Thermodynamic properties of Pt nanoparticles: Size, shape, support, and adsorbate effects


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This study presents a systematic investigation of the thermodynamic properties of free and γ-Al2O3-supported size-controlled Pt nanoparticles (NPs) and their evolution with decreasing NP size. A combination of in situ extended x-ray absorption fine-structure spectroscopy (EXAFS), ex situ transmission electron microscopy (TEM) measurements, and NP shape modeling revealed (i) a cross over from positive to negative thermal expansion with decreasing particle size, (ii) size- and shape-dependent changes in the mean square bond-projected bond-length fluctuations, and (iii) enhanced Debye temperatures (θ_D, relative to bulk Pt) with a bimodal size-dependence for NPs in the size range of ~0.8–5.4 nm. For large NP sizes (diameter d > 1.5 nm) θ_D was found to decrease toward θ_D of bulk Pt with increasing NP size. For NPs ≤ 1 nm, a monotonic decrease of θ_D was observed with decreasing NP size and increasing number of low-coordinated surface atoms. Our density functional theory calculations confirm the size- and shape-dependence of the vibrational properties of our smallest NPs and show how their behavior may be tuned by H desorption from the NPs. The experimental results can be partly attributed to thermally induced changes in the coverage of the adsorbate (H)) used during the EXAFS measurements, bearing in mind that the interaction of the Pt NPs with the stiff, high-melting temperature γ-Al2O3 support may also play a role. The calculations also provide good qualitative agreement with the trends in the mean square bond-projected bond-length fluctuations measured via EXAFS. Furthermore, they revealed that part of the θ_D enhancement observed experimentally for the smallest NPs (d ≤ 1 nm) might be assigned to the specific sensitivity of EXAFS, which is intrinsically limited to bond-projected bond-length fluctuations.

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I. INTRODUCTION

Metal nanoparticles (NPs) have been shown to display anomalous electronic and thermodynamic properties, including metal to nonmetal transitions,1,2 superheating,3 and negative thermal expansion.4-7 However, despite decades of intense research, the origin of these effects is still heavily debated. Consensus exists regarding the strong influence of the NP size on the thermal properties of nanoscale materials, but further investigations are required in order to understand specific size-dependent trends. It has been suggested that NPs within different size regimes must be treated differently. For example, nonmonotonic variations in the melting point (T_m) of small (<200 atoms) size-selected clusters have been observed9,10 and assigned to the interplay of electronic and geometric effects.9 However, the relative contribution of such effects could not be separated. For larger NPs (>200 atoms) monotonic size-dependent trends in T_m were observed.11 For a given material system the specific thermal behavior was found to be drastically affected by environmental influences such as the presence of a support, an encapsulating matrix, the internal defect density within a NP, the structural and chemical nature of the NP/support interface, and the presence of ligands or surface adsorbates.12-17

Reduced melting and Debye (θ_D) temperatures with respect to bulk have been generally reported for free-standing as well as supported NP systems.11-18-25 In addition a correlation between T_m and the NP diameter has been commonly observed: decreased T_m with decreasing NP size.3 Since for bulk systems T_m is proportional to θ_D2 (Lindemann’s criterion26), the Debye temperature is also expected to decrease in clusters relative to the bulk.27 Nevertheless, increased θ_D and superheating have been observed via a variety of methods [e.g., transmission electron microscopy (TEM), x-ray diffraction, differential scanning calorimetry, extended x-ray absorption fine-structure spectroscopy (EXAFS), etc.] for several nanoscale material systems, including supported or embedded Pt,5,6,28-29 Ag,17 and Ge NPs,16,30,31 as well as unsupported nanocrystalline agglomerates such as Ag,32 Au,32 ZnS,12 and thiol-capped CdS23 and CdTe14 nanocrystals. A comparison between the different references is challenging due to the distinct sample preparation and characterization conditions and, in some cases, the lack of detail on the specific structure of the systems investigated. However, some interesting trends could be extracted from the literature. Enhanced thermal stability and superheating was detected for faceted NP shapes with good crystallinity and coherent or semicoherent (nearly epitaxial) interfaces around the embedded NPs, or when NPs were coated by a high melting-point matrix.16,33,34 On the other hand reduced T_m values were found for NPs randomly embedded (e.g., without epitaxial relationships) in similar matrixes. According to previous studies, internal defects within the NPs or at the NP/support interface, voids, impurities, grain boundaries, as well as low-coordinated surface atoms (for NPs not fully embedded in a support matrix) act as nucleation sites for the onset of heterogeneous melting.3 Therefore, a global understanding of the thermodynamic properties of nanoscale materials requires in-depth insight into...
their geometrical structure, including its modifications in the presence of an environment (support and/or adsorbate).

In addition to the anomalous melting/vibrational behavior described previously, a number of additional material properties were found to be modified at the nanoscale. For instance, changes in the electronic properties (e.g., discretization of the energy levels) of small NPs, together with the interaction with the NP support, were held responsible for a size-dependent crossover from positive to negative thermal expansion observed with decreasing NP size for some NP systems or with increasing sample temperature for a given NP size. However, most of the experimental data reported thus far were collected on NPs exposed to a certain environment, for example, in the presence of hydrogen, and the role of such adsorbates on their thermodynamic properties is yet to be fully understood. It is well known that H lifts the contraction that the bonds of Pt NPs undergo because of low coordination either partially or almost totally. On the other hand the effective hydrogen coverage on the NP surface might vary in the course of an experimental thermal cycle. Interestingly, while Pt(111) can be saturated with hydrogen at 85 K and nearly complete H desorption has been observed in vacuum above 400 K, Pt NPs on Al2O3 have been reported to become free of H only above 550 K. An in-depth investigation of the role of H desorption from NPs in the thermal expansion or contraction observed experimentally under constant H2 flow is still lacking. The calculations presented here provide insight into the thermal stability of adsorbed H species on Pt NPs and help evaluate the changes in the bond lengths brought about by the adsorption of H and their contribution to the negative thermal expansion observed for small Pt NPs.

