The strengths and limitations of effective centroid force models explored by studying isotopic effects in liquid water

Ying Yuan,¹ Jicun Li,² Xin-Zheng Li,^{1,3} and Feng Wang^{2,a)}

¹State Key Laboratory for Mesoscopic Physics and School of Physics, Peking University, Beijing 100871, People's Republic of China

²Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA

³Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, People's Republic of China

(Received 1 March 2018; accepted 20 April 2018; published online 8 May 2018)

The development of effective centroid potentials (ECPs) is explored with both the constrained-centroid and quasi-adiabatic force matching using liquid water as a test system. A trajectory integrated with the ECP is free of statistical noises that would be introduced when the centroid potential is approximated on the fly with a finite number of beads. With the reduced cost of ECP, challenging experimental properties can be studied in the spirit of centroid molecular dynamics. The experimental number density of H₂O is 0.38% higher than that of D₂O. With the ECP, the H₂O number density is predicted to be 0.42% higher, when the dispersion term is not refit. After correction of finite size effects, the diffusion constant of H₂O is found to be 21% higher than that of D₂O, which is in good agreement with the 29.9% higher diffusivity for H₂O observed experimentally. Although the ECP is also able to capture the redshifts of both the OH and OD stretching modes in liquid water, there are a number of properties that a classical simulation with the ECP will not be able to recover. For example, the heat capacities of H₂O and D₂O are predicted to be almost identical and higher than the experimental values. Such a failure is simply a result of not properly treating quantized vibrational energy levels when the trajectory is propagated with classical mechanics. Several limitations of the ECP based approach without bead population reconstruction are discussed. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5027433>

I. INTRODUCTION

Methods to perform molecular dynamics simulations on electronic structure based potential energy surfaces (PESs) have received a lot of attention in recent years. One way to carry out such a simulation is to perform electronic structure calculations on the fly to integrate the equation of motion. This type of approach is generally referred to as *ab initio* molecular dynamics.¹ Variants of this method include Born-Oppenheimer molecular dynamics (BOMD),^{2,3} Car-Parrinello molecular dynamics (CPMD),⁴ or Atom centered Density Matrix Propagation (ADMP) method.^{5–7} Another approach is to fit the electronic structure PES to a model potential that is significantly less expensive computationally to evaluate. In other words, perform simulations through a purely electronic structure based force field. Popular routes along this direction include potentials based on many-body decomposition,⁸ symmetry adapted perturbation theory (SAPT),⁹ or force matching (FM).^{10–16} However, most of these approaches assume that the nuclear degrees of freedom evolve classically on or around a PES determined at the ground electronic state, thus completely leaving out the quantum effects of atomic nuclei.

Such an approximation can occasionally lead to fairly large discrepancies when compared to experiments, especially

for systems containing hydrogen atoms or at low temperatures. Because a particle's thermal de Broglie wavelength is inversely proportional to the square root of particle mass and temperature,¹⁷ quantum nuclear effects are more pronounced under those conditions.

Treating such contributions due to nuclear quantum effects is challenging. For systems with more than 100 atoms, most practical approaches rely on exploiting the isomorphism between the discrete path-integral formalism¹⁸ and the liquid-polymer thermodynamics in classical statistical mechanics.¹⁹ Popular methods that exploit such an isomorphism include path-integral molecular dynamics (PIMD),^{19–21} path-integral Monte-Carlo (PIMC),^{22–24} centroid molecular dynamics (CMD),^{25–28} ring polymer molecular dynamics (RPMD),^{29–32} etc.

With such an approach, each particle is approximated by a collection of beads. The bead distribution reflects the density matrix elements in the Cartesian space for the quantum mechanical particle. With proper sampling of the bead degrees of freedom, which is not trivial by itself,³³ many thermodynamic properties can then be calculated by integrating over the bead distribution in the phase space.

Compared to thermodynamic properties, the calculation of quantum dynamical correlations is even more challenging. Partly due to its conceptual simplicity, the CMD approach, while having several well-documented limitations,^{34–36} is still one of the top choices among competing methods.^{31,37}

^{a)}Author to whom correspondence should be addressed: fengwang@uark.edu

The focus of this work is to explore CMD through fitting to an effective centroid potential (ECP). By performing the fit on a small system, such a centroid potential can be used on systems of much larger size and allows sampling to be performed on time scales that are challenging to address directly with CMD. The significant reduction in computational cost brought by the ECP allows properties that are challenging to converge numerically to be studied.

One goal of the study is to investigate which properties could be captured by fitting to an ECP and which properties will still require either CMD or PIMD. We will investigate two different methods to fit the ECP. In addition, we will study the convergence behavior of effective centroid forces (ECF).

We note that one of the two fitting procedures, the quasi-adiabatic procedure, has been used in the past for the development of ECPs for hydrogen³⁸ and water.³⁹ Although the concept of ECF fitting is not entirely novel, this work provides significant new insight into the general performance and limitations of the methodology. A careful investigation of the properties of liquid water as a result of nuclear quantum effects is also reported.

The paper will be arranged in five sections, following the Introduction, the basic idea of CMD and the philosophy of the ECP are discussed in Sec. II, the fitting procedure and the final parameters for the ECPs are described in Sec. III, and the properties of H₂O and D₂O as predicted by the ECPs are reported in Sec. IV. Summary and conclusion are given in Sec. V.

II. CMD AND THE PHILOSOPHY OF EFFECTIVE CENTROID POTENTIALS

The philosophy of CMD has been well described in the literature.^{26,40–42} In a standard PIMD stimulation, each particle is discretized into a number of beads connected by harmonic springs. With the Trotter theorem, it can be shown that the bead distribution reflects the real space density matrix elements of the quantum mechanical particle in a constant temperature ensemble as the number of beads approaches infinity. The premise of CMD is to treat the centroid of the beads as a special variable and approximate the quantum mechanical partition function,

$$Z = \text{tr}\{e^{-\beta\hat{H}(\hat{x},\hat{p})}\}, \quad (1)$$

by the partition function of the centroid evaluated through a classical phase space integral.⁴³ The centroid is propagated according to the potential of mean force averaged over the bead distribution. The integral can be written as

$$Z_{\text{CMD}} = \iint \frac{e^{-\beta H(x_c, p_c)}}{2\pi\hbar} dx_c dp_c, \quad (2)$$

where the quantum mechanical trace in Eq. (1) is replaced by an integral in the centroid phase space and the quantum mechanical Hamiltonian operator is reduced to the effective Hamiltonian of the mean force at the centroid.

