Finite Systems Under Pressure: Assessing Volume Definition Models from Parallel-Tempering Monte Carlo Simulations

Aleš Vitek^{†,*}, Daniel J. Arismendi-Arrieta^{§,#,*}, Martina Šarmanová^{†‡^a}, René
Kalus[†], and Rita Prosmi^{†§*}

[§] *Institute of Fundamental Physics (IFF-CSIC), CSIC, Serrano 123, 28006 Madrid, Spain*

[†] *IT4Innovations, VŠB – Technical University of Ostrava, 17. Listopadu 2172/15, 708 00
Ostrava-Poruba, Czech Republic*

[#] *Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018
Donostia-San Sebastián, Gipuzkoa, Spain*

[‡] *Olga Havlová Grammar School, Marie Majerové 1691, 708 00 Ostrava-Poruba, Czech
Republic*

E-mail: ales.vitek@vsb.cz; darismendi@dipc.org;

rita@iff.csic.es; Phone: +34-91-5616800Ext.941131

^aCurrent address: Faculty of Mathematics and Physics, Charles University, Ke Karlovu 2027/3, 121 16 Praha 2, Czech Republic

Abstract

We have investigated different approaches to handle parallel-tempering Monte Carlo (PTMC) simulations in the isothermal-isobaric ensemble of molecular cluster/nanoparticle systems, for predicting structural phase diagram transitions. We have implemented various methodologies that consist in treating pressure implicitly, through its effect on the volume. Thus, the main problem in the simulations under non-zero pressure, becomes the volume definition of the finite non-periodic system, and we considered approaches based on the particles' coordinates. Various volume models, namely *container-volume*, *particle-volume*, *average-volume*, *elipsoides-volume*, and *convex hull-volume* were employed, and the required corrections for each of them in the Monte Carlo computations were introduced. Finally, we explored the effects of volume/pressure changes for all models on structural phase transitions of a test system, such as the small "ice-like" $(\text{H}_2\text{O})_{12}$ water cluster. The temperature and pressure dependence of the cluster's heat capacity, and energy-volume Pearson correlation coefficient was studied, phase diagrams were constructed, using a multiple-histogram method, and attempts were made to identify phase transitions to particular cluster structures. Our results show significant differences between the employed volume models, and we discuss all pressure-induced, such as solid-solid, solid-liquid and liquid-gas like, phase transformations in the present study.

Introduction

The study of finite-size systems, such as clusters, nanoparticles, or molecular complexes, under pressure has acquired an increasing scientific and technological interest.¹ Such systems are built up by a finite number of particles (*e.g.* atoms and molecules), that can show very rich structural organization originating from the inter-particle interactions, as well as the interaction with the surroundings. Applying pressure to a given system, may cause electronic structure changes that could also modify the properties of the system leading to a completely new behavior.² Thus, nowadays, pressure effects are of great importance

in controlling properties of materials with technological implications in the future designs of such nanobjects.^{3,4} Besides the general interest in understanding the mechanism of the phase transformation sequences, it is also fundamental to explore how such pressure-induced structural transformations occur in the small-scale systems, and how they proceed as a function of their structure size.

Computer molecular dynamics simulations at both classical and *ab initio* levels have been devoted to treat constant-pressure periodic boundary systems, where the system's volume is well defined by the simulation cell. Contrary, in computational studies of finite systems under pressure there are conceptual difficulties, regarding the issue of how pressure can be applied to the system. In this respect, different approaches have been reported to treat the problem. In some of them the pressure is explicitly included in the calculations by introducing a pressurizing medium, *e.g.* an external fluid as a conveyor to control pressure, that mimics the way pressure is applied to clusters/nanostructures in real experiments,⁵ or the Langevin random forces scheme by Kohanoff *et al.*,⁶ and more recently the generalized Langevin-Hull approach.⁷ Such methods are in principal more suitable for heterogeneous mixtures, such as clusters/nanostructures inside fluids, as both the system and surrounding environment can be explicitly considered in simulations. In the case of finite nonperiodic (cluster) systems, we should highlight that in order to obtain a well-defined T-P reservoir the number of particles and the volume of external pressurizing fluid should be large enough, which requires an extra computational cost and could limit the size of the systems to be treated. In addition, one must also determine how the external fluid particles interact to each other, as well as with the cluster, so that such fluid does not crystallize or undergo glass or any other relevant transition of the clusters under study.

Another class of methods are those treating pressure implicitly as a thermodynamic variable, through its effect on volume, its conjugate variable. In this case, the volume of the system becomes very important, and the major problem is how to define the volume for a finite/non-periodic molecular system. An appropriate volume definition is essential, although

there is no a unique prescription on that, and various methods have been reported to calculate finite system volume as a function of particles coordinates. Thus, volume definition methods are varying from those that use all particle coordinates to the ones estimated by some of them, such as the triangulation elimination procedures^{8,9} to identify particles lying on the surface of the system. On the one hand, Berry and co-workers¹⁰ have proposed an isotropic spherical approximation, in which the volume of a cluster configuration is replaced by the volume of a sphere with a radius given by the distance from the center of mass to the outermost atoms. Sun and Gong¹¹ have estimated the total volume as the geometrical volume of an ellipsoid defined by the radii of gyration of the cluster, or as a sum of individual atomic volumes,¹² while Landau¹³ has defined the system volume from the average inter-particle distances. On the other hand, more sophisticated approximations have been also proposed, such as the one by Cococcioni *et al.*¹⁴ who have introduced the quantum volume occupied by the electronic charge density obtained from first-principles calculations,¹⁵ or those based on surface dependent volume definitions,^{8,9,16,17} which rely on finding the minimal polyhedron enclosing the finite system, and thus its respective volume, by performing a search of the smallest convex set that includes all system particles.^{18,19}