It is evident that the trends described previously are intimately related to the complex structure of the nano-sized materials, and a detailed atomic-scale investigation of the origin of these anomalies is yet to be undertaken. This study focuses on the investigation of the influence of the NP geometry (size and shape) and environment (adsorbate and support) on the thermal properties of structurally well-defined, free-, and γ-Al2O3-supported Pt NPs. For this purpose we have taken advantage of state-of-the-art nanostructure fabrication (micelle encapsulation) and characterization methods (EXAFS, TEM, and cluster-shape modeling), as well as of first-principles theoretical calculations [density functional theory (DFT)]. In particular, insight into the evolution of important material characteristics such as the thermal expansion coefficient (α) and the Debye temperature with decreasing NP size is provided. Our calculations serve to separate intrinsic (free NPs) from adsorbate (H)-induced changes in the Pt-Pt distances measured at different temperatures. They also revealed drastic differences between the conventional mean square atomic displacement (MSD) and the mean-square bond-length fluctuations (MS-BLF) parallel to the bond obtained from the analysis of EXAFS data of NPs.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Sample preparation and morphological characterization (TEM)

Size- and shape-selected Pt NPs were prepared by micelle encapsulation methods. Commercially available poly(styrene)-block-poly(2vinylpyridine) [PS-P2VP] diblock copolymers were dissolved in toluene to form inverse micelles. Size-selected Pt NPs are created by dissolving H2PtCl6 into the polymeric solution. Subsequently, the nanocrystalline γ-Al2O3 support (average size ~40 nm) is added. The encapsulating ligands are eliminated by annealing in O2 at 648 K for 24 hours. Different NP sizes can be obtained by changing the molecular weight of the head (P2VP) of the encapsulating polymer, the metal/P2VP ratio (micelle loading), and the post preparation annealing treatment and atmosphere. Our micellar synthesis normally leads to 3D-like NP structures. Nevertheless, the NP shape can be changed from 3D to 2D by decreasing the metal loading into the initially spherical polymeric micelles. Further details on the sample preparation method and synthesis parameters can be found in Refs. 28, 38, and 41–44, and Table I.

TEM samples were prepared by making an ethanol suspension of the Pt/γ-Al2O3 powder and placing a few drops of this liquid onto an ultrathin C-coated Cu grid and allowing the sample to dry in air. High-angle annular dark-field (HAADF) images of the Pt/γ-Al2O3 samples were acquired under scanning mode within a JEM 2100F TEM operated at 200 kV. The probe size of the scanning transmission electron microscopy (STEM) is about 0.2 nm. The Pt NP diameters were determined by measuring the full width at half maximum of the HAADF intensity profile across the individual Pt NPs. Average and volume-weighted TEM diameters are shown in Table I. The TEM images shown here were acquired after the EXAFS measurements. NP sintering did not take place in the course of the EXAFS measurements since the samples were previously stabilized by a 24-h annealing treatment at the maximum temperature of the EXAFS thermal cycle (648 K).

B. Structural and vibrational characterization (EXAFS) and NP shape modeling

EXAFS data were acquired at beamline X18B of the NSLS at Brookhaven National Laboratory in transmission mode using the Pt L3 edge. The EXAFS samples were prepared by pressing the Pt/γ-Al2O3 powders into thin pellets, which were mounted in a sample cell that permitted sample heating and liquid nitrogen cooling, as well as the continuous flow of gases during data acquisition. A bulk Pt foil was measured simultaneously with all samples (in reference mode) for energy alignment and calibration purposes. Multiple scans (up to 6) were collected at each temperature of interest and averaged in order to improve the signal-to-noise ratio. Measurements were done at different temperatures under H2 (50% H2 balanced with He for a total flow rate of 50 ml/min, samples S1–S9 in Table I) and He (S2) atmospheres.

Data processing was conducted with the IFEFFIT package by simultaneously analyzing the first shell Pt-Pt contribution of the data acquired at different temperatures. The EXAFS Debye-Waller factors (σ2) were obtained by using the Correlated Debye Model (CDM), as described in Ref. 28. From the analysis of temperature-dependent EXAFS data, the dynamic mean-square relative bond-length disorder σd was extracted, and through that ΘD. In the high-temperature approximation σd = kBT/kT ∼ T/θD, with k being the effective...
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TABLE I. Parameters used for the synthesis of micellar Pt NPs, including polymer type (PS-PVP) and the ratio \( (L) \) between the metal-salt loading and the molecular weight of the polymer head (P2VP). Also included are the mean and the volume-weighted TEM diameters. By comparing structural information obtained via EXAFS (first–fourth NN coordination numbers) and TEM (NP diameters) with a database containing fcc-cluster shapes, the ratio of the number of surface atoms to the total number of atoms in a NP \( (N_s/N_t) \) and the ratio of the number of atoms in contact with the substrate to the total number of atoms \( (N_c/N_t) \) were obtained. The static disorders \( (\sigma^2_t) \) obtained from the analysis of EXAFS data are also shown. The largest values of \( \sigma^2_t \) were generally observed for the samples with the largest NP/support interface (S1 and S4).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Polymer</th>
<th>( L )</th>
<th>TEM diameter (nm)</th>
<th>Volume-weighted TEM diameter (nm)</th>
<th>( \sigma^2_t ) (Å²)</th>
<th>Model cluster shapes</th>
<th>( N_s )</th>
<th>( N_s/N_t )</th>
<th>( N_c/N_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>PS(27700)–P2VP(4300)</td>
<td>0.06</td>
<td>0.8 (0.2)</td>
<td>0.9 (0.3)</td>
<td>0.0023 (2)</td>
<td>22</td>
<td>0.86</td>
<td>0.55</td>
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</tr>
<tr>
<td>S2</td>
<td>PS(27700)–P2VP(4300)</td>
<td>0.1</td>
<td>0.8 (0.2)</td>
<td>0.9 (0.2)</td>
<td>0.0013 (2)</td>
<td>44</td>
<td>0.84</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>PS(27700)–P2VP(4300)</td>
<td>0.2</td>
<td>1.0 (0.2)</td>
<td>1.2 (0.2)</td>
<td>0.0010 (3)</td>
<td>85</td>
<td>0.74</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>PS(16000)–P2VP(3500)</td>
<td>0.05</td>
<td>1.0 (0.2)</td>
<td>1.1 (0.2)</td>
<td>0.0028 (3)</td>
<td>33</td>
<td>0.82</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>PS(16000)–P2VP(3500)</td>
<td>0.1</td>
<td>1.0 (0.2)</td>
<td>1.2 (0.3)</td>
<td>0.0019 (2)</td>
<td>55</td>
<td>0.75</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>PS(16000)–P2VP(3500)</td>
<td>0.2</td>
<td>1.0 (0.2)</td>
<td>1.1 (0.3)</td>
<td>0.0015 (2)</td>
<td>140</td>
<td>0.64</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>PS(16000)–P2VP(3500)</td>
<td>0.4</td>
<td>1.8 (1.5)</td>
<td>5.7 (2.2)</td>
<td>0.0015 (2)</td>
<td>90</td>
<td>0.64</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>S8</td>
<td>PS(27700)–P2VP(4300)</td>
<td>0.3</td>
<td>3.3 (1.5)</td>
<td>6.0 (2.8)</td>
<td>0.0016 (1)</td>
<td>120</td>
<td>0.64</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>S9</td>
<td>PS(27700)–P2VP(4300)</td>
<td>0.6</td>
<td>5.4 (3.0)</td>
<td>15.0 (10.0)</td>
<td>0.0012 (1)</td>
<td>180</td>
<td>0.64</td>
<td>0.13</td>
<td></td>
</tr>
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</table>

force constant.\(^{47,48}\) Hence, the slope of the temperature dependence of \( \sigma^2_t \) is inversely proportional to \( \Theta^2_2 \). The static disorders \( (\sigma^2_t = \sigma^2 - \sigma^2_s) \) are shown in Table I. The latter parameter is considered a measure of the degree of anisotropy in the internal structure of NPs (distribution in bond lengths), which for small clusters can be intrinsic\(^{49}\) but are also strongly influenced by the underlying support.\(^{50}\)