In addition, CMD approximates the quantum time correlation by the correlation of the centroid variable under the ECP, which is equivalent to the potential of mean bead force at the centroid location. Although the premise of CMD is fairly simple, a number of numerical tests have shown that CMD

is indeed capable of capturing the main quantum effects of challenging condensed phase systems.^{44–50}

By mapping the quantum distribution of a particle to a bead centroid that propagates classically according to an effective Hamiltonian, there is inevitably some loss of information. For example, probability densities are replaced by the precise trajectory of the centroid leading to a violation of the uncertainty principle since both the centroid position and momentum are known.

For certain thermodynamic properties, the missing information can sometimes be recovered since the centroid potential is approximated on the fly by sampling the bead degrees of freedom. With the associated bead distribution, it would be possible to evaluate the kinetic energy as

$$K_C = \frac{p_c^2}{2m} + \frac{1}{P} \sum_{i=1}^P \left[\frac{1}{2} (x_c - x_i) F_i(x_i) \right], \quad (3)$$

where the sum is performed over the P beads, F_i is the force on bead i at x_i ,^{43,51} and x_c is the location of the bead centroid. Similarly, the potential energy can be estimated as

$$V_C = \frac{1}{P} \sum_{i=1}^P V_i(x_i). \quad (4)$$

The sum of K_C and V_C is frequently referred to as the centroid Hamiltonian,⁴³

$$H_C = K_C + V_C. \quad (5)$$

We note that this Hamiltonian is not the Hamiltonian that gives the effective centroid forces for the trajectory propagation.⁴³ By integrating out the bead distribution in the derivation of the latter, it would be impossible to evaluate the virial term in Eq. (3).

For direct comparison with experiments, the radial distribution function (RDF) is also better approximated by the RDF of the beads rather than the RDF of the centroid.⁵² This has been well recognized in literature. For isotropic systems, a deconvolution algorithm has been devised that will allow the experimental RDFs to be obtained from the centroid RDFs.⁵³

Since the centroid degrees of freedom are propagated along the potential of mean force experienced by the bead centroids, it will be natural to use force matching to fit such an effective centroid potential. Indeed, several publications have explored such a possibility.^{38,39} Such an approach has two immediate advantages. In a CMD simulation, typically, not much more than 100 beads are used due to computational cost limitations. In order to improve the approximation of the mean centroid force, the sampling of the beads is generally enhanced with the use of an adiabaticity parameter⁴² that accelerates the motion of the beads in a normal mode based sampling technique. However, this approach will necessarily lead to oscillations of instantaneous centroid forces around the true gradients of the ECP. Such an oscillation in CMD is similar to oscillations around the Born-Oppenheimer surface that occurs in a typical CPMD simulation.¹ When the ECP is approximated by force-matching, it will be possible to use converged effective centroid forces obtained with constrained centroid sampling. Such a procedure will thus reach the true adiabatic limit by removing the noises in the centroid gradients.

Assuming that the fitting error is smaller than the noises introduced by limited number of the beads, the fitted potential will better follow the true potential of mean force of the centroid. Eliminating such sampling noises as a result of incomplete adiabatic separation may lead to improved accuracy especially for dynamical properties.

The second immediate advantage for force matching ECP is to allow much larger time and length scales to be studied. The reliable determination of many properties requires large box sizes and long simulation durations. Diffusion constants, dielectric constants, and surface tension are all known to be difficult to converge. Even tight convergence of the density could require multi-nanosecond simulations. In this work, we will study the density difference between H₂O and D₂O. The experimental difference in the number density of the two liquids is around 0.4%. It is thus very challenging to converge this property with either CMD or PIMD.

Without the associated bead distribution, a disadvantage of an ECP based simulation is the loss of information needed to evaluate certain properties, such as the internal energy described above. However, the bead distribution could be easily reconstructed by constrained centroid sampling of uncorrelated configurations obtained with classical MD with the ECP. In other words, short constrained centroid PIMD simulations could be performed using conformations sampled with the ECP potential to recover the missing bead distribution.

III. DEVELOPMENT OF THE EFFECTIVE CENTROID POTENTIALS AND THE CONVERGENCE OF EFFECTIVE CENTROID FORCES

In this work, the potential of mean bead force at the centroid will be referred to as the effective centroid potential, with its gradients giving rise to the effective centroid forces with a customary negative sign. Previous work on force matching has mostly focused on fitting the instantaneous forces that oscillate around the true ECFs saved in a CMD simulation. We will refer to such an approach as quasi-adiabatic centroid force matching. The other possibility is to fit the ECFs obtained by constrained-centroid simulations.

For developing ECPs, it will be most appropriate to perform CMD simulations with a potential that was fitted to reproduce the electronic structure PES rather than using a potential that was fit directly to experiments. For this purpose, we use the BLYPSP-4F potential⁵⁴ for water, which was developed by fitting to a coupled cluster quality PES⁵⁵ with the adaptive force matching method.^{13,56}

The BLYPSP-4F potential is a flexible four-site model for water with each hydrogen atom carrying a positive charge q_H , and a negative charge q_M is placed on a virtual site M. The M site location is defined as

$$\vec{r}_{OM} = a(\vec{r}_{OH_1} + \vec{r}_{OH_2}), \quad (6)$$

with a geometrical scaling parameter a of 0.2. $\vec{r}_{OH_1}$ and $\vec{r}_{OH_2}$ are the two O–H bond vectors.

The oxygen atoms interact with each other according to a Buckingham potential of the form

$$U_{OO}(r) = A_{OO}e^{-\alpha r} - C_{OO}/r^6, \quad (7)$$

where r is the O–O distance. In addition, a repulsion term is placed between the hydrogen atom and the M site to improve the description of short-range hydrogen bond interactions,⁵⁷

$$U_{HB}(r_{MH}) = \begin{cases} A_4/r_{MH}^4 - A_4/r_c^4 + 4A_4(r_{MH} - r_c)/r_c^5 & r_{MH} \leq r_c \\ 0 & r_{MH} > r_c \end{cases}, \quad (8)$$

with a cutoff distance r_c .

