Thermal behavior of a 13-molecule hydrogen cluster under pressure

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The thermal behavior of a 13-molecule hydrogen cluster is studied as a function of pressure and temperature using a combination of trajectory and density functional theory simulations. The analysis is performed in terms of characteristic descriptors such as caloric curve, root-mean-square bond length fluctuation, pair correlation function, velocity autocorrelation function, volume thermal expansion, and diffusion coefficients. The discussion addresses on the peculiarities of the transition from the ordered-to-disordered state as exhibited by the cluster under different pressures and temperatures. © 2010 American Institute of Physics. [doi:10.1063/1.3359460]

I. INTRODUCTION

Hydrogen is an essential component of Jovian planets, brown dwarfs, and other objects discovered recently beyond the limits of the solar system (Refs. 1 and 2 for a list of extrasolar planets). The typical conditions in the environments of these stellar objects are those of high pressure and high temperature. This prompted extensive interest in the properties of bulk hydrogen under the conditions of high pressure and temperature. Ideally, one would want to have an equation of state (EOS) that could help to understand the interior versus the exterior structure of hydrogen-containing stellar objects and their radiation spectra.3 The issue of EOS for bulk hydrogen has been addressed both experimentally and theoretically;4–41 for a review that also contains a discussion of early work on structural and thermodynamic properties of solid hydrogen, see Ref. 4.

The experimental investigations of bulk solid hydrogen cover a broad spectrum of properties, which include index of refraction studied by interferometry,7 crystal structure explored by neutron4 and x-ray diffraction techniques,8,12,23 and vibrational13 and band gap characteristics investigated via optical spectroscopies. Shock-wave experiments,15,24 were used to obtain Hugoniot curves and to measure sound velocity, reflectivity, and electrical conductivity.31

The majority of theoretical explorations of bulk hydrogen are computational. These can be divided into two classes.12 Those in the first class use semiempirical potentials, usually of pairwise additive form, to mimic the interatomic interactions (see, e.g., Refs. 5, 27, and 28). These studies are capable of addressing structural, dynamical, and thermal aspects, but not ones that require explicit inclusion of electrons (e.g., the pressure-induced plasma state12,13). Studies of the second class include explicit treatment of electrons by solving the Schrödinger equation. The formalism of choice is usually density functional theory (DFT) in its either local42,21,25,34 or nonlocal29,32,36 implementations, although the path integral19,22 and quantum Monte Carlo35,37 techniques have also been employed. The structural, dynamical, and thermal aspects are then studied by computing the forces acting on the atoms via the Hellmann–Feynman theorem, and performing molecular dynamics simulations to mimic the time evolution of the system, or by Monte Carlo statistical sampling of the nuclear configuration space using first-principles-based configurational energies. Studies in the second class address issues as the pressure-induced transition to metallicity42,43 and to plasma state19,22 (cf. also Refs. 14, 20, and 28), high-pressure isotherms,38 and a rapid increase in dc conductivity along the Hugoniot curve.15

In recent DFT-based computational studies we explored the effects of pressure on structural and electronic properties of small molecular hydrogen clusters at zero temperature.39–41. The results indicate a gradual atomization of the constituent H2 molecules and a transition from nonmetallic to metallic state as the pressure on the clusters is increased. The goal of this study is to explore the behavior of a 13-molecule hydrogen cluster encapsulated in a 60-atom hydrogen cage as defined by simultaneous effects of pressure and temperature. The ranges of pressure and temperature covered are those of 65 to 70 GPa and 10 to 600 K, respectively. Such ranges correspond to the conditions of an envelope of Jupiter’s interior.3 In this regard, the investigation becomes important to understand the behavior of matter under extreme conditions from a bottom-up point of view. The methodological background and computational procedure are outlined in Sec. II. The results are presented and discussed in Sec. III. A brief summary is given in Sec. IV.

II. CONFINE MODEL

The molecular simulation of a system of particles under confinement and with temperature demands the presence of confining walls in contact with a heat reservoir. However, in practice, the atomic structure of the walls makes the molecu-
lar simulations computationally expensive. In this context, alternative approaches have emerged making use of extended Lagrangians that include barostat and thermostat effects through virtual particles. These methods have shown excellent results for systems with translational symmetry, such as crystals, but their application to finite systems remains questionable. In this work we assume a confinement cage with atomic structure and interaction with the enclosed particles. The forces of the cage are responsible of the pressure over the enclosed particles. The enclosed particles also appear under the effects of temperature to determine the main thermodynamic variables.

