

Hydrogen induced melting of Palladium clusters

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Abstract. To investigate the effect of adsorbates on structural transitions in small palladium aggregates, we have performed molecular dynamics simulations of cluster “melting” in presence of atomic hydrogen. Intriguing questions are how the exposure to hydrogen modifies the metal-metal interaction, and whether hydrogen could lower the onset of melting. Various structural and calorimetric methods were used to capture signatures of melting. We present results for the bare icosahedral Pd₅₅ cluster and also Pd₅₅ exposed to different amounts of hydrogen. Our results indicate that the melting transition is significantly lowered as hydrogen adsorbs on the cluster, and that the decrease in melting temperature depends sensitively on the hydrogen loading.

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During the last few years, considerable theoretical effort has been invested to understand thermodynamical properties of finite systems, such as atomic clusters [1, 2]. This research area is truly challenging because of the complexity of the total energy surface of finite aggregates, and the existence of many energetically near-degenerate isomers. It is well understood how the absence of the long-range order, and a large surface-to-volume ratio in a qualitative way modify the thermodynamic properties of small particles [3]. Early experiments have shown that the melting temperature decreases with decreasing particle size [4]. Later observations have reported details in the thermodynamical properties, such as structural instabilities [5], and surface pre-melting [6]. The cluster analog to the solid-liquid phase transition in bulk samples has recently also been investigated by means of molecular dynamics simulations [7, 8]. Cluster size effects have been well established, same as facet specific phenomena of surface pre-melting, suggesting that icosahedral clusters with closed-packed (111) facets should not show any surface pre-melting, whereas this should be the case for Wulff polyhedral clusters with more open (100) facets [8].

In a very recent study [9], we have investigated thermodynamical properties of small icosahedral palladium aggregates. We have observed large size variations in the onset temperature of melting, as well as the absence of surface

pre-melting and an almost size independent heat of transformation per atoms for Pd₁₃, Pd₅₅ and Pd₁₄₇. In connection with reactions involving clusters, an especially interesting question is the influence of adsorbates and a carrier gas atmosphere on the thermodynamical properties of metal clusters. In this work we study this issue by molecular dynamics simulations of palladium clusters melting in presence of hydrogen. We will present results for the bare icosahedral Pd₅₅ cluster, as well as Pd₅₅ exposed to various amounts of hydrogen.

To study the temperature dependent dynamics of palladium clusters, we need an accurate description of interatomic interactions. The Hamiltonian describing the system should be capable of correctly selecting between different minima in the potential energy surface, and also account for the re-hybridization due to adsorbed hydrogen. We have used the Many-Body-Alloy (MBA) Hamiltonian [10], which is based on the second-moment approximation for the electronic density of states, and a pairwise repulsive Born-Mayer interaction. The parametrized binding energy for each atom is given by

$$E_b(i) = -\left\{ \sum_{i \neq j} \xi_0^2 e^{-2q(\frac{r_{ij}}{r_0} - 1)} \right\}^{\frac{1}{2}} + \sum_{i \neq j} \epsilon_0 e^{-p(\frac{r_{ij}}{r_0} - 1)}. \quad (1)$$

The first part represents the many-body binding term, and the second the pairwise repulsion. The parameters, ξ_0 , ϵ_0 , p , q and r_0 , have been determined using *ab initio* local density functional results for bulk Pd and PdH [11], and depend on the interacting atoms. The scheme has been successfully used in various problems involving the hydrogen/palladium system [11, 12]. We also notice that the MBA scheme compares favorably with SCF-CI calculations [13] for Pd₁₃. The MBA value 2.50 Å for the radius of the Pd₁₃ icosahedron compares well with the SCF-CI value of 2.60 Å, and the energy difference between the icosahedral and the octahedral isomers is 0.12 eV in both techniques. Furthermore, the simple analytic expressions for the forces in the MBA scheme make the method suitable for molecular dynamics simulations involving long simulation times.

The dynamics of the system has been described by numerically solving the Euler-Lagrange equations of motion. To perform the simulations in a canonical rather than a mi-