Quantitative determination of the NP shape was carried out by analyzing low temperature EXAFS data up to the fourth nearest-neighbor (NN) contribution, including multiple scattering (MS), as described in Refs. 38, 43, and references therein. The data were acquired in H\(_2\) after NP reduction. References 28, 38, and 43 contain analogous information for the rest of the samples discussed in the present article. The shapes of our Pt NPs have been resolved by matching structural information obtained experimentally via EXAFS (coordination numbers up to the fourth NN, \( N_1-N_4 \)) and TEM (NP diameter, \( d \)) to analogous data extracted from a database containing \(~4000\) model fcc NP shapes. In our analysis, after taking into consideration the error bars in the EXAFS coordination numbers as well as the TEM diameters, we have found on average three model fcc cluster shapes consistent with all experimental parameters \( (N_1, N_2, N_3, N_4, d) \) for the small NPs. A larger degeneracy of NP shapes in agreement with the previous experimental parameters was found for the large NPs (>1.5 nm, S7–S9), and, therefore, representative model cluster shapes for those samples are not shown here. Further details on the selection of the model NP shapes can be found in Refs. 28 and 43. A comparison of the EXAFS and model coordination numbers for the two NP shapes that best represented S1 is shown in supplementary material Table III.\(^{51}\) In order to determine the most representative NP shape, we have used volume-weighted TEM diameters. In general the use of the volume-weighted diameters is preferred when comparing TEM and EXAFS structural information, since EXAFS is a volume-weighted technique. Examples of the NP shapes typical of similarly prepared but larger micellar Pt NPs resolved by STM can be found in Refs. 38, 43, and 52. Table I also contains information on the total number of atoms within each NP \( (N_t) \), the ratio of the number of Pt atoms at the NP surface and perimeter to the total number of atoms \( (N_s/N_t) \), and the ratio of the number of Pt atoms in contact with the substrate to the total number of atoms within a NP \( (N_c/N_t) \) extracted from the selected model NP shapes. The distinction between 2D- and 3D-like NPs obtained from the former analysis is in agreement with the general trends observed here for the EXAFS static disorders, with the highest values corresponding to the 2D NPs (S1 and S4, 0.0023 and 0.0028 Å\(^2\), respectively).
Changes in the morphology of our samples as a function of temperature have not been accounted for in our study, since the analysis of the thermal properties of our NPs was conducted up to a maximum annealing temperature of 648 K (for about 1.5 hours), which is the same temperature used for the 24-h sample calcination and stabilization treatment carried out prior to the EXAFS measurements. If any changes in the NP morphology (size and/or shape) were to occur at 648 K, they should have already taken place before the EXAFS measurements.

C. Computational details

Within the framework of DFT\textsuperscript{53} implemented in the Vienna \textit{ab initio} simulation package (VASP),\textsuperscript{24} total-energy periodic super-cell calculations were performed to relax the structure and obtain the vibrational modes of clean and H-covered platinum NPs of various sizes: Pt\textsubscript{22}, Pt\textsubscript{131}, Pt\textsubscript{244}, Pt\textsubscript{55,} and Pt\textsubscript{85}; Pt\textsubscript{22}H\textsubscript{22}, Pt\textsubscript{131}H\textsubscript{22}, Pt\textsubscript{244}H\textsubscript{22}, Pt\textsubscript{55}H\textsubscript{22}, and Pt\textsubscript{85}H\textsubscript{22}. The model NP shapes and sizes were inferred from Ref. 28 and the analysis of EXAFS and TEM data described previously. We have used pseudopotentials obtained via the projected-augmented-wave-method\textsuperscript{55} included in VASP and applied the generalized gradient approximation for the electron-exchange correlation via the Perdew-Burke-Ernzerhof functional.\textsuperscript{56} The Kohn-Sham orbitals are expanded in-plane waves with an energy cut off of 400.0 eV.

The intrinsic thermal expansion of a Pt\textsubscript{22} NP (model shape of S1) was obtained by using \textit{ab initio} molecular dynamics (MD) calculations also implemented in VASP. The simulations were carried out in a canonical ensemble using a Nosé-Hoover thermostat. The relaxed structure of the Pt\textsubscript{22} NP (0 K) was thermalized at 100, 300, 500, and 700 K for 3 ps using a time step of 3 fs. In order to determine the thermal expansion, the thermal evolution of each first NN bond was traced, and an average over the entire NP obtained. Since the atoms within NPs are characterized by a wide distribution of bond lengths,\textsuperscript{57} we report the median of the calculated first NN bond-length distribution, \( R \).

In order to gauge the expansion induced in the Pt NPs by H desorption as a function of temperature, the evolution of the bond lengths of Pt\textsubscript{22} with varying H coverage was monitored. In principle the energetics and vibrational properties of the many possible structures that result from varying not only the H coverage but also the position and tilt angle of the H atoms should be explored. However, such an exhaustive study is computationally prohibitive. In this work we have investigated the main trends in the adsorption of hydrogen on small Pt NPs. To find the preferred sites for hydrogen adsorption, the binding energy of one H atom at the top, fcc, hcp, and bridge positions around atoms at Pt-facets and Pt-edges were obtained. Based on this information, the Pt\textsubscript{22} NP was saturated with H atoms (Pt\textsubscript{22}H\textsubscript{22}) at the most preferred sites (top and bridge), with \( M = 22 \) at facets and edges or only at edges, 25 only at edges, 27 or 29 mostly at edges, and 31 at facets and edges. In addition, it was ensured that after relaxation the nominal preferential site for H adsorption (top and bridge) remained the same. For selected H coverages, the gain in the Gibbs free energy (\( G^{\text{GAIN}} \)) per NP upon H adsorption was calculated according to

\[
G^{\text{GAIN}} = E^{\text{DFT}}(\text{Pt}_N H_M) + F_{\text{vib}}(\text{Pt}_N H_M) - E^{\text{DFT}}(\text{Pt}_N) - F_{\text{vib}}(\text{Pt}_N) - \frac{M}{2} E^{\text{DFT}}(H_2) - \frac{M}{2} \mu_{H_2}(T, P). \tag{1}
\]

