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Computational investigations of the thermodynamic properties of size-selected water and Ar–water clusters: High-pressure transitions

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Classical parallel-tempering Monte Carlo simulations in the isothermal-isobaric ensemble were carried out for the (H₂O)₂₀ and Ar(H₂O)₂₀ clusters, over a wide ranges of temperatures (30–1000 K) and pressures (3 kPa–10 GPa) in order to study their thermodynamical properties and structural changes. The TIP4P/ice water model is employed for the water-water interactions, while both semiempirical and *ab initio*-based potentials are used to model the interaction between the rare-gas atom and water molecule. Temperature-pressure phase diagrams for these cluster systems were constructed by employing a two-dimensional multiple-histogram method. Structural changes were detected by analyzing the heat capacity landscape and the Pearson correlation coefficient profile for the interaction energy and volume. Those at high pressure correspond to solid-to-solid transitions and are found to be related to clathrate-like cages around the Ar atom. It is also shown that the formation and thermodynamic stability of such structures are determined by the intermolecular interaction between the rare-gas atom and host water molecules.

1 Introduction

Clusters of finite size are to a certain extent an ideal tool to investigate macroscopic properties on a microscopic level and to answer fundamental questions on the transition from the gas to condensed phase. As model microsolutions they retain many characteristics of the bulk, are theoretically tractable, and represent thus a useful approach to more complicated systems. In the case of water clusters, specific size systems are currently receiving considerable attention, as models for inclusion compounds of different type of clathrate hydrates. By assuming that hydrate formation starts from conceivably stable clusters¹, and considering that usually these systems, *e.g.* specific size gas-water clusters, are not accessible to experimental investigations, then employing water clusters as the building blocks of those hydrate lattices can be used as a model to probe the relevant guest/host interactions^{2–7}, as well as to derive and to test intermolecular potentials that can be also used under different thermodynamic conditions^{8–11}.

In order to provide insights into these aspects, rare-gas (Rg) hydrates are significant model systems for the study of water-gas interactions, especially if we want to describe the nature of repulsive interactions under high pressure conditions^{9–12}.

A number of spectroscopic and diffraction studies have been conducted to explore at which conditions (pressure, temperature, composition of the aqueous solution) bulk rare-gas hydrates may be formed or decomposed and what types of them may be obtained at these conditions^{12–14}. The light He and Ne atoms are too small to stabilize any cage, forming clathrates very similar to the original ice frameworks^{4,15}, although there is some evidence for the formation of Ne hydrate¹⁶. In turn, the heaviest Rg hydrates are the most notable exception to the rules that enable the prediction of the expected clathrate by considering the relationships between guest size and cage size. At pressure of 30 MPa for both Ar and Kr hydrates the sII (cubic structure II) is the stable structure, while Xe forms sI (cubic structure I). In high-pressure regimes (see Refs. 12,14 and references therein) Ar clathrate hydrate transforms to the sH (hexagonal structure H) form at 0.46 GPa, while the Kr hydrate transforms from the initial sII to sI at 0.45 GPa before transforming to sH at 0.75 GPa, and Xe sI hydrate transforms to a sH at 1.6 GPa. However, there is not always a good agreement between different sets of experiments and accepted resolution of the discrepancy.^{17–21} Therefore, theoretical attempts to describe structural transitions in these clathrate hydrates could provide useful information, and could serve to settle such disagreement.

The majority of results reporting structural changes for water clusters doped with impurities do not consider the temperature and pressure effects^{22,23}, and only recent studies have addressed this issue employing genetic algorithms^{24,25} or more

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advanced Monte Carlo simulations^{26–28}. Simulations of such systems is a computational challenge, as their potential energy landscapes are often rugged, with a large number of close-lying local minima that requires considerable computer time for sampling across them. Thus, in this article computer simulations are performed based on the parallel tempering Monte Carlo method in the isothermal-isobaric (*NPT*) ensemble, aiming to sample the full configuration space of the system and to provide a complete description of the cluster phase behavior under various temperature–pressure conditions. In this context, it is clear that grids of simulated temperatures and pressures will usually be strongly limited due to the computational demands, and to this end we adopt a recently implemented interpolation scheme, called multiple-histogram technique²⁸, for constructing heat capacity phase diagrams for specific size clusters. The goal of our study is twofold: (a) to calculate thermodynamical properties and structural changes caused by a heavy Ar atom embedding in the small polyhedral cages of the sI, sII and sH structures, and (b) by employing two completely different type of Rg-water interaction potentials and examining the conditions at which such structures are formed and stabilized, more information about the underlying intermolecular potential energy surface (PES) between the Rg and host water molecules will be revealed.

The article is organized as follows. In the next section we briefly discuss the methods employed and the computational details of the simulations, together with the description of the potential terms used for the water–water and Ar–water interactions. The results on the (H₂O)₂₀ and Ar(H₂O)₂₀ systems are presented and discussed in section 3. The structural changes observed in the phase diagrams, induced by increasing pressure/temperature, are examined in terms of the intermolecular Ar–water potential and a comparison with experimental data available for Ar hydrate is presented. Finally, some concluding remarks are given in the last section.

2 Methods and Computational details

2.1 Parallel-tempering Monte Carlo and 2D Multiple-histogram calculations

A two-dimensional parallel-tempering (PT) algorithm has been used to accelerate the convergence of the present *NPT* Monte Carlo (MC) simulations²⁹. The PT methodology consists in simulating many systems of identical composition (replicas), but under different external conditions (temperature and pressure), in parallel and in periodically exchanging generalized configurations between different systems. Usually, only neighboring systems are selected for this exchange move to keep the exchange probability sufficiently large. Here, an exchange move has been proposed for a randomly selected pair of neighboring systems each time one MC step has been

completed for all replicas.

In the *NPT* ensemble, the residual part of the mean value of a dynamical parameter, F , if it depends on the system configuration only through the interaction energy and system volume, is expressed at particular temperature T and pressure P as,

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

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

$$Z_{T,P} = \int_V \int_{E^{\text{int}}} \exp\left(-\frac{E^{\text{int}} + PV}{k_B T}\right) \Omega(E^{\text{int}}, V) dE^{\text{int}} dV \quad (2)$$

is the system configuration integral, V is the volume of the system, E^{int} is the interaction energy of the system, and k_B is the Boltzmann constant.