The enclosed system consists of 13 hydrogen molecules. The particle species are due to the fact that hydrogen is the main component of Jovian planets. In a previous investigation, the pressurized molecular system of 13 hydrogens was observed to present icosahedral symmetry and great energetic stability. In particular, the small clusters are notorious for the magic-number behavior of many of their properties, and \(N=13\) is a well-known magic number for many clusters such as rare-gases. In addition, a number of 13 molecules have shown to provide results compatible with experiments on the solid. On the other hand, a fullerene cage conformed by 60 hydrogen atoms is considered as the confining box. The cage interacts with the encapsulated hydrogens and can be shrunk to reproduce different pressures. The application of a cage like this has shown the self-assembly of hydrogen molecules into hydrogen clusters of different sizes and geometries with the pressure and, in addition, has shed light on the atomization process of molecular hydrogen under extreme pressures. The consideration of a confined system with higher particle density reduces the range of pressures that can be explored with the 60 hydrogen atom cage. Also, the computational expense of the proposed system is not prohibitive when the total number of particles, including those of the cage, is reasonably low. In this regard, the model (consisting of 13 confined hydrogen molecules in a 60-atom hydrogenic fullerene cage) appears appropriate enough to consider cluster stability with pressure and temperature.

In order to classify the thermodynamic state of the confined hydrogen cluster, expressions for the pressure, temperature, and volume should be provided. Thus, it is relevant to recall the pressure of a system of interacting particles with validity in the classical regime \((k_B T \gg \hbar \nu\), with \(\nu\) the average vibrational frequency of the particles),

\[
PV = Nk_BT + \frac{1}{3} \sum_{a=1}^{N} \mathbf{R}_a \cdot \mathbf{F}_{\text{int}}^a,
\]

where \(N\) and \(V\) are the number and volume of the confined particles and \(P\) and \(T\) are the equilibrium pressure and temperature. The set of coordinates \(\mathbf{R}_a(t_0), \mathbf{R}_a(t_1), \mathbf{R}_a(t_2), \ldots\) gives the trajectory of the \(a\)th particle in its interaction with all the other particles of the compressed cluster and cage. The time dependence of the coordinates defines an instantaneous pressure, which should be averaged to obtain the final pressure [the brackets in Eq. (1) denote time average]. The first term is associated to elastic collisions producing pressure on the walls (it is also observed to appear in other derivations, such as the virial expansion of the pressure). The second term corresponds to the pressure produced by the internal forces. The quantity \(\mathbf{F}_{\text{int}}^a\) is the force exerted over the \(a\)th particle by the other compressed particles, excluding the (external) force exerted by the container. The present expression is not amenable computationally because the total force \(\mathbf{F}_{\text{tot}}^a\), and not the internal one, is determined in the molecular simulation. In order to deal with the internal force, the external force is subtracted from the total force, \(\mathbf{F}_a = \mathbf{F}_{\text{tot}}^a - \mathbf{F}_{\text{ext}}^a\). Since the external force can be estimated from additional molecular calculations (to be explained below), then the internal force is determined in terms of the total and external forces. In particular, the external force is computed by working with a hydrogen atom located in the fullerene cage at different distances \(R_a\) from the cage center. The approximate spherical symmetry of the cage allows to consider the external force as a radial force, given in the form \(\mathbf{F}_{\text{ext}} = -\hat{R}_a \partial V(R_a) / \partial R_a\). The potential \(V\) is created by the cage atoms. The coordinate \(\mathbf{R}_a(t)\) is taken from the simulation in which all the interactions of the \(a\)th particle with the cage particles and the cluster particles are considered. The proposal of the external force is physically admissible as it does not incur in additional suppositions than these already established in Eq. (1), and is compatible with the Born–Oppenheimer approximation implicitly assumed in the equations. Therefore, the pressure acquires the form

\[
F = Nk_BT/V + \frac{1}{3V} \sum_{a=1}^{N} \mathbf{R}_a \cdot \left[ \mathbf{F}_{\text{tot}}^a + \hat{R}_a \frac{\partial V(R_a(t))}{\partial R_a} \right].
\]

