Thermodynamic States of Nanoclusters at Low Pressure and Low Temperature: The Case of 13 \( \text{H}_2 \)

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ABSTRACT: A confinement model of finite-size systems that embodies an equation of state is presented. The temperature and pressure of the system are obtained from the positions and velocities of the enclosed particles after a number of molecular dynamics simulations. The pressure has static and dynamic (thermal) contributions, extending the Mie–Grüneisen equation of state to include weakly interacting anharmonic oscillators. The model is applied to a system of 13 \( \text{H}_2 \) molecules under low-pressure and low-temperature conditions in the classical regime. The confining cage in this case is a spherical hydrogen cavity. The Born–Oppenheimer molecular dynamics in conjunction with density functional theory are used for the time evolution of the particle system. The hydrogen molecules form a noncrystalline cluster structure with icosahedral symmetry that remains so in the whole temperature range investigated. The fluctuations of the interatomic distances increase with the temperature, while the orientational order of the enclosed system of molecules fades out, suggesting a gradual order–disorder transition.

INTRODUCTION

The investigation of atomic clusters represents one of the most active fields in material sciences. A particular challenge consists in understanding the way in which the properties of matter change with the size. In this sense, the clusters are considered unique entities as they introduce the size as a new physical variable. In other words, they are not simply a fraction of matter, as initially thought, but constitute new entities with characteristics of their own: with a change in the size of a cluster, its morphology (spatial structure) and electronic properties are likely to change, too. In the macroscopic world, the properties of matter are mostly determined by the temperature and the pressure and not by the size of the system. In contrast, size effects in the microscopic world produce the unfolding of clusters from two-dimensional to three-dimensional (3D) spatial conformations, the variation of magnetic properties,” etc. An additional feature that makes clusters attractive and different from solids is the large number of isomers that they exhibit. The isomers increase with the cluster size and usually show energies close to each other. The existence of different isomers is common in a single experiment. The properties described above represent a few examples among many others that explain the interest in this field, apart from the potential technological use of clusters in different aspects of life. Clearly, when a cluster is composed by a very large number of atoms, the properties of the bulk solid start being reproduced. In such a limit, the addition of more atoms hardly changes the overall structure or physical—chemical characteristics and the usual thermodynamic expressions of pressure and temperature determine the thermodynamic state of the particle system. However, the application of thermodynamical expressions to finite size systems is questionable as these are held a priori only in the thermodynamic limit \( N \to \infty \). As a starting point, most investigations have focused on clusters in the gaseous phase, for which the thermodynamic state of the particles is simple. Nevertheless, questions emerge regarding the behavior of clusters in environments different from the vacuum, in particular their structural and energetic stability with changes in the pressure and temperature. In short, the study of clusters under pressure and temperature is of paramount importance to have a complete picture of their behavior under different and real physical conditions.

Received: May 10, 2011  
Revised: July 15, 2011  
Published: July 29, 2011
In a series of papers we have presented a model for the confinement of systems with a small number of particles together with the expressions that determine the thermodynamic state of the confined system at relatively high temperatures and pressures. The confinement model has been applied to the particular case of hydrogen clusters, giving results in excellent agreement with experimental measurements on the solid. Incidentally, the investigation of hydrogen clusters under confinement has also called attention in the context of hydrogen storage, where clusters are confined in either fullerene or clathrate cages. In experiments with diamond anvils, confined hydrogen has been obtained under high pressure in a xenon solid. Though xenon is too heavy and expensive for practical use in hydrogen-storage applications, these results open a new road in forming novel hydrogen-storage compounds and, more generally, in the synthesis of new materials by means of pressure. As shown later, our methodology presented in this work may represent the theoretical counterpart of the experimental results obtained by this new pressure-induced chemistry.

The purpose of the present work is to complement our previous efforts by proposing a set of thermodynamic expressions for a confined cluster under low temperature and low pressure conditions, but without reaching the region where quantum effects are prominent. The strategy consists in determining the main thermodynamic variables from the basic mechanical variables of the particles, namely, positions, velocities, and forces generated from molecular dynamics simulations. The relevance of this research unfolds as follows: (i) it shows the possibility of assigning a thermodynamic state to clusters in the classical low-pressure, low-temperature regime, (ii) we have the possibility to elucidate and quantify “phase” transitions from a bottom-up perspective, thus complementing the collective phenomena picture observed in the macroscopic world, and (iii) the ability to explain the thermodynamic behavior of clusters and their features at the atomic level through molecular simulations.

In particular, the analysis of equilibrium structures of confined hydrogen clusters at pressures lower than 100 GPa suggests the presence of a molecular orientational order (Figure 1 of ref 5). On the other hand, the orientational order in bulk hydrogen is a well-known phenomenon (see the review of Silveira for orientational ordering at very low pressures and Mao and Hemley for pressure-modulated orientational ordering). Subsequent theoretical works have studied the order—disorder transition associated with the orientation of H₂ molecules in the solid phase. A quantitative explanation of the experimental observations (including some pronounced changes in rotational excitations) is given in terms of quantum versus classical orientational ordering in the dense solid. Therefore, we are also interested in the present work in quantifying the orientational order in hydrogen clusters with the use of an order parameter.

The paper is structured as follows: First, a confinement model of finite-size systems is presented. In a second stage, the main thermodynamic variables such as the volume, temperature, and pressure are defined in analogy with their macroscopic thermodynamic counterparts. In a third stage, we illustrate the method by studying the thermodynamic states of a set of 13 hydrogen molecules confined in a H₆₀ fullerene cage. A detailed study of the orientational order of the 13 H₂@H₆₀ system is also given. The present investigation is restricted to particles systems at low pressure and low temperature conditions, because the expressions that we develop take the oscillatory character of the atoms into consideration, which is the observed behavior of particles at low pressure and low temperature. Still, the approximations are within the classical limit. The conditions of high pressures and high temperatures, together with the appropriate thermodynamic expressions, have been reported elsewhere. These last expressions also apply to the low pressure/temperature limit; however, they take no specific oscillatory character of the particles into consideration.

