Shake-Rattle-and-Roll: A Model of Dynamic Structural Disorder in Supported Nanoscale Catalysts

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We investigate the effects of “dynamic structural disorder” (DSD) on the behavior of supported nano-scale catalysts. DSD refers to the intrinsic fluctuating, inhomogeneous structure of such nano-scale systems. In contrast to bulk materials, nano-scale systems exhibit substantial fluctuations in energy, charge, and other extensive quantities as well as large surface effects. The DSD is driven by the stochastic librational motion of the center of mass and fluxional bonding at the nanoparticle surface due to thermal coupling with the substrate. Our approach for calculating DSD is based on a combination of statistical mechanics, transient coupled-oscillator models, and real-time DFT/MD simulations. This approach treats thermal and dynamic effects over multiple time-scales, including bond-stretching and -bending vibrations, DSD, and transient tethering to the substrate at longer ps time-scales. Model calculations of molecule-cluster interactions and molecular dissociation reaction paths are presented in which the reactant molecules are adsorbed on the surface of dynamically sampled clusters. This model suggests that DSD affects both the prefactors and distribution of energy barriers in reaction rates, and thus can strongly affect catalytic activity at the nano-scale.

I. INTRODUCTION

The structure and behavior of materials at the nanoscale are both of fundamental and technological importance and are particularly relevant to the understanding of supported nanoscale catalysts. This challenging problem is complicated by the fact that nano-scale properties differ from those of condensed systems, especially at high temperature. Their unusual thermodynamic properties have been widely recognized at the structural, catalytic, and spectroscopic level. They differ from the bulk since the thermodynamic limit does not apply for small N, where N refers to the number of atoms in the nanocluster. For example, cluster surface effects of O(N^{2/3}) are crucial and thus nano-scale systems are necessarily inhomogeneous. Moreover, statistical physics arguments imply that nano-scale systems exhibit substantial O(N^{1/2}) fluctuations in extensive physical quantities like total energy and charge, and hence O(N^{-1/2}) fluctuations in local temperature. In addition, supported nano-scale catalysts exhibit an intrinsic fluctuating, inhomogeneous structure referred to as dynamic structural disorder (DSD). Thus, in contrast to bulk materials, they have no well-defined “equilibrium structure,” particularly at high temperatures. The presence of these intrinsic fluctuations suggest that it would be useful to examine their behavior from a dynamical perspective. This approach is in contrast to conventional surface science approaches typically based on time-independent structural properties. Indeed, there has been a growing interest in such real-time approaches in recent years. Dynamic effects have also been postulated to play a role in other treatments of catalysis, ranging from heterogeneous catalysts at surfaces and in the catalytic activity in biostructures. The difference in the treatment here is the emphasis on the effects of nano-scale dynamics on catalytic properties which are investigated using nudged-elastic-band (NEB) transition state theory (TST) calculations.

Our approach for modelling the effects of DSD is based on a concept dubbed picturesquely as “Shake-Rattle-and-Roll” (SRR). This approach was inspired by observations of unusual behavior in nanoscale supported Pt and Pt-alloy catalysts: In particular, x-ray absorption spectra (XAS) studies showed that small Pt nano-clusters exhibit negative thermal expansion, anomalously large disorder, and temperature dependent shifts in XAS threshold energies. These anomalous properties were subsequently explained by finite-temperature DFT/MD calculations, which showed that they are dynamical in origin, involving multiple time-scales. They include 1) fast bond vibrations (i.e., shaking) 2) soft anharmonic or fluxional modes, particularly involving the nano-particle surface atoms; and 3) librational motion of the center of mass (CM), which is due to the thermal contact of the nano-clusters tethered to the support bonding sites. As discussed below, these CM dynamics are analogous to hindered 2-dimensional Brownian motion. When combined with the stochastic thermal coupling to the support, these low-frequency modes induce a rattle-like motion in the system, typically at sub-THz frequencies. At longer time scales (tens of ps for supported Pt clusters on γ-alumina at high temperatures), bonding to the support is transient. When those bonds break, the nano-clusters can then roll or slide to new positions on the support. The combined motion of many such clusters eventually leads to sintering, which typically reduces catalytic activity. This rattle-like motion has recently been interpreted as dynamic structural disorder, in contrast to static bond distortions or substitutinal disorder typical in condensed systems. Instead, the DSD is “non-equilibrium” in character, in the sense that the system exhibits fluctuations from from mechanical and thermal equilibrium, even though, of course, the full system (cluster plus support) is in overall “thermal-equilibrium,” with a well defined global temperature T. Thus the geo-
metric structure of nano-clusters is amorphous and fluctuating, rather like that in a partly-melted solid. Indeed, DSD affects the nano-cluster behavior through stochastic fluctuations in structure, cluster charge and center of mass position.