The intramolecular potential of BLYPSP-4F water contains a quartic bond term and a harmonic angle term with the form

$$U_{\text{intra}}(r_1, r_2, \theta) = \frac{k_2}{2}(r_1 - r_e)^2 + \frac{k_3}{3}(r_1 - r_e)^3 + \frac{k_4}{4}(r_1 - r_e)^4 \\ + \frac{k_2}{2}(r_2 - r_e)^2 + \frac{k_3}{3}(r_2 - r_e)^3 + \frac{k_4}{4}(r_2 - r_e)^4 \\ + \frac{k_\theta}{2}(\theta - \theta_e)^2, \quad (9)$$

where r_1 and r_2 are OH bond lengths and θ is the HOH angle. The parameters for the BLYPSP-4F model is summarized in Table I for convenience.

For the ECP, we will use the same energy expressions as the BLYPSP-4F potential except for the OH stretch term. Instead of a quartic bond term, we will use a Morse potential for each bond,

$$U_{OH}(r) = E_0(1 - e^{-c(r-r_e)})^2. \quad (10)$$

The Morse potential was chosen because it showed better numerical stability during force-matching. We note that technically a Morse potential will allow dissociation of water, which is undesirable. However, in practice, this is not an issue at most temperatures where the quantum nuclear effect is expected to be appreciable. At higher temperatures, it might be better to truncate to a more stable quartic form.

For the fitting of the ECP, we used a droplet containing 216 water molecules at 298 K in vacuum. We chose a droplet rather than a periodic box to avoid the need to use Ewald summation⁵⁸ during the fitting step. Fitting ECP with Ewald is significantly more costly. The good agreement between ECP and CMD shown below indicates that the use of a droplet is sufficient; the extra cost for Ewald based fits is thus not warranted. The droplet was equilibrated without PIMD for 300 ps and then with PIMD for 450 ps. All the PIMD or CMD simulations were performed with 24 beads.

For the constrained centroid force matching, 200 conformations were saved with 5 ps separation between each conformation from 1 ns worth of PIMD trajectory after the

TABLE I. Parameters for the BLYPSP-4F model.

Parameters	Value	Parameters	Value
q_M (e)	-1.3290	r_e (Å)	0.951
q_H (e)	0.6645	k_2 (kcal/mol Å ²)	1255.19
A_{OO} (kcal/mol)	210 710	k_3 (kcal/mol Å ³)	-4503.57
α (1/Å)	4.055	k_4 (kcal/mol Å ⁴)	7020.31
C_{OO} (kcal Å ⁶ /mol)	610.578	θ_e (deg)	106.678
A_4 (kcal Å ⁴ /mol)	81.489	k_θ [kcal/(mol rad ²)]	82.658
r_c (Å)	2.483		

initial equilibration. For each conformation, 200 000 steps of constrained centroid PIMD simulations were performed with a time step size of 0.005 fs for the beads and an adiabaticity parameter of 0.025. The adiabaticity parameter accelerates the normal modes orthogonal to the centroid motion to achieve better bead sampling without affecting the time evolution of the centroid. In the constrained centroid simulation, although a typical time step and adiabaticity parameter choice for CMD was used, the centroid locations were never allowed to change. Thus the simulations only sample the bead degrees of freedom. The average forces from the 200 000 frames will be used as the reference ECFs for force matching.

Figure 1 shows the convergence errors of the atomic and molecular forces obtained with constrained centroid simulations. The molecular force is the sum of the atomic centroid forces. The convergence error of the forces as a function of the number of frames, N_F , can be evaluated as

$$\sigma_F(N_F) = \sqrt{\frac{1}{N} \sum_i^N \left(\frac{\sum_{j=1}^{N_F} \vec{F}_i(j)}{N_F} - \langle \vec{F}^{ref}_i \rangle \right)^2}, \quad (11)$$

where N is the number of atoms or molecules in each frame, i is the atomic or molecular index, and j is a frame index. The arrow on top indicates a vector. Although the instantaneous centroid forces, $\vec{F}_i(j)$, were obtained by averaging over the 24 beads, the reference force, $\langle \vec{F}^{ref}_i \rangle$, was calculated by averaging the instantaneous forces over the entire 200 000 frames of one conformation.

From Fig. 1, it can be seen that the convergence error reduces slowly. It takes around 1100 frames for the convergence error on the molecular forces to reduce to

FIG. 1. Convergence error of the centroid effective atomic forces (a) and molecular forces (b) as a function of the number of frames in a constrained CMD simulation.

0.1 kcal/(mol Å) and it took about 10 000 frames for the convergence error for atomic forces to reduce to 1 kcal/(mol Å). The much slower convergence of atomic forces is expected since small errors in the density matrix elements will lead to relative large deviations in intramolecular forces due to the stiffness of the OH bond. For the constrained CMD sampling, we intentionally picked parameters similar to those being used in typical CMD simulations. With a 0.005 fs time step, for every femto-second, 200 evaluations of the centroid forces are performed. The convergence error for 200 evaluations is around 0.2 kcal/(mol Å) for intermolecular forces and 4.0 kcal/(mol Å) for atomic forces. We note that the root mean square deviation (RMSD) of the force matching fit is around 0.08 kcal/(mol Å) for molecular forces and 2.1 kcal/(mol Å) for the atomic forces; both are significantly smaller than the corresponding force convergence error typically obtained in a CMD simulation when averaged over 1 fs.

The 0.2 kcal/(mol Å) convergence error for intermolecular forces in a typical CMD simulation should not be considered large; it is likely not going to influence any properties happening on a time scale much longer than a few femto-seconds. However, the atomic force convergence error is much larger at the femto-second scale.

For the quasi-adiabatic fit, we simply fit the potential to the centroid forces saved from a typical CMD simulation. The word “quasi-adiabatic” comes from the assumed adiabatic separation of the fast bead degrees of freedom and the slow centroid degrees of freedom used in a typical CMD simulation. For the quasi-adiabatic force matching, the CMD simulations were performed with the same time step and adiabaticity parameter as the constrained centroid force matching. In the CMD, although the velocity distribution of the beads was controlled by one Nosé-Hoover chain³³ with a length of four for each degree of freedom of the beads, the centroids are only weakly coupled to a single thermostat for the entire system. The system thermostat is a single Nosé-Hoover thermostat with a relaxation time of 0.2 ps.