For a sufficiently accurate estimate of $\Omega(E^{\text{int}}, V)$, we employed the multiple-histogram (MH) approach (see Ref. 28 and references therein). First, 2D energy-volume histograms are collected from a series of *NPT* PTMC simulations performed over a sufficiently broad range of temperatures and pressures, and then the 2D density of states, $\Omega(E^{\text{int}}, V)$, required for the evaluation of ensemble averages, is obtained by an iterative scheme over the grid of interaction energies and volumes. The PTMC calculations are carried out for 414 replicas of the system covering 23 values of pressure (P_m) in the range of 3 kPa to 10 GPa, and 18 temperatures (T_n) in the range of 30 to 1000 K. We should note that the upper limit in the temperature, which goes beyond a physically relevant value, is necessary for achieving convergence in the PT simulations. In Table 1 all possible combinations of these 414 systems simulated in parallel are listed. For both temperatures and pressures, an exponential increase of spacing is used, in order to efficiently sample the system configuration space, as energy and volume fluctuations are small at low temperature and high pressure. The external pressure is modeled by a hard-wall spherical container of a variable radius, with an upper limit set to 200 Å to control the volume growth at low pressures and high temperatures.

It should be noted here that the high temperature values are used for achieving a rapid convergence in the PTMC calculations. In total, 5×10^7 MC steps are performed for reaching each system at thermodynamic equilibrium, and 5×10^7 more MC steps are then used to generate the energy-volume histograms by collecting data from every 50th of these additional steps. The 2D density of states is calculated from 414 energy-volume histograms, each of them having 2000000 points (1000 different energies and 2000 different volumes), with exponential increase of spacing for increasing interaction energy and volume. From the 2D density of states, we finally computed heat capacities and Pearson correlation coefficients

Table 1 Temperature (T_n) and pressure (P_m) values used in the present PTMC simulations.

n/m	T_n [K]	P_m [GPa]
1	30	0.000003
2	38	0.00001
3	47	0.00003
4	62	0.0001
5	80	0.0003
6	104	0.001
7	132	0.003
8	166	0.01
9	203	0.03
10	240	0.1
11	261	0.15
12	294	0.2
13	330	0.3
14	400	0.5
15	490	0.7
16	600	1
17	750	1.4
18	1000	2
19		2.7
20		3.8
21		5.4
22		7.5
23		10

for 400 different temperatures and 400 different pressures, in total 160000 values of measured parameters in the (T, P) plane. One can see the main advantage of the method: from the *NPT* PTMC calculations we obtained values of thermodynamics parameters only for 414 temperature-pressure pairs, while with the 2D MH method the thermodynamics parameters are evaluated for 160000 temperature-pressure points.

We used the heat capacity as the tool for studying the phase change properties of the clusters in the direction of temperature and the Pearson correlation coefficient in the direction of the pressure. In this work, the residual part of the constant-pressure heat capacity is used,

$$C_P^{\text{res}} = \frac{1}{k_B T^2} \left[\left\langle \left(H^{\text{int}} \right)^2 \right\rangle - \left\langle H^{\text{int}} \right\rangle^2 \right], \quad (3)$$

where $H^{\text{int}} = E^{\text{int}} + PV$, and the Pearson correlation coefficient for volume and energy,

$$\rho_{E^{\text{int}}, V} = \frac{\langle E^{\text{int}} V \rangle - \langle E^{\text{int}} \rangle \langle V \rangle}{\sigma_{E^{\text{int}}} \sigma_V}, \quad (4)$$

with $\langle E^{\text{int}} \rangle$ and $\langle V \rangle$ denoting the mean values and $\sigma_{E^{\text{int}}}$ and σ_V being the variances of the interaction energy and volume, respectively.

Using C_P^{res} and $\rho_{E^{\text{int}}, V}$, we constructed temperature-pressure phase diagrams for the specific size clusters ($N=20$) corre-

sponding, as we mentioned above, to the building blocks (small or medium cage) of sI, sII and sH hydrate lattices¹⁴. We should also note that in finite systems, the phase changes are not sharp and occur over a more or less wide region of temperatures and pressures. We represent these regions in a simplified way by curves, namely coexistence curves, corresponding to the maxima of the heat capacity along the temperature axis, and the minima/maxima of the Pearson correlation coefficient for interaction energy and volume detected along the pressure/temperature axis²⁸. For analyzing the structures under different T, P conditions, local enthalpy optimizations are also carried out for 128 randomly selected configurations for each T, P point from the PTMC simulations, with temperatures values up to 240 and 294 K for the (H₂O)₂₀ and Ar-(H₂O)₂₀ cluster, respectively, and pressure values up to 5.4 GPa. Such minimizations are performed via the simulated annealing method³⁰ for a NPT statistical ensemble using a probability weight of $\exp(-\frac{(E^{\text{int}} + PV)}{k_B T})$ for sampling the cluster configurations and volumes, with starting temperature of 5 K and final one 0.01 K. Current temperature has been decreased every 50th MC step by a factor of 0.999. We should note that the fast cooling and the low initial temperature were adopted so that a local optimization to the nearest local minimum be performed.

2.2 Model interaction potentials

Water model potential: For the water-water interactions the TIP4P/ice model³¹ is used. Comparison between different water models have shown that the TIP4P/ice reproduces in a very good agreement with the experiment three phase coexistence lines in methane-hydrate¹¹, and in general, there is also a good correspondence with the relative isomer energetics for the (H₂O)₂₀ (D-cage) and (H₂O)₂₄ (T-cage) clusters compared with results from other water model potentials,^{32,33} as well as with those from MP2 and DFT calculations (see Refs. 34,35 and references therein). In the TIP4P/ice model a negative charge is placed (M-site) 0.1577 Å from the O atom along the the C₂-axis of the water molecule. The parameters of the TIP4P/ice are given in Table 2, with the a fixed C_{2v} geometry for each water molecule with the OH distance of 0.9572 Å, and $\angle HOH$ of 104.5°.

Ar-water potential: For describing the Ar-water interaction, we choose two different types of interaction potentials based on semiempirical and *ab initio* parameterized forms. In this way we could analyze the effect of the Ar-H₂O interaction on the structural stability and changes in the Ar-water cluster.