CONFINEMENT MODEL OF FINITE-SIZE SYSTEMS

The molecular simulation of a system of particles under confinement and temperature requires the presence of confining walls in contact with a heat reservoir. In practice, the consideration of a large number of particles together with the atomic structure of the containing walls makes molecular simulations computationally intractable. Despite that, alternative approaches have emerged making use of extended Lagrangians and non-Hamiltonian theory to include barostat and thermostat effects via virtual particles. Such methods give excellent results for systems with translational symmetry like crystals, but their application to finite systems remains questionable. In this work, we consider a confinement cage with atomic structure interacting with the enclosed particles. The cage exerts a compressive stress on the enclosed particles and may be (isotropically or anisotropically) shrunk or expanded to reproduce different pressures. The encapsulated system of particles is in contact with an equilibrium thermal bath at temperature T. The thermalization may be achieved either by taking the vibrations of the cage into consideration, implying momentum transfer among the particles of the cage and the enclosed ones, or by stochastically scaling the velocities of the encapsulated particles while holding the positions of the cage atoms fixed. We chose the latter option for simplicity. The computational cost of the proposed system is not prohibitive and quite reasonable to investigate the properties of finite-size systems at various pressures and temperatures. The expressions for the computation of the pressure, temperature, and volume are provided in the following subsections.

Volume. Let us consider a cage with atomic structure. There are N particles inside the cage. In principle, the cage can take any geometry and, like in the real world, the geometry may induce particular structures on the confined particles. We choose here a fullerene-like cage which is approximately spherical. The radius R₉ of the spherical cage is related to the pressure. The cage radius is determined from the distances R between the cage atoms and the cage center

\[ R_c = \frac{1}{M} \sum_{i=1}^{M} R_i \]  

where M is the number of atoms forming the cage. In the case of a vibrating spherical cage, the radius should be time averaged. On the other hand, we define the radius R₀ of the confined cluster as

\[ R_0 = \langle R_{np} \rangle + \delta R; \quad \delta R = (R_c - \langle R_{np} \rangle) / 2 \]  

The quantity Rnp(t) is the average distance between the outer atoms of the cluster and the cage center at time t. The inner atoms of the cluster are excluded in the computation of the volume of the enclosed particles. The center of mass of the cluster coincides with the center of the cage as, otherwise, the center of mass of the cluster has to be translated to the center of mass of the cage to compute Rnp(t). The quantity \( \langle R_{np} \rangle \) is the time average of Rnp(t) in the molecular dynamics simulation. The cage electron cloud also participates in the
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The compression process. When the cage and cluster atoms are of the same species, the space between them is equally shared by their electron clouds. The difference $\delta R$ represents half the thickness of the electron clouds, which are located between the outer part of the confined atoms and the inner part of the cage atoms. The cluster volume $V_c$ of confinement is that of a uniform sphere, namely, $V_p = 4\pi R_p^3/3$, which is determined from radii $R_c$ and $R_{ap}$.

**Temperature.** In principle, the confining cage is immersed in a heat bath, causing vibrations of the cage walls, which in turn modify the kinetic energy of the encapsulated particles. In our case, the heat flow is simulated stochastically or, more precisely, without assuming vibrating walls but considering scaled velocities of the confined particles

$$T = \frac{2}{N_{df}k_B} \left( \langle E_{kin}(t) \rangle \right)$$

$$= \frac{1}{N_{df}k_B} \left( t_{init} - t_{fin} \right) \sum_{i=1}^{N} \sum_{\alpha=1}^{3} M_\alpha \left( \lambda V_\alpha(t) \right)^2$$

(3)

The quantities $k_B$, $M_\alpha$, and $V_\alpha$ are, in that order, the Boltzmann constant, mass, and velocity vector of the $\alpha$th particle, while $t_{init}$ and $t_{fin}$ are the initial and final times of that part of the molecular simulation referring to the thermodynamic equilibrium. In this regard, the difference $t_{fin} - t_{init}$ is the period where the particle system is in thermodynamic equilibrium and where the averages of relevant physical observables are computed. The number $N_{df}$ is the number of momentum degrees of freedom. The brackets indicate a time average, once the equilibration temperature is achieved. The value of $\lambda$ is determined from the new $(T_{new})$ and old $(T_{old})$ temperatures in the form: $\lambda^2 = T_{new}/T_{old}$. The $T_{new}$ temperature may be equal to the equilibrium temperature, while $T_{old}$ is the instantaneous temperature of the system. Once the “new” temperature is decided, the scale factor is automatically determined in terms of $T_{new}$ and $T_{old}$. The scaling algorithm is commonly implemented in many molecular dynamics programs and is usually called in the molecular dynamics simulation automatically or by default.20

**Pressure.** The pressure contains a static and a thermal contribution, $P = P_{stat} + P_{therm}$. The static part takes the usual thermodynamic form

$$P_{stat} = -\frac{\partial U}{\partial V_p}$$

(4)

where $U$, the static energy of the system, depends on the confined volume. The thermal, or dynamical, part is

$$P_{therm} = 3\gamma N_0 k_B T / V_p$$

(5)

where the factor $\gamma$ (a priori temperature dependent) is of particular interest.21 We have adopted in this expression the usual notation in experimental studies. The above decomposition is well-established for several model systems, frequently used to describe real systems at low temperatures and pressures. However, it can be computed more generally from simulation data as explained in the following subsections. For instance, an analytical expression of $\gamma$ can be derived for a set of $N_0$ weakly interacting harmonic oscillators and, as shown in Appendix A, the dynamic part of the pressure can be extended to include weakly interacting anharmonic oscillators throughout the use of $\gamma$. The pressure of weakly interacting three-dimensional harmonic oscillators in the classical regime is given by the so-called Mie–Grüneisen equation of state (MG-EOS)$^{22}$

$$P_{MG} = -\left( \frac{\partial U}{\partial V} \right)_T + \gamma \frac{3 N_0 k_B T}{V}, \quad \gamma_G = -\frac{V}{\nu} \frac{\partial P}{\partial V}$$