Recently, motivated by experimental studies we have investigated structural transitions in rare-gas clathrate-like clusters^{20–34} by constructing phase diagrams as a function of temperature and pressure, in order to identify specific solid-solid like phase transitions, and assist to clarify findings reported by the experiments,^{24,26,27,35,36} especially at the low-temperature regime. Our PTMC simulations aim to provide insights regarding the formation, and pressure transitions of some selective host water networks,^{32,34,37,38} that are able to leverage experimental efforts. We should note that, in general, the investigation of pressure effects on finite systems has been initiated to understand strongly bound system, such as ionic or metallic nanoparticles/nanostructures. Although by extending such approaches to weaker bound molecular systems, we aim to investigate how hydrogen-bonded (water-containing) clusters hold their shape under confinement, and to explore how the bulk properties (e.g.

the 2D polymorphism of confined water,^{39,40} "minimal-ice" crystals, or structure of water nanodroplets^{41–43}) are recovered as the size of the clusters increases. We have found^{32,34} that in connection with the nature of the intermolecular interaction, the effect of the volume definition for simulations at isothermal-isobaric (NPT) ensembles on finite non-periodic systems should be also considered. In this sense, more axiomatic and general methods should be implemented to provide a better description of the finite system shapes. Through the MC configurations' sampling, the employed volume model could directly affect the formation of specific isomeric structures, especially under high pressures, so we have emphasized the need to test and check the effect of volume models on thermodynamic properties of specific cluster systems.^{32,34,44–47}

The goal of our work is to undertake a general investigation of the effects of pressure on cluster structures. Since the probability of sampling cluster's configuration space is governed, under NPT conditions, by the enthalpy, $H = E^{(int)} + PV$, the PV term may become important at high pressures. More specifically, at low pressures $|E^{(int)}| \gg PV$ and the cluster interaction energy dominates, so structures with low energies are preferred to higher-energy structures, more or less independently of their volume. At high pressures, on the other hand, the PV term becomes comparable to the cluster energy, and structures with smaller volume may be favored over those with lower interaction energy. Consequently, there should exist a region on the pressure axis along which a transformation takes place dragging the cluster from the low-energy regions of the cluster configuration space to more compact structures with smaller volumes.^{32,34,45,46,48}

The article is organized as follows: in next section we briefly describe the volume models and their variants implemented in the present study, as well as computational details on how to calculate thermodynamic averages from standard NPT PTMC simulations performed for finite molecular systems by incorporating the corresponding volume model dependent corrections. In section Results and Discussion we focus on NPT PTMC simulations for testing and applying the different types of volume models on specific thermodynamical properties

of an “ice-like” cluster formed by 12 water molecules, and in particular, to illustrate the volume model implication on cluster structural transitions under medium to high pressures. Finally, we summarize our conclusions in the last section.

Methods and Computational Details

Volume Definition Models and Their Variants

In this work, we employed six different volume definition methods for NPT Monte Carlo simulations of finite systems (see Fig. 1). We divided these methods into three groups, depending on how the volume of the cluster is defined. In the first group, the cluster is compressed by a hard-wall spherical container with a variable radius, R_C , and volume is given by $\mathcal{V} = \frac{4}{3}\pi R_C^3$, while the remaining two groups include direct computation of the cluster volume depending on particles’ coordinates.

Figure 1: Schematic representation of volume models for a finite system (see text).

In the first group, we considered two variants, namely M1 and M2 (see the left panel in Fig. 1, respectively), depending on the variable radius of the spherical container. In the simplest M1 model (or *container-volume model*) the radius could be equal or larger than the distance from the center of mass of the cluster to the outermost point-particle,^{10,32,34,45} while in the M2 model the smaller spherical container radius is extended by including the van der Waals radius of an atom in the cluster, *e.g.* the oxygen atom in Fig. 1 (see gray-color spheres).

The second group of methods includes another three methods, namely M3, M4, and M5, while the third group includes the M6 method, as shown in Fig. 1 (see middle and right panels). The key point of these approaches is the computation of the minimal volume of the system, $\mathcal{V}_{\min}(\vec{q})$, as a function of particle coordinates, $\vec{q}$. For the M3, M4 and M5 methods the volume definition depends on all particle positions, while in M6 method the volume of the system only depends on the coordinates of surface particles. Also, we should point out that the M6 model could predict more general system volume shapes than those of the isotropic M1, M2, M4 or even M5 ones.