The semiempirical potential combines van der Waals (vdW) interactions between the Ar atom and the water molecule, and electrostatic interactions between the point charges q_i and q_j centered on M-site and H atoms of each water molecule, and is given by

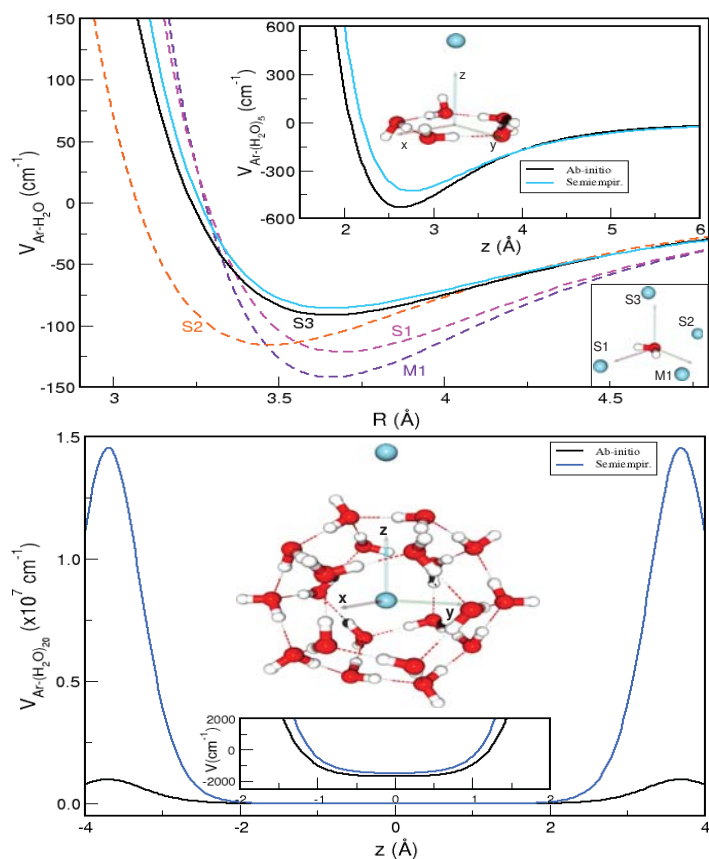


Fig. 1 Top panel: *Ab initio* and semiempirical potential energy curves are plotted for the Ar–H₂O complex as a function of the Ar–O distance. For the *ab initio* curves the structures of the minimum (M1, see color-dashed line) and saddle-points (S1, S2, and S3, see color-dashed and black-solid line, respectively) of the ArH₂O system are also displayed (lower-side inset plot). In the upper-side inset plot the potential curves are shown as a function of the distance along the z-axis between the Ar atom and the center of mass of a pentagon of water molecules. Bottom panel: *Ab initio* and semiempirical potential energy curves are shown as a function of the distance between the Ar atom and the center of mass of the 5¹² cage formed by 20 H₂O molecules (see upper-side inset plot and text).

Table 2 Partial atomic charges and LJ parameters for the TIP4P/ice³¹ and the Ar atom⁵ used in the present PTMC simulations. The LJ potential parameters between Ar–O atoms are determined by combination rules (see text).

Atom	q[e]	σ [Å]	ϵ [kJ/mol]
O(water)	0.0	3.1668	0.882159
H(water)	+0.5897	0.0	0.0
M(water)	-1.1794	0.0	0.0
Ar	0.0	3.359	1.183

$$V_{Ar-H_2O} = \sum_i \sum_{j>i}^N \left\{ \frac{q_i q_j}{4\epsilon_0 r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\} \quad (5)$$

where i and j summation runs over Ar and all O, H, M-site centers on each H₂O molecule, respectively. The standard Lorentz-Berthelot combination rules are used to determined the Lennard-Jones (LJ) parameters between unlike atoms, $\epsilon^{ij} = (\epsilon^{ii}\epsilon^{jj})^{1/2}$ and $\sigma^{ij} = (\sigma^{ii} + \sigma^{jj})/2$. The LJ parameters between similar type atoms, ϵ^{ii} and σ^{ii} corresponding to the O atom from the TIP4P/ice water model³¹, and ϵ^{jj} and σ^{jj} corresponding to the Ar atom⁵, are listed in Table 2 together with the partial charges for the Coulombic interactions.

The *ab initio* PES for the Ar–water interaction is taken from Ref. 3. This intermolecular potential has been constructed by fitting an analytical many-body expression to high level CCSD(T) *ab initio* data refined at the complete basis set limit by evaluating its correction at four stationary points of the PES. The most stable geometry for the Ar–H₂O interaction corresponds to a planar configuration, namely M1, as well as the next S1, and S2 ones corresponding to saddle-points of the PES, while the S3 has an out of plane configuration with the Ar atom in an almost perpendicular position to the H₂O plane (see the lower inset in the top panel of Fig. 1).

To compare the Ar–water interactions predicted by the semiempirical (see Eq. 5) and *ab initio* potentials, we plot the potential curves as a function of the Ar–O distance in Fig. 1 (see top panel) for the orientations corresponding to the M1, S1, S2 and S3 stationary points of the complex (see the lower inset in the top panel of Fig. 1).

One can see that the semiempirical and *ab initio* curves for the S3 orientation of the Ar–H₂O system are very similar to each other, although the *ab initio* potential shows a deeper and more anharmonic well than the semiempirical one. In addition, in the upper inset we display comparisons of these potential curves for the interaction between the Ar atom and a pentagon formed by water molecules, as part of the 5¹² (D-cage). As can be seen the differences between the semiempirical and *ab initio* potential wells are now larger, as well as in the repulsive part of the curves. Finally, in Fig. 1 (see bottom

