Does hydrogen pre-melt palladium clusters?

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Abstract

We use molecular dynamics simulations to study the influence of an ambient atmosphere on the melting process in the icosahedral palladium clusters Pd_{13}, Pd_{55} and Pd_{147}. Novel methods to capture the character of melting in finite systems are presented. The signature of melting in clusters heated by inert carrier gas collisions closely resembles that in systems heated in a Nosé-Hoover thermostat. Exposure to hydrogen instead of an inert carrier gas, however, significantly lowers the melting temperature.

Recent studies of finite-sized systems have addressed the intriguing question of how the physical properties of atomic clusters evolve with their increasing size [1]. Equally interesting is to follow the signature and changing nature of bulk phenomena, such as phase transitions, as the size of the system decreases. Melting is a well-defined first-order phase transition in the bulk, which involves the loss of long-range order, a stepwise increase in the free energy and a singularity in the specific heat. The large portion of surface atoms in small systems is expected to change the nature of the transition, and the absence of long-range order to smear out the transition region over a finite temperature interval [2]. Early experiments on small gold aggregates reported a drastic decrease in the melting temperature with decreasing particle size [3]. Later experiments on metal particles have also observed structural instabilities [4] and surface pre-melting [5]. Recently, several authors investigated the atomistic origin and nature of this "phase transition" in homonuclear clusters [6-10].

In this Letter, we focus our interest on the effect of an ambient atmosphere on structural transitions in small Pd aggregates. We will study how the general thermodynamical behavior and melting transition are affected by the presence of hydrogen which modifies the metal-metal interaction. The key question is whether the presence of adsorbates could drive a "chemical" melting transition. To address these issues, we have to revisit two basic topics in finite systems, namely the temperature control and the characterization of melting in both a thermodynamical and structural fashion.

The systems we investigate are the icosahedral clusters Pd_{13}, Pd_{55} and Pd_{147}. We describe the rehybridization of Pd orbitals in clusters exposed to hydrogen using the many-body alloy (MBA) potential [11,12]. This potential consists of a many-body binding term, based on the second-moment of the electronic density of states, and pairwise repulsive Born-Mayer interactions. Our parameterization, based on ab initio local density functional results for bulk Pd and PdH [12], has proven successful in describing hydrogen embrittlement of palladium [13] and hydrogen-induced softening of Pd surface phonon modes [12]. Also for bare Pd aggregates, the MBA results compare favorably

with self-consistent field – configurational interaction (SCF-CI) calculations [14] for geometry optimized Pd_{13} clusters. The MBA value 2.50 Å for the radius of the Pd_{13} icosahedron compares well with the SCF-CI value of 2.60 Å, and the energy difference between the icosahedral and octahedral isomers is 0.12 eV in both techniques. The level of accuracy of the potential, combined with simple analytic expressions for the interatomic forces, makes the MBA scheme ideally suitable for molecular dynamics simulations.

We describe the dynamics of the system by solving numerically the Euler–Lagrange equations of motion. To describe a canonical system with constant temperature rather than a microcanonical ensemble with fixed energy, the equations of motion are modified according to the Nosé–Hoover scheme [15] which describes the coupling to an external heat bath. Atomic trajectories are determined using a fourth-order Runge–Kutta integration scheme [16]. Our focus on the changed dynamics of Pd clusters in the presence of hydrogen justifies a classical description also of the light H atoms. Due to the small mass of the H atoms we use a short time step $\Delta t = 0.4$ fs for simulations involving H, while $\Delta t = 2.0$ fs is used as the time step in bare Pd clusters. These choices guarantee energy conservation over long simulation times. We consider the time evolution of each system during 1.1 ns real time. To investigate thermally induced transitions, we increased the heat bath temperature from 200 to 2000 K in small steps of 50 K, each followed by 30 ps equilibration time. The collection of statistical data started 5 ps after each increase of the heat bath temperature. Since ergodicity is not guaranteed for small systems, we also performed an ensemble average over forty different trajectories for Pd_{13}, ten trajectories for Pd_{55} and five trajectories for Pd_{147}. The initial configurations at $T = 100$ K have been prepared with zero rotational and translational motion of the cluster.

