It is well-known that the thermodynamic phase transitions in small systems are broadened due to finite size effects: dynamical coexistence of phases is observable over a finite energy or temperature. A classic example is that of the liquid-solid phase coexistence in atomic clusters. Here we show by MD simulations that anionic gold clusters can exhibit a novel, free-standing two-dimensional liquid phase. This phase exhibits a liquid-liquid coexistence (LLC) with a normal three-dimensional liquid. It is further shown that upon cooling with experimentally realizable cooling rates, the entropy-favored 3D-liquid clusters with \( N \geq 12 \) get supercooled and solidify into the “wrong” dimensionality. This indicates that experimental validation of theoretically predicted Au\(_N\) ground states might be more complicated than hitherto expected.

**Small gold cluster have planar ground states to large cluster sizes -are they also thermodynamically stable?**

- **Changes in the dimensionality...**
  - ...are related to the bimodality of the potential energy
  - ...with both in liquid phase:
    - large bond length fluctuations
    - heat capacity 160\% Dulong-Petit
    - diffusion constant
    - visual inspection (movie in EPAPS)

**What enables LLC?**
- low barriers within the different basins...
- ...separated by high barrier, which is overcome far less frequently

**LLC has experimental consequences:**
- the conditions enabling LLC favor supercooling into higher lying isomers in experiments

**Cooling simulations (SCC-DFTB):**
- 5 cooling runs for \( N=11,12,13 \) and 14
- He buffer gas @50 mbar, \( \sigma=100 \text{ Å} \)
- \( dE/dt=0.04 \text{ eV/ns} \)
- 0.01 eV/coll, collisions every 0.3 ns

**References:**