\( E^{\text{DFT}} \) denotes the DFT total energy (static energy at 0 K), \( F_{\text{vib}} \) denotes the vibrational Helmholtz free energy, \( N \) is the number of Pt atoms constituting the NP (\( N = 22 \)), \( M \) is the number of H atoms on the NP, \( \mu_{H_2} \), is the vibrational and kinetic part of the H\textsubscript{2} chemical potential taken from experiments,\textsuperscript{58} \( T \) is the temperature, and \( P \) is the H\textsubscript{2} pressure, which is considered to be 1 atm. The preference of H adsorption on edge atoms of Pt\textsubscript{22} was tested through the Gibbs free energy for Pt\textsubscript{22}H\textsubscript{22} by considering that (i) all H atoms adsorb at the edges and (ii) some atoms may be at facets.

The atomic MSD (\( x^2 \))\textsubscript{in} and the bond-projected MSBLF (\( \sigma_j^2 \))\textsubscript{in} were calculated within the harmonic approximation from the eigenfrequencies and eigenvectors. The selectivity of EXAFS for bond-length fluctuations parallel to the bond is taken into account in (\( \sigma_j^2 \))\textsubscript{in} by following the general theory of the EXAFS Debye-Waller factor developed by Beni and Platzman.\textsuperscript{59} The details on the calculation of (\( \sigma_j^2 \))\textsubscript{in} are described elsewhere.\textsuperscript{57}

As previously mentioned, \( \Theta_{\text{slope}} \) is a parameter defined in correspondence with the Debye temperature of bulk Pt and can be obtained as follows

\[
\Theta_{\text{slope}} = \Theta_{\text{D bulk Pt}} \sqrt{\frac{\Delta_{\text{bulk Pt}}}{\Delta_{\text{NP}}}}, \tag{2}
\]

where \( \Theta_{\text{D bulk Pt}} \) is the Debye temperature of bulk Pt (244 K), \( \Delta_{\text{bulk Pt}} \) is the slope of \( \sigma_j^2 \) for bulk Pt derived from EXAFS measurements \((1.528 \times 10^{-5} \text{ Å}^2/\text{K})^6 \), and \( \Delta_{\text{NP}} \) is the slope of (\( \sigma_j^2 \))\textsubscript{in} calculated for the NP.

III. RESULTS

A. Morphological characterization (TEM)

The average NP-size distribution in the polymer-free micellar Pt NPs supported on γ-Al\textsubscript{2}O\textsubscript{3} was obtained from HAADF-STEM images. Figure 1(a) shows a representative STEM image of Pt NPs in S1. The corresponding NP diameter histogram is displayed in Fig. 1(b), and average values for the rest of the samples are given in Table I. Additional TEM images of other samples included in this study are shown in supplementary material Fig. 1\textsuperscript{31} and Refs. 38 and 43. All of our samples containing small NPs are characterized by narrow-size distributions according to in-depth TEM analysis, while wider-size distributions were observed for some of the larger clusters. Histograms of the TEM NP diameters for all samples are given in supplementary material Fig. 2.\textsuperscript{51}

B. Structural and thermodynamic properties (EXAFS)

EXAFS spectra in \( r \)-space from micellar Pt NPs supported on γ-Al\textsubscript{2}O\textsubscript{3} (S1, S2, S8) are shown in Fig. 2(a). The spectra were acquired in H\textsubscript{2} at room temperature. The thermal evolution of the \( r \)-space EXAFS spectra of S1 measured in H\textsubscript{2} at temperatures ranging from 173 K to 648 K is shown
FIG. 1. (Color online) (a) HAADF-STEM image of micellar Pt NPs on γ-Al₂O₃ (S1). (b) Histogram of the NP diameter distribution.

in Fig. 2(b). With increasing temperature, a decrease in the intensity of the EXAFS signals is observed, indicative of an increase in the Pt-Pt bond-length disorder. A representative MS fit of the 173 K spectrum is included as an inset in Fig. 2(b). Supplementary material Fig. 3 shows exemplary EXAFS data from additional samples (S1, S8, and S9) at all temperatures in k-space. Representative fits in r-space to temperature-dependent data from S1 and S8 are shown in supplementary material Figs. 4 and 5, respectively.

Figure 3(a) displays Pt-Pt distances (R) in the temperature range of 150 K to 700 K for samples S1, S2, S7, S8, and a bulk Pt foil. All measurements were carried out under continuous H₂ flow. The data points shown in Fig. 3(a) correspond to the best fit results of the experimental EXAFS spectra obtained for the first NN Pt-Pt bond lengths (R, averaged over all bonds within one NP) at different temperatures. The solid lines in Fig. 3(a) represent a linear fit of the experimental data. From the slope of such fit, the average thermal expansion coefficient (α) can be extracted: \( \alpha = \left( \frac{1}{R_0} \right) \left( \frac{\partial R}{\partial T} \right) \), where \( R_0 \) is the Pt-Pt distance obtained for each sample at the lowest measurement temperature. Due to the enhanced noise of the experimental data of sample S1 at high temperature, the Pt-Pt distance shown in Fig. 3(a) at \( \sim 700 \) K was not included in the linear fit.

Figure 4(a) depicts \( \alpha (a) \) as a function of the average first-NN EXAFS coordination number for all samples investigated and (b) as a function of the average TEM NP diameter. In general, large coordination numbers (close to 12 for bulk Pt) are associated with large NPs and small values with small NPs, although NPs with different shapes will also display distinct coordination numbers. Our data reveal a size-dependent trend in the thermal expansion coefficient, namely, a cross-over from positive (S3, S5–S9) to negative (S1, S2, S4) thermal expansion with decreasing NP size. The effect of hydrogen chemisorption in the thermodynamic properties of our NPs will be discussed in more detail in the theoretical section.

