Physical and chemical properties of gold in the nanoscale have attracted significant cross-disciplinary interest during recent years, motivated by some key observations of remarkable chemical and catalytic activity, electronic transport, and optical properties. A large body of various structural investigations have led to the conclusion that gold in general prefers lower dimensional structures than other noble or late-transition metals due to strong relativistic bonding effects [1,2]. This is manifested by its tendency to form relatively large planar [2–4] or cage-like [5] clusters. Another example is the formation of stable monatomic wires up to 7–8 atoms as seen in mechanical break junctions, [6] in separating tip-surface contacts, [7], or as a ‘‘nanobridge’’ in a freestanding thin gold film after intense electron irradiation [7,8].

Atomic clusters offer an ideal ‘‘laboratory’’ to study the structure of matter as a function of size. The small scale introduces also phenomena that are not present in the bulk matter. For example, it is well known that first order phase transitions in small systems are broadened due to finite size effects. There, instead of the concurrent coexistence of phases in bulk matter, a dynamical coexistence is observable over a finite, system-size-dependent range of a thermodynamical parameter, such as the temperature [9]. A classic example is that of the liquid-solid phase coexistence in atomic clusters [10–12].

Until now considerable effort has been put forth to resolve preferred (static) atomic geometries of anionic gold clusters (Au$_N^-$, N ≤ 20) in the gas phase. Mobility measurements have previously detected a crossover between 2D and 3D structures at N = 12 [3]. On the other hand, density-functional theory (DFT) calculations employing the generalized gradient approximation (GGA) predicted planar ground states for N = 13 and 14 [3,4] leading to the suggestion that GGA-DFT overestimates the stability of planar anionic clusters. This is a puzzling and unsatisfactory situation, especially given that GGA-DFT correctly describes the energetic sequence of smaller gold cluster isomers, as has been confirmed by photoelectron spectroscopy, e.g., for N = 4, 8, 10, and 12 [4].

Motivated on one hand by this discrepancy between theory and experiment, and on the other hand by the fundamental question of the thermodynamic stability of low-dimensional nanostructures, we have investigated the dynamics of the liquid phase and the solidification transition of gold cluster anions from Au$_{13}^-$ to Au$_{14}^-$ using a recently established charge self-consistent density-functional based tight-binding (DFTB) model for gold [13]. Because our DFTB model is more than 3 orders of magnitude faster to solve than the full Kohn-Sham DFT model, while still retaining the essential electronic-structure effects, we were able to calculate thermodynamical properties and simulate the cluster cooling process within an experimentally realistic time scale. These simulations resulted in two unexpected and novel phenomena that we now discuss.

**Dynamical coexistence of two liquid phases for Au$_{13}^-$...Au$_{14}^-$.**—We first investigated the dynamics of hot liquid clusters via several microcanonical and canonical DFTB molecular dynamics (MD) trajectories at elevated temperatures up to 1100 K. Figure 1(a) shows the evolution of the planarity parameter of Au$_{13}^-$ (defined as the minimum thickness of the cluster) during a representative microcanonical MD trajectory with an average temperature of about 750 K. Surprisingly, the cluster remained for comparatively long periods of time in the planar or 3D configurational space [see insets of Fig. 1(a) for representative snapshots] and these periods were abruptly terminated by changes in the dimensionality, suggesting a dynamical coexistence of two heterodimensional phases. Interestingly, this coexistence could be observed for all clusters in the size range considered in this Letter and became even more pronounced with increasing cluster sizes; see Fig. 1(b) for the dimensionality parameter of Au$_{14}^-$ for T = 750 K and Fig. 1(c) for the evolution of the corresponding potential energies. The potential energy distribution has a bimodal character [see inset of Fig. 1(c)] which is directly connected to the abrupt changes in the dimensionality of the cluster [Fig. 1(c)]. A careful analysis of the trajectories revealed that both the 2D and 3D phases

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**PACS numbers:** 64.70.Ja, 36.40.Ei, 36.40.Mr, 61.46.Bc

**DOI:** 10.1103/PhysRevLett.98.015701

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are liquid, and since the bimodality is characteristic of dynamical coexistence [14], we conclude that the clusters display a novel liquid-liquid coexistence (LLC). To the best of our knowledge, this is the first report of a free-standing two-dimensional liquid phase. This is not necessarily a typical behavior of two-dimensional systems; corresponding simulations with small graphene clusters, for example, resulted in branched carbyne molecules instead of the establishment of a stable two-dimensional carbon liquid.