Our force-matching algorithm relies on solving the singular value decomposition (SVD) problem. In force-matching, generally the number of equations, m , is much larger than the number of parameters n . In this case, the cost of SVD scales as m^2n . With a 216 water box, each conformation will result in 1944 equations just for atomic forces; this makes it very computationally demanding to fit all the frames from a long CMD simulation. For the quasi-adiabatic fitting, we performed five CMD simulations starting from properly equilibrated PIMD configurations and saved 400 conformations at 0.5 fs interval from each simulation. This procedure provided 2000 instantaneous centroid forces for force-matching.

Of all the parameters of the ECP, additional discussion is warranted for the C_6 parameter for dispersion. While the density of water is strongly regulated by dispersion, our past experience indicates that the C_6 parameter is very challenging to fit reliably. For a completely homogeneous system, it is easy to understand that the total force due to dispersion will be exactly zero regardless of the actual C_6 parameter. This is a result of total cancellation of dispersion forces from all the directions. Liquid water is nearly homogenous beyond the second hydration shell. Thus determining the C_6 parameter

by force matching is hampered by the numerical difficulty in capturing weak contributions resulting from the remaining inhomogeneity. In such a case, the C_6 fitted could be biased to improve the short-range description of repulsion rather than trying to capture the weaker longer range dispersion.

One way to address this issue is to assume that nuclear quantization has minimal influence on dispersion. This is likely a good approximation at least for the BLYPSP-4F model. In this model, dispersion is only present between oxygen atoms, which are not significantly delocalized into wave-packets under ambient conditions. Under this assumption, it will be sufficient to fix the C_6 to the BLYPSP-4F value and only fit the remaining parameters.

The final parameters for both the constrained-centroid and the quasi-adiabatic fits are reported in Table II for both H_2O and D_2O . While for the quasi-adiabatic fits, we allowed the C_6 parameters to be fit, for the constrained-centroid FM, two ECP models were fitted for each type of water with either the dispersion term being fit or remaining fixed. We anticipate that the models with the C_6 fixed to the classical value will provide better densities and better represent the true ECPs as a result of the improved numerical stability of the C_6 . The ECP model where the C_6 is constrained to the BLYPSP-4F dispersion parameter will be referred to as ECP with classical dispersion (ECP_CD).

For convenience, the classical BLYPSP-4F model is also reported in Table II after the intramolecular term was refitted to a Morse potential [Eq. (9)]. It is clear that the ECP parameters produced by the quasi-adiabatic fit are in good agreement with that from the constrained-centroid fit. The difference in parameters is comparable to the uncertainty of the fit estimated with boot-strap resampling.

Since the energy expressions fitted with the constrained-centroid and the quasi-adiabatic fits are very similar, we will focus only on the H_2O and D_2O models fitted with the constrained-centroid approach. The main difference between the ECPs and the classical model is clearly in the intramolecular stretching model. Since the OH bond in the BLYPSP-4F model has a negative cubic contribution, it is anticipated

that quantum nuclear effects will lead to a small increase of the equilibrium bond length. Although the equilibrium bond length of D_2O ECP at 0.954 Å is slightly larger than the classical BLYPSP-4F model of 0.951 Å, the equilibrium bond length of H_2O ECP is 0.952 Å, which is shorter than that of D_2O . This is somewhat surprising, considering H_2O having a stronger intramolecular quantum nuclear effect. The observed shorter bond length of the H_2O ECP than that of the D_2O ECP clearly indicates a problem.

In order to understand the problem of ECP bond lengths, we simulated an isolated OH bond with CMD. Figure 2(a) shows the bead density distribution and centroid density distribution for the BLYPSP-4F water. The numerical solution of the one-dimensional Schrödinger's equation for a single BLYPSP-4F O–H bond obtained with a 4th order Numerov method⁵⁹ is also shown as a comparison. It is clear from Fig. 2(a) that the bead distribution indeed captures the correct quantum solution with a maximum at 0.968 Å. However, the centroid distribution has a maximum of 0.952 Å. The presence of the 0.952 Å centroid density maximum explains the 0.952 Å equilibrium bond length of the corresponding ECP potential. Figure 2(b) shows the density plots from a CMD simulation of the OH bond, where the stretching potential is truncated to be harmonic. For a harmonic potential, the density maximum is expected to be the same as the equilibrium bond length of the potential. Although this is true for the bead density distribution, the density maximum of the centroid once again shifted to a shorter value.

The shorter equilibrium bond length of the ECP is actually consistent with the previously described curvature problem in CMD.^{34,35} With the stiff OH bond, the beads distribute in two narrow bands around the equilibrium bond length leading to the centroid location appearing at the shorter OH distance. The short equilibrium bond length of the ECP simply reflects the position of the maximum density of the centroid. This is expected since the ECP is simply the potential of mean force of the centroid, which should be zero at a maximum.

Although the small error in equilibrium bond length reflects the curvature problem, the difference is very small at

TABLE II. Parameters for the H_2O and D_2O ECPs obtained using the constrained centroid method and the quasi-adiabatic method. The error bars on the constrained centroid parameters were reported as the 1σ uncertainty of the last significant number shown. The error bars were calculated with boot-strap resampling, and we anticipate the error bar for the quasi-adiabatic fit to be comparable.

Parameters	BLYPSP-4F	ECP- H_2O			ECP- D_2O		
		ECP	ECP_CD	Quasi-ECP	ECP	ECP_CD	Quasi-ECP
q_M (e)	−1.3290	−1.3254(0)	−1.3254	−1.3256	−1.3276(0)	−1.3276	−1.3274
q_H (e)	0.6645	0.6627(0)	0.6627	0.6628	0.6638(0)	0.6638	0.6637
A_{OO} (kcal/mol)	210 710	230 360(367)	228 001	230 221	220 096(325)	218 795	219 100
α (1/Å)	4.055	4.091(1)	4.087	4.091	4.072(0)	4.068	4.069
C_{OO} (kcal Å ⁶ /mol)	610.578	605.259(654)	610.578	603.225	606.548(631)	610.578	607.893
A_4 (kcal Å ⁴ /mol)	81.483	82.680(16)	82.679	82.714	82.387(8)	82.380	82.335
r_c (Å)	2.483	2.508(0)	2.508	2.507	2.495(0)	2.495	2.494
r_e (Å)	0.951	0.952(0)	0.952	0.952	0.954(0)	0.954	0.954
E_0 (kcal/mol)	110.284	164.095(434)	164.034	161.654	125.566(121)	125.432	126.153
c (1/Å)	2.380	1.783(6)	1.785	1.798	2.134(1)	2.136	2.129
θ_e (deg)	106.678	106.957(0)	106.925	106.956	106.838(0)	106.800	106.836
k_θ [kcal/(mol rad ²)]	82.658	79.170(12)	78.998	79.243	80.838(6)	80.811	80.810

FIG. 2. Probability distribution of a single isolated OH bond modeled with the BLYSP-4F parameters (a) and the harmonic terms of the BLYSP-4F bond potential (b). The exact distributions were approximated with the Numerov method, and the bead and centroid distributions were obtained with CMD.

