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Anomalous Structural Disorder in Supported Pt Nanoparticles

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Abstract

Supported Pt nanocatalysts generally exhibit anomalous behavior, including negative thermal expansion and large structural disorder. Finite temperature DFT/MD simulations reproduce these properties, showing that they are largely explained by a combination of thermal vibrations and low frequency disorder. We show here that a full interpretation is more complex, and that the DFT/MD mean square relative displacements (MSRD) can be further separated into vibrational disorder, “dynamic structural disorder” or DSD, and long-time equilibrium fluctuations of the structure dubbed “anomalous structural disorder” (ASD). We find that the vibrational and DSD components behave normally, increasing linearly with temperature while the ASD decreases, reflecting the evolution of mean nanoparticle geometry. As a consequence the usual procedure of fitting the MSRD to normal vibrations plus temperature independent static disorder results in unphysical bond strengths and Grüneisen parameters.

Graphical TOC Entry

Supported metal nanoparticles (NPs) are widely used as catalysts in applications ranging from chemical synthesis to petroleum refining.^{1,2} Consequently their nanoscale structure and behavior are of considerable technological interest. Their properties as a function of size, temperature, and interaction with the support are important determinants of catalytic activity and specificity. However, understanding their behavior is challenging, due partly to their inhomogeneous structure and substantial differences *vs* the bulk, especially at high operating temperatures and in the presence of support and ligands.^{3–5} EXAFS studies of nanoscale Pt clusters on γ -Al₂O₃ reveal several anomalous properties:^{6,7} First, EXAFS analysis⁶ shows that ~ 1 nm NPs exhibit negative thermal expansion (NTE) and have shorter average Pt–Pt bond lengths than in bulk Pt. In contrast ~ 2.9 nm NPs have positive thermal expansion on average and mean bond lengths closer to those in the bulk. Using DFT/MD simulations,^{8,9} this behavior was attributed to “dynamic structural disorder” (DSD), i.e. the inhomogeneous, fluctuating nature of structure at the nanoscale. In particular the DSD exhibits multiple time-scales, being driven by the chaotic motion of the center of mass (CM) of the NPs, their librational motion and transient tethering to the support in the ps time-scale, and their internal fluxional bonding at substantially slower time-scales. Second, EXAFS data for small NPs exhibit unusually large Pt–Pt bond length fluctuations, i.e., mean-squared relative-displacements (MSRD), compared to vibrational motion at $T = 0$ K. These quantities are important for interpreting vibrational properties such as bond strengths and Grüneisen parameters. Our main goal here is to understand this behavior. The large corrections to the zero-point MSRD are usually interpreted as temperature-independent “static” disorder, reflecting the inhomogeneous structure of the NPs.¹⁰ As we show below, however, this interpretation is problematic. For example, the Pt–Pt bond strengths $k \sim \Theta_E^2$ based on Einstein models (EM) of the MSRD with Einstein temperatures Θ_E are anomalous. Indeed, fits for 0.9 nm NPs gave an anomalously large $\Theta_E = 300$ K, equivalent to a mean vibrational frequency $\nu_E = 6.3$ THz. This mean frequency is larger than that observed for the strongest known Pt–Pt bonds and is hence unphysical. Similarly the Grüneisen param-

eters¹¹ γ derived from the variation of the ν_E with cluster size are anomalous, being more than 50% larger than in bulk.

We show here that this seemingly anomalous behavior of the MSRD can be accounted for by a reinterpretation of the dynamic disorder. The MSRD σ_P^2 for a single Pt_{*i*}-Pt_{*j*} (*i, j* = 1 $\cdots$ *N*) bond trajectory $r_P(t) = |\vec{r}_i(t) - \vec{r}_j(t)|$ is defined as the time average

$$\sigma_P^2(T) = \frac{1}{\tau} \int_0^\tau [r_P(t) - \bar{r}_P]^2 dt, \quad (1)$$

where $P = \{i, j\}$ denotes a bond pair, and $\bar{r}_P$ is the mean bond distance computed as a time-average over the same long-time time τ , (10 ps in our simulations). To obtain the total MSRD $\sigma_{Tot}^2(T)$, we average over all initial conditions and over pair trajectories chosen to minimize tail effects (see Supplementary Information):