Thus, in the M3 method (or *particle-volume model*) the total volume of the finite system is expressed as a sum of individual particle volumes, $\mathcal{V}_{\min}(\vec{q}) = \sum_j^N \mathcal{V}_i$, where $\mathcal{V}_i$ is the volume of the i -th particle, and can generally be written as a cubic homogeneous function, f , of its nearest-neighbor distance r_{ij} , i.e. $\mathcal{V}_i = \sum_{j \neq i} f(r_{ij}^3)$.¹² The M4 method (or *average-volume model*) is based on the volume estimation¹³ from the average inter-particle distance, $R = \left(\frac{1}{N(N-1)} \sum_{i,j=1,j \neq i}^N [\sum_{\alpha} (r_{i,\alpha} - r_{j,\alpha})^2] \right)^{1/2}$, where $\alpha = x, y, z$. The total volume is proportional to the cube of R given by, $\mathcal{V}_{\min} = V_{(\text{in})} \frac{R^3}{R_{\text{in}}^3}$, where R_{in} and $V_{(\text{in})}$ are initial characteristic size and volume estimates of the system, respectively, *e.g.* values obtained from the M1 volume model. As shown in Fig. 1, in the M5 method (or *elipsoides-volume model*) the volume of the simulated system is computed from a referential ellipsoid as $\mathcal{V}_{\min} = \frac{4}{3}\pi R_1 R_2 R_3$, where $R_i = \sqrt{\frac{CI_i}{N}}$, ($i = 1, 2, 3$) are the gyration radii, and I are the principal inertia moments of the system with respect to its center of mass. The value of C could be adjusted to an initial

estimate of the volume depending to the general shape of the systems, *e.g.* for a spherical caged structure $C = \frac{3}{2}$.¹¹

In turn, in the M6 method (or *convex hull-volume model*) the total volume of the system is given by the convex hull approximation, that consists in finding the subset of particles forming the minimal convex polyhedron enclosing all point-particles of the cluster.¹⁶ We employed the “Quickhull” algorithm¹⁹ for computing the convex hull of particle configurations. As it can be seen in Fig. 1, in the case of water clusters, we replace the convex hull of points (see inner black line) by convex hull of particles centered on the oxygen atoms with a radius equal to their van der Waals radius of 1.52 Å (see color blue line). So, the total cluster volume for the M6 model reads: $\mathcal{V}_{\min} = V_C + \sum_{i=1}^h S_i R + \sum_{i=1, j \neq i}^{3h/2} \frac{1}{2} R^2 \alpha_{ij} l_{ij} + \frac{4}{3} \pi R^3$, where V_C is the sum of the triangular pyramids volumes, h is the number of convex hull walls, S_i is the i th convex hull wall, α_{ij} is the angle of two adjacent convex hull walls, and l_{ij} is the length of edge at which they intersect.

Thermodynamic Averages from Monte Carlo Simulations

In turn, we aim to compare the different volume approaches in simulations of finite systems using a standard isothermal-isobaric Monte Carlo combined with a parallel-tempering approach (PTMC).^{49,50} Briefly, a thermodynamic quantity, F , is calculated as a weighted mean of the corresponding dynamical parameter, $\mathcal{F}$, averaged over a properly chosen ensemble of systems. The ensemble is uniquely defined by a weight distribution function,

$$F^{(\text{res})} = \frac{1}{Q_{NPT}} \int_0^{+\infty} \left(\int_{\vec{q}} \left[\mathcal{F}^{(\text{res})}(\vec{q}, \mathcal{V}) e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{q}) + P\mathcal{V})} \right] d\vec{q} \right) d\mathcal{V}, \quad (1)$$

where $\beta = k_B T$ and $Q_{NPT} = \int_0^\infty \left(\int_{\vec{q}} \left[e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{q}) + P\mathcal{V})} \right] d\vec{q} \right) d\mathcal{V}$ is the isothermal-isobaric configuration integral. The superscript “res” (residual) means that only interaction part of the system Hamilton function, $\mathcal{E}^{(\text{int})}$, is considered. Since Monte Carlo simulations employing the volume definitions of the first group (M1 and M2 methods) are based on different

algorithm than those employing the other volume definitions (M3–M6 models), we described them separately for each case. For simplicity, the explanations will be provided considering point-particles.

First, let us consider the Monte Carlo simulations using methods M1 and M2. This approach has been previously reported in detail in Ref.,⁴⁵ so we just summarize its main points here. Initially, we use dimensionless coordinates $\vec{\eta} \equiv \vec{q}\mathcal{V}^{1/3}$ to remove the dependence of the limits of the domain of the inner integral in Eq. 1, which yields,

$$F^{(\text{res})} = \frac{1}{Q_{NPT}} \int_0^{+\infty} \left(\int_{B_1^N} \left[\mathcal{F}^{(\text{res})}(\vec{\eta}\mathcal{V}^{1/3}, \mathcal{V}) \mathcal{V}^N e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{\eta}\mathcal{V}^{1/3}) + P\mathcal{V})} \right] d\vec{\eta} \right) d\mathcal{V}, \quad (2)$$

where B_1 is a 3D ball of unit volume centered at the origin of coordinates. Then, we sample N rigid molecules, with translation moves consisting of isotropic displacements of the molecules, and random rotation moves implemented as three subsequent rotations around the laboratory frame axes shifted to the center-of-mass of the rotated molecule. In turn, volume changes have been proposed randomly, and in order to avoid divergences of the volume at low pressures and high temperatures, the maximum radius of the spherical container has been set to $R_{\text{max}} = 200 \text{ \AA}$. Finally, sampling of coordinates $\vec{q}$ and container volume $\mathcal{V}$ have been performed using the standard Metropolis criterion, $P_{\text{old} \rightarrow \text{new}} = \min\{1, \frac{\mathcal{V}_{\text{new}}^N}{\mathcal{V}_{\text{old}}^N} e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{\eta}_{\text{new}}\mathcal{V}_{\text{new}}^{1/3}) - \mathcal{E}^{(\text{int})}(\vec{\eta}_{\text{old}}\mathcal{V}_{\text{old}}^{1/3}) + P(\mathcal{V}_{\text{new}} - \mathcal{V}_{\text{old}}))}\}$, for accepting or rejecting translation, rotation, and volume moves.⁴⁵