0.01 Å. Whether the curvature problem will lead to significant errors for water simulations not too far away from ice-water equilibrium temperature is still a subject of debate.^{60,61}

Despite the curvature problem, which affects the equilibrium bond lengths of the ECP, the ECP for the O–H(D) stretching mode does appear to be softer than the classical BLYSP-4F potential as shown in Fig. 3. This is anticipated since the delocalized ground state density feels the negative cubic term in the stretching mode leading to a lower zero point energy of vibration.

The influence of nuclear quantization to the intermolecular potential is more subtle. Figure 4 shows a very minor difference between the classical BLYSP-4F potential and the H₂O and D₂O ECPs. Figure 4(b) shows the difference between the ECPs and the classical potential. The intermolecular potentials for both the fitted C_6 ECP and that of the ECP_CD are shown. Both the ECP and ECP_CD show a similar change from the classical potential, although the magnitude of the change is slightly different. At shorter distances, the ECPs become more

FIG. 3. OH stretching potentials of the BLYSP-4F potential (black) and ECP models for H₂O (red) and D₂O (green). To better emphasize the curvature change, the minimum of the potentials was shifted to the same position.

FIG. 4. Comparison of the O–O repulsion in the BLYSP-4F potential and the H₂O and D₂O ECPs. Since the Buckingham repulsion (a) is almost superimposable, the difference between each ECP to the BLYSP-4F model is reported in panel (b).

repulsive than the classical potential probably due to delocalization of the particles into a more repulsive region at shorter interatomic distances. It is interesting that the H₂O ECPs seem to be less repulsive than the classical model from 2.57 to 3.65 Å. This most likely reflects tunneling of the particle density into a classically forbidden region.

IV. PROPERTIES OF LIQUID WATER INVESTIGATED BY THE ECP POTENTIALS

In this work, we focus studying the differences between H₂O and D₂O due to nuclear quantum effects by developing ECPs for both H₂O and D₂O. It is known that the H₂O and D₂O have slightly different number densities. At 298 K, the number density of H₂O is 55.35 mol/l, which is slightly higher than that of D₂O at 55.14 mol/l.⁶² The classical partition function factorizes into an ideal gas term and a configuration energy term. The result of this factorization is that the particle masses cannot influence any thermodynamic properties within classical statistical mechanics. Thus, the observed difference in number densities between H₂O and D₂O has to be a result of quantum nuclear effects. However, confirming this argument with either PIMD or CMD is very challenging since the difference is only 0.38%. Long simulation is required to ensure proper convergence.

All the property calculations using the ECPs were performed with the Groningen MACHine for Chemical Simulation (GROMACS) simulation package.⁶³ For the determination of density, 20 ns NPT simulations were performed at 298 K with a Nosé-Hoover thermostat with a relaxation constant of 1.0 ps and the Parrinello-Rahman barostat with a relaxation time of 5.0 ps. Long range corrections to pressure

and energy were incorporated to account for the truncation of van der Waals interactions at 9.0 Å. For the BLYPSP-4F ECPs, the densities for H₂O and D₂O were measured to be 55.71 (±0.01) mol/l and 55.63 (±0.02) mol/l, respectively, showing a 0.15% higher density for H₂O. With the ECP_CD, the densities for H₂O and D₂O are 55.90 (±0.01) mol/l and 55.66 (±0.01) mol/l, respectively, showing a 0.43% higher density for H₂O. Thus, both the fitted C_6 ECPs and the ECP_CDs are able to capture the increased number density of H₂O. The agreement is almost quantitative with the ECP_CD model without refitting the C_6 parameter. As discussed previously, we anticipate the ECP_CD to be more accurate due to numerical challenges associated with fitting long range dispersion in a nearly homogenous environment. This slightly higher density for H₂O might be due to the presence of the slightly less repulsive region in the H₂O intermolecular potential shown in Fig. 4.

We note that the BLYPSP-4F water density is 55.73 mol/l in a classical simulation. This density is lower than that of H₂O but higher than that of D₂O. This is not surprising considering that the D₂O ECP is more repulsive than the classical BLYPSP-4F model in the entire range shown in Fig. 4(b). Only the H₂O ECP has a region that is less repulsive than the classical model. This suggests that if classical water does exist in real life, its density is likely not smaller than that of D₂O. Extrapolation of H₂O and D₂O densities to obtain the hypothetical classical water density is thus not straightforward.

The diffusion constant is also anticipated to be influenced by nuclear quantum effects. At 298 K, the H₂O diffusion constant is 0.230 Å²/ps,⁶⁴ which is 29.9% higher than that of D₂O at 0.177 Å²/ps.⁶⁵ Computational determination of the diffusion constant is challenging due to strong finite size effects.⁶⁶ One way to address the finite size effect is to measure the diffusion constant with different box sizes and extrapolate to infinity. Figure 5 shows the diffusion constant of H₂O and D₂O calculated as a function of box sizes containing from 343 to 1728 water molecules. The simulation was performed under the NVT condition using the average volume that gives the corresponding model density at 1 bar. 10 ns of simulation was performed for each box size. As shown in Fig. 5, a good linearity can be seen when the diffusion constant is plotted against 1/ L , where L is the length of the cubic box. The fit to a linear equation reveals an intercept of 0.291 Å²/ps for H₂O and 0.241 Å²/ps for D₂O for the fitted C_6 ECP. The corresponding diffusion constants for the ECP_CD are 0.293 Å²/ps for H₂O and 0.240 Å²/ps for D₂O, respectively. Thus the fitted C_6 ECPs and the ECP_CDs, respectively, predict H₂O to have diffusion constants 21% and 22% higher than that of D₂O. Both are in good agreement with experiments.