$$\sigma_{Tot}^2(T) = \left\langle \frac{1}{N_P} \sum_P \sigma_P^2(T) \right\rangle, \quad (2)$$

where the brackets indicate the average over initial conditions. We show that in addition to low frequency dynamic fluctuations, the MSRD also contains a temperature dependent quasi-equilibrium component, which we dub anomalous structural disorder (ASD). To compute the ASD and analyze its origin, we perform a spectral analysis of the temperature and size dependence of the different components of disorder in supported Pt NPs. We partition the MSRD into three components according to their dynamic timescales: Vibrational disorder (σ_{Vib}^2), associated with fast nuclear motion with frequencies higher than 1 THz, dynamic structural disorder (σ_{DSD}^2) arising from slower dynamics in the 0 to 1 THz range, and anomalous structural disorder (σ_{ASD}^2) associated with mean quasi-static Pt-Pt disorder over the duration of the simulation. The partitioning is done by convolving a trajectory $r(t)$

$$r_L(t) = \int_{-\infty}^{+\infty} r(\tau) F(t - \tau) d\tau, \quad (3)$$

with a low-pass filtering function $F(t)$ defined as

$$F(t) = \begin{cases} \frac{\pi}{2}\nu_L \cos(\pi\nu_L t) & |t| < 1/2\nu_L \\ 0 & |t| > 1/2\nu_L. \end{cases} \quad (4)$$

Here ν_L is the cutoff frequency (set to 1 THz), and $r_L(t)$ is the low frequency component of the trajectory. From $r_L(t)$ we define the high frequency component as $r_H(t) = r(t) - r_L(t)$. The partitioned σ_{Vib}^2 and σ_{DSD}^2 are obtained similarly to σ_P^2 in Eq. 1. The ASD component is defined as

$$\sigma_{ASD}^2(T) = \langle (\bar{r}_L - \langle \bar{r}_L \rangle)^2 \rangle, \quad (5)$$

where the brackets indicate an average over all selected trajectories and initial conditions, and where the mean trajectory distance $\bar{r}_L$ is

$$\bar{r}_L = \frac{1}{\tau} \int_0^\tau r_L(t) dt. \quad (6)$$

A simpler version of this partitioning that did not separate the ASD from DSD was previously used^{9,12} to investigate dynamic effects on Pt and PtSn NPs.

Physically the effective pair potentials in NPs depend strongly on the NP-support interaction and other environmental factors that make them indirectly temperature-dependent, similar to the temperature dependence of the mean geometrical structure in the quasi-harmonic approximation. We show that the apparent anomalous MSRD behavior arises from neglecting the temperature dependence of the ASD and disappears when the ASD is taken into account. Thus the ASD is critically important in attaining an all-encompassing explanation for understanding NP properties including NTE, MSRD and γ . Consequently, we propose that, although widely used in the NP community, the concept of temperature-independent static disorder should be revised since it yields incorrect behavior for small supported NPs.

To study the behavior of the NPs under realistic conditions, we carried out DFT/MD

simulations of γ -Al₂O₃-supported Pt₁₀ and Pt₂₀ clusters for temperatures ranging from 165 to 573 K. Given that acquiring adequate statistics, especially at lower temperatures, requires careful sampling,¹³ the results for each temperature are obtained by averaging over six independent trajectories starting from different initial conditions. (See Computational Methods section.) Fig. 1 shows the total MSRD averaged over all internal bonds for both supported and unsupported Pt₁₀ and Pt₂₀. We find that the diameter cutoffs for finding 95% of the atoms are 0.82 and 1.04 nm for Pt₁₀ and Pt₂₀, respectively. Thus, these results are compared to those measured for the 0.9 and 1.1 nm NPs⁷ and found to be in reasonable agreement, with an average error of about 10%.