The dynamic correlated mean-square bond length disorder (\( \sigma_d^2 \)) obtained from the fits of the experimental EXAFS data following the CDM are shown in Fig. 5(a). As was described in the experimental section, the slope of the temperature dependence of \( \sigma_d^2 \) is inversely proportional to \( \Theta_d^2 \) in the high
temperature approximation. Above 100 K, our experimental data display a good linear dependence at least up to our maximum measurement temperature of \(\sim 650\) K. Deviations from the linear behavior of \(\sigma_D^2\) might be found in the proximity of the melting temperature,\(^6\) which, even for small Pt NPs,\(^2\) is expected to be significantly higher than 650 K. Our results indicate that the majority of Pt atoms in our NPs are characterized by smaller bond-projected bond-length fluctuations (correlated displacements) than those in bulk Pt samples.

The Debye temperatures obtained from the CDM analysis of our EXAFS data are displayed in Fig. 6(a) as a function of the TEM NP diameter and in Fig. 6(b) as a function of the total number of atoms in the NP normalized by the number of atoms at the NP surface and perimeter (\(N_t/N_s\)). All data correspond to samples passivated by H\(_2\) under identical conditions. Figure 6(b) does not include data from the large NPs (S7–S9) due to the degeneracy in the model shapes obtained for those samples. A bimodal trend in \(\Theta_D\) as a function of the NP diameter is observed in Fig. 6(a). For NPs \(\leq 1\) nm, an overall decrease of \(\Theta_D\) was found with decreasing NP size [Fig. 6(a)] or decreased \(N_t/N_s\) [Fig. 6(b)]. Nevertheless, relative differences were observed for NPs with the same TEM diameter but different shape (\(\sim 0.8\) nm, S1 and S2; \(\sim 1\) nm, S3–S6). For larger NPs (>1 nm), decreasing...
Debye temperatures were observed with increasing NP size (TEM diameter), approaching the bulk $\Theta_D$ value for sizes above 5 nm. Interestingly, $\Theta_D$ of all experimental NP samples was found to exceed that of bulk Pt. A detailed description of possible origins for these intriguing size- and shape-dependent trends is given in the discussion section.

C. Calculated structural properties and thermal expansion

DFT calculations were carried out to gain insight into the intrinsic size- and shape-dependent structural and thermodynamic properties of our NPs and the role played by the adsorbate (H$_2$) present during our experiments. Table II presents a comparison of the EXAFS bond lengths measured in H$_2$ for Pt NPs supported on $\gamma$-Al$_2$O$_3$ and the DFT-calculated median bond lengths for unsupported adsorbate-free Pt NPs (S1–S5). All values shown in Table II were normalized by the respective (experimental or calculated) bulk Pt-Pt distances at the given temperatures. Clean and unsupported model NPs show an overall contraction of 3.4–5.9% with respect to the bulk-bond lengths. Since the experiments were conducted in H$_2$, calculations of the effect of H chemisorption on the Pt-Pt bond lengths of one of the samples (Pt$_{22}$, S1) were also carried out and included in Table II. It was observed that H prefers to adsorb at top-like positions or at bridge sites (between two atoms), and binding at edge atoms is preferred, as compared
TABLE II. Experimental (EXAFS) and theoretical (DFT) average first-NN bond lengths of Pt NPs with different sizes and shapes given as a fraction of the respective bulk values. All experimental samples but S2 were H$_2$-passivated and supported on γ-Al$_2$O$_3$. S2 was also measured in He. The NPs analyzed theoretically were unsupported and free of adsorbates, with the exception of S1, which was also investigated with different H coverages. The experimental bulk Pt-Pt reference distances are 2.762 (2) Å at 154 K, 2.765 (4) Å at 300 K, and 2.78 (1) Å at 700 K. The calculated bulk Pt-Pt distance is 2.805 Å at 0 K. The DFT calculations were only carried out on Pt NPs containing less than 100 atoms.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Pt-Pt bond lengths relative to bulk (EXAFS)</th>
<th>Pt-Pt bond lengths relative to bulk (DFT)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>172–188 K</td>
<td>300 K</td>
</tr>
<tr>
<td>S1</td>
<td>0.996</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>0.999 (H$_{2}$)</td>
<td>0.996 (H$_{2}$)</td>
</tr>
<tr>
<td></td>
<td>0.996 (He)$^{28}$</td>
<td>0.991 (He)</td>
</tr>
<tr>
<td>S3</td>
<td>0.994</td>
<td>0.999</td>
</tr>
<tr>
<td>S4</td>
<td>0.996</td>
<td>0.997</td>
</tr>
<tr>
<td>S5</td>
<td>0.997</td>
<td>0.997</td>
</tr>
<tr>
<td>S6</td>
<td>0.999</td>
<td>1.001</td>
</tr>
<tr>
<td>S7</td>
<td>0.999</td>
<td>0.997</td>
</tr>
<tr>
<td>S8</td>
<td>0.998</td>
<td>0.997</td>
</tr>
<tr>
<td>S9</td>
<td>0.998</td>
<td>0.997</td>
</tr>
</tbody>
</table>

The intrinsic thermally driven bond-length expansion of a support-free Pt$_{22}$ NP was calculated via ab initio MD (open symbols). The theoretical thermal-expansion coefficient $\alpha$ was found to be positive ($\sim$28 $\times$ 10$^{-6}$ K$^{-1}$) and larger than that of bulk Pt. Figure 3(b) also displays similar data obtained for H-covered NPs (closed symbols). The latter data were based on the Gibbs phase diagram (see Eq. (1)) calculated for Pt$_{22}$H$_{29}$, which is displayed in Fig. 3(c). From the H coverages studied, the thermodynamically stable configurations are those with all H atoms around edge Pt atoms, namely, Pt$_{22}$H$_{29}$ below 400 K, Pt$_{22}$H$_{25}$ at $\sim$500 K, and Pt$_{22}$H$_{22}$ above 600 K. Our calculations for the H coverages selected suggest that, at a constant H$_2$ pressure of 1 atm, H desorption sets in at about 420 K, marked by a vertical dotted line in Fig. 3(c). The latter is the temperature for which an intercept from those of the “real” (uncorrelated) MSDs, $(\sigma^2)_{th}$, More specifically, smaller slopes of the $(\sigma^2)_{th}$ versus temperature plots were observed for the majority of the clean NPs as compared to bulk Pt (exp.), which is in qualitative agreement with.