For the second and third groups of methods (M3–M6 volume models), based on the direct computation of system volume, we rewrite Eq. 1 as follows:

$$F^{(\text{res})} = \frac{1}{Q_{NPT}} \int_{\vec{q}} \left(\int_{\mathcal{V}_{\min}(\vec{q})}^{\infty} \mathcal{F}^{(\text{res})}(\vec{q}, \mathcal{V}) e^{-\beta(P\mathcal{V})} d\mathcal{V} \right) e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{q}))} d\vec{q}, \quad (3)$$

$$Q_{(NPT)} = \int_{\vec{q}} \left(\int_{\mathcal{V}_{\min}(\vec{q})}^{\infty} e^{-\beta(P\mathcal{V})} e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{q}))} d\mathcal{V} \right) e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{q}))} d\vec{q}, \quad (4)$$

where $\mathcal{V}_{\min}(\vec{q})$ is the “minimal volume” enclosing the simulated system at configuration $\vec{q}$,

as calculated by M3 to M6 models.

The mean value of a thermodynamic quantity F , such as the mean interaction energy, $E^{(\text{int})}$, and mean volume, V , has been obtained by analytically calculating the inner (volume) integrals in Eqs. 3 and 4, as follows:

$$E^{(\text{int})} = \frac{\int_{\vec{q}} \mathcal{E}^{(\text{int})}(\vec{q}) e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{q}) + P\mathcal{V}_{\min}(\vec{q}))} d\vec{q}}{\int_{\vec{q}} e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{q}) + P\mathcal{V}_{\min}(\vec{q}))} d\vec{q}}, \quad (5)$$

and,

$$V = \frac{1}{\beta P} + \frac{\int_{\vec{q}} \mathcal{V}_{\min}(\vec{q}) e^{-\beta(E^{(\text{int})}(\vec{q}) + P\mathcal{V}_{\min}(\vec{q}))} d\vec{q}}{\int_{\vec{q}} e^{-\beta(E^{(\text{int})}(\vec{q}) + P\mathcal{V}_{\min}(\vec{q}))} d\vec{q}}. \quad (6)$$

As mentioned above, the Monte Carlo algorithm is slightly different from the algorithm implemented for simulating a cluster using the M1 and M2 volume models. In the M3–M6 cases, we only sample molecular translations and rotations using the Metropolis criterion reads now as, $P_{\text{old} \rightarrow \text{new}} = \min\{1, e^{-\beta(\mathcal{E}^{(\text{int})}(\vec{q}_{\text{new}}) - \mathcal{E}^{(\text{int})}(\vec{q}_{\text{old}}) + P(\mathcal{V}_{\min}(\vec{q}_{\text{new}}) - \mathcal{V}_{\min}(\vec{q}_{\text{old}}))}\}$. The mean energy of the system, E , is calculated by considering only the simple average of sampled energies, $\mathcal{E}^{(\text{int})}(\vec{q})$, while in order to compute the mean volume of the simulated system, V , we need to add a correction of $1/\beta P$ to the average value of $V_{\min}$, *i.e.* $V = V_{\min} + \frac{1}{\beta P}$. In turn, the enthalpy, H , of the system is computed as $H = E + PV_{\min} + k_B T$, while the heat capacity, C_p , and the Pearson correlation coefficient for volume and energy, $\rho_{\mathcal{E}, \mathcal{V}}$, are given by,

$$C_p^{(\text{res})} = \left(\frac{\partial H}{\partial T} \right)_P = \frac{1}{k_B T^2} (\langle (\mathcal{E} + P\mathcal{V}_{\min})^2 \rangle - \langle \mathcal{E} + P\mathcal{V}_{\min} \rangle^2) + k_B, \quad (7)$$

and

$$\rho_{\mathcal{E}, \mathcal{V}} = \frac{\langle \mathcal{E}\mathcal{V}_{\min} \rangle - \langle \mathcal{E} \rangle \langle \mathcal{V}_{\min} \rangle}{\sigma_{\mathcal{E}} \sigma_{\mathcal{V}_{\min}}}, \quad (8)$$

respectively, with $\sigma_{\mathcal{E}}$ and $\sigma_{\mathcal{V}_{\min}}$ being the variances of the interaction energy and volume, respectively. We should also note that the volume correction $1/(\beta P)$ is significant only for low pressures and high temperatures, and the related correction just raises the heat capacity by a constant factor of k_B .

In the specific case of a dynamical parameter that depends on the system configuration only through the interaction energy and system volume, $F = F(\mathcal{E}^{(\text{int})}(\vec{q}), \mathcal{V})$, such as enthalpy, heat capacity and energy-volume Pearson coefficient, corresponding mean value is expressed at particular temperature T and pressure P as,

$$F^{(\text{res})} = \frac{\int_V \int_{\mathcal{E}^{(\text{int})}} F(\mathcal{E}^{(\text{int})}, \mathcal{V}) \exp\left(-\frac{\mathcal{E}^{(\text{int})} + P\mathcal{V}}{k_B T}\right) \Omega(\mathcal{E}^{(\text{int})}, \mathcal{V}) d\mathcal{E}^{(\text{int})} d\mathcal{V}}{\int_V \int_{\mathcal{E}^{(\text{int})}} \exp\left(-\frac{\mathcal{E}^{(\text{int})} + P\mathcal{V}}{k_B T}\right) \Omega(\mathcal{E}^{(\text{int})}, \mathcal{V}) d\mathcal{E}^{(\text{int})} d\mathcal{V}}, \quad (9)$$

by replacing the complicated high-dimensional integral in Eq. 1 by a computationally much cheaper two-dimensional integration, with $\Omega(\mathcal{E}^{(\text{int})}, \mathcal{V})$ being the classical density of states of the system. The multiple-histogram (MH) approach has been used to obtain accurate estimate of $\Omega(\mathcal{E}^{(\text{int})}, \mathcal{V})$ by constructing two-dimensional energy-volume histograms from the NPT PTMC simulations over a broad range of temperatures and pressures.⁴⁶