The basic thermodynamic signature of melting and other first-order phase transitions is a discontinuous change in the total energy $E(T)$ as a function of temperature. Our results for Pd_{13}, Pd_{55} and Pd_{147} clusters are presented in Fig. 1a. We find the temperature dependence of the total energy characterized by two linear regions, separated by a smooth transition region which we attribute to melting. Our results also show that this transition gradually smears out with decreasing size of the system. We further noted that the
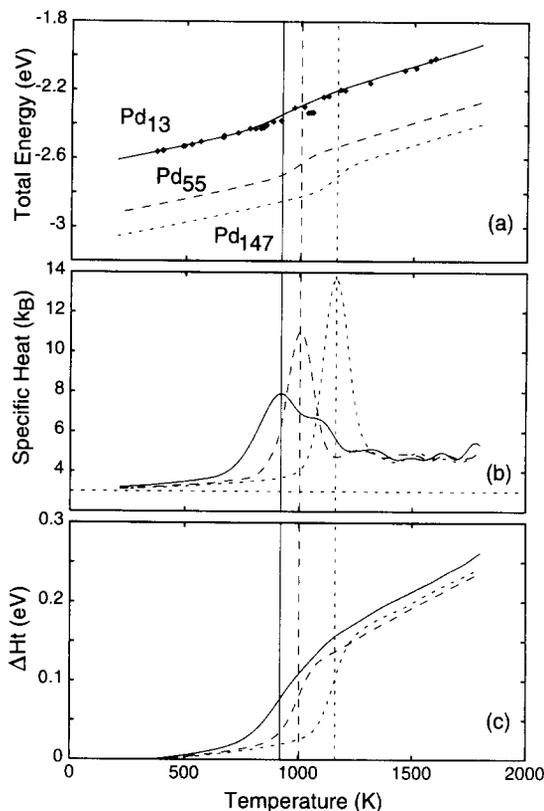

Fig. 1. (a) Temperature dependence of the total energy per atom for the Pd_{13} (solid line), Pd_{55} (dashed line) and Pd_{147} cluster (dotted line). The cluster temperature is controlled using a Nosé–Hoover thermostat (continuous lines) or alternatively by collisions with Ar atoms (◇). (b) Corresponding results for the specific heat per atom. (c) The latent heat of transition, reflecting caloric changes in the system as a function of temperature. The vertical lines indicating the melting temperatures of Pd_{13}, Pd_{55} and Pd_{147} are for visual guidance.

transition of the ensemble spans a larger temperature range than that of a single trajectory, where melting appears to occur from one temperature step of the heat bath to the next. The small clusters were found to melt within a temperature range from 800 to 1300 K, which lies substantially below the observed melting temperature of bulk Pd, $T_{M,expt} = 1825$ K, or the calculated value $T_{M,MBA} = 2000$ K [13]. As known from previous simulations [6,7] and experiments [3], the onset temperature for melting decreases with decreasing cluster size.

In order to further investigate the caloric character of melting, we show in Fig. 1b the specific heat c, computed as the derivative of the total energy $E(T)$

per atom with respect to temperature. The crystalline and liquid-like state of the clusters are seen to be separated by a large peak. At low temperatures, the specific heat is close to the classical value of $3k_B$. At temperatures above the melting transition, however, the specific heat lies above this classical value. We associate the higher value of c with a series of structural transformations which gradually leads to a less coordinated structure. The transition region was also investigated by calculating the latent heat of transition per atom, defined by $\Delta H_t = \int_{T_0}^{T}[dE/dT - 3k_B]\, dT$, which we show in Fig. 1c. Surprisingly, we do not find large differences in ΔH_t between the different systems investigated. Our results rather suggest a cluster size independent change in the atomic environment upon melting and absence of strong surface effects that would depend on the cluster size. Also the results for the latent heat indicate that the transition becomes sharper with increasing cluster size, and approaches a step function in the bulk limit.

Temperature control in free clusters poses considerable problems both to the experiment and the simulation, since efficient thermal contact between a cluster and an external heat bath necessarily perturbs the dynamics of the system. In the experiment, such thermal contact is established via collisions with a noble carrier gas. The simplest way to control the temperature in simulations is by straight velocity scaling, with uncontrollable effects on the cluster dynamics. The more physical Nosé–Hoover thermostat controls the cluster temperature by transferring heat into a virtual degree of freedom. Since even this scheme can modify the dynamics of small clusters significantly, we propose an alternative computational approach to check the Nosé–Hoover dynamics in our simulations of the Pd_{13} cluster.