D. Vibrational properties

The eigenfrequencies and eigenvectors of unsupported, clean Pt NPs and H-covered NPs were calculated from first principles. Both $(\sigma^2)_{th}$ and $(\sigma^2)_{th}$ were obtained exactly within the harmonic approximation from the discrete spectrum of the NPs. Figure 5(a) contains information on the thermal evolution of $(\sigma^2)_{th}$ of Pt$_{22}$H$_{22}$, Pt$_{22}$H$_{25}$, Pt$_{22}$H$_{29}$, and (b) of clean Pt NPs (Pt$_{22}$, Pt$_{33}$, Pt$_{44}$, Pt$_{55}$, and Pt$_{85}$). The evolution of $(\sigma^2)_{th}$ for the former adsorbate- and support-free Pt NPs is shown in (c). The thermal evolution of $(\sigma^2)_{th}$ of Pt$_{22}$H$_{22}$, Pt$_{22}$H$_{25}$, and Pt$_{22}$H$_{29}$ shows that $(\sigma^2)_{th}$ and its slope varies as H desorbs with increasing temperature. Furthermore, the slopes of $(\sigma^2)_{th}$ for all three H-covered NPs (Pt$_{22}$H$_{22}$, Pt$_{22}$H$_{25}$, and Pt$_{22}$H$_{29}$) are larger than that of bulk Pt (exp.) and Pt$_{22}$ (theory). By comparing Figs. 5(b) and 5(c) it is evident that the trends obtained for $(\sigma^2)_{th}$ corresponding to the correlated motion of atom pairs within the NPs parallel to the bond are clearly different from those of the “real” (uncorrelated) MSDs, $(\sigma^2)_{th}$. More specifically, smaller slopes of the $(\sigma^2)_{th}$ versus temperature plots were observed for the majority of the clean NPs as compared to bulk Pt (exp.), which is in qualitative agreement with.
clean and unsupported NPs depends on the size and shape of the NPs.58

Figure 6(a) displays βslopeth, a parameter defined in correspondence with the Debye temperature (see definition for bulk materials in the experimental section47) extracted from the slope of the theoretical (σσσσ22th) versus T plots of clean Pt22 (S1) and Pt22H22 [see Eq. (2)]. The Pt22H22 coverage was selected because it is stable at the highest temperature investigated (T > 600 K). The error bar corresponds to the variations of βslopeth with H coverage, considering only those that are thermodynamically stable. Overall, the adsorption of hydrogen was found to lead to a reduction of βslopeth for all H coverages studied. Nevertheless, the observed changes were nonmonotonic, being largest for Pt22H29 (βslopeth = 226 K) and smallest for Pt22H25 (βslopeth = 203 K), with Pt22H22 (βslopeth = 220 K) in between [Fig. 6(a)].

IV. DISCUSSION

Our calculations show that clean and unsupported NPs display an overall bond length contraction (averaged over all bonds within a NP) of about 6% at 0 K for Pt22 with respect to bulk Pt, whereas for the smallest experimental NPs measured in H2 (S1), the contraction measured at 172–188 K is only 0.4% (Table II). This cannot be assigned to the difference in the experimental and theoretical temperatures [see Fig. 3(a)] but rather to the presence of H2 (dissociate adsorption) on the experimental Pt NPs. Indeed, a better agreement is obtained when H is incorporated into the model of the unsupported NP. Our calculations corroborate that H partially lifts the Pt-Pt bond-length contraction caused by the low-coordination of surface atoms of the small NPs. More specifically, while for clean Pt22 the calculated R is contracted by ∼5.9% with respect to the calculated value for bulk Pt (see Table II), for Pt22H29 (stable configuration below ~420 K), Pt22H25 (stable between ~420 and ~550 K), and Pt22H22 (stable above ~550 K), contractions of only ~2.3, 3.1, and 4.0%, respectively, were obtained. However, it should be mentioned that our calculations for the flat Pt22 NP did not result in the enhanced structural ordering expected for such NPs in the presence of H.39

All of our NP samples were found to have smaller thermal expansion coefficients than bulk Pt [α ~ 11 × 10−6 K−1 is the reference value extracted from EXAFS measurements on a Pt foil or 8.8 × 10−6 K−1 from Ref. 61]. This effect can be partially assigned to the influence of the NP/support interface, since γ-Al2O3 is characterized by a smaller α of −4.5 × 10−6 K−1.62 The latter has also been held responsible for the reduced coefficient of thermal expansion measured for superheated Al NPs in Al2O3.63 Furthermore, for identically synthesized NPs, Fig. 4 constitutes a clear example of the influence of the NP size and geometry on their thermal properties. For reference, model shapes for our small NPs extracted from the analysis of EXAFS and TEM data are included in Table I and as insets in Fig. 6(b). Interestingly, Fig. 4(b) reveals a cross-over from positive to negative thermal expansion at/below 1 nm. This result is in agreement with data from Kang et al.5 and Sanchez et al.6 obtained for 0.9–1.1 nm Pt NPs supported on γ-Al2O3 prepared by impregnation precipitation. According to previous DFT calculations for Pt13 on dehydrated

![Graph of Vibrational DOS](image_url)
γ-Al2O3 (with relatively strong metal/support interactions), the impregnation-precipitation preparation method is likely to result in 2D-shaped NPs. In our study, the three samples displaying negative thermal expansion coefficients include the smallest NPs (S1 and S2, ~0.8 nm with 2D and 3D shape, respectively) and a sample with slightly larger NP size but 2D shape (~1 nm, S4). Since other samples with average NP size of ~1 nm but 3D shape did not show such effect (S3, S5, S6), both the NP/support interface and the ratio Pt surface atoms shape (respectively) and a sample with slightly larger NP size but 2D shape (~1 nm, S4) showed a lower but still negative thermal-expansion coefficient. When samples containing small NPs with the same size and analogous surface area for H2-chemisorption are compared (e.g., S1 and S2, ~0.8 nm; Nt/Ns = 0.84–0.86, Table I), the negative thermal-expansion effect was found to be more pronounced for sample S1 with the highest NP/support contact area (Nt/Ns = 0.55 for S1 versus Nt/Ns = 0.23 for S2). The specific role of the NP support is yet to be determined, since our present calculations were carried out on unsupported NPs, and only one support (γ-Al2O3) was used for all experiments. Nevertheless, a recent EXAFS study by Sanchez et al. revealed clear changes in the thermal-expansion behavior of Pt NPs prepared by the deposition-impregnation method and supported on γ-Al2O3 and C substrates, with positive α values reported for the clusters deposited on the more weakly interacting C support and negative α on γ-Al2O3.