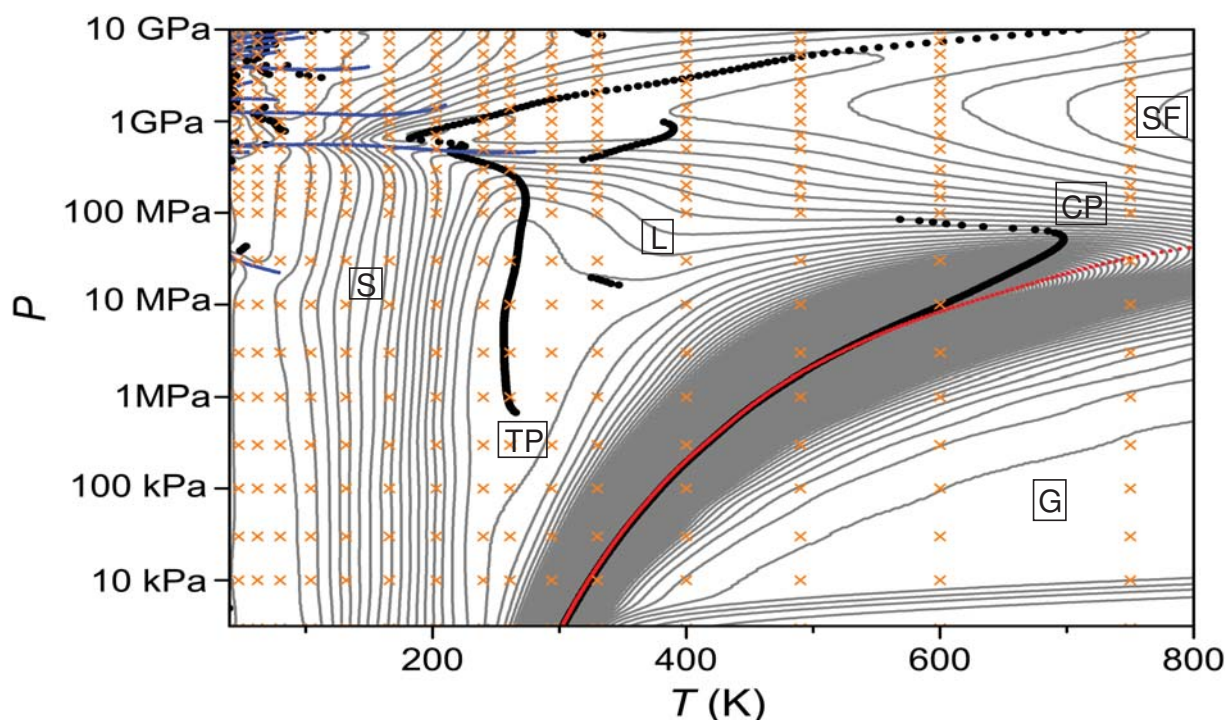


Fig. 2 Temperature-Pressure phase diagram of the $(\text{H}_2\text{O})_{20}$ cluster (see text for symbols labelling various regions).

panel) we show the potential curves corresponding to the total interaction of the Ar atom with 20 H_2O molecules forming a 5^{12} cage. The Ar atom could be inside (encapsulated) or outside the cavity (see upper inset in bottom panel of Fig. 1) as it moves along the z -axis.

The main differences between the two, *ab initio* and semiempirical, types of curves (solid black and blue lines, respectively) are in the repulsive part of the PESs, with the high barriers corresponding to the “on surface” position of the Ar atom. The *ab initio* potential is close to the semiempirical one only in the flat minimum area, at energies of about -1700 cm^{-1} , corresponding to configurations with Ar inside the cage. In contrast, the semiempirical curve is very different with much larger repulsion at configurations nearby the surface of the cage. As we can see in the bottom panel of Fig. 1, the barriers for the formation of the Ar–cage hydrate are much higher for the semiempirical interactions than for the *ab initio* ones. The repulsive parts of the potentials, as we will discuss below, are related to the outside-to-inside structural transition of the Ar atom in the high pressure regimes.

3 Results and Discussion

Pure water cluster:

As we mentioned above, the TIP4P/ice water model is employed here for the water-water interactions. Previous studies on selected medium-size water clusters, with up to 24 molecules, have been reported^{25,35,36}, although all of them are mainly dealing with structural transformation of such clusters at zero temperature and pressure obtained from global cluster structure optimization methods, while more recently the phase behavior of such cluster sizes have been presented up to pressures of 1 GPa²⁸. Here, as we are interested in structural changes in the region of higher pressures, we extend this study up to pressures of 10 GPa.

As we described in section 2, we used the C_P^{res} and $\rho_{E_{\text{int}},V}$ in order to construct temperature-pressure phase diagrams for the specific size clusters. In Fig. 2 we display the phase diagram for the $(\text{H}_2\text{O})_{20}$ pure water cluster. In general, the contour lines correspond to the C_P^{res} values, while the coexistence curves indicate different types of cluster transformation in the (T, P) -plane between three main regions corresponding to solid-like (S), liquid-like (L), and gas-like (G) phase of the cluster. We are using here the same nomenclature as used in the bulk, however, we should emphasize that the coexistence curves are just a simplified representation of much broader coexistence regions typical for finite systems, and thus the analogy with the bulk is only loose. The coexistence curve shown by black dot lines correspond to the maxima of the heat capac-

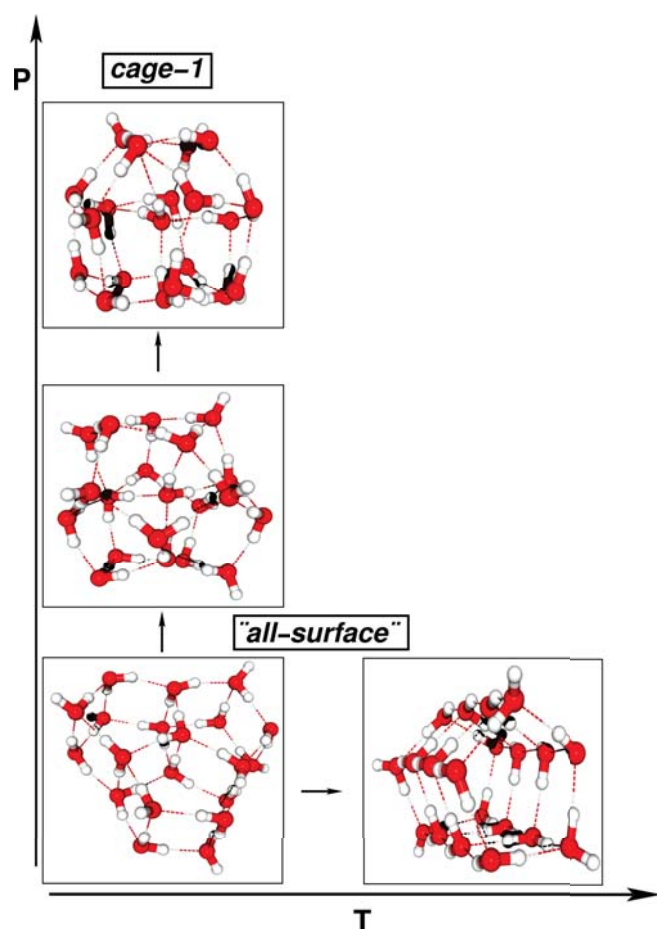


Fig. 3 Structural changes occur for the $(\text{H}_2\text{O})_{20}$ cluster at low temperatures as pressure increases. The “all surface” correspond to the edge-sharing (left side) and face-sharing (right side) pentagonal prisms.

ity, while blue and red dot lines depict the minima and maxima of the Pearson correlation coefficient, respectively, and cross symbols indicate the grid points (see Table 1) in (T, P) -plane used in the PTMC calculations. At low pressure the coexistence curves for the solid-like to liquid-like and liquid-like to gas-like transitions are getting very close to each other as they enter to the triple-point (TP) region of the cluster, a finite-size analogue to the macroscopic picture. Also, at high pressures the solid-liquid curve disappears, the cluster approaches the critical-point (CP) region, and something like supercritical fluid (SF) phase emerges.