These remarkable observations have motivated us to reinvestigate the structure and catalytic behavior of supported nanoclusters in terms of their dynamic structure. To this end, we introduce the SRR concept based on a combination of statistical mechanics, transient coupled-oscillator models, and real-time DFT/MD simulations. As discussed below, SRR can explain the anomalous properties observed for supported nano-clusters, including both DSD and charge fluctuations. As an illustration, we have applied this approach to calculations of the interaction between the supported nanocatalysts and prototypical molecules, and their dissociation reaction paths. These show that the DSD provides a mechanism for increasing reaction rates. Although still preliminary, the SRR model offers tantalizing insights into dynamic mechanisms that contribute to catalytic processes.

II. THERMAL FLUCTUATIONS AT THE NANOSCALE

As noted in the introduction, thermal properties of nano-structures with relatively small \( N \) differ substantially from those in macroscopic condensed matter due to finite-size effects enhanced by their poor thermal coupling to the support. In contrast to bulk systems, their mean energy \( \bar{E} \) is not sharply defined, but exhibits substantial energy fluctuations of order \( kT\sqrt{N} \) leading to fluctuations in the local temperature (or energy per particle) of order \( T/\sqrt{N} \). This effect is not immediately obvious since the global temperature \( T \) is a constant throughout the system. To understand these results, we recount the classical arguments of statistical thermodynamics. We consider a nano-cluster with \( N \) atoms weakly bound to a support at fixed temperature \( T \), which serves as a heat-bath. For simplicity of argument the cluster volume \( V \), charge \( Q \), and composition can be regarded as fixed, but these contraints are not essential and will be relaxed below. Due to contact with the support, which is in continuous thermal and vibrational motion, energy will fluctuate between the cluster and the support, with a probability distribution

\[
P(E, T) \approx \Omega(E)e^{-\beta E} = e^{-\beta F(E, T)}
\]

where \( F(E, T) = E - \frac{3}{2}TS\) and \( k \ln \Omega(E) = S(E) \) is the net cluster entropy due to distinguishable configurations \( \Omega(E) \) of the nano-cluster at energy \( E \). Thermal equilibrium corresponds to the maximum probability or, equivalently, \( \min F(E, T) = F(T) \), i.e., the Helmholtz free energy. The mean total cluster energy \( \bar{E} \) is then fixed by the relation \( \partial S(E)/\partial E|_{\bar{E}} = 1/T \), and hence both the nanocluster and the support have the same equilibrium temperature \( T \). The cluster entropy \( S(E) \) is additive in terms of the independent \( 6N \) degrees of freedom in the cluster dynamics. In addition to the \( (3N-3) \) internal vibrational modes (including both potential and kinetic degrees of freedom), the dynamics includes four additional degrees of freedom from the 2-d librational modes of the CM parallel to the support, and additional modes binding the cluster to it. The distribution \( P(E, T) \) is sharply peaked for large \( N \) and approximately Gaussian near the peak at \( \bar{E} \). The mean square fluctuations \( \sigma_E^2 \) are obtained from the 2nd derivative of the entropy \( \sigma_E^2 = k/\partial^2 S(E)/\partial E^2 \).

The quantity \( \sigma_E^2 \) is clearly \( O(N) \) since both the total energy \( E \) and entropy \( S(E) \) of the cluster are extensive. At high temperatures, where equipartition is valid, \( \bar{E} = 3NkT \) and \( S(E) \approx 3Nk \ln E \). Thus the energy fluctuations are given by \( \sigma_E \propto kT\sqrt{3N} \) and similarly since \( T = \bar{E}/3Nk \), fluctuations in the internal temperature of the cluster are \( \sigma_T = T/\sqrt{3N} \). The effect is rather like that of a fluctuating thermostat for which any non-linear effects (e.g., reaction rates) on temperature do not cancel. Consequently, one may expect substantial DSD effects on reaction rates. For example, for \( N = \text{20} \) at 600 K, \( \bar{E} \) is distributed within a few tenths of an eV of the mean \( \bar{E} = 3NkT \approx 3 \text{ eV} \), and \( \sigma_T \approx 75 \text{K} \). In contrast, the thermal fluctuations of the substrate itself are negligible. This statistical argument suggests why finite temperature DFT/MD approaches may be more efficient than full canonical ensemble sampling for calculating the physical properties of nanoclusters, since they naturally probe the range of accessible phase space within a few \( \sigma_E \) of \( \bar{E} \) over a time-scale comparable to the periods of vibrational and librational motion.