The conventional way to estimate mean bond strength in EXAFS experiments is to fit the EXAFS $\sigma^2(T)$ to an EM plus an additional temperature-independent “static-disorder” term σ_S^2 .^{14–16}

$$\sigma^2(T) = \sigma_S^2 + \frac{\hbar^2}{2\mu k_B} \frac{1}{\Theta_E} \coth\left(\frac{\Theta_E}{2T}\right). \quad (7)$$

Here μ is the reduced mass of a Pt–Pt pair, k_B is Boltzmann’s constant, and $\Theta_E = h\nu_E/k_B$ is the Einstein temperature. However, this approach becomes questionable when the system is inhomogeneous and σ_S^2 has significant contributions from DSD.¹⁷ This inhomogeneity is difficult to determine experimentally since EXAFS gives global average quantities. Our simulations show, however, that the NPs have distinct populations of surface and interior atoms and bonds (Supplementary Figs. S1 and S2). One of our key findings is that the NPs undergo a smooth homogenizing transition with temperature, resulting in a quasi-static $\sigma_S^2(T)$ that is temperature-dependent. Therefore the conventional interpretation of fitted EM plus “static disorder” in terms of bond strengths is unreliable, and must be modified. To demonstrate this for small NPs, the parameters for traditional EM fits are given in Table 1. The simulations reproduce the large σ_S^2 observed in the experiment within error bars, and their fitted Θ_E have the correct decreasing trend with increasing size although slightly lower than experiment. The bonds in unsupported Pt₁₀ are weaker and become less disordered with increasing temperature than those on the support. In contrast, results for supported

Table 1: Einstein model fit parameters for the total and decomposed MSRDs of supported and unsupported Pt₁₀ and Pt₂₀, and for bulk Pt. Einstein temperatures (Θ_E) in K, static disorder (σ_S^2) in $10^{-3} \text{ \AA}^2$. Errors correspond to the 95% confidence interval. The σ_S^2 for σ_{Vib}^2 and σ_{DSD}^2 are statistically indistinguishable from 0. Experimental data refitted from Ref. 7.

Comp.	Param.		Pt ₁₀ /γ-Al ₂ O ₃	Pt ₂₀ /γ-Al ₂ O ₃	Pt ₁₀	Pt ₂₀	Pt foil
σ_{Tot}^2	Θ_E	Theo.	239±76	197±14	198±18	221±26	184±4
		Expt.	300±22	223±12			181±2
	σ_S^2	Theo.	5.8±2.0	4.3±0.6	1.7±0.8	4.2±0.8	0.0±0.2
		Expt.	6.9±0.4	4.5±0.4			0.2±0.2
σ_{Vib}^2	Θ_E	Theo.	196±8	182±7	193±3	192±8	
σ_{DSD}^2	Θ_E	Theo.	81±22	63±18	96±10	59±5	

and unsupported Pt₂₀ are similar. Our simulations also reproduce bulk Pt with smaller Θ_E and no static disorder.

Assuming the conventional EM interpretation for the sake of argument, the fitted Θ_E for Pt₁₀ would imply an effective vibrational frequency of 6.3 THz, which is much higher than the $\nu_E = 3.8$ THz observed for the bulk. Such an increase is consistent with well-known many-body bonding effects^{18,19} that result in bond strengthening with reduced coordination number.^{20–22} That is, the smaller the system, the lower the mean coordination of the bonds, and higher ν_E (Supplementary Figs. S3 and S4).^{12,13} However, the observed ν_E are too high to be physically plausible: a value of 6.3 THz in Pt₁₀ is comparable to that in the strongly-bound isolated Pt₂ dimer,²³ which is 5.8 THz in a supercooled jet,²⁴ and 6.5 THz in a noble gas matrix.²⁵

Fig. 1 also shows the components of the MSRD as a function of temperature, while the parameters for their EM fits are presented in Table 1. σ_{Vib}^2 shows normal behavior for both supported and unsupported systems, with a Θ_E 45 K lower for Pt₁₀ than that for the total MSRD. In fact, σ_{Vib}^2 is quite similar to that in the bulk, with a Θ_E of 196 K *vs* the bulk value of 184 K. The small difference arises from the shorter and stronger cluster bonds. The σ_{DSD}^2 also shows normal linear behavior with increasing temperature, although with a significantly smaller slope than σ_{Vib}^2 . Given that the DSD originates from low frequency dynamics associated with the motion of the CM (see Supplementary Information), we use

the total mass of the cluster in the EM fits instead of the Pt–Pt reduced mass, resulting in a Θ_E of about 60-80 K.