A Test Study on the "ice-like" Water Cluster

Water clusters have been extensively studied by both theory and experiment,^{45,51–59} and considerable insight has been gained on lower-energy structures as a function of the cluster size, classified into two broad categories, such as 2-D (ring or chain) structures and 3-D (cage, prism, or cube and so on) structures.⁶⁰ However, there is still a considerable lack of understanding of the transitions from properties and structures of small-, intermediate-sized clusters to those of the large-sized clusters.^{43,61–63} Previous studies on selected medium-size water clusters, with up to 30 molecules, have been reported,^{56,58,59,64} although most of them deal mainly with the structural transformation of such clusters from global cluster structure optimization methods, while phase diagrams of small water clusters have been only presented up to pressures of 1 GPa.⁴⁶ Also, just recently different techniques have been employed to sample various potential energy surfaces available, for extracting thermodynamic properties, and the contribution of the potential features at finite temperatures has been explored^{52,58} for small water clusters. Here, we are interested in the effect of pressure on structural changes

by implementing various types of volume models in the NPT PTMC simulations. We choose as a test case the $(\text{H}_2\text{O})_{12}$ cluster, as it is large enough to show various isomeric structures, and at the same time accessible for performing a series of calculations for various volume models' assessment.

Following our previous studies, we employed the TIP4P/ice water model⁶⁵ for representing the intermolecular interactions, as it yields the best estimations of the water solid-phase properties, and there is in general a good correspondence with the relative isomer energetics for various water clusters compared with other water models and *ab initio* calculations.^{56,66} The TIP4P/ice is a three-site description of water molecule (rigid at fixed C_{2v} geometry with OH distance of 0.9572 Å and $\angle\text{HOH}$ of 104.5°), with partial charges of -1.1794 e, placed at 0.1577 Å aside from the O atom along the C_2 -axis of the molecule, and +0.5897 e placed at each hydrogen atom, while a single Lennard-Jones interaction site is placed on oxygen atom, with parameters $\sigma=3.1668$ Å and $\epsilon=0.0382540446$ eV.

Briefly, we have employed a two-dimensional parallel-tempering algorithm in the present NPT MC simulations,⁶⁷ using periodic swaps of configurations and volumes between replicas of the simulated system. The standard Metropolis-Hasting criterion⁶⁸ for the acceptance probability has been applied, as mentioned above, for randomly selected pairs of replicas with neighboring temperatures or pressures. The MC simulations have been carried out in parallel for 23 values of pressure (from $P_1 = 3$ kPa to $P_{23} = 10$ GPa) and 18 values of temperatures (from $T_1 = 30$ to $T_{18} = 1000$ K) with nonuniform exponential increase of spacings for an efficient configuration sampling at low temperatures and in the high pressure region. All the above mentioned M1-M6 volume models, including the volume corrections as described in Section 2, are used to approximate the effect of the external pressure. In total, 414 replicas of the system have been simulated for each volume model, in parallel, performing 5×10^7 MC steps to reach the thermodynamic equilibrium of the system, and another 5×10^7 MC whole-cluster and volume moves were carried out for each replica to collect data for subsequent averaging. The data for the final analysis were collected every 50 MC steps to

avoid correlations. The MH method was used to calculate the 2D density of states, $\Omega(\mathcal{E}^{\text{int}}, \mathcal{V})$, needed in Eq. 9. For all the 414 replicas, we have produced 2D energy-volume histograms over an exponentially distributed energy-volume 600×600 grid using the raw data extracted from performed NPT PTMC calculations. Subsequently, we have used them to compute mean thermodynamic parameters over 200×200 temperature-pressure points, instead of the initially 414 ones to allow for a subtle analysis needed for phase diagrams construction.⁴⁶

Results and Discussion

Meanwhile, thermodynamic averages, such as enthalpy, H , constant-pressure heat capacity, C_p , and Pearson correlation coefficient for energy and volume, $\rho_{E^{(\text{int})}, V}$, have been computed, and temperature-pressure phase diagrams have been then constructed for each M1-M6 volume models for the $(\text{H}_2\text{O})_{12}$ cluster. Resulting phase diagrams are shown in Figure 2. The contour lines correspond to the C_p values, and coexistence curves are also plotted showing how the phase diagram is divided into several regions related to different structural transformations of the cluster. We should note however, that clusters exhibit smooth phase changes compared to sharp transitions seen in the bulk. In Figure 2, maxima of heat capacity along temperature (see circle symbols) are used to indicate liquid-to-gas like (evaporation) and solid-to-liquid like (melting) transitions, while minima of the Pearson correlation coefficient along pressure (see square symbols) correspond to solid-to-solid like transitions. Phase transitions are defined for macroscopic systems, however terms such as evaporation and melting are also used in finite systems indicating the temperature-pressure region where the cluster starts to explore larger phase space, though structural transformations similar to phase transitions.⁶⁹