The above arguments can be generalized for other conserved physical quantities, for example total volume \( V_{\text{tot}} = V + V_S \), net electronic charge \( Q_{\text{tot}} = Q + Q_S \), chemical composition, etc., where the subscript \( S \) refers to the support. To this end one must generalize the calculations of accessible states in terms of \( S(E, V, Q, N_i) \) with varying \( V, Q, \) etc. These additional physical quantities are stabilized by those from the support bath, so that \( F \rightarrow F - pV + \mu Q/e + \sum \mu_i N_i \) where \( p \) is the pressure, \( \mu \) the chemical potential, \( Q/e \) is the number of electrons in the cluster, and \( N_i \) the number of atoms of species \( i \). Since quantities like \( V \) and \( Q \) are extensive, one also expects their fluctuations to be of order \( \sqrt{N} \). The charge (and hence chemical potential) fluctuations, are important to explain the variation of the Fermi energy with temperature in the XAS studies. Due to the strength of Coulomb forces and the importance of oxidation states in many catalytic reactions, these charge fluctuations may play a key role in controlling nano-scale properties and chemical reaction rates.

III. TRANSIENT COUPLED OSCILLATOR MODEL

The thermodynamic behavior of tethered Pt nanoclusters can be understood in terms of a “transient coupled oscillator model.” That is, we consider the inter-
vibrational modes with respect to fluctuating instantaneous-equilibrium structures, which is presumably valid over a ps time-scale long compared to the vibrational periods. The dominant modes of the system coupled to the support thus consist of: i) vibrational modes; ii) soft and fluxional modes, particularly close to the cluster surface; and iii) CM librational modes, i.e., soft modes about which the cluster center of mass fluctuates. For Pt, the vibrational modes are of THz scale, while the soft and librational modes are sub-THz. The model is transient, since anharmonicity and bond-breaking can be substantial, and hence the characteristic modes of oscillation fluctuate. The thermodynamic quantities of interest can be obtained from the free energy e.g., \( \langle F(T) \rangle \) averaged over several such models, each of which can be calculated over sufficiently short (e.g., ps time-scale) time-intervals within a quasi-harmonic approximation using the relation \( \frac{\partial^2 F}{\partial \beta^2} = kT \).

\[
F(T) = E_0(\bar{R}) + kT \int d\omega \rho(\omega) \ln[2\sinh(\beta\hbar\omega/2)].
\]

Here \( \rho(\omega) \) is the total density of modes per unit frequency and \( E_0(\bar{R}) \) is the electronic energy at the transient mean atomic positions. The thermodynamic average \( \langle F(T) \rangle \) is given by the same expression with \( E_0(\bar{R}) \) replaced by \( \langle E_0(\bar{R}) \rangle \) and \( \rho(\omega) \) by \( \langle \rho(\omega) \rangle \). This approach is efficient, since despite the fluctuations in structure, the average spectrum \( \langle \rho(\omega) \rangle \) is relatively stable. The term \( E_0(\bar{R}) \) is important since it contains the transient effects of charge fluctuations and affects changes in potential energy that dominate the reaction paths. The support provides both a heat bath and charge reservoir at fixed \( T \) which give rise to stochastic CM motion and DSD. Since we are primarily interested in catalytic behavior at high-temperatures, we focus our discussion here to the classical limit with mean phonon occupations \( n(T) \approx kT/\hbar\omega \gg 1 \). At 600 K this limit is a reasonable approximation for Pt which has a Debye-temperature of 240 K and an equivalent Debye frequency of 5.2 THz. In this limit

\[
F(T) = E_0(\bar{R}) + kT \int d\omega \rho(\omega) \ln(\beta\hbar\omega).
\]

This statistical approach can also be directly compared to experiment, since observed physical properties are usually defined as averages over a statistical ensemble, and are equivalent to time-averages over a long time interval sufficient to cover the accessible phase space. Low frequency modes are important since \( n(T) \) varies inversely with \( \omega \). However, the effect of breathing modes is expected to be small since for a 3-d system \( \rho(\omega) \approx \omega^2 \) at long-wavelengths. From the identity \( \ddot{E} = \partial^2 F/\partial \beta^2 \), we obtain a mean energy \( \ddot{E} = 3NkT \) at high temperatures, consistent with the equipartition theorem. This energy includes contributions from the 2-d librational motion in the \( x-y \) plane, which can be approximated by low frequency (sub THz) vibrational modes of the CM (Fig. [1]). Thus the mean stochastic librational kinetic energy \( (1/2)Mv_{lib}^2 = kT \). This result is the analog of Brownian motion, the difference being that such motion is hindered and 2-dimensional in character in nanoparticles tethered to the support. This stochastic CM motion is crucial to the origin of DSD and drives non-equilibrium fluctuations in the internal structure.