However, the first two terms on the right hand side cancel each other by the equipartition theorem (in our simulations, the addition of such terms practically gives zero), and the pressure reduces to

\[
F = \frac{1}{3V} \sum_{a=1}^{N} R_a \frac{\partial V(R_a(t))}{\partial R_a}.
\]

All the particles contribute to build the pressure. The potential can be parametrized for making it accessible in the molecular simulations, or easily computed in a posterior calculation to the simulation. Since the particle at the center of the cage achieves the minimum energy, because the forces on the particle are of equal magnitude but symmetrically opposed at that location, the parametrization acquires the form

\[
V(R_a) = A + B_1 R_a + B_2 R_a^2 + B_3 R_a^3 + B_4 R_a^4,
\]

where \(A = -33.6709, B_1 = 0.00255, B_2 = -0.00257, B_3 = 0.00467, \) and \(B_4 = 0.00141\). When the polynomial expansion is depicted, a quadratic curve is essentially observed with the \(B_i\) coefficients controlling the fast/slow growing of \(V\), for the values of \(R_a\) delimited by the cage radius. As expected, the minimum energy is reproduced when the particle is located at the center of the cage \((R_a=0)\). Finally, the force is easily computed by differentiation of the functional form of the potential.

In addition to the pressure, the cluster volume requires consideration. Suppose that the confining fullerene cage is spherically symmetric and rigid. The sphere radius is used as...
a parameter to simulate different pressure conditions (for the case of a vibrating cage, it is always possible to define an average radius). The cage radius $R_c$ appears in terms of the $M = 60$ atom distances $R_i$, measured from the fullerene cage center,

$$R_c = \frac{1}{M} \sum_{i=1}^{M} R_i. \quad (4)$$

On the other hand, the volume $V_p$ of the encapsulated particles corresponds to that of a uniform sphere, $V_p = (4\pi/3)R_p^3$, where $R_p$ is the (electronic) radius of the particles under pressure, calculated in the form

$$R_p = R_{np} + (R_c - R_{np})/2. \quad (5)$$

The quantity $R_{np}$ is the average radius of the nuclear positions of the enclosed particles (taking care of excluding the inner particles of the cluster that do not contribute to its external volume). Thereby, the volume of the confined particles is determined from the basic variables $R_c$ and $R_{np}$.

The heat flow from a heat reservoir is simulated stochastically or, more precisely, by scaling the velocities of the confined particles in the form

$$T = \frac{2}{3Nk_B} \left( E_{kin}(t) \right) = \frac{1}{3Nk_B} \left( \sum_{a=1}^{N} M_a (\lambda V_a)^2(t) \right). \quad (6)$$

The quantities $M_a$ and $V_a$ are the mass and velocity vector of the $\alpha^{th}$ particle. The brackets stand for the time average over a sufficiently large time interval. The value of $\lambda$ is determined from the new and old temperatures of the system in the form $\lambda^2 = T_{\text{new}}/T_{\text{old}}$. In other words, once the “new” temperature is decided, the scale factor is automatically determined in terms of $T_{\text{new}}$ and $T_{\text{old}}$.

Note that, under high pressure and/or high temperature, the confined atoms may escape from the cavity due to the porous nature of the cage. In these conditions, the force of the cavity over the confined atoms remains valid, although the pressure diminishes due to a reduction in the particle density. Thus, the method permits the investigation of the stability of confined atoms with the temperature and pressure.

It is with the previous proposals for pressure, temperature, and volume that the thermodynamic state of the confined cluster is determined.

**III. METHOD**

We have recourse to the classical Born–Oppenheimer scheme to perform the molecular dynamics simulations. In this approach the Newtonian equations of motion for each hydrogen nucleus are solved at every time step, thus generating a trajectory of the system. The forces over the nuclei are obtained from the electron wave function, which is computed for the (presumed) instantaneously static nuclei. The electron wave function corresponds to a single determinant of molecular orbitals which, in turn, are obtained by self-consistently solving the Kohn–Sham density functional theory equations. The self-consistent approach is finished when a convergence of $10^{-5}$ au in the energy and density is obtained. We use the generalized gradient version of DFT with the expressions of Becke for exchange and Lee–Yang–Parr for correlation. Such a level of theory classifies within the nonlocal approximations of DFT, appropriate in the investigation of energetic features and properties that are highly dependent of the charge distribution anisotropy. We use double-$\zeta$ valence polarization basis sets to build the molecular orbitals, as these are characterized to give small basis set superposition errors. The Verlet’s integrator is taken into consideration to evolve the positions and velocities of the classical particles. The time step in the dynamics is 1 fs, with simulations extending up to 5 ps. The number of particles allowed to freely move in the system corresponds to the 26 compressed hydrogen atoms. The system is not translating in space and the degrees of freedom considered are $3N−3$. The origin of the particle system corresponds to the cage center. The cage radius is fixed at 3.0 Å. The chosen temperature range is 10–600 K. The volume and temperatures proposed are based on a section of the phase diagram of bulk hydrogen, where the solid and liquid phases presumably coexist.