Our computational approach mimics the experiment by heating the cluster in collisions with an inert gas of constant temperature. We consider Ar carrier gas, and describe the Ar–Ar and Ar–Pd interaction by a Lennard-Jones potential $V(Ar-Ar) = V(Ar-Pd) = \epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, with $\epsilon = 0.0416$ eV and $\sigma = 3.4$ Å [17]. To minimize the influence on the cluster dynamics, the temperature of the carrier gas is maintained by rescaling the velocity of Ar atoms *outside the cluster exclusion zone*, i.e. in the region where the closest Ar–Pd distance exceeds the cut-off value

$r_c = 6$ Å for the Ar–Pd interaction. The remaining interacting system is treated as a microcanonical ensemble. We use twenty Ar atoms and a time step of $\Delta t = 0.2$ fs to thermalize the cluster in collisions, and apply periodic boundary conditions with cubic unit cells of side length $a = 20$ Å. Thermal equilibration of the cluster is achieved after a sufficient number of collisions, which for a Pd_{13} cluster translates into a residence time of $\gtrsim 0.2$ ns in the Ar atmosphere. The comparison between the Nosé–Hoover and the rare gas thermostat, shown in Fig. 1a, proves the adequacy of the ensemble-averaged Nosé–Hoover dynamics for the temperature control of this small system.

To learn more about the element-specific effect of the carrier gas on structural transformations in clusters, we also performed simulations of the cluster melting process in the presence of hydrogen [1]. Molecular hydrogen is known to react readily with Pd clusters [18], presumably by a non-activated dissociation. Furthermore, saturation experiments indicate that small Pd clusters can absorb large amounts of hydrogen, resulting in a saturation concentration $x > 1$ [18] which exceeds the bulk value $x \approx 0.7$ [19]. Upon hydrogen absorption in metallic Pd, the Pd 4d states are filled and the Pd 5s states are charge depleted [20]. The cohesive energy and bulk modulus of the metal increase, whereas the shear modulus decreases in the presence of hydrogen. Since hydrogen dissociates and solves spontaneously upon contact with Pd clusters, we can concentrate on the atomic species and neglect the H_2 dissociation step when studying the influence of hydrogen on the melting process in Pd_{55}. The initial geometry consists of an equilibrated Pd_{55} cluster surrounded by ten hydrogen atoms placed randomly on a sphere with a 1.5 Å larger radius than the cluster radius. During the first few picoseconds, all hydrogen atoms adsorb on the cluster, preferably in hollow and bridge sites, from where they can diffuse into the subsurface region. Thermal evolution of the interacting $Pd_{55}H_{10}$ system is then described using Nosé–Hoover molecular dynamics.

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[1] No experimental data are available on the effect of hydrogen on the melting of bulk Pd, since hydrogen evaporates from the bulk at a temperature well below the melting point [19]. This is to be expected, since the binding of Pd atoms in the bulk is much stronger than that of H atoms. In contrast to this, little H evaporation prior to melting is expected in Pd_nH_m clusters, where the binding energies of Pd and H atoms are comparable.

To obtain a quantitative understanding of "chemical melting" and the differences between the melting process in bare and hydrogen-loaded clusters, we monitored both thermodynamic and structural quantities during this transition. The basic thermodynamic quantity is the specific heat *per Pd atom* which we display in Fig. 2a for Pd_{55} and $Pd_{55}H_{10}$. The initial low-temperature specific heat in $Pd_{55}H_{10}$ is somewhat larger than the classical value $3k_B$, reflecting the increased number of degrees of freedom in hydrogen loaded clusters. In spite of strengthening the binding of Pd atoms on average by 0.1 eV [2], hydrogen lowered the melting temperature of Pd_{55} by about 200 K, as seen in the corresponding shift of the dominant peak in the specific heat of the hydrogen-loaded cluster.