(6)

The number of oscillators $N_0$ should be distinguished from the number of confined particles $N$. The quantity $\nu$ is the characteristic frequency of the harmonic oscillators, $V$ the confining volume, $U$ the static energy of the particle system, $k_B$ is the Boltzmann constant, and $\gamma_G$ is the Grüneisen factor obtained after averaging the vibrational frequencies of the confined particles and differentiating with respect to the volume. The MG-EOS is largely used in the laboratory to establish the pressure. One may then ask how eq 6 would be modified in the presence of anharmonic effects, mimicking stronger interactions between oscillators at higher pressure and temperature. For this purpose, we have calculated in Appendix A the pressure of a system of weakly interacting anharmonic oscillators in the quasi-harmonic approximation, which in the classical limit reads

$$P_{anh} = -\left( \frac{\partial U}{\partial V} \right)_T + \gamma \frac{3 N_0 k_B T}{V}$$

(7)

Our expression maintains the functional form of the pressure as it appears as the sum of a static and dynamic contribution. However, the factor $\gamma$ generalizes the Grüneisen result. Both factors coincide in the low temperature and low pressure limit, where the interaction among particles is weak and the anharmonic effects are small.

$$\gamma \bigg|_{T \to 0} = \gamma_G$$

(8)

$$P \to 0$$

Interestingly, a linear behavior of the pressure with the temperature has been observed beyond the harmonic oscillator approximation for confined hydrogen (refer to Figure 1, inset B of ref 6). The linearity is also consistent with the extended validity of the Mie–Grüneisen equation of state inferred from experimental observations.22 We indicate below the way to compute each pressure contribution separately.

**Static Pressure.** The static energy $U$ is determined by averaging the electronic energies of the confined system of particles

$$U = \langle E_{elec}(t) \rangle = \frac{1}{(t_{fin} - t_{init})} \sum_{t_{init}}^{t_{fin}} [E_{elec}(t) - E_{elec}^{cage}]$$

(9)

The average is performed in the time interval $[t_{init}, t_{fin}]$ when the system is in thermal equilibrium. The thermal equilibrium is determined when the fluctuations of the temperature are lower than 10%. The total electronic energy of the whole system (cage and confined atoms) at the $i$th time step is $E_{elec}^{tot}(t_i)$. The contribution $E_{elec}^{cage}$ is the electronic energy of the cage. In our case, it is time independent as the cage remains rigid during the simulation. The difference $[E_{elec}(t) - E_{elec}^{cage}]$ gives the electronic energy of the confined particles system by excluding the cage energy.

The static energy exhibits an exponential behavior as a function of the volume due to the general repulsive character of the potential energy when the particles get close to each other. It is convenient to parametrize the static energy obtained from the
simulations with, for instance, the form proposed by Vinet\textsuperscript{23}

\[ U^{\text{V}} = -\frac{9B_0V}{\eta^2} \left\{ 1 - \eta \left[ 1 - \left( \frac{V_p}{V_0} \right)^{1/3} \right] \right\} \exp \left( \eta \left[ 1 - \left( \frac{V_p}{V_0} \right)^{1/3} \right] \right) \]

(10)

\[ \eta = \frac{3}{2}(B_0' - 1) \]

This energy involves the bulk modulus \( B_0 \), its first derivative \( B_0' \), a volume \( V_0 \) at ambient conditions, and the cluster volume \( V_p \).\textsuperscript{24} The parametrization of the static energy \( U^{\text{V}} \) displayed in eq 10 is computationally cheap due to the small number of parameters to fit. Once the parametrization is proposed, the static pressure is obtained by differentiation of the static energy with respect to the cluster volume (eq 4).

\[ P_{\text{stat}} = -\frac{\partial U^{\text{V}}}{\partial V_p} = \frac{3B_0}{V_p} \left\{ \left( \frac{V_p}{V_0} \right)^{-2/3} - \left( \frac{V_p}{V_0} \right)^{1/3} \right\} \exp \left( \frac{1}{3}(B_0' - 1) \right) \left\{ 1 - \left[ \frac{V_p}{V_0} \right]^{1/3} \right\} \]

(11)

It must be noted that this equation differs from that published in ref.\textsuperscript{7} in the exponent of the factor \((V_p/V_0)\), which is now \(-2/3\) instead of \(+2/3\). Both equations reproduce approximately the same pressure but the coefficient \( B_0 \) now represents the bulk modulus (which was not the case of the coefficient \( K_0 \) in ref.\textsuperscript{4}). This EOS was proposed by Loubeyre et al.\textsuperscript{25} for the case of bulk hydrogen, but the zero pressure volume \( V_0 \) was there taken equal to the original value \((23 \text{ cm}^3/\text{mol})\) given in\textsuperscript{17} as recommended in ref.\textsuperscript{26} Thereby, while the pressure (eq 11) is determined in experiments, the energy (eq 10) is the quantity determined in our molecular simulations. Still, the pressure obtained from the energy is consistent with the expression of the pressure used in experiments.

**Thermal Pressure.** To obtain the dynamical pressure of eq 5, the computation of the \( \gamma \) factor is required. The estimation of \( \gamma \) represents a challenge in experiments as it requires the measurements of various thermodynamic properties (such as the volume coefficient of the thermal expansion, the crystal volume, the isothermal compressibility, and the heat capacity at constant volume).\textsuperscript{21} The computation of \( \gamma \) also represents a challenge theoretically because one needs to know all the anharmonic constants of the oscillators (refer to Appendix A). Thus, it is necessary to implement a simpler approach without forgetting to include anharmonic effects in the computation of \( \gamma \). At the experimental level, one alternative consists in focusing on the asymptotic limit \( T \rightarrow 0 \text{ K} \).\textsuperscript{21} We resort to a similar procedure here.