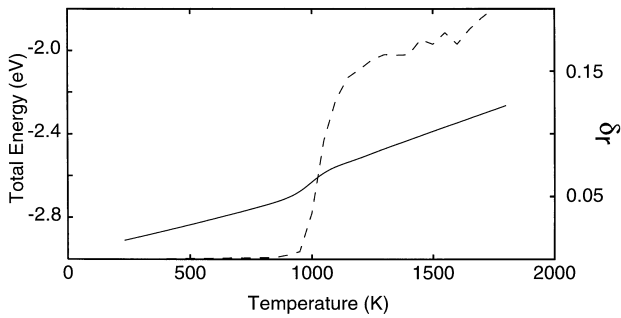


Fig. 1. Total energy per atom as a function of temperature (solid line) and the radial diffusion index (dashed line) for the hydrogen-free Pd₅₅ cluster

crocanonical ensemble, a Nosé-Hoover [14] thermostat has been used. This thermostat models the coupling to an external heat bath, by including a virtual degree of freedom in the equations of motion. In our previous work [9], we have shown how the Ar carrier gas thermostat gives results in close resemblance with those obtained using the Nosé-Hoover scheme. The atomic trajectories have been determined using a fourth-order Runge-Kutta integration scheme [15]. Since we follow the time evolution of a system which contains very light hydrogen beyond the heavy Pd atoms, very short time steps are needed for the alloy to describe correctly the dynamics and to guarantee energy conservation over long simulation times. We have used $\Delta t = 0.4$ fs for the Pd₅₅H_x system, and $\Delta t = 2.0$ fs for the bare Pd₅₅ cluster. The heat bath temperature was increased in steps of 50 K from 200 K to 1600 K. After each temperature increase, the system was allowed to evolve for 30 ps, and data were collected after a relaxation period of 5 ps. Since ergodicity is generally not guaranteed in small systems, we performed – beyond time averaging – an ensemble average over ten different trajectories for the Pd₅₅ and Pd₅₅H_x clusters. The effect of hydrogen loading was investigated by studying the thermodynamical evolution of Pd₅₅H_x with $x = 2, 6$ and 10 hydrogen atoms.

To investigate the signatures of melting, we show the temperature dependence of the total energy *per atom* for Pd₅₅ in Fig. 1 (solid line). At low and at high temperatures, the total energy increases almost linearly with the temperature. These two regimes are separated by a smooth transition region, which describes the melting transition. We notice that in each individual trajectory, the transition occurs from one temperature step to another, and that the smooth transition in Fig. 1 is an effect of the ensemble averaging. The slopes of the two linear regions are different. As we will discuss below, the slope at low temperatures corresponds to the classical value of $3k_B$, while at temperatures above the melting transition, the slope is steeper. This is interpreted as a series of transitions, gradually leading to a less coordinated cluster.

To study also the signatures of melting in a structural fashion, we have defined a radial diffusion index δ_r as

$$\delta_r = \left\langle \frac{\sum_i [d_i(t) - d_i(0)]^2}{\sum_i d_i(0)^2} \right\rangle, \quad (2)$$

where $d_i(t)$ is the distance of atom i from the center of mass of the cluster at time t . This definition of δ_r targets the onset of radial diffusion in the cluster upon melting, while ignoring the translation and rotation of the rigid body. The

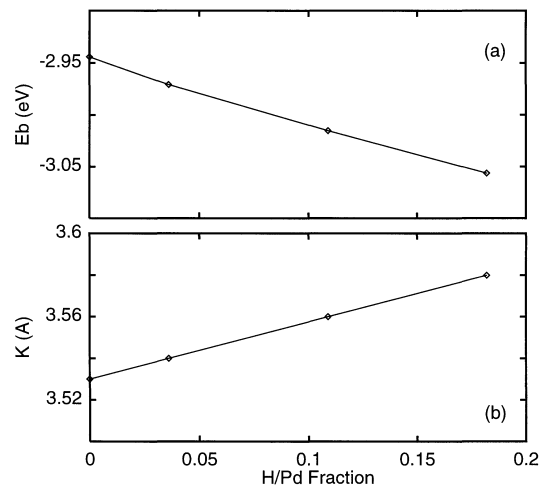


Fig. 2. The effect of hydrogen on cluster stability **a**, and volume **b**. The presented values are ensemble averages at 200 K

result for Pd₅₅ is shown in Fig. 1 (dashed line). We see how the onset of radial diffusion matches the caloric signature of the melting transition. We find δ_r to level off at a value of ≈ 0.15 above the melting transition, which corresponds to a diffusion of about one atomic layer in the icosahedral palladium cluster.

Next we investigated the effect hydrogen exposure on the properties of Pd₅₅. We focussed on Pd₅₅H_x with $x = 2, 6$ and 10. Hydrogen is known to readily react with palladium, both at surfaces [16] and with clusters [17], and solves spontaneously upon contact with the metal. The observed dissociation of hydrogen molecules upon contact with Pd eliminates the need to address the molecular species. Therefore, we started each simulation by placing the hydrogen atoms on a sphere surrounding the Pd₅₅ cluster at a distance of 1.5 Å. During the first few pico seconds of the simulation, the hydrogen atoms adsorbed on the cluster, preferably occupying hollow and bridge sites. Several of the atoms thereafter diffused into the cluster and occupied sub-surface sites. In Fig. 2a and b we show data for the Pd₅₅H_x system at a temperature of 200 K. The binding energy, E_b *per atom* and the mean radius of gyration, K , are displayed as a function of hydrogen loading. The binding energy of palladium atoms increases as hydrogen is introduced to the system, indicating stabilization of the cluster due to hydrogen. The almost linear relationship between loading and binding energy is likely to be valid as long as the hydrogen concentration is low and interaction between hydrogen atoms negligible. Subsurface diffusion results in an expansion of the Pd₅₅ cluster, that is reflected in the increasing mean radius of gyration.