The liquid nature of the phases was confirmed using various, well-established measures [15]. First, inspecting the case of Au_{14} more closely, Fig. 1(d) shows that the mean bond length fluctuation $\delta$ in the coexistence region remains above 20%, a value identified with a liquid phase for even smaller clusters [16]. Second, the diffusion constant $1-5 \times 10^{-5} \, \text{cm}^2/\text{s}$ in the coexistence region is in a typical range of values for liquid, even though we find that the it is typically 20%–30% lower in the 2D phase [17]. This accounts for the fact that since the cluster remains strictly planar without any jumps out of the plane, the motion of the atoms in two dimensions becomes more collective and correlated than in three dimensions, which diminishes bond length fluctuations. Third, the heat capacities of both planar and three-dimensional clusters increased from the almost exact Dulong-Petit value for low temperatures by more than 60% upon heating to $T = 750$ K—an increase characteristic for a hot liquid phase. Finally, a visual inspection of trajectories of the atoms over 300 ps periods at high- and low-potential energy regimes of the simulation confirms the existence of liquidlike 3D “drops” and 2D “disks” [insets of Fig. 1(d)].

The characteristics of the DFTB potential energy landscape were investigated by calculating transition interconversion barriers for different stable isomers by the nudged elastic band method [18]. Figure 2 shows a portion of the DFTB potential energy landscape, exhibiting a few 2D and 3D local minima (marked by $m$). The barriers within 2D and 3D regions are relatively low, which enables the separate 2D and 3D liquid phases. On the other hand, the phases are separated by a much higher 2D/3D barrier, which is a necessary condition for LLC. Note that the 2D/3D transitions are found to be preceded by a strongly excited 2D bending mode, such as the configuration before the 2D/3D transition state (marked by $c$). The DFTB barrier structure was confirmed by making similar nudged elastic band calculations using GGA-DFT [19,20]. In order to have reasonable guesses for low transition pathways on the DFT Born-Oppenheimer surface, a 10 ps MD trajectory at 1250 K was simulated. Starting from the planar ground state, it was observed that also in GGA-DFT the planar structures are thermodynamically very stable. The heights of the chosen 2D/2D and 3D/3D barriers were signif-

FIG. 1 (color online). Dynamical coexistence of 2D and 3D liquid clusters. Time evolution of planarity parameter $D_{\text{rms}}$, for (a) Au_{11} and (b) Au_{14}. The insets in (a) are representative snapshots of the Au_{11} geometry in different phases. (c) Time evolution of the potential energy $E_{\text{pot}}$ for Au_{14}. Inset: the corresponding histogram of $E_{\text{pot}}$ short time averages (same energy scale as main panel). (d) rms bond length fluctuation $\delta$ for Au_{14}. Insets: 300 ps atomic trajectories at high- and low-$E_{\text{pot}}$ regimes. For both Au_{11} and Au_{14} data were taken from 3.5 ns microcanonical DFTB simulations corresponding to average temperatures of $T \sim 750$ K, where panels (b)–(d) correspond to the same simulation.

FIG. 2 (color online). Characteristic barriers of Au_{14}. A portion of the DFTB potential energy landscape at $T = 0$, showing a few 2D and 3D local minima (marked by $m$), appearing also at high-temperature DFTB molecular dynamics runs. The very low 2D/2D barrier ($m'/m''$) represents a partial rotation of the 2D ground state, where the inner square rotates inside the 10-atom ring.
FIG. 3 (color online). Cooling simulations. (a) Planarity parameter $D_{\text{rms}}$, versus cooling time (top axis, counted backwards) and total energy (bottom axis). Runs were started at $E = 3, 3.3, 3.5,$ and $3.8$ eV above the ground states of $N = 11, 12, 13,$ and $14$, respectively, corresponding roughly to $T = 1000$ K. (b) rms bond length fluctuation $\delta$ for the $N = 14$ run. In the dynamical 2D-liquid–3D-liquid coexistence region the fluctuation is well above the conventional criterium $\delta > 0.1$ for liquid clusters. The cluster enters the 3D-liquid–3D-liquid coexistence region near $E_{\text{tot}} = 1.1$ eV and becomes 3D solid around $E_{\text{tot}} = 0.77$ eV. (c) Caloric curve for $N = 14$ (averaged over five simulations and separated into 2D and 3D phases using $D_{\text{rms}}$). The planar clusters form the hot, low-potential energy phase. The 3D liquid phase has the heat capacity of $c_v = 4.05k_B$ and the 3D solid phase $c_v = 3.06k_B$ per atom. A similar decrease of the heat capacity is obtained for the 2D solid-liquid transition. (d) The partial entropies for 2D and 3D phases versus potential energy. The entropy curves (from multiple histogram calculations [23,24]) crossover around $E_{\text{tot}} = 1.5$ eV.

cantly lower than the 2D/3D barriers, confirming the qualitative features of the DFTB energy landscape.

Even though we have used Au$_{14}$ as an example to demonstrate the features of LLC, we want to stress once more that the LLC is observed for Au$_{11}$ and Au$_{13}$ as well as for Au$_{13}$, for broad temperature ranges. This demonstrates that LLC is a persistent phenomenon, not confined to exist only in narrow parameter or cluster size ranges.