We first recall the expression of the pressure as given by the Virial (Vir) theorem\textsuperscript{6}

\[ P^{\text{Vir}} = \frac{1}{3V} \sum_{\alpha=1}^{N} R_{\alpha}^3 \left\langle \frac{\partial^2}{\partial R_{\alpha}(t)^2} \right\rangle_T \]

(12)

where \( \langle \rangle_T \) is the potential of the wall to which the \( \alpha \)-th enclosed particle is subject to. The quantity \( R_{\alpha}(t) \) is the trajectory of the \( \alpha \)-th particle as determined from the interaction with all the other confined particles and cage atoms in the molecular dynamics simulation. The differentiation of \( \langle \rangle_T \) is performed with respect to the radial distance \( R_{\alpha} \). The brackets indicate time average as in eq 3. The difference \( P^{\text{Vir}} - P^{\text{Vir}}_{\text{eq}} \) represents the thermal pressure. By combining eq 5, one obtains the \( \gamma \) factor

\[ \gamma = \frac{(P^{\text{Vir}} - P^{\text{Vir}}_{\text{eq}})}{3Nk_BT} \]

(13)

In this form, the \( \gamma \) factor may be interpreted as a friction coefficient, according to the approach of Nosé and Hoover.\textsuperscript{27} Obtaining \( \gamma \) with eq 13 is relatively cheap computationally since the Virial pressure simply depends on the atom trajectories retrieved from the molecular dynamics simulation. For simplicity, it is convenient to parametrize the potential \( U \) of eq 12 with an \( m \)-order polynomial. The value of \( m \) is determined by the cage potential, which depends on the cage radius. It is observed that large radii require more terms because the potentials are non-monotonic. The Virial pressure becomes

\[ P^{\text{Vir}} = \frac{1}{3V} \sum_{\alpha=1}^{N} \sum_{n=1}^{m} nB_nR_{\alpha}^n(t) \]

(14)

We record the atomic coordinates at every time step of the molecular dynamics. Afterward, they are used to compute the Virial pressure and, finally, the \( \gamma \) factor. The final pressure corresponds to the sum of the static (eq 11) and thermal (eq 5) pressures.

\[ P = \frac{3\gamma Nk_BT}{V_p} \]

\[ + 3B_0 \left\{ \left( \frac{V_p}{V_0} \right)^{-2/3} - \left( \frac{V_p}{V_0} \right)^{1/3} \right\} \exp \left( \frac{1}{3}(B_0' - 1) \right) \left\{ 1 - \left[ \frac{V_p}{V_0} \right]^{1/3} \right\} \]

(15)

The EOS is both computationally and experimentally amenable. It is expected to work reasonably well for systems of confined particles at low temperatures and low pressures, even beyond the anharmonic approximation, but, of course, within the classical regime. Note that the above expression of the pressure differs from that of ref.\textsuperscript{24} as knowledge of both the Debye frequency distribution and the Einstein dominant frequency is not required in the case of atomic clusters.

**METHOD**

The molecular dynamics simulations are performed under the classical Born–Oppenheimer (BO) scheme where the Newtonian equations of motion of the atoms are numerically solved at discrete times. The collection of all atomic coordinates over time represents the system trajectory. The forces exerted on the atoms are obtained from the electron wave function which is computed for instantaneously static nuclei. The electron wave function is represented by a single determinant of molecular orbitals which, in turn, are determined by self-consistently solving the DFT Kohn–Sham one-electron equations. The self-consistent iterations of the energy and density are converged to values lower than \( 10^{-5} \text{ au} \). We use the generalized gradient version of DFT with the expressions of Becke for exchange\textsuperscript{28} and Lee–Yang–Parr for correlation\textsuperscript{29} because they are appropriate for investigating the energetic features of systems with highly inhomogeneous charge distributions. Basis sets of the type DZVP (double-\( \zeta \) valence plus polarization) render small basis set superposition errors and are used to build the molecular orbitals. The velocity Verlet’s integrator is applied to evolve the positions and velocities of the particles. The time step in the dynamics is 1 fs and the simulation times reach up to 5 ps. The thermal equilibrium is
determined in terms of the fluctuations of the temperature with the time. The thermal equilibrium is achieved when temperature fluctuations become less than 10% of the average temperature. For a cage with radius 3.7 Å, the thermal equilibrium is obtained after 1 ps; however, for a cage with radius 3.0 Å the thermal equilibrium is obtained after a half ps. Despite that, our time averages are taken over the last 2 ps when the simulations are of 5 ps. Given the small number of particles and the spatial constrains on their motions, we assume that ergodicity is achieved in the simulations. The equilibrium temperature is obtained by averaging the instantaneous temperatures in the time interval corresponding to thermal equilibrium.

Note that in the classical BO approach the motion equations of the atoms are Newtonian and, clearly, not appropriate for the study of quantum phenomena at very low temperatures. Therefore, the method is only valid at temperatures where quantum effects play a negligible role. In order to estimate the lower bound temperature for the application of the classical equations of motion, it is important to consider the critical temperature of para-H$_2$ for Bose-Einstein condensation, which is 6.6 K. According to Grether et al.’s arguments, the critical temperature is expected to be smaller for harmonically trapped quantum gases. On the other hand, there is evidence that superfluidity appears on the surface of small para-hydrogen clusters at temperatures close to 2 K. For the classical limit to be valid, the cavity radius is capable of explaining molecular dissociation of intermolecular potentials. Unfortunately, the approach implemented there is incapable to explain molecular dissociation and the transition to the metallic state as no effective with the new GPU computing technologies and strategies discussed in ref 37; work in this direction is currently in progress.