Figure 6 reports the infrared spectra for H₂O and D₂O. The spectra determined with the fitted C_6 ECP and the ECP_CD are superimposable and in close agreement with the CMD spectra. While the CMD spectra were obtained with a 60 ps trajectory, the corresponding ECP trajectories are 800 ps. The much longer trajectories for the ECP spectra are probably responsible for the ECP spectra being much smoother than the CMD one. The CMD spectra might also be noisier due to the oscillating effective centroid forces as a result of the oscillative forces.

FIG. 5. Diffusion constants of H₂O (red) and D₂O (green) calculated for the fitted C_6 ECP (a) and ECP_CD (b). The diffusion constants are plotted as a function of $1/L$, where L is the length of the cubic simulation box.

For H₂O, compared with the classical BLYPSP-4F model, CMD shows a redshift of 220 cm⁻¹ for the intramolecular OH-stretch. This shift is around 280 cm⁻¹ for both the ECPs, which brings the ECP stretch at 3380 cm⁻¹ into closer agreement with experiments at 3404 cm⁻¹.⁶⁷ It would be difficult to judge if the slightly larger redshift for the ECP H₂O is due to the better converged centroid forces by the elimination of strong fluctuations or simply fortuitous.

For the D₂O, the difference between the ECPs and CMD is negligible; both redshift the OD stretch by 100 cm⁻¹ from the

FIG. 6. The infrared spectra of H₂O (a) and D₂O (b) calculated with the classical BLYPSP-4F model, CMD, fitted C_6 ECP, and ECP_CD. The spectra obtained with the fitted C_6 ECP and ECP_CD are superimposable. The experimental curves are also shown as a comparison.

classical model. The resulting peak position for the OD stretching band is around 2500 cm^{-1} which is in good agreement with the experimental value of 2504 cm^{-1} .⁶⁷

We focused our attention on the intramolecular stretching model since it is most strongly influenced by quantum effects. For all the other peaks, good agreement between the ECPs and CMD predictions is observed. We also note that the IR intensities from the simulations should not be considered reliable. The underlying BLYPSP-4F model is not designed to properly capture the dipole derivative surfaces, and thus it is expected to give wrong intensities. In order to capture the proper gradients of the dipole with respect to geometry distortions, a polarizable model with proper modeling of geometry-dependent charge-flow is required.

As discussed previously, mapping to an ECP will necessarily lead to some loss of information. The quantum density profile encoded in the bead distribution will no longer be available. It would be impossible to evaluate the centroid Hamiltonian [Eq. (5)] without reconstructing the bead distribution. With the ECP Hamiltonian, both the heat of vaporization and the heat capacity will be over-estimated as with typical flexible water potentials in a classical simulation.

This effect is best understood with the equipartition theorem. In a classical simulation, each intramolecular vibrational mode will contribute approximately R to the heat capacity, whereas the contribution from the vibrations is very small for the stiff OH bonds when the energy levels are properly quantized. The reason for the constant contribution to heat capacity in classical statistical mechanics can be shown by an integration over the phase space to calculate the average vibrational energy. Assuming that the vibrational models are totally harmonic, such an integration will lead to an average energy of RT for each intramolecular vibrational mode, regardless of the actual parameter for the harmonic stretch. The average internal energy will lead to an associated heat capacity of R in a classical simulation. The true heat capacity cannot be recovered unless the quantum nature of vibration is properly considered.

With classical MD, it is thus not surprising that most flexible water models tend to over-estimate the heat capacity, whereas rigid models frequently give better agreements with experiments.^{68,69} When the equation of motion is integrated classically with ECPs, one would expect the constant pressure heat capacities C_p of the H_2O and D_2O to be overestimated. In our simulation, the C_p for H_2O and D_2O are 101.40 J/(K mol) and 102.92 J/(K mol) , respectively. These values are significantly higher than the experimental values of 75.34 J/(K mol) for H_2O ⁷⁰ and 84.67 J/(K mol) for D_2O .⁷¹ Without properly treating the quantum nature of the vibrations, one should not be able to capture the difference in heat capacities between H_2O and D_2O , which is clearly shown with our results. We emphasize that a CMD simulation would have no trouble recovering the proper heat capacities, since the bead distribution is available to evaluate H_C in Eq. (5).

We note that for the heat capacity, and all the properties below, only the ECP_CD results are reported since they are almost identical to the fitted C_6 ECP results (not shown). We anticipate the ECP_CD models to be more reliable due to the more accurate long range dispersion.

The experimental heat of vaporization for H_2O and D_2O are 10.52 kcal/mol and 10.85 kcal/mol , respectively.^{72,73} ECP_CD models gave a heat of vaporization of 13.30 kcal/mol for H_2O and 13.44 kcal/mol for D_2O . It is not surprising that the liquid heat of vaporizations is also over-estimated when the heat capacities are over-estimated.

As shown in Fig. 7, the RDF obtained by the ECP_CD model for H_2O is identical to the centroid RDF from the CMD simulations. Both are different from the bead RDFs obtained from the same CMD simulations. It has been known that the experimental RDF corresponds to the bead RDF and not the centroid RDF.⁵² One possible method to reconstruct the bead RDF is to perform short PIMD simulations from uncorrelated configurations sampled with the ECP. In this work, we will, however, use a deconvolution algorithm proposed previously by Blinov and Roy,⁵³

$$g(r) = \int dr_c g_c(r_c) F(r, r_c), \quad (12)$$

where the RDF, $g(r)$, is calculated from the RDF of the centroid, $g_c(r_c)$, and $F(r, r_c)$ is a transformation function for the deconvolution.

For isotropic and homogenous potentials, the transformation function is

$$F(r, r_c) = (6\mu \cdot k_B T / \pi \hbar^2)^{3/2} e^{-\frac{6\mu(r-r_c)^2 k_B T}{\hbar^2}}, \quad (13)$$

FIG. 7. The RDFs of H_2O at 298.15 K . The centroid RDF (centroid) from a CMD simulation is in good agreement with the RDFs using the corresponding ECP_CD models. The bead RDFs (bead) from the CMD simulation and the deconvoluted ECP RDFs (deconv.) are also reported.

where μ is the reduced mass of a pair of particles. For the calculation of the O–O RDF, μ was chosen to be the reduced mass of a pair of water molecules. It can be seen in Fig. 7(a) that the deconvolution algorithm does a very good job recovering the “true” O–O RDF. Although it might be appropriate to approximate the overall water–water interaction as isotropic, applying such an approximation for the OH and HH RDFs is more problematic. For the calculation of the OH and HH RDFs, the reduced masses of the two corresponding atom pairs were used in Eq. (13). However, it is not surprising that the deconvolution algorithm only shows an improvement to the ECP_CD RDF and is not able to fully recover the corresponding bead RDFs, especially at short ranges. Water shows strong short-range orientational orders as a result of the highly anisotropic OH and HH interactions at small separations. Thus, the isotropic transformation function is not expected to be completely adequate.