**Supercooling of the metastable 3D phase.**—Next we turn our attention to the cooling processes that take place in the experiments. In a typical experimental source, noble metal clusters are grown in helium buffer gas by aggregation of metal atoms. Each aggregation event rises the internal temperature of clusters of sizes as considered here by about 1000 K; during aggregation and especially after the last atom attachment, the clusters are cooled down again by collisions with the helium carrier gas. Rough estimates as well as previous theoretical work [21] yield a typical cooling rate of about 0.1 eV/ns for a cluster with a kinetic temperature of around 700 K in a laser evaporation source (helium pressure about 100 mbar) and of about 0.001 eV/ns in a magnetron sputter gas aggregation source (helium pressure ≤ 1 mbar). These cooling rates imply time scales in the range of 0.1 to 10 μs, which are accessible with our DFTB molecular dynamics.

The collisional cooling was simulated via extensive DFTB-MD simulations where a single trajectory consisted of sequential microcanonical parts; between two successive parts the kinetic energy of the cluster was reduced by $-0.013$ eV through randomized virtual collisions. We performed in total 20 independent cooling runs, five per cluster size in the range of Au$_{11}$ to Au$_{14}$. Figure 3(a) shows the time evolution of the planarity parameter $D_{\text{rms}}$ for representative runs in this size range. Here we can note that all cluster sizes exhibit LLC at large temperatures (bimodality of $D_{\text{rms}}$), even though for $N = 11$ and $N = 12$ it is not as clearly shown in the figure due to shorter flipping times. It can be seen that the smallest clusters Au$_{11}$ and Au$_{12}$ rather continuously and smoothly anneal and solidify to the planar ground state, whereas Au$_{13}$ and Au$_{14}$ solidify to higher energy 3D structures from the 3D-liquid–3D-solid coexistence phase; note that both GGA-DFT and DFTB predict planar ground-state structures in this size range. The solidification dynamics is nicely reflected in the evolution of the root-mean-square bond length fluctuation [Fig. 3(b)]; for Au$_{14}$ the LLC ends at $E_{\text{tot}} \sim 2$ eV followed by a 3D-liquid–3D-solid coexistence for $E_{\text{tot}} < 1.1$ eV corresponding roughly to temperatures around 300 K [see Fig. 3(c) for the partial caloric curves $T(E_{\text{tot}})$ of both dimensionalities].

Why do the larger clusters get supercooled and solidify into the energetically higher lying 3D isomer space in the time scale of our simulation? Out of the aforementioned five cooling runs for each cluster size, all the runs resulted in the ground-state isomer for Au$_{11}$ and Au$_{12}$, whereas for
Au$_{13}$ only two and for Au$_{14}$ only one simulation resulted in planar ground-state isomers. We can suggest a combination of two factors that increases the tendency for supercooling to the wrong dimensionality. First, as Fig. 3(d) shows, in the LLC region with $E_{\text{tot}} > 2$ eV, the entropy of the 3D liquid phase is more than 2$k_B$ larger than the entropy of the 2D liquid phase. This results in longer dwelling times in the 3D phase, as displayed by Figs. 1(b) and 3(a). Second, as discussed already in the context of Fig. 2, the phases with different dimensionalities are separated by high-potential energy barriers. Upon cooling, this causes the 2D/3D barrier to become impenetrable already at a relatively high total energy where the equilibrium constant (the ratio [time in 2D]/[time in 3D]) is still small due to free energy differences. The larger entropy at higher temperatures thus favors supercooled 3D clusters.

After the theoretical prediction of the liquid-liquid coexistence and the supercooling into metastable structures for some sizes at experimental cooling rates, let us briefly discuss the experimental situation. As discussed in the introduction, earlier collision cross-section measurements with drift tubes [3] suggested the 2D/3D transition size at $N = 12$, which lead to the speculation that GGA-DFT overestimates the 2D stability regime. Although this might be correct, our simulations indicate that it is not permissible to base this conclusion on a disagreement of experimentally determined isomers and theoretically predicted ground-state structures, since it is possible that with experimentally realizable cooling times one cannot reach a possibly existing 2D ground state. Thus, our results clearly underline the fact that even in small homogeneous systems the possibility for supercooling (preferred formation of non-ground-state structures) exists, and this possibility must be taken into account when comparing experimental and theoretical results.

The dodecamer anion Au$_{13}$ deserves special attention in this context since this is the only gold cluster anion with a bimodal arrival distribution in mobility experiments [3]. Various independent studies report a 2D GGA-DFT ground state and a more than 0.5 eV higher lying 3D structure [3,4]. Furthermore, the theoretical collision cross sections of these isomers agree with the two peaks in the experimental mobility data. There are two explanations for the observed experimental coexistence of both isomers at low temperatures: (i) energetic degeneracy of the 2D and 3D structure or (ii) LLC + supercooling. Option (i) would imply a serious overestimation of the 2D/3D energy gap by the present gradient corrected density functionals. Although this can not be excluded, we consider option (ii) as the more likely explanation. In conclusion, this work underlines the need to pursue further investigations of dimensionality crossover of gold cluster anions in two parallel fronts. On the experimental side, our predic-

**References**

[15] See EPAPS Document No. E-PRLTAO-98-013702 for an animated impression of the LLC for Au$_{13}$ corresponding to Figs. 1(b)–1(d) around 2.4, ..., 2.9 ns. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.