![Typical trajectory for a bound Pt-Pt pair in Pt_{15}Sn_{5} on γ-Al_{2}O_{3} at 298 K decomposed into structural disorder and vibrational components by applying a 0.5 THz low-pass filter (top), and average projected density of states for the vibrational and dynamic structural disorder components of bound Pt-Pt pairs in Pt_{15}Sn_{5} as a function of temperature (bottom).](image)

**IV. DYNAMIC STRUCTURAL DISORDER**

In order to investigate DSD in more detail we consider the effect of their large fluctuations on the dynamic structure of the cluster. This structure can be described formally as a point in 6N-dimensional phase space defining the nuclear coordinates and momenta \( \{\vec{R}_i(t),\dot{\vec{R}}_i(t), i = 1 \ldots N\} \). Due to the fluctuations in the structure, e.g., the change in shape due to the librational motion and fluxional surface bonds, the cluster potential energy surface \( V(\{\vec{R}_i\}, t) \) will also fluctuate on a time-scale comparable to the librational motion, which is much slower.
than typical bond vibrations. Thus it is reasonable to assume that a transient harmonic oscillator approximation is valid for characterizing short-time motion. During that time the motion of the cluster is vibrational with respect to the instantaneous minima on its PES, i.e., fluctuating equilibrium positions, denoted by \( R_i \). Next we introduce the mean pair distribution function \( g(R) \) defined as the average distance between all bond pairs \((i,j)\) in the cluster,

\[
g(R) = \frac{1}{N(N-1)} \sum_{i \neq j} \langle \delta(R - |R_i(t) - R_j(t)|) \rangle.
\] (4)

This PDF can be measured in experiment. For example the XAFS signal

\[
\chi(k) = \int dR g(R) \frac{f_{\text{el}}(k)}{k R^2} \sin(2kR + \Phi)e^{-2R/\lambda}
\] (5)

is closely related to the Fourier transform of \( g(R) \). In conventional XAFS analysis, however, one usually restricts consideration to the near neighbor bonds, e.g., by Fourier filtering over the first coordination shell, which is described by the near-neighbor distribution function \( \tilde{g}(R) \). Physical quantities of interest are then obtained from the cumulant moments of \( \tilde{g}(R) \), e.g. the mean near-neighbor distance \( \bar{R} = \langle R \rangle = \int dR \bar{R} \tilde{g}(\bar{R}) \), and the mean-square radial disorder (MSRD) by \( \sigma^2 = \langle (R - \bar{R})^2 \rangle \).

Note, however, that the quantities \( \bar{R} \) and \( \sigma^2 \) refer to averages over the entire cluster and thus can give a misleading picture of the structure of inhomogeneous systems. This difference is important in the Pt nano-clusters, for which the mean Pt-Pt bond length and fluctuations depend on the local environment and thus their locations inside the cluster. Simulations of \( \sigma^2 \) can be carried out in terms of the distribution of (partial) PDFs at each site \( g_i(R) = \sum_{j \neq i} g_{ij}(R) \). The local near-neighbor distributions \( \tilde{g}_{ij}(R) \) have net weights \( \tilde{g}_i = \int dR \tilde{g}_{ii}(R) \), mean near neighbor bond lengths \( \bar{R}_i = \int dR R \tilde{g}_{ii}(R) \), with fluctuations \( \sigma^2 = \int dR (R - \bar{R}_i)^2 \tilde{g}_{ii}(R) \). Consequently the global average near-neighbor bond distance \( \bar{R} \) and MSRD \( \sigma^2 \) corresponding to experimental measurements are

\[
\bar{R} = \sum_i \bar{R}_i \tilde{g}_i, \quad \sigma^2 = \sigma^2_D + \sigma^2_V,
\] (6)

where the local bond fluctuations are \( \sigma^2_V = \sigma^2 \tilde{g}_i \), and the mean-squared disorder due to cluster inhomogeneity is \( \sigma^2_D = \sum_i (\bar{R}_i - \bar{R})^2 \tilde{g}_i \). Interestingly both of these contributions have DSD contributions from low frequency fluctuations. This procedure is illustrated in Fig. 2 which shows the decomposition of \( \tilde{g}(R) \) vs mean bond length. In particular, much of the width of the first neighbor peak in \( \tilde{g}(R) \) comes from cluster inhomogeneity, and thus explains the anomalously large disorder observed for the nanoclusters. Moreover, the individual PDFs in Fig. 2 are not randomly distributed, suggesting a correlation between the mean Pt-Pt bond length and the associated MSRD of the bond. This correlation is clearly shown in

Fig. 3 with an increase in the MSRD as the Pt-Pt bonds get longer/weaker.

