



Two-dimensional multiple-histogram method applied to isothermal–isobaric Monte Carlo simulations of molecular clusters



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ABSTRACT

A two-dimensional multiple-histogram method for isothermal–isobaric ensemble is discussed in detail, implemented for isothermal–isobaric Monte Carlo simulations of molecular clusters, and employed in a case study on phase changes in pure water clusters containing 15 through 21 water molecules. Full phase diagrams of these clusters are reported in the temperature–pressure plane over a broad range of temperatures ($T = 30\text{--}800\text{ K}$) and pressures $P = 10^3\text{--}10^9\text{ Pa}$. The main focus of the work is on the structural transformation occurring in the solid phase of these clusters and leading from cluster structures with all molecules on the cluster surface to cage-like structures with one molecule inside, and on how the transformation is influenced by increased pressure and temperature.

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1. Introduction

Numerical simulations play a key role in cluster science since they provide a deep insight into the physics and chemistry of these objects which is not directly accessible to experimental investigations. Even at the classical level, numerical simulations can provide valuable qualitative as well as quantitative data. Among two main branches of molecular simulations methods, molecular dynamics methods and Monte Carlo methods, the latter represent a computationally cheaper alternative and have been frequently used in the past. Up to now, however, free clusters have usually been studied using canonical Monte Carlo approaches [1–6]. This may ultimately provide complete information about the evolution of the properties of various clusters along the temperature axis for temperatures for which the evaporation of monomers from the cluster is negligible. A more detailed approach based, e.g., on isothermal–isobaric Monte Carlo simulation techniques [7] has been much less frequently applied despite the fact that it may provide a basically complete information about the cluster phase behavior in the temperature–pressure plane.

A couple of problems are closely linked to numerical simulations. The most important problems may be (a) how to achieve a sufficient convergence of simulated data and avoid quasergodicity, which becomes particularly important if a coexistence region of

two phases of a particular system is simulated, and (b) how to obtain values of the quantities of interest (like internal energy, heat capacity etc.) at thermodynamic conditions (temperatures, pressures etc.) not included in particular simulation runs. Both problems have been addressed in the past and efficient procedures have been developed to surmount them. *Parallel-tempering* techniques, proposed originally for canonical, constant-temperature simulations [8] and extended later to isothermal–isobaric calculations [7], have been developed to deal with the quasergodicity problem and have soon become a simulation standard, at least for canonical, constant-temperature studies. To deal with latter problem, reliable interpolation schemes must be used since the size of the grids of simulated temperatures and pressures is usually strongly limited due to computational demands. *Multiple-histogram* techniques have proven to be very efficient in this respect. The original multiple-histogram approach by Ferrenberg and Swendsen [9] was first developed, similar to the evolution of the parallel-tempering methodology, for canonical, constant-temperature simulations and only recently has been generalized to be used in isothermal–isobaric calculations [10], building on the *weighted histogram analysis method* [11], an extension of the original multiple-histogram method [9] towards multi-parameter simulations. If combined with isothermal–isobaric Monte Carlo calculations, the two simulation methods, parallel tempering and multiple histograms, seem to be well suited for getting converged thermodynamic data of the system under study for basically arbitrary values of the temperature and pressure at acceptable computational costs. Since almost smooth dependences

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of thermodynamic parameters on the temperature and pressure, e.g., for the system heat capacity or internal energy, can be obtained in this way, they can be used in a detailed analysis of phases and phase transitions in the system [12,2], leading eventually to a full phase diagram in the temperature–pressure plane.