By comparing with the phase diagram for the $N=20$ water cluster using the TIP4P water model reported in Ref. 28 for pressure values up to 1 GPa, we see a similar pattern at the pressure range between 10–100 MPa, while some differences are found at the higher pressure regime, $P > 0.5$ GPa.

In particular, we found that the transition at pressures around 30 MPa (15–60 MPa for the TIP4P) and low temperatures occurs from the “all-surface” (all water molecules on the surface of the cluster) to internally solvated or cage-1 like (one molecule at the center with the remaining ones forming a cage around it) structures. In Fig. 3 we depict the evolution of the corresponding configurations, obtained from local enthalpy minimizations, as we discussed in section 2, as temperature and pressure increase. At $3 \text{ MPa} < P < 30 \text{ MPa}$ and $T < 60 \text{ K}$ we only observe “all-surface” configurations that correspond to the edge-sharing and face-sharing pentagonal prisms (see lower-side structures in Fig. 3), as well as few irregular fused-cubes structures. Although the edge-sharing structure is the most abundant isomer, after a slight increase of the temperature the face-sharing configurations are also detected. For comparison reasons, in Table 3 we list the total binding energies of the four lowest $(\text{H}_2\text{O})_{20}$ minima from MP2 complete basis set (CBS) calculations³⁵, as well as those predicted by the TIP4P/ice³¹ and TIP4P³⁶ models. As we mentioned above, the TIP4P/ice water model has been designed to describe solid-phase water properties, and as it was expected larger deviations are obtained in the total binding energies compared to the TIP4P and MP2 results. However, we should point out that the relative energies are comparable, with the edge-sharing pentagon prisms being the global minimum of the MP2/CBS calculations and TIP4P/TIP4P/ice water models, and lower in energy by 5.3 and 0.9/0.9, 2.9 and 1.4/1.7 and 17.8 and 11.2/13.8 kcal/mol than the fused-cubes, face-sharing pentagon prism and pentagon dodecahedron (D-cage) isomers, respectively.^{35,36} Further, we should note that these potential minima are separated by high barriers, which might lead to non-ergodic behavior by causing convergence problems in the simulations. However, all low-lying isomeric configurations have been observed during the present simulations indicating that the PTMC methodology efficiently prevents such effect. For pressures just above 30 MPa we start to observe irregular internally solvated structures that the population of which rapidly grows as the pressure is increasing.

Table 3 Total binding energies (in kcal/mol) for the four low-lying families of minima of the $(\text{H}_2\text{O})_{20}$ calculated at the MP2/CBS level of theory³⁵ and compared with the values from the TIP4P/ice³¹ and TIP4P³⁶ water models.

Cluster structure	Energy		
	MP2/CBS	TIP4P	TIP4P/ice
Dodecahedron	-200.1	-197.5	-237.7
Fused cubes	-212.6	-207.8	-250.6
Face-sharing pentagon prisms	-215.0	-207.3	-249.8
Edge-sharing pentagon prisms	-217.9	-208.7	-251.5

As we mentioned above, in this study we focus on transitions at high pressures, and therefore, as one can see in Fig. 2, the grid of the points is denser in the high pressure/low temperature regime. By analyzing the minima of the Pearson correlation coefficient, one can see that various structural transitions appear to take place for pressure values $P > 0.5$ GPa. At pressure value around 0.7 GPa, the first of such solid-solid changes takes place, and corresponds to the transition from irregular or cage-1 like to the regular cage-1 structure (see upper two structures in Fig. 3), with the regular cage-1 configuration to be the dominant one for $P > 1$ GPa. By examining the heat capacity anomalies in the TIP4P/ice phase diagram $(\text{H}_2\text{O})_{20}$ at this high pressure range, one should expect additional transitions, however we did not observe any further structural changes, especially the one corresponding to energetically higher family of pentagon dodecahedron (D-cage) minima on the $(\text{H}_2\text{O})_{20}$ cluster PES. We should note that such guest-free clathrates of sI and sII structures have been predicted theoretically as stable phase of water at negative pressures.³⁷

Note also that our PTMC results indicate only quantitative differences between the TIP4P and TIP4P/ice water models on the observed transitions at low/high temperature/pressure regimes for the water cluster under study.

Ar $(\text{H}_2\text{O})_{20}$ cluster: In Figure 4 we present the phase diagrams calculated for the Ar $(\text{H}_2\text{O})_{20}$ cluster using the *ab initio* and semiempirical potentials (see top and bottom panels of the figure, respectively). As previously, one can see the coexistence curves corresponding to evaporation of the systems (see red and black dotted lines) for $T > 300$ K, and to the cluster melting (black dotted line) for $P > 100$ kPa and $T > 250$ K, while at low temperatures and low pressures $P < 100$ kPa we detect some Ar evaporation (black dotted line).

The decomposition curve of Ar hydrates has been measured by differential thermal analysis, and Raman scattering up to pressures of 1.5, and 3 GPa, respectively, and temperatures between 233–443 K^{13,18,38,39}. Features on the curve, such as its maximum and fractures, have been used to suggest, initially, the formation of at least three hydrates in the Ar– H_2O system, with the sI structure to be stable at high pressures of 15 kbar and up to temperature of 348 K³⁸. Later on, more detailed diffraction studies^{17,20,39} have been carried out, where discrepancies have been found in the transition from the sII to sH structure at 0.46 GPa and ambient temperatures, while they agree in the formation of the tetragonal structural type of clathrate at pressure around 0.7 GPa, and also for the filled-ice structure at higher pressures^{20,39}. Here, one can see in Fig. 4 that the melting curves of the phase diagrams show the decomposition of the Ar $(\text{H}_2\text{O})_{20}$ cluster at high pressures (P between 1 and 2 GPa) and at temperatures around 350 K for both *ab initio* and semiempirical potentials. Below, we will discuss on the solid-solid structural changes predicted by the present re-

sults from the semiempirical interactions, and will try to draw some relation with the above experimental findings.