Another example of structural correlations is shown in Fig. 1 which depicts the mean Pt-Pt bond distance \( R_{\text{Pt-Pt}} \) as a function of its distance to the center of the nanoparticle (\( R_{\text{CC}} \)). Bonds near the surface of the cluster (\( R_{\text{CC}} \gtrsim 2.5 \text{Å} \)) are shorter, as expected from their reduced number of near neighbors. This threshold is in good agreement with previous results showing that the interior-surface transition zone occurs between 2.5 and 3 Å.

The low frequency DSD modes in Eq. (3) are particularly important in these calculations, since they give large contributions to the MSRD

\[
\sigma^2 = \frac{\hbar}{2\mu} \int d\omega \frac{\rho(\omega)}{\omega} \coth(\beta\hbar\omega/2) \approx \frac{kT}{\mu} \int d\omega \frac{\rho(\omega)}{\omega^2},
\] (7)

where the expression on the right is the high temperature limit. Here \( \mu \) refers to the reduced mass of a given bond.
is to use DFT/MD calculations of $\langle \sigma^2 \rangle$, in real time over a sufficiently long interval $\tau$,\[ \langle \sigma^2 \rangle = \frac{1}{\tau} \int_0^\tau dt \sigma^2(t) = \int d\omega \sigma^2(\omega), \tag{8} \]
where $\sigma^2(\omega) = \rho(\omega)/\mu \omega^2$. Such real-time calculations naturally account for the transient coupled-oscillator motion and effects of charge fluctuations on the dynamics of the cluster, as illustrated in Fig. 1 (bottom). Alternatively $\rho_R(\omega)$ can be obtained from the FT of real-time DFT/MD trajectories or from equation of motion techniques.

\[ \rho_R(\omega) = \frac{2}{\pi} \int_0^{t_{\max}} \langle Q_R(t)Q_R(0) \rangle \cos(\omega t)e^{-\epsilon t^2}. \tag{9} \]

V. NANOSCALE REACTION RATES

Formally, calculations of catalytic properties such as reaction rates depend on free energies from equilibrated statistical ensembles that contain all accessible regions of phase space. The effects of disorder\textsuperscript{15,16} and the presence of a variety of possible transition paths\textsuperscript{17,18} have been addressed in the past. Due to its simplicity, however, transition state theory (TST) is still the most widely used approach for rate calculations in molecular and nanoscale systems.\textsuperscript{19} This approach is usually based on time-independent nanoparticle potential energy surfaces and the assumption of quasi-equilibrium between reactants and transition state. In contrast, our SRR model based on finite-temperature DFT/MD calculations avoids many of these difficulties. We stress that \textit{ab initio} DFT is crucial for many properties, as classical MD simulations with model potentials do not adequately capture charge fluctuations, bond-breaking, diffusion and other non-equilibrium effects.\textsuperscript{20} Moreover DFT/MD is a good approach for non-equilibrium structural and physical properties at high temperatures, since it builds in anharmonic and structural disorder.

Statistical thermodynamic arguments similar to those in Sec. II. can be applied to nano-scale reaction rates. Our analysis suggests that it may be important to treat the behavior of reactant molecules on the dynamically fluctuating surface of a nano-cluster, e.g., with our SRR model, rather than on selected static structures. Thus, the slow fluctuating modes of both the cluster and the reactant molecules can couple, resulting in an statistical ensemble of reaction barriers and reaction rates.

The SRR catalysis model thus consists of a system of reactant molecules in contact with a fluctuating cluster that can exchange energy to and from it. Our treatment below focuses on the rate limiting step of crossing the transition barrier; more detailed approximations should take into account the diffusion rates of the molecules on the surface of the nano-clusters to the reaction site.