By comparing the phase diagrams obtained from each of the M1-M6 volume models (see Figure 2), one can see similarities between few of them, such as the M1 and M2 models, and clear differences between most of them, especially in the high pressure regions. In particular,

Figure 2: Temperature-pressure phase diagrams of the $(\text{H}_2\text{O})_{12}$ cluster obtained from the NPT PTMC simulations for each of the M1-M6 models (see text).

the coexistence curve corresponding to the melting transition shows similar behavior for all models, with small deviations around 200 K to the melting temperature at low pressures, and significant differences at high pressures, while the curve for the liquid-gas transition seems to be more sensitive to the volume model employed. The evaporation of the cluster starts to occur at temperatures above 250 K for the M6, 300 K for the M1/M2 and M4, and 400 K for the M3 and M5 models. Also, significant differences are observed in the solid-solid like transitions at low-temperature/high-pressure regime. We will discuss this later on in connection to structural changes predicted for the $(\text{H}_2\text{O})_{12}$ cluster by each model.

Figure 3: Mean volume, V , as a function of pressure at the indicated temperatures, as computed by the NPT PTMC simulations using each M1-M6 volume model for the $(\text{H}_2\text{O})_{12}$ cluster. Solid and dashed lines correspond to estimates obtained with and without the correction in the M3-M6 models, respectively (see text in Section 2).

So, in the following, we describe in more details the above mentioned aspects of the phase diagrams. First, Figure 3 shows the dependence of the system mean volume as a function of

the pressure at selected values of temperature $T = 62, 166, 249$ and 600 K , for all volume models considered (see Fig. 1). One can see that volume corrections (see solid and dashed lines of the same color in Fig. 3) in the volume models M3 up to M6 are very significant at the low pressure and temperature regimes, and by including them, the computed volume values of these models are then comparable with volume predictions from the M1 and M2 models. We found that the M2 model overestimates volume at all pressure and temperature values studied compared to all other models considered. The M2 and M4 models predict close volume values for pressures above $\approx 2 \times 10^8$ Pa for all temperatures, while in contrary the M5 and M6 models show similar behavior for pressures below 10^9 Pa. Also the M1 model shows a faster volume decrease than the M6 for pressures lower than 10^9 Pa, while for higher pressures both models predict similar volume values. We observe such trends in the volume definition by each model as temperature increases up to ≈ 250 K, while at very high temperatures, as expected all volume models show almost the same dependence, with the M6 model predicting the lowest volume of the cluster at high values of pressure. As we can see in Fig. 3 the convex-hull volume falls down to zero, that, as we will see later on, it is due to the sampling of planar and linear configurations of the system.

It is not straightforward to analyze the effect of each volume model at specific T-P conditions, as no clear trends are seen in the mean volume dependence at moderate-pressure values and low temperatures. However, one can rationalize on the differences of the implemented volume models, as displayed in Fig. 3 for different TP thermodynamic conditions. Such differences are due to the overestimation of the minimal volume of the cluster, either by the isotropic or anisotropic volume changes of the cluster, *e.g.* the vdW-container M2 model, or the more sophisticated convex-hull M6 one. The volume model directly affects the NPT MC configurations sampling and thus the preference of specific cluster structures, especially at high pressures. The probability of sampling the cluster configuration space is governed by enthalpy, so as pressure increases the PV term becomes important, and low-energy cluster structures are transformed to compact (smaller volume) configurations. Thus,

one can also identify structural transitions, when a sudden drop-off appears in the volume curves in Fig. 3, such as those of solid-to-solid like at low temperatures of $T = 62$ and 166 K, and at pressures values above 10^8 Pa. Thus, for the lower temperature of 62 K, the first step occurs at pressure values of 0.35 , 0.25 , 1.3 , 3 , and 1.9 GPa, for the M1, M2, M4, M5 and M6 model, respectively, while there is no step for the M3 model.

Figure 4: Heat capacity, C_p , as a function of temperature and pressure as estimated from the NPT PTMC calculations using the M1–M6 volume models for the $(\text{H}_2\text{O})_{12}$ cluster.

In Figure 4 we display the calculated heat capacity, C_p , curves as a function of the temperature at selected pressure values for all volume models as obtained by the NPT PTMC simulations. The most prominent peaks correspond to the evaporation of the $(\text{H}_2\text{O})_{12}$ cluster, while smaller peaks observed at lower temperatures represent the solidification/melting of the cluster. By analyzing the effect of each volume model on the $C_p(T)$ curves, we found that for pressure values below 10^8 Pa the melting peak is around 200 K, and presents slight

mutual shifts for the M1-M6 volume models. For example at $P = 1$ MPa this $C_p(T)$ peak can be easily identified at $T = 215, 220, 191, 196, 196$ and 201 K, while at higher pressure of $10/100$ MPa it becomes more pronounced at $220/215, 220/201, 191/196, 196/205, 196/205$, and $196/205$ K for the M1 to M6 volume models, respectively. As it can be seen for pressures up to 10^8 Pa the volume models do not affect significantly the cluster melting temperature. These values of the melting/solidification temperature are found in an overall good agreement with estimates reported previously for $(\text{H}_2\text{O})_{12}$ from $C_v(T)$ calculations using the TIP4P/ice, as well as other water model potentials for this cluster.^{52,54,57,58}

In turn, as the temperature increases a sharper evaporation peak could be observed at lower pressures, although its position is highly dependent on the type of volume model employed. We should note that the M1 and M2 container-based models overestimate volume during the evaporation of the cluster, stabilizing in this way the liquid-like phase, while the M6 method provides a more reliable volume estimate than that of container-based models under study, when one or a few molecules drift away for the liquid-like cluster. In addition, as pressure increases (*e.g.* 10^8 Pa) the $C_p(T)$ curves obtained from each volume model show further remarkable differences. Given that the M1 model is the most widely used and that the M6 model represents the most axiomatic approach to the finite system volume specification, we thus consider to discuss below their results in more detail.