In Figure 5 (see top panel) we plot the dependence of the system mean volume, interaction energy, and Pearson correlation coefficient as a function of pressure at a temperature of 50 K. One can see in Fig. 5 that the interaction energy and volume of the system become strongly anti-correlated in the solid-to-solid transition region and, as a consequence, the ρ coefficient develops sharp minimum close to -1. Similar behavior is also observed at other temperatures close to $T = 50$ K, with such transitions to take place at pressure values around 100 MPa, 2.2 GPa, and 3.8 GPa, as we discuss below in Fig. 4. In the bottom panel of Fig. 5 we show, as a function of temperature, the distance of the Ar atom from the center of mass of the 20 water molecules, as well as the radius of the surrounding pressure container at pressures of 3 and 30 kPa. One can observe the Ar evaporation at low temperatures of 50–70 K and 60–100 K at 3 and 30 kPa pressure values, respectively, while the water molecule(s) evaporation takes place at higher temperatures of 300–320 K for the low pressure value, as well as above 320 K for $P=30$ kPa. This is in accord with the evaporation coexistence curves of Fig. 4, as we mentioned above.

Based on the Pearson correlation coefficient profile, for pressure values $P > 0.5$ GPa, we observed transitions corresponding to solid–solid changes for both the *ab initio* and semiempirical potentials. In particular, by performing local enthalpy optimizations and analyzing various optimized configurations along the MC calculations performed at various temperatures and pressures we detected 3 main transitions in the Ar $(\text{H}_2\text{O})_{20}$ cluster, when the semiempirical Ar– H_2O potential is used. They are denoted by the labels A, B and C in Fig. 4 and typical structures, obtained from local enthalpy minimizations, as we discussed in subsection 2.1, which appear prior and after each particular transition are given in Fig. 6. At low temperature, $T < 100$ K, and pressure values below 100 MPa we observed structures corresponding to the Ar atom attached to “all-surface” configurations, such as the edge-sharing pentagonal prisms, and as the pressure is increased one can see that the pentagonal prisms structures are deformed and for $P > 100$ MPa we detect the transition to the water cage-1 structures with the Ar atom outside. As we mentioned above, such a transition was observed at slightly lower pressure of 30 MPa in the phase diagram of the $(\text{H}_2\text{O})_{20}$ cluster (see Figs. 2 and 3). For pressure values $P < 2$ GPa we only observe structures with the Ar atom attached to the pentagonal or cage-1 structures of the $(\text{H}_2\text{O})_{20}$ cluster (see region A in Figs. 4 and 6), while at pressure of 2 GPa a transition from outside to inside Ar configurations occurs. This transition is sharp at low temperatures, and it proceeds gradually as the temperature increases (see region B in Figs. 4 and 6). One can see that at low temperatures and high pressures we obtain configurations with the Ar atom inside to an irregular cage formed

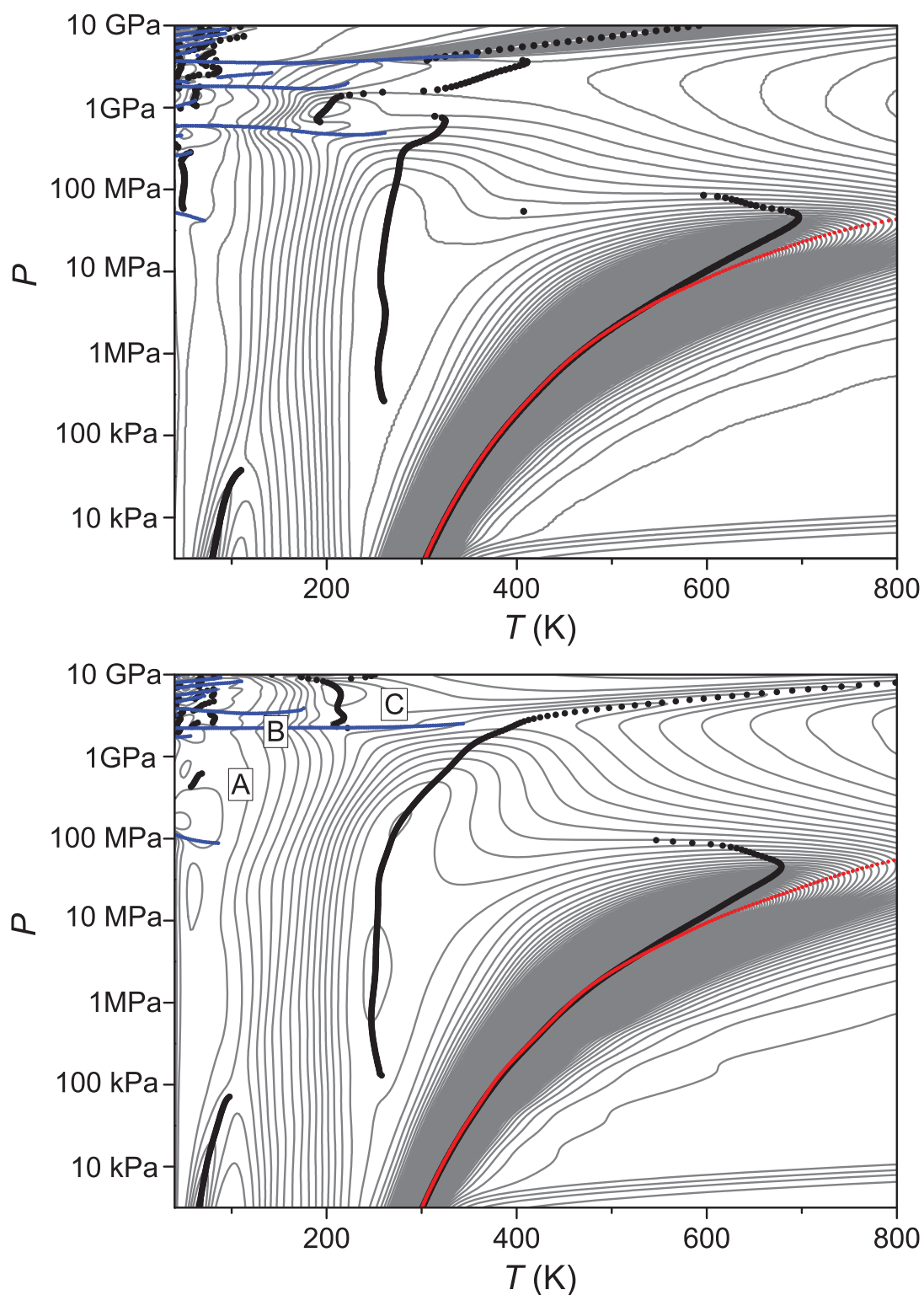


Fig. 4 Phase diagrams of the $\text{Ar}(\text{H}_2\text{O})_{20}$ cluster using the *ab initio* (top panel), and semiempirical (bottom panel) Ar–H₂O PESs. Black dot lines correspond to the maxima of the heat capacity, blue and red dot lines depict the minima and maxima of the Pearson correlation coefficient profile, and the A, B, and C are for the different solid–solid transitions (see in the text and Figure 6).