A CASE STUDY: 13 CONFINED H$_2$ MOLECULES

Confined hydrogen has traditionally represented a challenging system and little is known on the behavior of finite-size hydrogen systems under compression. The number of 13 hydrogen molecules is chosen as it is a magic number for which the hydrogen molecules remain energetically stable at high pressures. This number of molecules has been shown capable of reproducing some results compatible with those observed experimentally on the bulk. The confining cage is a fullerene conformed by M = 60 hydrogen atoms. The pressure created by the cage makes the hydrogen molecules self-assemble into clusters. The atomization energy with respect to the cluster structure. As in the 30 K simulations, the outcome was a static energy with dependence on the parametrization of the static case. For simplicity, we shall use the parametrization of the static volume $V_p$ is used in the parametrization of the static energy (eq 10). Numbers in brackets are experimental measurements of ref 24.

<table>
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<tr>
<th>$R_c$ (Å)</th>
<th>$V_p$ (cm$^3$/mol)</th>
<th>parameter</th>
<th>value</th>
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<td>2.30</td>
<td>1.215</td>
<td>$V_0$</td>
<td>23 [19.93, 23.0]</td>
</tr>
<tr>
<td>2.40</td>
<td>1.374</td>
<td>$B_0$</td>
<td>0.2540 [0.166, 0.33]</td>
</tr>
<tr>
<td>2.50</td>
<td>1.545</td>
<td>$B'_0$</td>
<td>7.1239 [6.6, 7.29]</td>
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<td>3.80</td>
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</table>

The units of $V_0$ are cm$^3$/mol, units of $B_0$ are GPa, and $B'_0$ is dimensionless. The volume $V_p$ is used in the parametrization of the static energy (eq 10). Numbers in brackets are experimental measurements of ref 24.

RESULTS AND DISCUSSION

We compare the results obtained in the low-temperature and low-pressure regime with available experimental measurements. The comparison is to assess the similarities and differences between the cluster (the finite-size matter) and the bulk. We first discuss the behavior of the static energy, continue with the gamma factor, to finally determine the total pressure. The orientational order of the confined hydrogen molecules is discussed at the end.

Static Energy. The static energy $U$ was obtained after averaging the DFT energies as indicated in eq 9. The time interval considered for most time averages was the last 2 ps of each molecular dynamics simulations, usually with a total duration of 5 ps. We obtained the static energy $U$ as a function of the cluster volume $V_p$ for a temperature of 30 K. A parametrization of $U$ vs $V_p$ using eq 10 was performed for the 30 K simulations. Concurrently, we performed static minimizations of the electronic energy with respect to the cluster structure. As in the 30 K simulations, the outcome was a static energy with dependence on the parametrization of the static case. For simplicity, we shall use the static parametrization to compute the static pressure in the following. The parameters are listed in Table 1; however, one must be aware that a better evaluation of the pressure requires in principle several parametrizations in order to account for temperature effects, specially at high temperatures. The values of the bulk modulus $B_0$, its pressure derivative $B'_0$, and of the volume $V_p$ are in fair agreement with experimental measurements.

Table 1. Cage Radius and Corresponding Cluster Volume, Together with the Parameters of the Static Pressure $P_{stat}$

\begin{tabular}{|c|c|c|}
\hline
$R_c$ (Å) & $V_p$ (cm$^3$/mol) & parameter & value \\
\hline
2.30 & 1.215 & $V_0$ & 23 [19.93, 23.0] \\
2.40 & 1.374 & $B_0$ & 0.2540 [0.166, 0.33] \\
2.50 & 1.545 & $B'_0$ & 7.1239 [6.6, 7.29] \\
2.60 & 1.697 & & \\
2.70 & 1.850 & & \\
2.80 & 2.045 & & \\
3.00 & 2.479 & & \\
3.20 & 2.972 & & \\
3.40 & 3.531 & & \\
3.60 & 4.162 & & \\
3.80 & 4.865 & & \\
\hline
\end{tabular}
The behavior of the thermal pressure (eq 5) with respect to $\gamma$ is of interest (Figure 2). According to expression 5, a positive $\gamma$ produces a compression of the cluster, whereas a negative $\gamma$ produces a tensile stress (negative thermal pressure). The stress acts through the electron system located between the cage and the cluster atoms. On the other hand, when $\gamma$ is constant and positive, the thermal pressure increases linearly with the temperature. In the case of a constant and negative $\gamma$, the tensile stress increases linearly with the temperature.

In the case of the cavity radius $R_c = 3.0$ Å, the cluster volume is 2.5 cm$^3$/mol, the gamma factor is positive and eq 5 gives a thermal pressure of 0.64 GPa for $T \sim 190$ K (Figure 2). In bulk hydrogen, a volume of 10.0 cm$^3$/mol with temperature 300 K produces the same thermal pressure. The present results are satisfactory given the differences between the finite-size system and the extended system, together with the use of different temperatures. For the cavity with radius $R_c = 3.7$ Å the values of $\gamma$ are larger and negative, producing a tensile stress (Figure 2).
In the case of the cavity of radius 3.0 Å the thermal pressure decreases. The two contributions compensate each other in this limit, with one central molecule surrounded by 12 others. In systems where all molecules point in the same direction, we have \( \mathbf{n} = \mathbf{n} \) (this is not the case here) and \( O \) is called the nematic order parameter.\(^4,5^\) At low temperatures, the individual molecules of the clusters are oriented in fixed directions (the vectors \( \mathbf{u} \) are roughly time independent) but the orientations differ from one molecule to another. In this limit, \( \langle (\mathbf{u} \cdot \mathbf{n})^2 \rangle = 1 \) for every index \( i \) in eq 17 and the orientational order parameter is maximal, \( O = 1 \). On the contrary, if each molecule rotates and takes any orientation with equal probability in the course of time, then \( \langle (\mathbf{u} \cdot \mathbf{n})^2 \rangle = 1/3 \), leading to \( O = 0 \), indicative of the absence of orientational order.