In Figure 5 we display 3D plots of the cluster heat C_p capacity, and Pearson $\rho_{E^{\text{int}},V}$ correlation coefficient versus temperature and pressure computed using the M1 and M6 volume models for the $(\text{H}_2\text{O})_{12}$ cluster. As is clear from Figure 4 all features are seen here for these two models, such as the two maxima on the heat-capacity landscape corresponding to solid-liquid like and liquid-gas like transitions, as well as the deep valleys (minima) on the $\rho_{E^{\text{(int)}},V}$ surface at low temperatures and high pressures corresponding to solid-solid like transitions of the cluster. Interestingly, one should also notice that a double evaporation peak appears in the heat-capacity plot of the M6 model (see upper-right panel of Fig. 5), that is attributed to a gradual disintegration of the cluster, with evaporation of one water

Figure 5: Heat capacity, C_p , (upper panels) and energy-volume Pearson correlation coefficient (lower panels) calculated from the NPT PTMC simulations using the M1 (left panels) and M6 (right panels) volume models, as a function of temperature and pressure for the $(\text{H}_2\text{O})_{12}$ cluster.

molecule, and proceeding with further fragmentation of the cluster, to more than two groups of molecules, at higher temperatures. For example, we found that at pressure of 10^6 Pa, the cluster starts to disintegrate gradually at temperature around 250 K with only one water molecule evaporated. Then, additional water molecules or even subgroups of molecules have been released from the cluster as its temperature increases up to $T = 330$ K, and finally the cluster is completely fragmented to gas-phase molecules at temperatures above $T = 400$ K.

Figure 6: Energies and (selected cubic and non-cubic) structures of $(\text{H}_2\text{O})_{12}$ local isomers determined by enthalpy optimizations of configurations sampled at low pressures in PTMC simulations using the M6 model.

In order to characterize the observed transitions of the cluster it is useful to refer to the distribution/abundance of local isomeric structures. The simulated annealing method⁷⁰ adapted to the NPT ensemble, with fast cooling and low initial temperature, has been used to optimize structures to the nearest local minimum on the interaction enthalpy surface. In Figure 6 we show the interaction energies of the lowest 176 isomers of a total of 762 isomers

obtained from such local enthalpy optimizations. In total 6912 configurations have been locally optimized, starting from 192 initial randomly selected configurations for each grid point from the PTMC calculations performed for the M6 volume model, for temperatures up to $T = 294$ K and pressures up to 10^5 Pa. Further, using a classification scheme based on O-O bond-distances we identified 39 different cubic like configurations and 723 configurations as non-cubic like structures up to energies of -5.3 eV. In the inset plots of Fig. 6 a few representative configurations of such isomers are depicted: the cubic isomer 1 with energy of -5.541 eV, then the isomers numbered 4 and 6 with energies -5.498 eV and -5.486 eV, respectively, as well as the non-cubic isomers 23 and 32. Specifically, the lowest three isomers are almost isoenergetic within 0.005 eV, followed by other cubic-like isomers, which are separated from the lowest group by gaps of 0.038 and 0.012 eV. Noteworthy, non-cubic structures appear at higher energies of -5.416 eV.

Figure 7 shows relative populations of the six lowest $(\text{H}_2\text{O})_{12}$ isomers (see color solid lines) as a function of temperature as obtained for pressures of 10^5 , 10^7 , 2×10^8 , and 1.4×10^9 Pa. In addition, relative abundances of cubic/non-cubic isomers are also shown in this figure (see dashed and dash-dotted lines, respectively). One can see that at pressures below 2×10^8 Pa the lowest two cubic isomers dominate the population of the $(\text{H}_2\text{O})_{12}$ cluster, with isomer 1 contributing by around 60% at low temperatures, while for temperatures above 80 K isomer 2 has the major contribution, around 50%. Isomer 3 also contributes to the overall populations of around 20% to the population, and as temperature increases (above 120 K), isomers 4-6 are also observed, although only at marginal abundances. One should also note the effect of pressure, especially on the cubic to non-cubic transition with the melting temperature shifted from 195 to 260 K as pressure increases, stabilizing/favoring in this way the cubic like isomers.

In turn, solid-solid like transitions are also observed at low temperatures as pressure increases. They are observed for M1/M2/M4/M5 and M6 models (see Figs. 2 and 5), and we could identify different structural changes in the transition regions depending on the volume

Figure 7: Relative abundances of the six low-lying (see Fig. 6) cubic-like $(\text{H}_2\text{O})_{12}$ isomers (color solid lines: blue=isomer 1, red=isomer 2, green=isomer 3, magenta=isomer 4, orange=isomer 5, cyan=isomer 6), and of the cubic/non-cubic structures (black dashed and dash-dotted lines, respectively) depicted for selected pressure values as a function of temperature. All data are obtained from the NPT PTMC calculations employing the M6 volume model.