In addition to the intriguing thermal-expansion behavior of our fcc Pt NPs supported on γ-Al2O3, Fig. 5(a) reveals clear differences in their thermodynamic properties with respect to bulk Pt, with smaller (σγ) versus temperature slopes for the H-coated experimental NP samples. This result can be partially explained by the fact that EXAFS measurements underestimate the relative contribution of low-energy vibrational modes to the total σγ, an effect that we have theoretically demonstrated to be significant for small unsupported NPs. This can be seen in Fig. 7, where the calculated VDOS of Pt22 and Pt22H5 is displayed together with the bond-projected VDOS (weighted similarly to the EXAFS data by only considering bond-length fluctuations parallel to the bond). From the comparison of the total and bond-projected VDOS in Fig. 7, it is confirmed that the main differences are observed at low energies, and that this region of the VDOS largely involves fluctuations perpendicular to the bond. Therefore, the experimental dynamic bond-projected bond length fluctuations can only be compared directly to σγ since the real MSD ⟨x2⟩th lacks the former EXAFS-weighting factor. Nevertheless, for the small (<1.5 nm) unsupported NPs, we have confirmed numerically that ⟨x2⟩th depends on the size and shape of the NPs, as shown in Fig. 5(c) and described in more detail.
in Ref. 57. Our calculations also demonstrate that \( (x_i)^2 \) and thereby \( (\sigma^2_{\text{th}}) \), correlate with the behavior of the VDOS at low energy (Fig. 7). Small \( (x_i)^2 \) versus T slopes [and \( (\sigma^2_{\text{th}}) \) versus T slopes] were observed for NPs with a large phonon confinement gap at low energies.\(^{37}\) Such a vibrational confinement gap\(^{38}\) is in turn determined by the NP size and shape.\(^{35}\) For example, Pt\(_{44}\) (S2) has the smallest \( (x_i)^2 \) and the widest phonon gap (5.7 meV), and Pt\(_{33}\) (S4) has the largest \( (x_i)^2 \) and smallest gap (\~{}2.5 meV).\(^{55}\) This apparently small difference in the VDOS is critical, as seen by the visible deviation of the \( (x_i)^2 \) and \( (\sigma^2_{\text{th}}) \) of Pt\(_{33}\) with respect to the rest of the samples in Figs. 5(b) and 5(c). Additionally, within the set of samples analyzed, an increase in the NP size for the same NP shape (S2 with 44 atoms versus S3 with 85 Pt atoms) was found to increase \( (x_i)^2 \) [Fig. 5(c)].

It is useful to point out that since a number of low-energy vibrational modes correspond to shear perturbations of surface atoms,\(^{55,66}\) if the NPs are strongly bound to a stiff substrate, the corresponding boundary condition might eliminate some of those modes.\(^{51,67}\) In addition, the presence of a strongly binding support might lead to an increase in the phonon gap present for small NPs.\(^{34}\) For instance, the vibrational gap increased from 0.2 to 4.2 meV for free versus pseudomorphic Ru(0001)-supported single-layer Au\(_{13}\).\(^{57,68}\) Therefore, for NPs supported on stiff substrates in which the low-energy VDOS might be suppressed, the differences between \( (x_i) \) and \( \sigma^2_{\text{th}} \) measured via EXAFS might not be as significant as those shown in Fig. 5 for the unsupported theoretical NPs. Thus, quantitative agreement between theoretical and experimental data requires also the consideration of the support in the calculations, which for the various NP sizes and shapes investigated here is beyond our possibilities based on first principle calculations. Moreover, it should be noted that the calculations shown in Fig. 5(a) of \( \sigma^2_{\text{th}} \) versus T curves for Pt\(_{22}\)H\(_2\), Pt\(_{22}\)H\(_3\), and Pt\(_{22}\)H\(_5\) intend to single out the effect of the limited sensitivity of EXAFS to low E-vibrational modes but do not take into consideration the expected changes upon gradual desorption of H\(_2\) with increasing temperatures, since they correspond to a constant hydrogen coverage.

From the slope of the \( \sigma^2_{\text{th}} \) versus T plot of the EXAFS data in Fig. 5(a), a Debye temperature was obtained for NPs in the size range of 0.8 to 5.4 nm (Fig. 6). As we have already mentioned, the behavior of the Debye temperature signifies here only the trends in the MSBLFs. It neither validates nor refutes the Debye model for the VDOS, which has been noted to be unsuitable for accurately describing the vibrational properties of small unsupported NPs (<500 atoms,\(^{34}\) <2 nm) due to the 3N-discretization of the vibrational energies\(^{66,69}\) and the observation of an excess VDOS at low phonon energies.\(^{70}\)

The following observations are made based on the analysis of the EXAFS data shown in Fig. 6: (i) an overall increase in the Debye temperature of all NP samples with respect to bulk Pt; (ii) the distinct thermal properties of small and large Pt NPs. For NPs \( \lesssim 1 \) nm, a decrease in \( \Theta_D \) is observed with decreasing NP size, while for larger NPs (>1 nm), the Debye temperature was found to decrease with increasing NP diameter [Fig. 6(a)]. The \( \Theta_D \) value of bulk Pt was not reached for the largest NPs investigated here (\~{}5.4 nm). The size dependency displayed by the NPs with sizes >1.5 nm is in agreement with that reported for superheated NPs with well-ordered (epitaxial) NP/support interfaces.\(^{33}\) (iii) For NPs <1.5 nm, a decrease in \( \Theta_D \) is also obtained with increasing relative number of atoms at the NP surface (\( N_s \)) [Fig. 6(b)]. It should be taken into consideration that \( N_s \) here includes surface and perimeter atoms (the latter in contact with the support). A plausible explanation for this observation is the consideration of the low-coordinated surface atoms as defects leading to a suppression of \( \Theta_D \), while the perimeter atoms in contact with the support might have the contrary effect. In fact if the interaction of Pt atoms with \( \gamma\text{-Al}_2\text{O}_3 \) is responsible for the large experimental \( \Theta_D \), increasingly large 3D NPs will have a smaller fraction of atoms in contact with the support, which would lead to the disappearance of the \( \Theta_D \)-enhancement (bulk limit). This trend is observed here for the largest NPs investigated (S9).

Although we did not measure the melting temperature of our NPs directly, according to Eq. (3), similar size-dependent trends are expected for \( T_m \) and \( \Theta_D \):\(^{27}\)

\[
T_m = \frac{2\pi m c^2 R^2 \Theta_D^2 k_B}{\hbar^2},
\]

with \( m \) being the atomic mass, \( c \) Lindemann’s constant,\(^{26}\) \( R \) the bond length, \( k_B \) Boltzmann constant, and \( h \) the Planck constant.