The computations are performed in a PC-cluster conforming by 16 nodes.

**IV. RESULTS**

In order to characterize the behavior of the confined hydrogen we have recourse to the different thermodynamic variables and indicators that are frequently used to explore the melting of solids. Some of the indicators are, for example, the interatomic-distance fluctuations, pair- and velocity-correlation functions, etc. The results correspond to time averages over the last 2 ps of the dynamics, where the fluctuations of the temperatures are lower than 10%, and the system is considered to have achieved thermal equilibrium.

**A. Pressure, volume, and temperature**

The cluster volume expands little for relatively large temperature changes, as observed in panel (a) of Fig. 1. In fact, a change of hundreds in Kelvins exhibits a change of tenths in Å$^3$. This disproportion corresponds to the disability of the cluster to freely expand, as the cavity radius is maintained fixed when the temperature is raised. Therefore, the volume expansion of the cluster is limited by the cavity. Panel (b) of the same Figure shows the temperature versus pressure. There is an almost linear relation between the two variables. However, care should be exercised in the very low temperature regime as the pressure calculation requires the consideration of quantum effects, and the present results are not expected to be the appropriate ones in such a temperature range (a work is in progress in this direction).

The volume thermal expansion coefficient, referred with $\alpha$ and computed in the form $\alpha = (1/V)dV/dT$, is estimated from our results in the high temperature regime. In the range of pressures $[66.5, 68.5]$ GPa, with an average value of 67.5 GPa, the value of $\alpha$ is $1.27 \times 10^{-5}$ K$^{-1}$. This value is slightly greater than the volume thermal expansion coefficient of a solid at null pressure$^{30}$ and lower than that of a liquid metal.
in standard conditions ($-3.5 \times 10^{-4}$ K$^{-1}$). In order to investigate the state of matter in more detail, we turn attention to the caloric curve.

**B. Caloric curve**

The caloric curve gives the variation of the total energy, considered as the sum of kinetic and potential energies, in terms of the cluster temperature. In principle, the caloric curve is capable to point out a melting process. Figure 2 shows the $E-T$ variation of the confined hydrogen cluster for the temperature range [10,600] K. An overall linear variation is observed. A possible explanation of this behavior is attributed to the fact that, under confinement, the cluster is constrained to occupy a limited number of energy states, related to small variations of the atomic positions, which in turn produce small conformational changes of the cluster. As a consequence, the energy changes linearly with the temperature. At high temperature, the cluster behavior corresponds to that obtained with the harmonic approximation, for which the normal modes are so highly excited that quantum effects are small enough. Still, the confined cluster is expected to be close to melting as hydrogen is known to have a low temperature fusion point. In short, the persistent linearity of the $E-T$ curve at high temperature points out an intermediate state, where the achievement of melting is frustrated under the particular thermodynamic conditions discussed above.

**C. Fluctuations of the interatomic distances**

The average behavior of the interatomic distances $r_{ij}$ with the temperature is elucidated with the root-mean-square bond length fluctuation given in the form

$$\delta(T) = \frac{2}{N(N-1)} \sum_{i<j}^N \frac{(r_{ij}^2) - (r_{ij})^2}{\langle r_{ij}^2 \rangle},$$

where $N$ is the number of atoms in the cluster and the brackets $\langle \cdots \rangle$ indicate a time average. The fluctuations are gauged with respect to the average interatomic distances $\langle r_{ij} \rangle$, which in turn depend on the temperature. Figure 3 depicts the fluctuations of the interatomic distances with the temperature as the pressure range is found to be practically constant, and the variations of the cluster conformations are essentially due to different temperatures.