Figure 8: Representative structural changes observed in the $(\text{H}_2\text{O})_{12}$ cluster at low temperatures as a function of pressure as obtained from NPT PTMC simulations employing the M1-M6 volume models.

model employed. Figure 8 depicts some of the most representative structural motifs detected in $(\text{H}_2\text{O})_{12}$ cluster at elevated pressures, such as cubic-like tubes, five- and four-membered water rings, water-centered cages with one molecule inside (*cage-1*), spheroid single cage, flat sandwich-like structures, and even chain-like structures. One can see that almost all the volume models predict a transition from cubic to non-cubic (formed by pentagons and tetragons rings) structures, although as pressure increases the M1-M2-M4-M5 results predict *cage-1* like structures, then the M1-M2 models predict spheroid-cage structures, the M4-M5 models lead to irregular *cage-1* ones, while the M6 model shows a transition to planar and also to linear chain-like isomeric structures. Clearly, the solid-solid transformations are hard to determine, and the differences obtained from the employed approaches reflect the effect of volume models used, indicating that the isotropic spherical models of cluster volume may oversimplify the underlying physics. In the case of the M6 model, it is able to predict water structures that correspond to anisotropic volume changes, as those reported recently,^{39,40} while the M1 model imposes a symmetric (spherical) compression on the cluster, and that explains the quasi-spherical cluster structures observed. In other words, the convex-hull method allows for a phase exploration without restrictions in volume shapes, thus at high pressures predicts planar and linear cluster structures, similar to the experimentally observed 2D polymorphism of confined water,^{39,40} while at low pressures the observed ice-like structures could be related to minimal-ice crystals^{41,43} or smallest-structures of water-nanodroplets.⁴² Thus, it would be possible, by employing the M6 model, to observe the evolution of such polymorphism of water as the number of water molecules grows.

Summary and Conclusions

In this study, we have undertaken a general investigation of the effects of pressure on finite nonperiodic systems, such as clusters or nanostructures, by treating pressure implicitly through its effect on system volume. Specifically, we have implemented different types of

volume models into NPT PTMC simulations, allowing to extend computations on larger size systems. Some of these models impose isotropic and other anisotropic compression of the cluster, with some of them being more axiomatic than others. By replacing the spherical *container-volume* approximations (M1 and M2 models) with models exploiting the information about the system configuration (M3-M6 models), which provide moderately more complicated particles' coordinates-dependent shapes, we have shown that one should incorporate the corresponding volume model dependent corrections to thermodynamic averages of interest, such as interaction energy, enthalpy, and heat capacity. In this way, we can explore the effects of pressure on the structural transitions and understand the stability of structural transitions of clusters/nanoparticles. Using such model approximations to define the system volume, structural and thermodynamic properties have been calculated and have been used to construct temperature-pressure phase diagrams. The performance of the tested models has been assessed for the specific case of $(\text{H}_2\text{O})_{12}$ cluster.

We found that depending on the volume definition the observable properties have different outcomes. In particular, by incorporating the effects of pressure in the study of both evaporation and melting phase changes of the $(\text{H}_2\text{O})_{12}$ cluster, our results show small deviations around 200 K for the melting transition at low and medium pressures, while much larger deviations are observed for most volume models at high pressures. The evaporation of single molecules and/or subgroups of molecules from the cluster is found to be more sensitive to the volume model employed, with liquid-gas transition observed between 250–400 K at low pressure, depending the model used. Noteworthy, a double-evaporation peak is observed for the M6 model (convex-hull) at low pressures attributed to the gradual disintegration of the cluster. We have also found that the effects of pressure are quite important in the solid-solid structural changes of the cluster and present some evidences for volume model dependent structural transformations at low temperatures. On the basis of the present NPT PTMC results, we may conclude that both M1 and M2 (rigid-wall container) and M3-M5 (particle coordinates-based) models overestimate the volume of the studied finite system, as

well as the M6 (convex-hull) model in the case of the evaporation, so the predicted transition pressures tend to be higher. Although, the convex hull-volume model estimates are the closest to minimal volume of the cluster at very high pressures due to its nature, it predicts planar and even linear structures, similar to 2D polymorphism of confined water reported in the literature. Thus, the M6 model could predict more general volume systems shapes than the remaining volume models, which show mainly compact and almost spherical caged structures. In spite of these, the volume values predicted by the M6 method are found to be very close to those of M5 method for pressures up to 2 GPa. We should highlight that solid-solid transformations are the hardest to be determined and thus, more efficient methods for structure identification and classification, such as machine-learning computational tools employing, for example, order parameter metrics,⁷¹⁻⁷³ should be implemented and/or developed.

In general, as the volume of a finite cluster is an important parameter that facilitates to identify structural changes in the systems along the pressure axis, it is essential to check for its best description depending on the most general overall shape of the nanoparticle system. Although there is not a unique volume definition of a finite (nonperiodic) system, work is in progress to check approaches based on electronic coordinates of the clusters by carrying out quantum *ab initio* electronic structure calculations.^{14,15} We consider that both convex-hull (M6) and such quantum-volume approaches could be the most axiomatic volume models, to serve as parameter-free reference methods for studying weakly-bound cluster systems under pressure. In principle, the trends seen here for $(\text{H}_2\text{O})_{12}$ cluster should be general, and will also remain for larger-size water clusters considering the same TIP4P/ice potential model. Thus, it would be a natural extension of the present work to investigate the pressure-induced structural transitions of larger, *e.g.* up to an estimated critical cluster size, water clusters, which could provide information on stabilization of metastable configurations, and insights for understanding the relation with bulk transitions.

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Graphical TOC Entry