In Fig. 3 we monitor several caloric and structural quantities as potential signatures of the melting transition in Pd₅₅H_x. As mentioned above, melting of bulk systems is a first-order transition, characterized by a stepwise increase in the free energy and a singularity in the specific heat. In small systems, the transition is smeared out over a finite temperature interval, resulting in a broad peak in the specific heat. In Fig. 3a we show the specific heat c , that we calculate as the derivative of the total energy *per Pd atom* with respect to temperature. At low temperatures, the specific heat is close to the classical value of $3k_B$. The effect of hydrogen load-

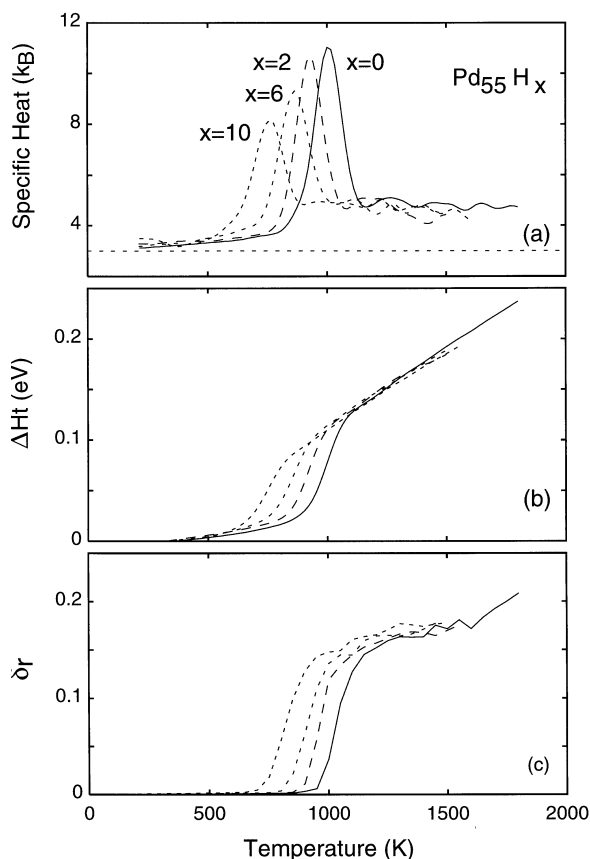


Fig. 3. Caloric and structural changes in Pd₅₅H_x clusters, for different hydrogen loading x

ing is a shift of the melting transition to lower temperatures. At temperatures below the melting point, the specific heat is somewhat larger than $3k_B$, reflecting the increase in the number of degrees of freedom upon hydrogen loading. We further investigate the caloric signatures of the melting transition, by computing the latent heat of transition per atom, defined by $\Delta H_t = \int_{T_0}^T [dE/dT - 3k_B]dT$. The ΔH_t curve shows clearly that the heat of transition decreases as the concentration of hydrogen is increased, hence driving the transition to lower temperatures. We find the intriguing results that even though the system is stabilized in presence of hydrogen, the melting transition is lowered. This illustrates that the melting temperature is determined not by the absolute binding energy, but rather the shear modulus. Hydrogen is known to soften the metal-metal interaction, which at surfaces results in softening of surface phonon modes upon hydrogen exposure [11]. Structural changes upon melting are investigated in hydrogen loaded clusters by comparing δ_r with the result for the bare Pd₅₅. Also in this signature we see the clear reduction of the melting temperature due to hydrogen, in agreement with the caloric observables.

In conclusion, we have performed molecular dynamics simulations of the melting transition in finite systems. In particular, we have investigated the effect of hydrogen on the melting transition in palladium clusters, by studying Pd₅₅H_x for various values of x . We found a substantial lowering of the melting transition upon hydrogen loading, and a clear dependence of the melting temperature on the hydrogen con-

centration. Even for a single dissociated H₂ molecule, we obtained a lowering of the melting transition in comparison with the bare cluster. From this we concluded that even though hydrogen increases the cohesion of the palladium clusters, it also softens of the metal-metal bonds, resulting in lower melting temperatures. Hydrogen induced melting, that we have investigated, is most likely related to a structural instability which has been previously observed in small palladium clusters [17].

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