Figure 4 displays the average orientational order parameter \( O \) as a function of the temperature. As expected, a decreasing trend with fluctuations is observed when the temperature increases. A large drop of \( O \) occurs in the temperature range 30–600 K for the cage \( R_c = 3.0 \) Å (approximate pressure of 200 GPa) and a smaller drop in the temperature range 25–200 K for the cage \( R_c = 3.7 \) Å (approximate pressure of 40 GPa). The large fluctuations are attributed to the onset of molecular dissociation. In both cases (\( R_c = 3.0, 3.7 \) Å), the decrease of \( O \) concurrently follows the increase of the fluctuations of the interatomic distances.\(^6^\) Despite the fluctuations of Figure 4, the results show evidence of a gradual order-to-disorder transition when the temperature increases.

**Bond-Orientational Order.** This section analyzes a bond-orientational order parameter characterizing the 3D structure of the cluster as a whole. At low temperatures it is observed that the mass centers of the 13 molecules are arranged in an icosahedral manner, with one central molecule surrounded by 12 others. Icosahedral structures are noncrystalline but common in glasses and liquids.\(^4,5^\) The presence of an icosahedron can be inferred
and even quantified with a bond-orientational order parameter. In this context, “bond” should not be interpreted as a chemical bond but as a line joining two centers of mass of molecules i and j. Let \( r_i(t) \) be the center of mass of molecule i at time \( t \) and \( r_j(t) \) the instantaneous position difference \( r_j(t) - r_i(t) \). Taking the central molecule \( (i = 1) \) as a reference point, let us denote \( \theta(r_{ij}) \) and \( \phi(r_{ij}) \) the spherical polar angles of the bond \( 1 \rightarrow j \) with respect to a given reference frame (the time variable is omitted for simplicity). The \( qlm \) number is introduced45

\[
qlm(r_{ij}) \equiv Y^m_l(\theta(r_{ij}), \phi(r_{ij}))
\]

where \( Y^m_l \) are the spherical harmonics. The local environment around molecule 1 is represented by the average number \( \overline{qlm} \)

\[
\overline{qlm} = \frac{1}{12} \sum_{l=2}^{13} \sum_{m=-l}^{l} qlm(r_{ij})
\]

Only even-\( l \) spherical harmonics are considered because they are invariant under inversion \( (qlm \) is unchanged by the transformation \( r_{ij} \rightarrow -r_{ij} \)). For a given \( l \), the number \( qlm \) depends on the reference coordinate system, nevertheless, the following combination is invariant under the rotation of the coordinate axes

\[
q_l = \left[ \frac{4\pi}{2l+1} \sum_{m=-l}^{l} |qlm|^2 \right]^{1/2} ; \quad 0 \leq q_l \leq 1
\]

One defines the bond-orientational order parameter \( Q_l \) as the time average of \( q_l \).

\[
Q_l \equiv \langle q_l \rangle \quad (18)
\]

For a perfect icosahedron, the first nonzero \( \overline{qlm} \) numbers occur at \( l = 6 \) and \( l = 10 \), namely, \( Q_6 \approx 0.663 \) and \( Q_{10} \approx 0.37 \) independently of the reference frame.46 For structures other than the icosahedron, \( Q_6 \) and \( Q_{10} \) take lower values. In Figure 5, we show \( Q_l \) in terms of the temperature for the first values of even \( l \) and for the two cage radii. The parameter \( Q_l \) is not small compared to 1 in the cases \( l = 6 \) and \( 10 \), but negligible otherwise. Thus, we have a signature of icosahedral order. Our values are very close to those of an ideal icosahedron. Somewhat unexpectedly, this order persists in the whole temperature range 30 – 570 K considered in this work as the numbers \( Q_6 \) and \( Q_{10} \) decrease only mildly with the temperature. The order is even slightly more robust at a higher pressure \( (R_c = 3.0 \ \text{Å}) \). At high temperatures, the icosahedral structure persists whereas the individual molecular orientations are in the disordered state. Similarly, in ref 16, orientational molecular disorder was observed within crystalline \( \text{H}_2 \). Since the order parameters \( O \) and \( Q_l \) describe different broken symmetries, the corresponding order—disorder transition temperatures do not have to be the same.

For comparison, the \( Q_l \) coefficients were recalculated by translating at each time step the center of mass of each molecule from its physical position with a random vector, more precisely, \( \mathbf{R}_i(t) \rightarrow \mathbf{R}_i(t) + \mathbf{b}_i(t) \), where \( \mathbf{b}_i(t) \) is a vector whose coordinates are random numbers chosen from a Gaussian distribution with zero mean and variance \( \varepsilon/\sqrt{3} \) (thus \( \langle |\mathbf{b}_i(t)|^2 \rangle = \varepsilon^2 \)). With \( \varepsilon = 1 \ \text{Å} \), the structures obtained with the perturbation lost the icosahedral geometry, and the \( Q_6 \) and \( Q_{10} \) coefficients noticeably decreased from the ideal values, whereas the other coefficients became prominent (in fact, larger than 0.10, see \( Q_l \) with \( l = 2, 4, 8 \) in Figure 5). This confirms the fact that the nonperturbed molecules are located near the positions of a perfect icosahedron as indicated in Figure 5. The structure is depicted in Figure 1 of ref 5.