pair, e.g., $M_{Pt}/2$ for Pt-Pt bonds. Thus it should be possible to distinguish DSD from conventional vibrations by filtering the density of modes $\rho(\omega)$, as shown in Fig. 1. Similarly the contribution from each site $\sigma_i^2$ can be obtained by replacing $\rho(\omega)$ with the projected density of vibrational modes $\rho_i(\omega)$. In this way, one can analyze the net MSRD into contributions from different positions in the cluster and their vibrational and DSD components. A similar expression can be used to calculate the librational fluctuations of the CM, with $\mu$ replaced by $M_{CM}$ and $\rho$ the projected density of librational modes. Note that this expression implies that $\sigma^2$ for the Pt-Pt bonds is linear in $T$ at high temperatures with a slope depending on the inverse second moment of $\rho(\omega)$. Estimates of $\rho(\omega)$ can be obtained in various ways. For example one approach
Given that diffusion processes are dominated by low frequency modes, such rates are likely influenced by the slow nature of the DSD. Using arguments analogous to those of Sec. II, the probability distribution of reactant energies \( \epsilon \) is given by a statistical ensemble with a fluctuating cluster energy distribution \( E \) relative to the mean \( \bar{E} \):

\[
\Omega(E-\epsilon) \propto \exp[S(E)-\beta \epsilon] \quad \text{where} \quad \beta = \partial S(E)/\partial E = 1/kT
\]

is the fluctuating inverse local temperature at energy \( E \). Thus we obtain

\[
P(\epsilon) \approx \langle \Omega_R(\epsilon) e^{-\beta \epsilon} \rangle = \langle e^{-\beta f(\epsilon;\bar{T})} \rangle, \quad (10)
\]

where \( \Omega_R(\epsilon) \) is the configurational entropy of the reactant molecules on the cluster, and the average is carried out over the distribution of cluster energies \( E \) and hence values of \( \beta \). This result shows why the average over terms with \( \beta \) is not the same as that with fixed \( \beta \) when temperature fluctuations are large.

Consequently, calculations of reaction rates \( \kappa \) for the transition \([A] + [B] \rightarrow [AB^*] \rightarrow [P]\) require a generalization of transition state theory to the case with fluctuating barriers,

\[
\kappa = \frac{kT}{\hbar} \left( \frac{Z'_{AB}}{Z_A Z_B} e^{-\beta \epsilon_b} \right) \quad (11)
\]

Here \( \hbar \) is Planck’s constant and the averages in the partition functions are carried out over all nano-cluster configurations: \( Z'_{AB} \) is the partition function of the activated complex, and \( Z_A \) and \( Z_B \) the partition functions of the reactants \( A \) and \( B \), and again the average is carried out over the range of local temperatures \( \beta \). This result is analogous to the usual Arrhenius law, but with a dynamically averaged “attempt frequency” prefactor and fluctuating reaction barriers \( e^{-\beta \epsilon_b} \). Both of these factors are affected by DSD. It is easy to see, for example, using a first order cumulant expansion, why the latter average is always greater than the reactivity at the mean barrier \( \langle \epsilon_b \rangle \)

\[
\langle e^{-\beta \epsilon_b} \rangle = e^{-\beta \langle \epsilon_b \rangle} e^{(1/2)\beta^2 \sigma^2_{\epsilon_b}} \geq e^{-\beta \langle \epsilon_b \rangle}.
\]

The average leads to a reduced temperature dependent “effective barrier” \( \epsilon'_{b} = \epsilon_{b} - (1/2)\beta^2 \sigma^2_{\epsilon_b} \), which is comparable to the lowest barriers typically encountered during reactions. Note, however, that the cumulant estimate assumes small fluctuations in \( \epsilon_b \), more generally the inequality is always valid and the lowest barriers dominate.

Approximate calculations of the molecular partition functions in these fluctuating TST models can be carried out in terms of the local free energies of the molecules bonded to the fluctuating cluster or at the transition state using a generalization of the coupled-oscillator model discussed above. One expects that the low frequency modes of the reacting molecule will be strongly coupled to the cluster and depend both on the instantaneous orientation and local geometry of the molecule on the cluster surface at a given time. This coupling is expected to be transient and it is plausible that cluster fluctuations will assist a molecule in probing a wider range of degrees of freedom than on a static support. Within this model, the local free energy of an adsorbed molecule with position \( \vec{r} \) is given by

\[
f(\bar{T}) = \epsilon_0(\vec{r}) + k\bar{T} \int d\omega \rho_R(\omega) \ln[2 \sinh(\beta \hbar \omega/2)], \quad (13)
\]