In the literature\(^{3} \) the following factors have been discussed to contribute to the \( \Theta_D \) (or \( T_m \)) enhancement reported for some nanoscale systems: (i) the presence of a matrix (e.g., \( \gamma\text{-Al}_2\text{O}_3 \)) with a higher melting temperature than that of the NPs (e.g., Pt) or a high melting-temperature coating around the NPs, and/or a support that binds strongly the NPs; (ii) a low density of structural defects within the NPs, good crystallinity, and NP faceting; (iii) a NP/support interface with a low-defect density and, if possible, an epitaxial relation between the NP/support; and (iv) the absence of a significant number of grain boundaries, twinning, and other related structural defects. The sample preparation method is a key factor controlling the structural features affecting this anomalous thermodynamic behavior. Our large NPs (>1.5 nm) display a trend for the Debye temperature analogous to that reported for the melting temperature of melt-spun superheated\(^{33}\) in NPs embedded in \( \text{Al} \)\(^{33}\) or \( \text{Pb} \) NPs in \( \text{Al} \),\(^{71}\) namely, increasing \( \Theta_D \) with decreasing NP size. Interestingly, for the same experimental systems, differently prepared samples (ball-milled) with incoherent NP/matrix interfaces displayed the opposite trend, namely, decreasing \( T_m \) with decreasing NP size.\(^{33,71}\) These effects were explained in terms of an enhanced internal disorder and noncoherent NP/support interface for the latter set of samples. Cahn\(^{34}\) attributes superheating effects to a constraint in the amplitude of the vibration of atoms at the NP/support interface, highlighting the importance of an epitaxial relation between the metal NPs and the coating, matrix, or support material. In our case Fig. 5(a) might suggest an overall stiffening of our NPs because of the reduced bond-projected bond length fluctuations, although the data shown correspond to the entire NP, not only to atoms at the NP/support interface. Nevertheless, as is shown in Fig. 5(b), a large part of the reduction in \( \sigma^2_{\text{th}} \) of the experimental NPs as compared to bulk Pt (and therefore part of the reduction of the slopes giving rise to enhanced \( \Theta_D \)) can be assigned to the
distinct definition of the EXAFS $\sigma_h^2$ (correlated bond-projected bond-length fluctuations), as compared to the real mean-square vibrational amplitude $\langle x^2 \rangle_0$ [Fig. 5(c)]. On the other hand it should be kept in mind that our calculations suggest that $H$ reduces the slope of $\langle \sigma_h^2 \rangle_0$, but they do not include the $\gamma$-Al$_2$O$_3$ substrate, which is expected to increase it and thus play a pivotal role in the thermodynamic behavior of supported NPs.

Following the preceding ideas, the enhanced Debye temperatures observed for our large NPs ($1.5 \text{ nm} < d < 5 \text{ nm}$) and their size dependency appear typical of well-ordered, faceted NPs with coherent or semicoherent NP/support interfaces surrounded by a high melting-temperature matrix (or support in our case). The crystallinity of our large NPs can be seen in the EXAFS spectra included in Fig. 2(a) (4–6 Å range) (S8) as compared to a bulk Pt reference. On the other hand our small NPs (S1–S6 ≤ 1 nm) behave similarly to disordered NPs, for which a decreasing melting temperature was observed with decreasing NP size.33 Furthermore, when small NPs are considered, not just the NP size but also their shape might strongly affect their Debye temperatures. For example, we obtained different Debye temperatures for NPs of identical size (~1 nm TEM diameter, S3–S6), and a correlation was observed between the number of low coordinated atoms at the NP surface and $\Theta_D$, with lower $\Theta_D$ values for the NPs with the highest surface-to-volume ratio [Fig. 6(b)]. This trend can also be explained by the adsorbate effect since the higher the surface-to-volume ratio, the stronger the adsorbate effect will be. Our theoretical results on unsupported Pt$_{22}$H$_M$ revealed that the adsorption of hydrogen increases the MSBLFs and its slope $[\langle \sigma_h^2 \rangle_0 \text{ versus } T]$ respect to the corresponding values of adsorbate-free Pt$_{22}$, leading to a smaller $\Theta_D$ [Fig. 6(a)]. Nevertheless, it should be noted that the support, which is expected to have the opposite effect, still needs to be taken into account. Experimentally, it was observed that the flat NPs in S4 displayed a higher $\Theta_D$ than analogously sized 3D clusters (S3) with a lower contact area with the $\gamma$-Al$_2$O$_3$ substrate. This effect reveals the important role played by the NP/support interface in the thermodynamic properties of small NPs.

Summarizing, our experimental and theoretical data provide insight into the influence of the geometric structure (size and shape) and environment (adsorbates and substrate) in the thermodynamic properties of metal NPs. In particular the important role of H$_2$ desorption in the negative thermal expansion experimentally observed for small supported metal clusters is discussed. Furthermore, size-dependent changes in the Debye temperature observed via EXAFS are explained in terms of the NPs geometrical structure and NP/support interface but also as a function of intrinsic limitations of the experimental technique used.

V. CONCLUSIONS

A synergistic combination of EXAFS, TEM, NP-shape modeling, ab initio total energy, and MD calculations based on DFT have allowed us to gain insight into the structure and thermal properties of Pt NPs supported on $\gamma$-Al$_2$O$_3$. Our main experimental findings are (i) a size-dependent cross-over from positive to negative thermal expansion with decreasing NP size; (ii) the observation of enhanced experimental Debye temperatures for small Pt NPs bound to $\gamma$-Al$_2$O$_3$; (iii) the different vibrational behavior of large and small metal NPs. Small NPs ($\leq 1.5 \text{ nm}$) show a general decrease in the Debye temperature with decreasing NP size associated with the increase in the number of atoms at the NP surface. For large NPs ($>1.5 \text{ nm}$), decreasing Debye temperatures are observed with increasing NP size. For the latter samples the existence of a decreasing number of atoms within the NPs in contact with the support appears to contribute to the suppression of the matrix-induced $\Theta_D$-enhancement.

Our computational investigations revealed that the negative thermal expansion of the smallest NPs is not intrinsic and qualitatively suggest that thermal desorption of chemisorbed hydrogen is at least partially responsible for this effect. The comparison of the calculated bond-projected $\langle \sigma_h^2 \rangle_0$ (based on the CDM) and the total $\langle x^2 \rangle_0$ for unsupported and adsorbate-free NPs revealed smaller slopes in the $\langle \sigma_h^2 \rangle_0$ versus $T$ plots. Hence, the relatively small experimental $\sigma_d^2$ slopes, and therefore, the unusually large Debye temperatures obtained experimentally, can be partially assigned to the nature of the experimental probe used for its determination, since fluctuations in the bond length perpendicular to the bond, which might be present at low energies, are not accessible to EXAFS. Furthermore, our calculations traced the observed decrease in the MSDs or bond-length fluctuations to the possible elimination of low-energy vibrational modes of the NPs. We have shown that this might occur due to specific detection limits of the experimental technique used, by the presence of large gaps in the VDOS of the NPs, or due to NP/support interactions.

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