### CONCLUSIONS

A new methodology with name TMoFSS (acronym of thermodynamic model of finite size systems) is presented to study the properties of finite systems under low pressure and low temperature conditions in the classical regime. The method considers a cage with atomic structure and provides expressions for the pressure, volume, and temperature of the enclosed particles. The pressure is calculated in analogy with the Mie—Grüneisen equation of state, without resorting to the Debye distribution of frequencies or to the variation of the molecular stretching frequencies with the volume. This novel confinement method is illustrated with the study of hydrogen clusters at low temperatures and low pressures in the classical region. The method is flexible enough and can be easily adapted to investigate pressure and temperature effects of other systems of particles. The present method complements a previous one used for finite systems at high temperatures.5 When the model was applied to a set 13 hydrogen confined molecules, different physical quantities were compared with experimental data. Despite of the fact that the system \( 13 \text{H}_2@\text{H}_{60} \) represents a finite set of hydrogen confined molecules, the results compare favorably with experimental measurements. Also, two orientational order parameters were discussed with the purpose of characterizing the structure of the \( 13 \text{H}_2 \) confined molecules. The \( 13 \text{H}_2 \) confined system presents an order-to-disorder transition in the orientations of the molecules, whereas the molecular mass centers of the hydrogen molecules stay arranged in a noncrystalline icosahedral structure for the wide temperature range considered in this work. Further applications are in progress.

### APPENDIX A: PRESSURE EXERTED BY A SYSTEM OF WEAKLY INTERACTING ANHARMONIC OSCILLATORS

In this appendix we derive an expression for the pressure of a system of weakly interacting anharmonic oscillators. The derivation is similar to that used in ref 46 for the harmonic case.
The anharmonicity emerges from the interaction potential between atom pairs of a molecule. First consider a one-dimensional anharmonic oscillator described by a potential energy that includes quadratic and quartic terms in the displacement \((R - R_e)^2\) and \((R - R_e)^4\):

\[
V(R) = \frac{k}{2}(R - R_e)^2 + \lambda(R - R_e)^4
\]  

(A1)

The factors \(k\) and \(\lambda\) are spring constants with \(k \gg \lambda \geq 0\). In other words, the anharmonicity of the oscillator is small. The energy levels corresponding to the wave equation

\[
\left[ -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \nu^2} + V \right] \psi_n = E_n \psi_n
\]  

(A2)

given, at first order in perturbation theory, by

\[
E_n = \hbar \nu \left( n + \frac{1}{2} \right) + \alpha \left( n + \frac{1}{2} \right)^2 + \frac{\alpha}{4}
\]  

(A3)

where \(\alpha = 3\lambda k^2/(8\pi^2 M^2 \nu^4)\).\(^3^9\) We next consider \(N_o\) anharmonic oscillators in interaction resulting in an additional energy \(U\). Since the temperature of the oscillator system is low enough (the mass centers of the oscillators fluctuate very little around their average positions and have a low configurational entropy), then the energy \(U\) may be approximated by the static energy of the system.\(^4^6\) The energy of the model system consists of the interaction energy among oscillators plus the energy of each oscillator

\[
E(\{n_i\}) \approx U + \sum_{i=1}^{N_o} E_{ni}
\]  

(A4)

If the oscillator modes are independent and the static energy \(U\) is constant, the partition function takes the form

\[
Z = e^{-U/k_b T} Z_{\nu}
\]  

(A5)

where \(Z\) is the single oscillator partition function.

\[
z = \sum_{n=0}^{N_{\text{max}}} e^{-E_n/k_b T}
\]

\[
= \sum_{n=0}^{N_{\text{max}}} e^{-(n+1/2)\hbar \nu/(\alpha t/4h \nu)}
\]  

(A6)

\[ t \equiv \hbar \nu/k_b T \]

Here, the \(i\) index of \(n_i\) was dropped and the energy \(E_n\) was inserted in the partition function \(Z\). We are interested in working inside the limits established by both the classical region \((t \ll 1\) or \(h \nu \ll k_b T\)) and perturbation theory (where the anharmonic contribution is a perturbation energy, \((\alpha t/\nu) n^2 \ll nt\)). The number \(N_{\text{max}}\) is the value of \(n\) such that the perturbative anharmonic correction of quadratic order becomes comparable with the leading term \(nh \nu\) (thus, \(N_{\text{max}} \sim h \nu/\alpha\)).

Truncating the partition function at \(N_{\text{max}}\) is valid when the probability of occupying higher energy levels is simply negligible. Hence, the thermal energy \(k_b T\) must be smaller than \(N_{\text{max}} h \nu\) or, equivalently \(N_{\text{max}} > 1/\ell\). By using the definition of \(N_{\text{max}}\) such a condition implies an upper bound to the temperature, namely, \(k_b T \ll (h \nu)^2/\alpha\).

From the form of \(Z\) above, the Helmholtz free-energy function \(F = -k_b T \ln Z\) of the system is given by

\[
F = -N_o k_b T \ln z + U
\]  

(A7)

The pressure is computed by differentiating this expression with respect to the volume, namely,

\[
P = -\left( \frac{\partial F}{\partial V} \right)_T
\]

(A8)

with \(\gamma\) given by the general relation

\[
\gamma = \frac{V}{Z} \frac{\partial Z}{\partial V}
\]  

(A9)

The gamma factor thus reads

\[
\gamma = -\frac{V}{k_b T} \left[ \sum_{n=0}^{N_{\text{max}}} \frac{\partial E_n}{\partial V} \right] \left( \sum_{n=0}^{N_{\text{max}}} e^{-E_n/k_b T} \right)^{-1}
\]

\[
= -\frac{V}{k_b T} \frac{\partial E_n}{\partial V}
\]  

(A10)

In the temperature range \(h \nu \ll k_b T \ll (h \nu)^2/\alpha\) the ensemble average of \(\partial E_n/\partial V\) is obtained by neglecting the anharmonic part of \(E_n\) in the exponentials.

\[
\gamma \approx -\frac{V}{k_b T} \left( \sum_{n=0}^{N_{\text{max}}} \left( n + \frac{1}{2} \right) \frac{\partial \nu}{\partial V} \right)
\]

\[
+ \left[ \left( n + \frac{1}{2} \right)^2 + \frac{\alpha}{4} \right] \frac{\partial \alpha}{\partial V} e^{-t(n+1/2)} \left( \sum_{n=0}^{N_{\text{max}}} e^{-t(n+1/2)} \right)^{-1}
\]

\[
= -\frac{V}{k_b T} \left[ \frac{1}{4} \frac{\partial \alpha}{\partial V} + \frac{s''(t)}{s(t)} \frac{\partial \nu}{\partial V} - \frac{s'(t)}{s(t)} \frac{\partial \nu}{\partial V} \right]
\]  