where \( \rho_R(\omega) \) is the projected local density of vibrational states at a given reactant molecule at position \( \vec{r} \) on the surface of the cluster and \( \bar{T} \) is the effective temperature of the cluster. As with the total free energy of the cluster, the local free energy of the molecule \( f(\bar{T}) \) contains terms coupling to the fast vibrational density of states of the cluster, and to the relatively slow librational motion of the CM and other contributions to DSD. Since reactant molecular vibration frequencies are often large compared to thermal motion \( (\hbar \omega \gg kT) \), their vibrational states are typically frozen in their ground state, and the high temperature limit is inappropriate. On the other hand, relatively low energy bending and rotational modes may be thermally active and contribute strongly. As with DSD, one expects that the MSRD \( \sigma^2 \) of the reactant molecule will contain contributions from the low frequency librational modes, even for weak couplings as contributions to \( \sigma^2 \) are proportional to \( 1/\omega^2 \) (cf. Fig. 5 of Ref. [13]). Thus it is possible that these low frequency fluctuations can significantly increase the entropy fluctuations and hence the catalytic activity of reactants, though quantitative calculations will be needed to assess the net effect.
VI. MODEL CALCULATIONS

A. DSD and adsorbate dynamics

As an illustration of the theory discussed above, we present calculations and sample reaction paths for prototypical molecules adsorbed on nano-clusters. In order to address the effects of DSD on their catalytic activity we first address the “simpler” problem of adsorbate dynamics on the surface of the particles. For this purpose we have carried out MD simulations similar to those described in the previous sections, but with the addition of an adsorbate molecule (CO) on the surface of the nanoparticle. Fig. 6 shows a series of snapshots illustrating the high mobility of the molecule over the surface.

Qualitatively, while the CO molecule position is strongly coupled to the DSD of the nanoparticle, its internal structure is not expected to depend strongly on disorder. The MD simulations support this statement: First, the CO molecule is tethered to a Pt atom through its carbon-end for most of the simulation, so its position is modulated by the slow Pt motion. Nevertheless, brief incursions into bifurcated anchoring states are also observed. These noticeably affect the internal structure of the adsorbate by elongating the CO bond. Second, the low frequency dynamics associated with the DSD are likely to couple better with the low frequency C-Pt bonds, rather than with the high frequency adsorbate covalent bonds.

To investigate this coupling between the adsorbate dynamics and the nanoparticle DSD more quantitatively, we have have filtered out the slow, stochastic component from the intra-adsorbate (R\textsubscript{CO}) and adsorbate-particle (R\textsubscript{CPt}) dynamics, similar to that in Fig. 4. The fast transition between Pt anchoring points described above can be clearly seen in a typical trajectory (Fig. 6). Here the region between ~2-4 ps shows a quick transition between Pt anchoring points, with brief incursions into bifurcated anchoring states. These transient states have a clear effect on the R\textsubscript{CO} distance (see Fig. 7).

![Graph showing decomposition of R_{CPt} dynamics](image)

**FIG. 6.** Dynamics of the three shortest R\textsubscript{CPt} bonds in a typical trajectory for CO adsorbed on Pt\textsubscript{10}Sn\textsubscript{10} on γ-Al\textsubscript{2}O\textsubscript{3} at 598 K. The vertical green line indicates the end of the thermalization stage. The region between ~2-4 ps shows a quick transitions between Pt anchoring points, with brief incursions into bifurcated anchoring states. These states have a clear effect on the R\textsubscript{CO} distance (see Fig. 7).

![Graph showing decomposition of R_{CO} dynamics](image)

**FIG. 7.** Decomposition of the R\textsubscript{CO} dynamics into vibrational and disorder components for CO adsorbed on Pt\textsubscript{10}Sn\textsubscript{10} on γ-Al\textsubscript{2}O\textsubscript{3} at 598 K. The vertical green line indicates the end of the thermalization stage.

These spectra are shown in Fig. 8 (top), where ε is a broadening parameter added for convenience. The most prominent features correspond to the CO stretch for both on-top (between 60 and 64 THz) and on-bridge (small peaks between 54 and 58 THz). These frequency ranges are in good agreement with the experimental values.\textsuperscript{21–24} Also noticeable is a small feature between 12 and 16 THz associated with the molecule-particle interaction, as discussed below in further detail. As expected, the negligible weight of the disorder confirms that the intramolecular dynamics of CO are largely independent of DSD.

The disorder has a much larger role in the molecule-nanoparticle dynamics, as seen in Fig. 8 (middle), where the R\textsubscript{CPt} modes below 5 THz are highly coupled to the DSD. The vibrational component shows a prominent feature between 13 and 15 THz, in reasonable agreement with the experimental range of 13-14 THz for the C-Pt...
FIG. 8. Average projected density of states for the vibrational and dynamic structural disorder components of the $R_{CO}$ (top), $R_{CPt}$ (middle) and $P\tilde{t}CO (\alpha_{OCPt}, bottom)$ trajectories in Pt$_{10}$Sn$_{10}$ on $\gamma$-Al$_2$O$_3$ at 598 K. The experimental CO stretch frequency for on-top adsorption sites ranges from 61.5 to 63 THz, while for on-bridge sites it ranges from 54 to 55 THz. For the C-Pt stretch, the frequency ranges from 13 to 14 THz.

stretch mode. In addition, the $R_{CPt}$ dynamics show a broad feature between 10 and 13 THz which results from strong coupling to the $P\tilde{t}CO$ bending, as seen in Fig. 8 (bottom). These results point to the importance of nanoparticle fluctuations on the pre-dissociation regime where the reacting molecule both explores a variety of surface sites, and the physical properties of the sites themselves vary dynamically.