Of the three components of the MSRD, the ASD component is the only anomalous one, decreasing with increasing temperature and explaining the enhanced Θ_E . For Pt₁₀, σ_{ASD}^2 accounts for 70% of the total disorder at low temperature, decreasing linearly to 15% at high temperature. The σ_{ASD}^2 in unsupported Pt₁₀ is about half, showing that the support has a very large effect on the MSRD of small NPs. In contrast, the supported and unsupported Pt₂₀ clusters show both a much smaller variation with temperature and similar σ_{ASD}^2 . These results highlight two important observations: First, σ_{ASD}^2 is the only component that has significant size- and support-dependence. Second, the temperature variation of σ_{ASD}^2 for Pt₂₀ is already quite small, indicating that standard EXAFS analysis methods are likely valid for NPs with 30 atoms or more. To probe the origin of the temperature-dependence of σ_{ASD}^2 , Fig. 2 shows the $\bar{r}_L$ distribution as a function of temperature. The σ_{ASD}^2 decrease appears as a narrowing of the distribution caused by two main effects: i) the longer/weaker bonds are preferentially removed from the screening window as they become active, and ii) the shorter bonds become longer due to thermal expansion. The NTE of the NPs is visible as a left shift of the centroid of the distributions (Supplementary Fig. S4, bottom).

Finally, we discuss the anomalous Grüneisen parameter γ :

$$\gamma = -\frac{d \ln \nu_E}{d \ln V} = -\frac{1}{3} \frac{d \ln \nu_E}{d \ln R_{PtPt}} \quad (8)$$

which characterizes bond anharmonicity. Estimates of γ based on ν_E values from standard EM fits of the total MSRDs give γ values of 5 ± 2 and 4 ± 2 from experiment and theory, respectively. These estimates are counterintuitively larger than the $\gamma = 2.7$ measured for the solid.²⁶ Based on simple effective anharmonic potential models,²⁷ γ can be approximated as $\gamma = k_3 R / k_2$, where k_2 and k_3 are, respectively, the harmonic and anharmonic force constants of the effective potential. Thus, given that in the NPs R is smaller and k_2 is larger, if

we assume that the anharmonicity remains about the same we expect $\gamma_{NP} < \gamma_{Bulk}$. The anomalous values can be traced to the assumption of temperature independent static disorder in the EM fits; however, normal behavior is recovered when actual vibrational ν_E values are used. Fig. 3 shows the variation of ν_E as a function of R_{PtPt} for Pt₁₀ and Pt₂₀, compared to the variation for bulk Pt obtained by assuming a constant $\gamma = 2.7$, and $\nu_E = 3.8$ THz at 2.77 Å. The NPs ν_E were obtained as the mean frequencies of 1 ps wavelets generated from the $r_H(t)$ trajectories. Although the NPs exhibit a broad distribution of frequencies due to the bond length range, they show the expected inverse relationship between bond length and frequency. The distributions peak at the Pt₁₀ and Pt₂₀ mean R_{PtPt} distances of 2.60 and 2.63 Å, with mean frequencies of 4.4 and 4.1 THz, respectively, in reasonable agreement with the values of 4.1 ± 0.2 and 3.8 ± 0.2 THz obtained from EM fits of σ_{Vib}^2 . The red lines in Fig. 3 correspond to fits of ν_E vs R_{PtPt} assuming constant γ , which we find to be 1.3 ± 0.5 for both Pt₁₀ and Pt₂₀, thus lower than the bulk value, as expected from anharmonicity considerations.