V. SUMMARY AND CONCLUSION

By developing ECPs through constrained-centroid or quasi-adiabatic force matching, the virtue of performing classical simulations on the centroid potential of mean force is evaluated. With the ECP, which is fitted to reproduce the converged centroid forces, noises in the instantaneous centroid forces due to the use of limited number of beads are eliminated. In addition, the low cost ECPs allow the modeling of quantum nuclear effects in the spirit of CMD for much larger systems over longer simulation times.

The ECPs for H₂O and D₂O correctly predict that H₂O has a slightly higher number density under ambient conditions. When the long range dispersion is fixed to the corresponding value in the classical potential, the ECP_CD models predict the H₂O number density to be 0.42% higher than that of D₂O in good agreement with experimental density difference of 0.38%. In addition, the ECP models predict the H₂O diffusion constant to be about 21% higher than that of D₂O, which is in good agreement with the experimental difference of 30%. The diffusion constant is a challenging property to determine due to finite size effects. With the ECP, we were able to investigate such finite size effects and extrapolate to the infinite box limit. The ECP also gives good predictions of the positions of the vibrational peaks for both liquid H₂O and D₂O when compared to the corresponding CMD simulations.

Without the associated bead distribution, ECP potentials have trouble obtaining certain properties, such as the heat capacity and heat of vaporization. Although the ECP RDFs are in good agreement with the centroid RDFs in a corresponding CMD simulation, a deconvolution procedure will be required to capture the “true” RDFs without explicit reconstruction of the bead distributions with PIMD.

ACKNOWLEDGMENTS

The model development work in Wang research group was supported by the National Institutes of Health under Grant No. 1R01GM120578 and by National Science Foundation (NSF) under Grant No. DMR-1609650. Y.Y. and X.Z.L. were supported by National Basic Research Programs of China

under Grand Nos. 2016YFA0300900 and 2017YFA0205000 and the National Science Foundation of China under Grant Nos. 11774004 and 11634001. The computer resources for this study were provided by supercomputer TianHe-1A in Tianjin, China.

- ¹M. E. Tuckerman, *J. Phys.: Condens. Matter* **14**, R1297 (2002).
- ²T. Helgaker, E. Uggerud, and H. J. A. Jensen, *Chem. Phys. Lett.* **173**, 145 (1990).
- ³E. Uggerud and T. Helgaker, *J. Am. Chem. Soc.* **114**, 4265 (1992).
- ⁴R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ⁵H. B. Schlegel, J. M. Millam, S. S. Iyengar, G. A. Voth, A. D. Daniels, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **114**, 9758 (2001).
- ⁶S. S. Iyengar, H. B. Schlegel, J. M. Millam, G. A. Voth, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **115**, 10291 (2001).
- ⁷H. B. Schlegel, S. S. Iyengar, X. Li, J. M. Millam, G. A. Voth, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **117**, 8694 (2002).
- ⁸G. R. Medders and F. Paesani, *J. Chem. Theory Comput.* **9**, 4844 (2013).
- ⁹R. Bukowski, J. Sadlej, B. Jeziorski, P. Jankowski, K. Szalewicz, S. A. Kucharski, H. L. Williams, and B. M. Rice, *J. Chem. Phys.* **110**, 3785 (1999).
- ¹⁰F. Ercolessi and J. B. Adams, *Europhys. Lett.* **26**, 583 (1994).
- ¹¹P. Tangney and S. Scandolo, *J. Chem. Phys.* **117**, 8898 (2002).
- ¹²S. Izvekov, M. Parrinello, C. J. Burnham, and G. A. Voth, *J. Chem. Phys.* **120**, 10896 (2004).
- ¹³O. Akin-Ojo, Y. Song, and F. Wang, *J. Chem. Phys.* **129**, 064108 (2008).
- ¹⁴J. Sala, E. Guàrdia, J. Martí, D. Spångberg, and M. Masia, *J. Chem. Phys.* **136**, 054103 (2012).
- ¹⁵L.-P. Wang, T. J. Martinez, and V. S. Pande, *J. Phys. Chem. Lett.* **5**, 1885 (2014).
- ¹⁶A. Albaugh, H. A. Boateng, R. T. Bradshaw, O. N. Demerdash, J. Dziedzic, Y. Mao, D. T. Margul, J. Swails, Q. Zeng, D. A. Case, P. Eastman, L.-P. Wang, J. W. Essex, M. Head-Gordon, V. S. Pande, J. W. Ponder, Y. Shao, C.-K. Skylaris, I. T. Todorov, M. E. Tuckerman, and T. Head-Gordon, *J. Phys. Chem. B* **120**, 9811 (2016).
- ¹⁷M. E. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, New York, 2010), p. 142.
- ¹⁸R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
- ¹⁹D. Chandler and P. G. Wolynes, *J. Chem. Phys.* **74**, 4078 (1981).
- ²⁰M. Parrinello and A. Rahman, *J. Chem. Phys.* **80**, 860 (1984).
- ²¹B. J. Berne and D. Thirumalai, *Annu. Rev. Phys. Chem.* **37**, 401 (1986).
- ²²D. M. Ceperley, *Rev. Mod. Phys.* **67**, 279 (1995).
- ²³D. M. Ceperley and E. L. Pollock, *Phys. Rev. Lett.* **56**, 351 (1986).
- ²⁴E. L. Pollock and D. M. Ceperley, *Phys. Rev. B* **30**, 2555 (1984).
- ²⁵J. Cao and G. A. Voth, *J. Chem. Phys.* **99**, 10070 (1993).
- ²⁶J. Cao and G. A. Voth, *J. Chem. Phys.* **100**, 5093 (1994).
- ²⁷J. Cao and G. J. Martyna, *J. Chem. Phys.* **104**, 2028 (1996).
- ²⁸D. Marx, M. E. Tuckerman, and G. J. Martyna, *Comput. Phys. Commun.* **118**, 166 (1999).
- ²⁹I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.* **121**, 3368 (2004).
- ³⁰I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.* **122**, 084106 (2005).
- ³¹B. J. Braams and D. E. Manolopoulos, *J. Chem. Phys.* **125**, 124105 (2006).
- ³²S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller III, *Annu. Rev. Phys. Chem.* **64**, 387 (2013).
- ³³G. J. Martyna, M. L. Klein, and M. Tuckerman, *J. Chem. Phys.* **97**, 2635 (1992).
- ³⁴A. Witt, S. D. Ivanov, M. Shiga, H. Forbert, and D. Marx, *J. Chem. Phys.* **130**, 194510 (2009).
- ³⁵S. D. Ivanov, A. Witt, M. Shiga, and D. Marx, *J. Chem. Phys.* **132**, 031101 (2010).
- ³⁶T. J. H. Hele, M. J. Willatt, A. Muolo, and S. C. Althorpe, *J. Chem. Phys.* **142**, 191101 (2015).
- ³⁷S. Bonella and D. F. Coker, *J. Chem. Phys.* **122**, 194102 (2005).
- ³⁸T. D. Hone, S. Izvekov, and G. A. Voth, *J. Chem. Phys.* **122**, 054105 (2005).
- ³⁹F. Paesani, W. Zhang, D. A. Case, T. E. Cheatham III, and G. A. Voth, *J. Chem. Phys.* **125**, 184507 (2006).
- ⁴⁰J. Cao and G. A. Voth, *J. Chem. Phys.* **100**, 5106 (1994).
- ⁴¹J. Cao and G. A. Voth, *J. Chem. Phys.* **101**, 6157 (1994).
- ⁴²J. Cao and G. A. Voth, *J. Chem. Phys.* **101**, 6168 (1994).
- ⁴³S. Jang and G. A. Voth, *J. Chem. Phys.* **111**, 2357 (1999).