To monitor the atomic diffusion in a cluster during melting, we defined a dimensionless radial-diffusion index δ_r by the expectation value

$$\delta_r = \left\langle \sum_i [d_i(t) - d_i(0)]^2 / \sum_i d_i(0)^2 \right\rangle, \quad (1)$$

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 dependence of δ_r on temperature in Pd_{55} and $Pd_{55}H_{10}$ is shown in Fig. 2b. A comparison with the specific heat data in Fig. 2a proves δ_r to be a sensitive structural indicator of melting. Following the onset of melting, δ_r first rapidly reaches a value close to 0.15, corresponding to a radial diffusion of about one atomic layer, and then increases at a reduced rate. We note that, except for a rigid temperature shift, the temperature dependence of δ_r is similar in the bare and hydrogen loaded clusters, suggesting that the presence of hydrogen does not change qualitatively the diffusion of Pd atoms during the melting process.

We also monitor the atomic motion of hydrogen by defining an analogous quantity $\delta_r(H)$ and using the individual surface adsorption site for $d_i(0)$ in Eq. (1). The relatively large value $\delta_r(H) \approx 0.15$ below the melting point indicates the importance of subsurface diffusion in this temperature range. Lowering of the $\delta_r(H)$ value above the melting point can be traced
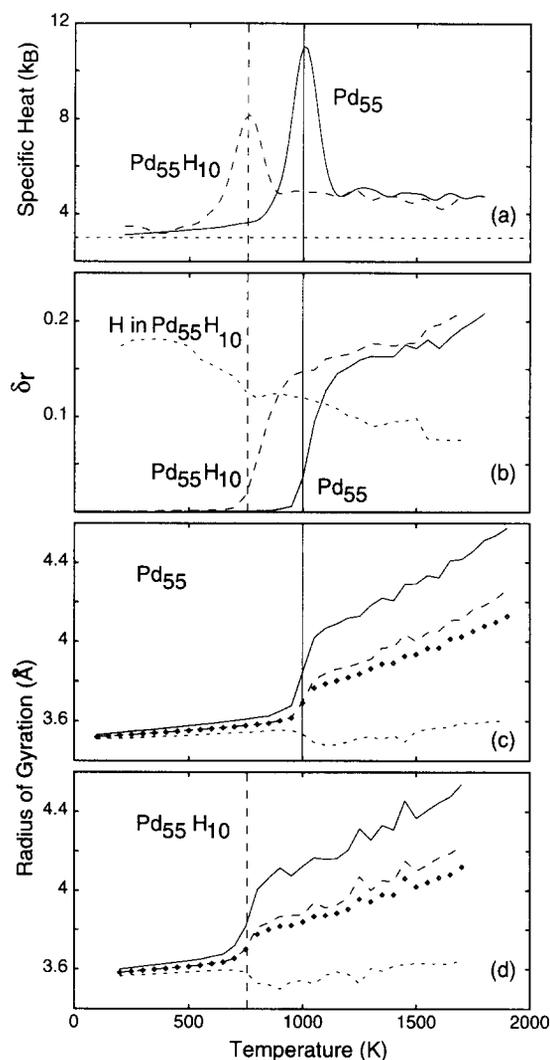
Fig. 2. Thermodynamic and structural signatures of the "melting transition" in Pd_{55} and $Pd_{55}H_{10}$ clusters. (a) Reproducible peaks in the specific heat (per atom) indicate energy changes during melting. (b) Nonzero values of the radial diffusion index δ_r signal the onset of diffusion in the cluster at the melting point. The changing shape of the cluster with increasing temperature is reflected in the three radii of gyration, which are given by the solid, dashed and dotted lines for Pd_{55} (c) and $Pd_{55}H_{10}$ (d). The geometrically averaged radius of gyration is shown by diamonds. The vertical lines indicating the melting temperatures of Pd_{55} and $Pd_{55}H_{10}$ are for visual guidance.

back to the expansion and changing shape of the cluster, causing hydrogen atoms to occupy sites which are further away from the center and hence closer to the original surface adsorption sites.