The main intention of this paper is to test the performance of combined parallel-tempering and multiple-histogram techniques in a case study on selected medium-sized water clusters, $[\text{H}_2\text{O}]_N$, with N ranging between 15 and 21 water molecules. The motivation for this choice is that, according to previous studies (see, e.g., Refs. [13–17]), a structural transformation occurs in isolated water clusters with $N \approx 16$ –21 molecules at zero temperature and zero pressure. This transformation consists in a gradual transition from the most stable structures having all water molecules on the surface of the cluster (*all-surface* structures) to structures with one molecule in the center of the cluster and with the remaining molecules forming a cage around it (*cage-1* structures). Let us briefly summarize the evolution of this observation. A first systematic study on the classical equilibrium structures of water clusters at zero temperature and zero pressure was reported for cluster sizes up to $N = 21$ by Wales and Hodges [13]. In their study, the authors used the simple TIP4P potential [18] for modeling the intra-cluster interactions and the *basin-hopping* methodology for cluster structures optimizations. They concluded from their calculations that up to $N = 21$ all the classical equilibrium structures of $[\text{H}_2\text{O}]_N$ are of the all-surface type except for $N = 19$, for which a disordered cage-like structure was reported as the most stable one. This conclusion was a bit later confirmed for the TIP4P water clusters by Hartke in a study employing a modified *genetic algorithms* approach [14]. In addition to the most stable, all-surface structures, Hartke found, however, that some metastable isomers of $[\text{H}_2\text{O}]_N$, $N = 16$ –18 and $N = 21$, were of the cage-1 type and that they were by 183 meV above the most stable structure for $N = 16$, but only by 22 meV, 48 meV, and 15 meV above the most stable structures for $N = 17$, 18, and 21, respectively. In the following studies [15,16], Hartke repeated the calculations using a more advanced TTM2-F potential [19] and found that, for this potential, the cage-1 structures are preferred in the $N = 16$ –21 range. More specifically, the all-surface structures were found as the most stable ones for $N = 18$ and 20, while the cage-1 structures became most stable for $N = 17$, 19 and 21. Consequently, the all-surface to cage-1 transition was reported to start at $N = 17$, to span the interval of cluster sizes of $N = 17$ –21, and probably to continue up to $N = 25$. Interestingly, another transition to cage-2 structures (two molecules inside) was reported to start at $N \approx 28$. A more recent study using another advanced interaction model (ABEEM/MM) [20], confirmed the observations of Refs. [15,16] up to $N = 24$ and only led to different predictions for $N \geq 25$. For example, the formation of cage-2 structures was predicted in this study to start at $N \approx 33$. A benchmark study on equilibrium structures of $[\text{H}_2\text{O}]_N$ for the size range of $N = 17$ –21 was reported from the group of Xantheas [17]. The calculations of this work were performed at the quantum chemistry level and employed the MP2 correlation method and augmented correlation-consistent basis sets of double and triple zeta quality. This state-of-the-art calculations confirmed the earlier results obtained for the TTM2F model [15,16]; namely, that the all-surface structures are the most stable ones for $N = 18$ and 20, while for $N = 17$, 19 and 21 the most stable structures are of the cage-1 type. To our best knowledge, no results have been reported up to now on the all-surface to cage-1 transition in water clusters of this size range going beyond the zero-temperature and, in particular, beyond the zero-pressure limit. In this work, we try to partly fill this gap. Moreover, we show that the methodology based on the combination of the parallel

tempering approach and multiple histograms can provide a firm base for such an analysis. The 15-molecules water cluster is also considered here since a detailed analysis of its thermodynamic behavior has been presented in a preceding study [21] which may be useful for interpreting the phase behavior of larger cluster sizes.

The paper is organized as follows. First, a summary of the method, code implementation, and computational details are given in Section 2; second, computational data are presented and discussed in Section 3 with the main focus on phase changes in water clusters of considered sizes and, in particular, on the all-surface to cage-1 transition in the solid phase; and finally, conclusive remarks are given in Section 4.

2. Methods and computations

2.1. 2D multiple-histogram method

In the isothermal–isobaric ensemble, the residual part of the mean value of a dynamical parameter, F , is expressed at particular temperature T and pressure P as an ensemble average,

$$\langle F \rangle_{T,P} = \frac{\int_V \int_q F(q, V) \exp\left(-\frac{E^{\text{int}}(q)+PV}{k_B T}\right) dq dV}{\int_V \int_q \exp\left(-\frac{E^{\text{int}}(q)+PV}{k_B T}\right) dq dV}, \quad (1)$$

where q and V are the system configuration and volume, respectively, E^{int} denotes the interaction energy of the system, and k_B is the Boltzmann constant. If the dynamical parameter depends on the system configuration through the interaction energy only,

$$F = F(E^{\text{int}}(q), V), \quad (2)$$

the complicated high-dimensional integral on the r.h.s. of Eq. (1) can be replaced by a computationally much cheaper two-dimensional (2D) integration,

$$\langle F \rangle_{T,P} = \frac{\int_V \int_{E^{\text{int}}} F(E^{\text{int}}, V) \exp\left(-\frac{E^{\text{int}}+PV}{k_B T}\right) \Omega(E^{\text{int}}, V) dE^{\text{int}} dV}{Z_{T,P}}, \quad (3)$$

where $\Omega(E^{\text{int}}, V)$ is the classical density of states and

$$Z_{T,P} = \int_V \int_{E^{\text{int}}} \exp\left(-\frac{E^{\text{int}}+PV}{k_B T}\right) \Omega(E^{\text{int}}, V) dE^{\text{int}} dV \quad (4)$$

is the system configuration integral. Since $\Omega(E^{\text{int}}, V)$ is a function of two independent variables, we denote it hereafter as *two-dimensional (2D) density of states* to distinguish it from the one-dimensional density of states, $\Omega(E^{\text{int}})$, considered in constant-volume calculations.

While the 2D integral on the r.h.s. of Eq. (3) can be rather simply calculated using any method of numerical quadrature, the calculation of $\Omega(E^{\text{int}}, V)$ may represent a rather tough task. However, a sufficiently accurate estimate of $\Omega(E^{\text{int}}, V)$ can be extracted at acceptable computational costs from two-dimensional energy–volume histograms collected from isothermal–isobaric simulations performed over a sufficiently broad range of temperatures and pressures. The methodology for doing so is based on the *multiple-histogram* (MH) approach proposed originally for canonical, constant-volume calculations [9] and extended later to the isothermal–isobaric case [10]. The method basically consists of two phases. First, histograms of E^{int} and V are collected from a series of isothermal–isobaric simulations carried out at various temperatures ($T = T_1, \dots, T_N$) and pressures ($P = P_1, \dots, P_M$). We call this initial phase the *production phase* since the production of 2D energy–volume histograms is the main task of this first step of the calculation. Second, the histograms recorded in the

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