In summary, we carried out DFT/MD simulations of supported Pt nanoparticles as a function of size and temperature, and analyzed their dynamic behavior by partitioning the MSRD of the Pt–Pt bonds into vibrational, DSD and ASD components. We show that the vibrational contribution arises from local Pt–Pt vibrations and is primarily controlled by the number of NN around the bonds. The DSD component, conversely, arises from the coupling between the global CM dynamics with the local Pt–Pt bond fluctuations. The ASD is due to the fraction of bonds that remain “frozen” for more than 10 ps at a given temperature and decreases linearly with increasing temperature. Our simulations reveal large inhomogeneity in the NPs, showing distinct surface and interior atom populations, thus challenging the conventional interpretation of bond-strengths from EM fits with static disorder that leads to anomalous values. Instead we found that the heretofore so-called static component is not constant but decreases with temperature. This decrease of the ASD component is caused by two effects: i) The activation of the longer, weaker Pt–Pt bonds and ii) the stretching of the

shorter bonds. This results in a narrowing of the equilibrium bond-distance distribution with increasing temperature and, given that it is dominated by the former, the system experiences an effective NTE. Physically this behavior is analogous to a smooth phase transition to a more homogeneous structure with increasing temperature. In contrast, the DSD and vibrational components display normal thermal behavior, with the vibrational component being similar to that in bulk Pt, and the DSD contributing about 10-20% of the total MSRD. Thus in order to obtain bond-strength-associated Grüneisen parameters from EXAFS, one has to subtract both the DSD and ASD components of the disorder. Finally, given that these anomalous properties likely arise from the synergistic effects of limited dimensionality of these systems,⁹ intra-particle heterogeneity,²⁸ and the effects of oxide support, our results may indicate the existence of other particle-support systems with similar anomalous properties.

Computational Methods

The computational approach here is similar to that used previously:¹³ All *ab initio* DFT/MD runs were done using VASP²⁹ using the Nosé-Hoover thermostat^{30,31} and the PBE functional.³² The simulations were non-relativistic, used spin-unpolarized densities at the Γ point, ultrasoft pseudopotentials, and a plane wave cutoff of 297 eV. (See Supplementary Information for more detailed information.) The initial structures for each temperature were generated by creating random clusters with appropriate bond distances (2.5-2.9 Å) which were then placed onto the “d” layer of the dehydroxylated [110] surface of γ -Al₂O₃, and fully optimized before starting the MD runs. The γ -Al₂O₃ surface is represented by 4 layers (2 fully relaxed and 2 frozen) in a supercell of 19.4 Å $\times$ 13.7 Å with an effective vacuum separation of 16 Å. Each run was 20 ps long, with the first 10 ps used for thermalization and discarded from the analysis. The equations of motion were integrated with the velocity-Verlet method with a 3 fs time step which captures the fastest fluctuations at the highest temperatures studied. In addition, we also carried out DFT/MD simulations for unsup-

ported Pt₁₀, Pt₂₀, and bulk Pt. These runs used the same computational details as those on γ -Al₂O₃ except that their simulation cells were different: for unsupported Pt₁₀ and Pt₂₀ we used a cubic cell with side 15 Å, while for bulk Pt we used a cubic simulation cell with side 11.898 Å and 108 atoms (a 3×3×3 replica of the conventional Pt cell).

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Supporting Information Available

Description of tail removal. Discussion of the relation between CM dynamics and disorder. Origin of sub-THz dynamics. Discussion of XC computational settings. Figures describing the internal structure of the NPs.

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Figure 1: Decomposition of the Pt–Pt MSD for supported (full) and unsupported (dashed) Pt_{10} (top) and Pt_{20} (bottom) clusters. The vibrational component corresponds to disorder with frequencies above 1 THz, the DSD to that between 0 and 1 THz, and the quasi-equilibrium ASD component to dynamics that are longer than the length of these simulations. The experimental values were taken from Ref. 7. The error bars correspond to estimated errors in the mean.

Figure 2: Comparison of the equilibrium pair distribution functions as a function of temperature for Pt_{10} (top) and Pt_{20} (bottom). Also included are Gaussian fits and vertical lines (dashed) indicating the spread and centroid of the distributions, respectively.

Figure 3: Probability distribution of the mean vibrational frequency ν_E of a Pt–Pt bond as a function of its mean bond length R_{PtPt} . The black line for bulk Pt was obtained by assuming a constant $\gamma = 2.7$ and a $\nu_E = 3.8$ THz at $2.77 \text{ \AA}$. The red line correspond to a fit of the Pt₁₀ data also assuming a constant γ .