In the region up to 70 K, the $\delta$ factor increases moderately (quasilinearly) with the temperature as expected. In the region from 70 to 300 K, the fluctuations rise sharply because the cluster particles have enough kinetic energy to overcome their local potential energy barriers. The fluctuations show a linear behavior after 300 K. In this limit, it is important to call attention to the Lindemann criterion, which for the fusion of the macroscopic solid establishes $\delta \approx 0.1$, but such a value may change for finite-size clusters. In the particular case of the hydrogen cluster, a plateau is observed from 300 K onwards, with a $\delta$ value of approximately
Based on the caloric curve behavior and the value of $\delta$, we conclude that the cluster appears in an intermediate state, presumably not far from the melting phase, in agreement with that portion of the phase diagram determined by pressures and temperatures in Ref. 30.

D. Pair correlation function

Additional structural information related to the way in which the particles are packed together with the temperature is obtained via the proton pair correlation function, defined as

$$g(r) = \frac{V_p}{4\pi r^2} \frac{\langle n_{r,r+\delta r} \rangle}{N} \langle n_{r,r+\delta r} \rangle = \frac{1}{N} \sum_{j=1}^{N} n_j(r, r + \delta r), \quad (8)$$

where $\langle n_{r,r+\delta r} \rangle$ represents the total number of neighbors located in a spherical shell of thickness $\delta r$ at a distance $r$ of each atomic center, for the $N$ encapsulated particles. The quantity $4\pi r^2 \delta r$ is the shell volume, while $N/V_p$ represents the reference number density. The resolution of the interval $\delta r$ is 0.01 Å. The previous expression is valid for a single frame of the dynamics, but it can be applied to all frames of the dynamics by summing over the total number of frames and introducing the corresponding normalization factor. Contrary to extended systems, for which $g(r)$ tends to 1 as $r$ gets large enough (see pages 54 and 140 of Ref. 55 and also Ref. 56), the pair correlation function becomes zero for spatially confined clusters at large $r$, as the probability of finding cluster particles beyond the confinement radius is naught. In this regard, if we wish to compare our results with those associated to a solid or liquid, the comparisons should be limited to the first two peaks of the pair correlation function. In Fig. 4 the pair correlation function is sketched at different temperatures. The differences are due to changes in the atomic positions or particle packing with the temperature. As the temperature increases, the first and second peaks of the correlation function decrease by spreading out. Such an evolution is also found in the melting of silicon clusters.56 In our situation, the spreading is limited by the cage. At 34 K, small secondary peaks are indicative of a positional order (associated to the $C_5$ axis of an icosahedral structure). They fade out as the temperature increases. At 543 K, the second peak is flattened. The characteristics of the second coordination shell are inherited from the low temperature peaks. In order to provide a comparison, the proton pair correlation function has been reported for bulk and dense metallic hydrogen (pressures beyond the molecular dissociation pressure) at temperatures of 1000 and 2000 K.19 The first two peaks in such a reference appear slightly shifted to higher distances from the origin than ours. In this regard, our results may be considered similar to those obtained for bulk matter. The main conclusion to this part is that the overall features of the correlation function are associated to that of an ordered solid in the transition to a disordered solid.55–57 The disordered solid, which starts at 70 K (Fig. 3), may be interpreted as a precursor of the liquid state at high temperatures, but such a liquid state is not observed in the present work.

E. The velocity autocorrelation function

Before dealing with the time correlations of atomic velocities and conclude on the possible thermodynamic state of the hydrogens under confinement, it is appropriate to check the atomic velocities by, for instance, comparing the velocity distribution function obtained from the simulation with the Maxwell speed distribution, $f(v) \sim v^2 \exp(-M_H v^2/2kT)$, where $M_H$ is the proton mass. A plot of both distributions exhibits a good agreement between the calculated and theoretical curves, indicating that thermal equilibration is achieved. In this regard, we proceed with the analysis of the autocorrelation function $C(t)$, defined in terms of the atomic velocities as
For simplicity, the latter option is considered, numerically integrating the velocity autocorrelation function or the atomic positions is defined in terms of the time as

\[ C(t) = \frac{1}{3N} \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle. \]  

(9)