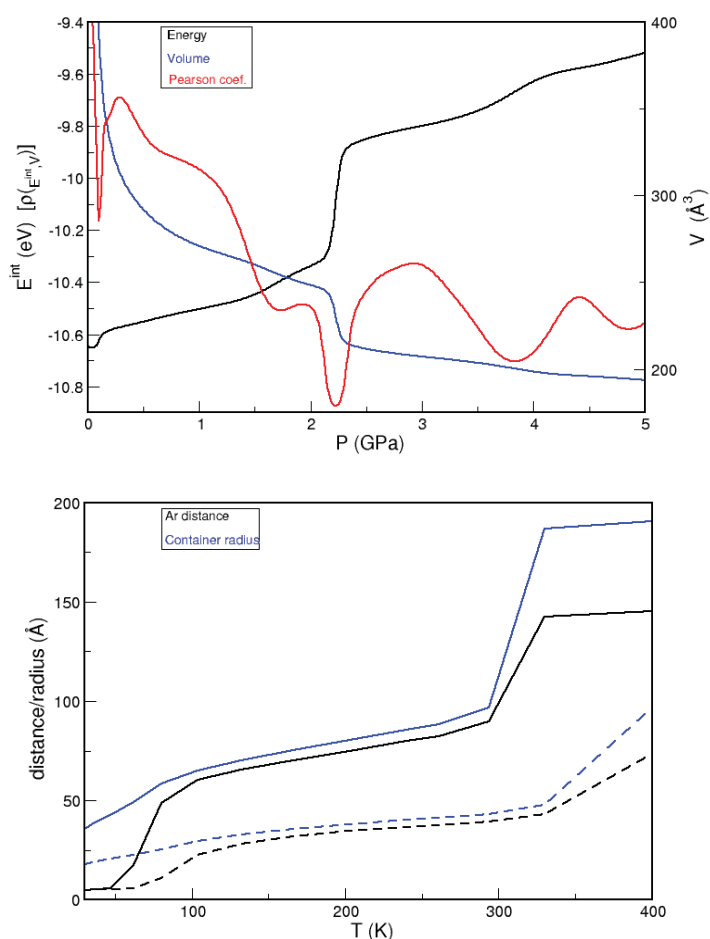


Fig. 5 Top panel: Mean volume (V), interaction energy (E^{int}) and Pearson correlation coefficient ($\rho_{E^{\text{int}},V}$) as a function of pressure at $T=50$ K. The range for the $\rho_{E^{\text{int}},V}$ is from -1.0 to 0. Bottom panel: The Ar distance from the center of mass of the 20 water molecules and the radius of the pressure container as a function of temperature at $P=3$ kPa (solid lines) and 30 kPa (dashed lines).

by the 20 water molecules. Although such structures are the most abundant ones even at higher pressures, up to 3.8 GPa, we also observe regular 5^{12} cages for the Ar clathrate (see region B), with a relative abundance about 10–15%. In addition, at $P=2.7$ GPa we found cages formed by tetragons and pentagons, similar to the irregular cages found at lower pressures, while by increasing the temperature at this pressure, as well as by increasing only the pressure, structures with tetragons, pentagons and hexagons (see region C in Figs. 4 and 6) are also detected. Similar type of cages, e.g. the medium size $4^35^66^3$ cage is one of building blocks of the sH clathrate structure, together with the 5^{12} cage that also appears in both sI and sII type of clathrates. By analyzing the cages observed, we gain more information on the structural changes and can draw some connections with phase transitions in bulk, reported from different experiments performed for the Ar hydrate.^{13,18,20,38,39}

In particular, on the basis of our results, we may speculate that structural changes from the irregular cage/Ar inside to the regular 5^{12} cage, taking place in region B of the phase diagram, corresponds to the formation of the Ar hydrate at pressure of 2 GPa, while the structural change from the small 5^{12} to the medium $4^35^66^3$ cage for the $\text{Ar}(\text{H}_2\text{O})_{20}$ cluster taking place at $P > 2.7$ GPa (region C) could be a germ of a transition from sI/sII to sH for the Ar hydrate observed experimentally at $P > 0.46$ GPa^{13,18,38,39}. However, such attempts should be seen as (partial) cluster approach to the unit shell of such clathrates, and thus, as a starting point since further calculations are still needed in order to provide solid insights.

By inspecting the phase diagram of the $\text{Ar}(\text{H}_2\text{O})_{20}$ cluster using the *ab initio* Ar–H₂O PES (see top panel of Fig. 4), we found several differences compared to that obtained with the semiempirical potential (see bottom panel of Fig. 4). One can see that the coexistence line corresponding to the Ar evaporation at low temperatures and pressures, shows a slight displacement to lower pressures and higher temperatures for the *ab initio* potential. The same occurs for the evaporation of the water monomers from the cluster at the high temperature regime. The slope of the melting coexistence curve is smaller for the *ab initio* potential at $T > 260$ K. In contrast to the semiempirical potential, the melting curve shows several discontinuities at pressure values between 1–2 GPa and 3.8–5.4 GPa. For the solid-solid transitions at high pressures, we can see that more structural changes are predicted for the *ab initio* potential, however, in contrast to the semiempirical PES results, we did not observe any transitions to clathrate-like structures in the range of T - P values studied. In particular, at low pressures, structures with the Ar atom outside the water cluster are found, like the ones in the region A of the Fig. 6, while by increasing the pressure the water molecules surround the Ar atom forming an open-irregular-cage. As we mentioned above, such behavior is related to the repulsive part of the potential, that is accessible at high pressures, and as it