- ⁴⁴E. Geva, Q. Shi, and G. A. Voth, *J. Chem. Phys.* **115**, 9209 (2001).
- ⁴⁵Y. Yonetani and K. Kinugawa, *J. Chem. Phys.* **119**, 9651 (2003).
- ⁴⁶T. D. Hone and G. A. Voth, *J. Chem. Phys.* **121**, 6412 (2004).
- ⁴⁷L. H. d. l. Peña and P. G. Kusalik, *J. Chem. Phys.* **121**, 5992 (2004).
- ⁴⁸L. H. d. l. Peña, M. S. G. Razul, and P. G. Kusalik, *J. Chem. Phys.* **123**, 144506 (2005).
- ⁴⁹M. Wang, Z. Lu, and W. Yang, *J. Chem. Phys.* **124**, 124516 (2006).
- ⁵⁰R. Welsch, K. Song, Q. Shi, S. C. Althorpe, and T. F. Miller III, *J. Chem. Phys.* **145**, 204118 (2016).
- ⁵¹J. Cao and B. J. Berne, *J. Chem. Phys.* **91**, 6359 (1989).
- ⁵²T. E. Markland, J. A. Morrone, K. Miyazaki, B. J. Berne, D. R. Reichman, and E. Rabani, *J. Chem. Phys.* **136**, 074511 (2012).
- ⁵³N. Blinov and P.-N. Roy, *J. Chem. Phys.* **120**, 3759 (2004).
- ⁵⁴F. Wang, O. Akin-Ojo, E. Pinnick, and Y. Song, *Mol. Simul.* **37**, 591 (2011).
- ⁵⁵Y. Song, O. Akin-Ojo, and F. Wang, *J. Chem. Phys.* **133**, 174115 (2010).
- ⁵⁶O. Akin-Ojo and F. Wang, *J. Comput. Chem.* **32**, 453 (2011).
- ⁵⁷O. Akin-Ojo and F. Wang, *J. Phys. Chem. B* **113**, 1237 (2009).
- ⁵⁸M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987), p. 156.
- ⁵⁹B. V. Noumerov, *Mon. Not. R. Astron. Soc.* **84**, 592 (1924).
- ⁶⁰F. Paesani and G. A. Voth, *J. Chem. Phys.* **132**, 014105 (2010).
- ⁶¹D. R. Moberg, S. C. Straight, C. Knight, and F. Paesani, *J. Phys. Chem. Lett.* **8**, 2579 (2017).
- ⁶²G. S. Kell, *J. Phys. Chem. Ref. Data* **6**, 1109 (1977).
- ⁶³D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, and H. J. C. Berendsen, *J. Comput. Chem.* **26**, 1701 (2005).
- ⁶⁴M. Holz, S. R. Heil, and A. Sacco, *Phys. Chem. Chem. Phys.* **2**, 4740 (2000).
- ⁶⁵W. S. Price, H. Ide, Y. Arata, and O. Söderman, *J. Phys. Chem. B* **104**, 5874 (2000).
- ⁶⁶I.-C. Yeh and G. Hummer, *J. Phys. Chem. B* **108**, 15873 (2004).
- ⁶⁷J.-J. Max and C. Chapados, *J. Chem. Phys.* **131**, 184505 (2009).
- ⁶⁸A. Wallqvist and O. Teleman, *Mol. Phys.* **74**, 515 (1991).
- ⁶⁹Q. Waheed and O. Edholm, *J. Chem. Theory Comput.* **7**, 2903 (2011).
- ⁷⁰W. Wagner, J. R. Cooper, A. Dittmann, J. Kijima, H. J. Kretschmar, A. Kruse, R. Mareš, K. Oguchi, H. Sato, I. Stöcker, O. Šifner, Y. Takaishi, I. Tanishita, J. Trübenbach, and T. Willkommen, *J. Eng. Gas Turbines Power* **122**, 150 (2000).
- ⁷¹M. Nakamura, K. Tamura, and S. Murakami, *Thermochim. Acta* **253**, 127 (1995).
- ⁷²W. Wagner and A. Pruß, *J. Phys. Chem. Ref. Data* **31**, 387 (2002).
- ⁷³F. D. Rossini, J. W. Knowlton, and H. L. Johnston, *J. Res. Natl. Bur. Stand.* **24**, 369 (1940).