Liquid-Liquid Phase Coexistence in Gold Clusters: 2D or not 2D?

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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 by calculations and photoelectron spectroscopy results that upon cooling with experimentally realizable cooling rates, the entropy-favored 3D-liquid clusters with N≥12 get supercooled and solidify into the “wrong” dimensionality. These results resolve the current controversy between theory and experiment regarding optimal cluster structures.

Liquid-liquid coexistence

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

Microcanonical simulation around 750 K:

Bimodality of potential energy...

...is related to changes in dimensionality

... with both in liquid phase:
- large bond length fluctuation
- heat capacity 160% Dulong-Petit
- diffusion constant
- visual inspection

What enables LLC?
- low barrier in two phases separately...
- ... separated by high barrier, which is overcome far less frequently

Supercooling

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, ~100 Å², dE/dt=0.04 eV/ns
- 0.01 eV/coll, collisions every 0.3 ns

Why do the clusters get supercooled?
- barrier structure (long 3D dwell times)
- phase space: larger entropy of 3D phase
- clusters often in 3D when the 2D/3D barrier becomes impenetrable!

Comparison to experiments (DFT and photoelectron spectra)

...is related to the change in slope of the caloric curve