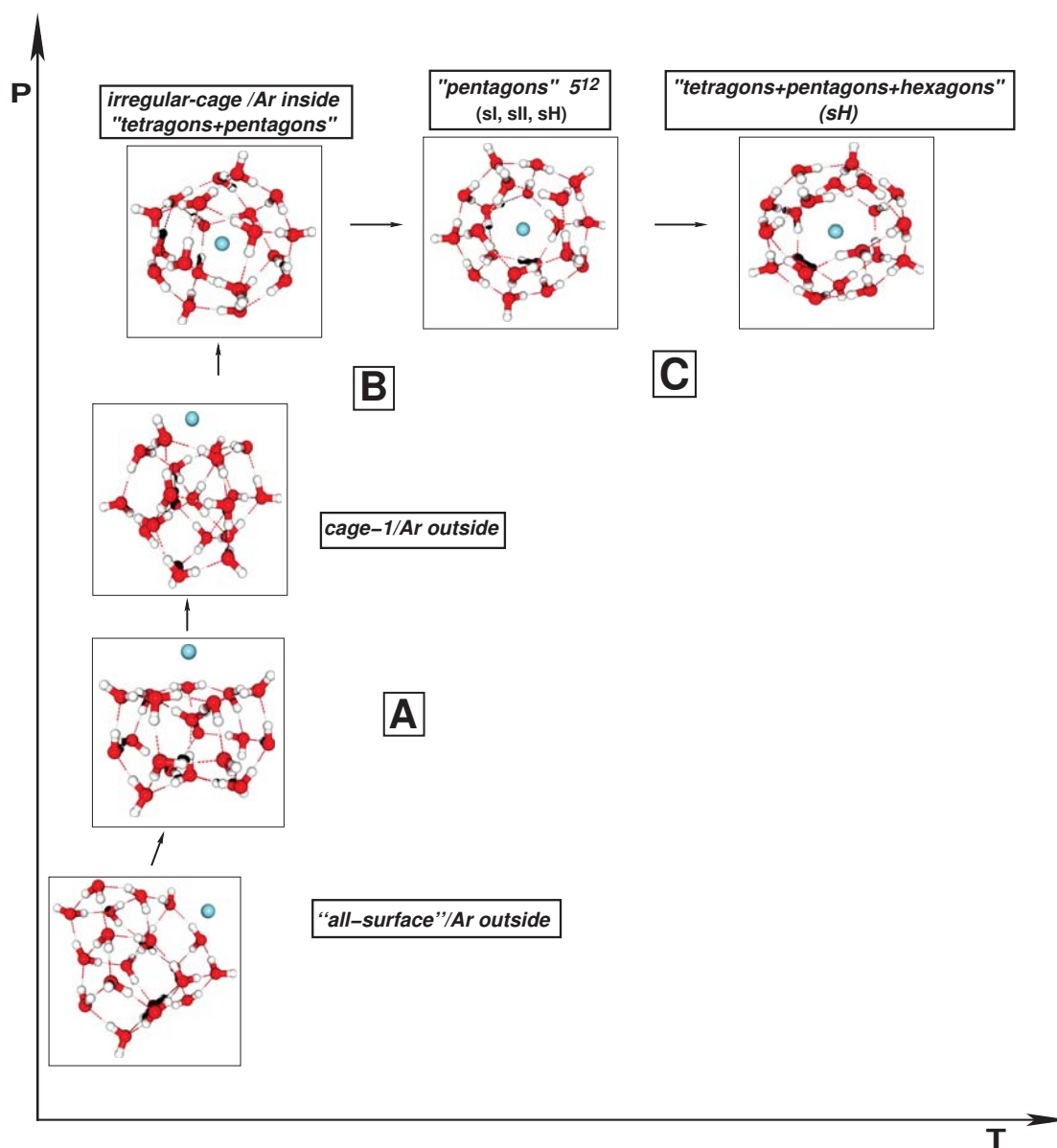


Fig. 6 Structural changes occurring in the $\text{Ar}(\text{H}_2\text{O})_{20}$ cluster as pressure and temperature increase using the semiempirical $\text{Ar}-\text{H}_2\text{O}$ PES. The A, B, and C regions are indicated in bottom panel of Fig. 4 for the different solid-solid transitions.

can be seen in the bottom panel of Figure 1, the semiempirical PES shows considerably higher barriers than the *ab initio* ones for the inside-to-outside transition (see structures in Fig. 6), indicating more stable encaged structures for the $\text{Ar}(\text{H}_2\text{O})_{20}$ cluster at higher pressure values.

4 Summary

Temperature-pressure phase diagrams are constructed using a two-dimensional multiple-histogram approach and from parallel-tempering isothermal-isobaric Monte Carlo simulations for $(\text{H}_2\text{O})_{20}$ and $\text{Ar}(\text{H}_2\text{O})_{20}$ clusters. The PTMC calculations are performed for a wide range of temperatures and pressures. Various thermodynamic and structural parameters are recorded, such as cluster energy and enthalpy, constant-pressure heat capacity, volume, and Pearson correlation coefficient for energy and volume, as well as structural isomers, that subsequently are analyzed. In the following we briefly summarize the main findings of this study, which is mainly focused on the high pressure and relatively low temperature regimes.

For the pure water cluster, $(\text{H}_2\text{O})_{20}$, we check the performance of the TIP4P/ice model potential and found only quantitative differences comparing with previously reported results using the TIP4P water model up to $P=1$ GPa. We observe structural changes corresponding to solid-solid transitions that at low pressures correspond to changes from the “all-surface” (edge- and face-sharing pentagonal prisms) structures to the cage-1 like structures, while at higher pressures transitions to the cage-1 isomeric structure occur.

For the $\text{Ar}(\text{H}_2\text{O})_{20}$ cluster we employed two different PESs for the Ar- H_2O interaction. Using the semiempirical Ar- H_2O surface leads, as we have shown, to specific transitions at the high pressure regime corresponding to structural changes from outside-to-inside structures, then to regular 5^{12} structures at about 2 GPa, while at higher pressures structures formed by tetragons and hexagons are also observed. Such transitions to regular 5^{12} structures are not observed in the simulations employing the *ab initio* Ar- H_2O PES, thus we relate this behavior to the shape of the repulsive part of the two potentials. Thus, structural transitions in Ar clathrates at high pressure are shown to be a consequence of the increasing intermolecular interaction at the repulsive region.

The present work is intended as a first step towards a more detailed description and understanding of structural changes in pure water and Ar-water clusters under high pressures. Ultimately, a direct comparison with available experiments on Ar clathrate hydrate is desirable. However, even the size of the unit cell of such clathrates are not tractable by such theoretical modelling, and to the best of our knowledge no experimental data are available for Ar-water clusters. Thus, we hope that by extending the present simulations to larger cluster

sizes, such as 24 and 36, as well as with higher occupancy in these large cages, we could then extract valuable information and insights for transitions occurring in the building blocks of the sI, sII and sH Ar clathrate hydrates.

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