We study the changing geometrical shape of the cluster during melting by monitoring the three radii of gyration, $K_i = (I_i/M)^{1/2}$, where I_i are the principal moments of inertia and M is the total cluster mass. The temperature dependence of K_i in Pd_{55} and $Pd_{55}H_{10}$ is shown in Fig. 2c and Fig. 2d, respectively. At low temperatures, the three radii of gyration of the initially spherical clusters are equal. The somewhat larger K_i value found in $Pd_{55}H_{10}$ indicates expansion due to subsurface hydrogen [19]. At the melting point, we observe a strong oblate deformation of both clusters, with two long and one short axis. The cluster expansion during melting is reflected in a stepwise increase of the averaged radius of gyration $(K_1 K_2 K_3)^{1/3}$ in Figs. 2c and 2d.

In conclusion, we have performed molecular dynamics simulations of the melting transition in finite systems. We evaluated several schemes for temperature control and identified thermodynamic and structural quantities which are suitable for monitoring specific signatures of melting. We found that melting in clusters heated by Ar carrier gas collisions closely resembles that in systems heated in a Nosé–Hoover thermostat, justifying the use of both schemes for simulations of finite systems. For the three icosahedral Pd clusters investigated, we found the melting temperature to decrease with decreasing cluster size. We found a substantial lowering of the melting temperature in Pd clusters upon exposure to hydrogen, but no qualitative changes in the atomistic diffusion processes. This hydrogen-induced "chemical melting" is most likely related to a structural instability which has been previously observed in this system [18]. It is worth noting that the presence of a hydrogen atmosphere can not only reduce the melting temperature, but also induce the melting of Pd clusters due to the heat released during the dissociative adsorption.

Acknowledgements

References

[1] H. Haberland, ed., Clusters of atoms and molecules (1) (Springer, Berlin, 1994).

[2] T.L. Hill, Thermodynamics of small systems (Benjamin, New York, 1964).

[3] Ph. Buffat and J.-P. Borel, Phys. Rev. A 13 (1976) 2287; J.-P. Borel, Surf. Sci. 106 (1981) 1.

[4] S. Iijima and T. Ichihashi, Phys. Rev. Lett. 56 (1986) 616.

[5] Y. Lerah, G. Deutscher, P. Cheyssac and R. Kofman, Europhys. Lett. 12 (1990) 709.

[6] R.S. Berry, J. Jellinek and G. Natanson, Phys. Rev. B 30 (1984) 919.

[7] F. Ercolessi, W. Andreoni and E. Tosatti, Phys. Rev. Lett. 66 (1991) 911.

[8] N. Ju and A. Bulgac, Phys. Rev. B 48 (1994) 2721; A. Bulgac and D. Kusnezov, Phys. Rev. Lett. 68 (1992) 1335.

[9] S. Valkealahti and M. Manninen, Phys. Rev. B 45 (1992) 9459; S. Valkealahti and M. Manninen, Z. Phys. D 26 (1993) 255.

[10] S.G. Kim and D. Tománek, Phys. Rev. Lett. 72 (1994) 2418.

[11] D. Tománek, S. Mukherjee and K.H. Bennemann, Phys. Rev. B 28 (1983) 665 [Erratum: B 29 (1984) 1076].

[12] W. Zhong, Y.S. Li and D. Tománek, Phys. Rev. B 44 (1991) 13053.

[13] W. Zhong, Y. Cai and D. Tománek, Phys. Rev. B 46 (1992) 8099; Nature 362 (1993) 435.

[14] G.L. Estiú and M.C. Zerner, J. Phys. Chem. 98 (1994) 4793.

[15] S. Nosé, J. Chem. Phys. 81 (1984) 511; W.G. Hoover, Phys. Rev. A 31 (1985) 1695.

[16] W.H. Press, S.A. Teukolsky, W.T. Vetterling and B.P. Flannery, Numerical recipes (Cambridge Univ. Press, Cambridge, 1992).

[17] N.W. Ashcroft and N.D. Mermin, Solid state physics (Saunders College, Philadelphia, PA, 1976).

[18] P. Fayet, A. Kaldor and D.M. Cox, J. Chem. Phys. 92 (1990) 254.

[19] G. Alefeld and J. Völkl, eds., Hydrogen in metals, Topics in Applied Physics 28 (Springer, Berlin, 1978).

[20] D. Tománek, Z. Sun and S.G. Louie, Phys. Rev. B 43 (1991) 4699.