(A11)

where \(S(t) = \sum_{n=0}^{N_{\text{max}}} e^{-t(n+1/2)}\) is \(e^{-t(1-\epsilon^{-tN_{\text{max}}+1})}/(1-\epsilon^{-t})\) and \(s(t), s'(t)\) are the first and second derivatives of \(S\) with respect to \(t\). \(N_{\text{max}}\) is such that \(1\geq e^{-t(N_{\text{max}}+1)}\) and we have \(s(t) = e^{-t/2}/(1-e^{-t})\). Expanding the above expression at small \(t\) yields the final result.

\[
\gamma = -\frac{V}{\nu} \frac{\partial \nu}{\partial V} - 2V \frac{k_b T}{(h \nu)^2} \frac{\partial \alpha}{\partial V} + \frac{\partial}{\partial V} \left( \frac{V}{k_b T} \frac{\partial \alpha}{\partial V} \right)
\]  

(A12)

This expression can be obtained from the partition function of a gas of anharmonic oscillators as proposed by Aly.\(^4^8\) A detailed analysis of \(\gamma\), and the inclusion of anharmonic effects based on thermodynamic expressions, is also given by Girifalco.\(^4^6\) The first term in the right-hand side of the above equation is the well-known Grüneisen factor, which is recovered in the absence of anharmonicity (\(\alpha = 0\)). Recalling that \(\alpha\) is proportional to \(h^2 \lambda \alpha / \nu \sim 0\), where \(\lambda\) is the anharmonic constant in the interaction potential, the second term represents the leading correction and, like the first leading term, it is independent of \(h\). In 3D space, there are more degrees of freedom and one can naturally define the \(\gamma\) factor in this case as

\[
P = \frac{3N_o k_b T}{V} \left( \frac{\partial U}{\partial V} \right)_T
\]

(A12)

which is eq 7 of the main body text. In conclusion, eq A12 confirms the experimental evidence of a Mie–Grüneisen-type
pressure that includes anharmonic effects and maintains a linear dependence on the temperature in the classical regime of low temperatures and low pressures.

**APPENDIX B: STEPS TO COMPUTE THE THERMODYNAMIC VARIABLES \( V_{\text{eq}}, \) \( T_{\text{eq}}, P_{\text{STAT}}, \) AND \( P_{\text{THERM}} \)**

The following steps indicate the procedure in the TMoFSS method to compute the pressure, temperature, and volume of the confined finite-size system.

1. Optimize the structure of the cluster with respect to the energy. At this first stage, the optimization considers the particle system in vacuum.
2. Build the confinement cage (possibly of fullerene type).
3. Insert the structure of step 1 in the cage of step 2. The cluster structure may need to be reduced to fit properly inside the cage.
4. Run the molecular dynamics at constant temperature, fixing the cage atoms but allowing the cluster atoms to move freely. The atom coordinates and velocities are recorded at every time step. If the coordinates are the only variables recorded, the atom speeds can be obtained from the sequence of frames of the molecular dynamics simulation.
5. Determine the instantaneous temperatures \( T(t) \) from the instantaneous kinetic energies \( E_{\text{kin}}(t) \). Analyze the curve “temperature vs time” to determine the temperature fluctuations. The time interval where the fluctuations are less than 10% is considered the time interval where the particles are in thermodynamic equilibrium. The average temperature in this interval defines the equilibrium temperature \( T_{\text{eq}} = 2\langle E_{\text{kin}}(t) \rangle / (N g k_B) \) (eq 3 with \( \lambda = 1 \)).
6. Compute the average cluster volume and average electronic energy in the time interval of thermodynamic equilibrium. This step gives a single point of the “static energy vs cluster volume” curve.
7. Repeat steps 4—6 for different cage radii using the same equilibrium temperature. This process provides several points that build the isothermal “static energy vs cluster volume” curve.
8. Parameterize the “static energy vs cluster volume” curve (eq 10) and get the static pressure by differentiation of the static energy with respect to the cluster volume (eq 11). The parametric expression of the static energy is somewhat arbitrary; nevertheless, the parametrization given in eq 10 has, in principle, physical meaning since mechanical or elastic constants appear in the expression. This gives a chance to compare with experimental results on the bulk. We are done with the static energy and static pressure at this stage.
9. In order to determine the thermal pressure, we need to know the \( \gamma \) factor as indicated in eq 13. First, the Virial pressure (eq 12) should be computed, which in turn requires knowledge of the wall potential \( \phi \) acting on a single particle located at different radial distances from the center of the cage (recall that the cage is supposed to have spherical symmetry). The latter calculations are “static” ones and require no molecular dynamics simulations of the system.
10. It is convenient to parametrize the wall potential to use it in the expression of the Virial pressure. This process allows introduction of an analytical expression (like this of eq 14) of the Virial pressure in an independent program code. We have a single Virial pressure for each molecular dynamics simulation with a given cage radius and fixed equilibrium temperature. The gamma factor results from the difference of Virial pressures (eq 13), as explained in the body text.

11. Once the gamma factor is known, the thermal pressure is obtained from eq 5. The thermal pressure should be added to the static pressure to obtain the total pressure (eq 15). At low temperatures the thermal pressure is small compared with the static pressure and, therefore, the static pressure is considered the total pressure. In such cases, there is no need of molecular dynamics simulations, however, it is necessary to obtain energy-optimized structures of the cluster in cages of different radii to determine the static energy in terms of the cluster volume and, finally, the static pressure.

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**ACKNOWLEDGMENT**

We wish to acknowledge DGSCA for use of KanBalam.

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