The \( C(t) \) data were divided by the first value of the velocity autocorrelation function \( C(0) \), as the purpose was that curves departed from unity at \( t=0 \). The function \( C(t) \) was made independent of the time origin by computing it at 1000 different initial times, and averaged afterwards. The curves depicted in Fig. 5 are the velocity autocorrelation functions calculated for the 13 hydrogen molecules, freely moving in the fullerene cage, under temperatures of 51 and 569 K. For both temperatures \( C(t) \) decreases from a maximum value to a negative minimum, as the particles evolve from a fully correlated stage to a lower correlation stage. In the 51 K case, the oscillations show large amplitudes, associated to the fact that atoms remain bonded (forming diatomic molecules) in a vibrational state of motion. However, at 569 K the amplitudes of the molecular vibrations are small, indicative of frequent collisions and constant changes in the velocity direction. In this case, privileged velocity directions are lost, becoming all directions equally possible and, in consequence, the correlation function becomes negligible with time. In short, the 51 K situation characterizes the cluster in the solid state (at this temperature, bulk hydrogen is known to be a solid\(^{13}\)), while the 569 K case corresponds to the cluster in an intermediate thermodynamic state.

The diffusion coefficient can be computed by either numerically integrating the velocity autocorrelation function or working with the mean square displacement of the atomic positions.\(^{59}\) For simplicity, the latter option is considered, namely, \( 3D = \lim_{t \to \infty} \langle r^2(t) \rangle / 2t \). The mean square displacement of the atomic positions is defined in terms of the time as

\[ \langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} [\mathbf{r}_i(t) - \mathbf{r}_i(t_0)]^2. \]  

(10)

where \( \mathbf{r}_i(t) \) is the position of the \( i^{th} \) particle at time \( t = 5000 \) ps, the initial time is \( t_0 = 3000 \) ps and \( N \) is the number of confined atoms. The average of the quadratic displacements gives \( D = 3.0 \times 10^{-8} \) cm\(^2\)/s for the 51 K case, and \( D = 3.2 \times 10^{-7} \) cm\(^2\)/s for the 569 K case. The latter value is typical of a diffusion coefficient close to the melting point of a solid (page 113 of Ref. 59), while the value of \( D \) for the case 51 K is 10 times smaller, and corresponds to a physically acceptable diffusion coefficient of a solid under hydrostatic pressure.\(^{60}\)

V. CONCLUSIONS

The characterization of hydrogen under a wide range of pressures and temperatures is of paramount importance to understand the interior of many stellar objects. In this work, we present Born–Oppenheimer molecular dynamics in combination with generalized gradient DFT to describe the thermal behavior of a 13-molecule hydrogen cluster under pressure. The model used to control pressure upon a system with a finite number particles follows similar lines to these developed in previous papers,\(^{39–41}\) namely, hydrogen is confined within a hydrogenic fullerene cage, whose radius may be changed to impose different pressures. However, in contrast to the previous works, temperature is considered in the present model. We obtain \( (V,T) \) and \( (P,V) \) phase diagrams. Based on such diagrams and data obtained from various phase-state descriptors such as the caloric curve, root-mean square distance, Lindemann criterion, volume expansion coefficient, velocity autocorrelation function, diffusion coefficient, etc., the thermodynamical behavior of the cluster is analyzed and discussed. For instance, the proton pair correlation function of the cluster exhibits a similar behavior to that of bulk hydrogen. On the other hand, the similar diffusion coefficients of the cluster and the bulk, together with the Lindemann criterion, indicate a phase state close to the liquid state. The results point out a smooth transition of the molecular cluster from an ordered solid state to an intermediate thermodynamic state as a precursor of a possible liquid state of the cluster. It is the confinement of the cluster which extends the persistence of the intermediate state over a wide range of temperatures (above 100 K and up to 500 K). The similar conditions of temperature and pressure to these corresponding to a molecular-hydrogen envelope of Jupiter’s interior,\(^3\) suggest the existence of hydrogen clusters in such an envelope of Jupiter. Finally, the confinement model is suitable not only to describe the pressure-induced clustering, but also to investigate the bulk solid from a bottom-up perspective in function of the temperature and pressure.

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FIG. 5. The velocity autocorrelation function [Eq. (9)] is depicted with the time for two temperature cases (51 and 569 K). The velocity autocorrelation function indicates an ordered solid cluster at \( T=51 \) K, and an intermediate state at \( T=569 \) K.