B. DSD in reaction barriers

As discussed in Sec. V, the dynamic disorder creates an effective activation barrier $\epsilon'_b \leq \epsilon_b$ due to barrier fluctuations. To study these fluctuations, we performed nudged elastic band (NEB) calculations of the dissociation of O$_2$ on Pt$_{10}$Sn$_{10}$ supported on $\gamma$-Al$_2$O$_3$. Fig. 9 shows results for three sample reaction paths, generated for nanoparticle conformations with different DSD, sampled from DFT/MD trajectories. These paths represent rather different behaviors, including exothermic and endothermic thermodynamics, and the presence of a high energy intermediate in path 2. From these results we can roughly estimate the mean barrier ($\epsilon_b \approx 0.8$ eV) and barrier fluctuations ($\sigma_{\epsilon_b} \approx 0.5$ eV). In addition, we can estimate the nanoparticle distortions induced during the dissociation process by analyzing the atomic displacements along the reaction path. For the paths shown in Fig. 9 the metal atoms directly bound to the O$_2$ molecule experience displacements of the order of 0.2 Å along the reaction path. Such nanoparticle distortions are of similar magnitude to those observed due to DSD (0.2-0.4 Å). The remainder of the nanoparticle also participates in the reaction, but with smaller displacements of O(0.1 Å).

FIG. 9. Typical NEB reaction paths for the dissociation of O$_2$ on fully relaxed Pt$_{10}$Sn$_{10}$ supported on $\gamma$-Al$_2$O$_3$. Paths energies have been shifted to match at the reactant state. The reaction path coordinate corresponds to the integrated displacement of all atoms in the system.

The effects of DSD on the reaction barriers are twofold: First, direct effects change the chemical nature of the reactants, transition states and products. These direct effects are usually visible as large energy changes, such as the shift from endothermic to exothermic behavior in paths 3 and 2, respectively, and are driven by major rearrangements of the structure of the nanoparticle and its
interaction with the adsorbate. Second, smaller fluctuations in structure that do not change the chemical nature of the different states yet still induce changes in the activation barrier. To quantify these indirect effects we have also computed reaction barriers where all atoms, except those in the dissociating O2 molecule, are fixed at the transition state structure of the paths in Fig. 10. These rigid nanoparticle paths are shown in Fig. 11. Overall, these paths are smoother than the fully relaxed ones. For instance, the nanoparticle fluctuations induce a variety of minima and shoulders in the reaction path. As expected, the reaction barriers are higher for the fully relaxed paths. The difference is only 0.1-0.2 eV; but the effect on the exponential character of reaction rates is nevertheless substantial. This result demonstrates our premise that DSD in nano-structures can significantly affect reaction rates.

VII. CONCLUSIONS

We have investigated the effects of dynamic structural disorder on the properties of supported metal nanoparticles, from both their morphological and reactivity perspectives. Our results suggest that a real-time approach that accounts for their fluctuating bonding and electronic structure may provide a useful approach to better understand of their catalytic activity. In particular, we have found that the dynamic structural disorder (DSD) in nanoclusters leads to a larger statistical ensemble of configurations than on solid surfaces. The shake, rattle and roll (SRR) concept makes it possible to simulate the statistical ensemble of possible reaction sites efficiently, compared to the effort needed for enumerating structures and Boltzmann factors. This can reveal both the surface structure and dynamics, which can be more important than the global average morphology. Since experimental probes measure global averages, it is important in the analysis to differentiate between surface and internal structure. The local electronic structure of the binding sites is highly heterogeneous. For instance, the oxidation state of a Pt atom varies significantly depending on its local environment. Thus, the DSD in these systems effectively induces additional active sites. Our results highlight the importance of large fluctuations driven by the stochastic motion of the center of mass of the nanoparticles and their transient bonding to the support. These fluctuations affect the internal energy distribution as well as the structure of the nanoparticles, thus having a measurable effect on both the properties observed by experimental probes like EXAFS, as well as the observed reaction rates.

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