Liquid metal nanodroplet dynamics inside nanocontainers

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Here we report direct observations of spatial movements of nanodroplets of Pb metal trapped inside sealed carbon nanocontainers. We find drastic changes in the mobility of the liquid droplets as the particle size increases from a few to a few ten nanometers. In open containers the droplet becomes immobile and readily evaporates to the vacuum environment. The particle mobility strongly depends on confinement, particle size, and wetting on the enclosed surface. The collisions between droplets increase mobility but the tendency is reversed if collisions lead to droplet coalescence. The dynamics of confined nanodroplets could provide new insights into the activity of nanostructures in spatially constrained geometries.

Results

Formations of nanodroplets inside nanocontainer. Our approach to create Pb nanoparticles inserted nanocontainer system is shown schematically in Fig. 1a. The nanocontainer, in the form of a carbon nanocup engineered from graphitic carbon, was fabricated by using precisely controlled short nanopores inside anodic aluminum oxide templates and thermal chemical vapor deposition of acetylene (C2H2) at 650°C. As shown in scanning electron microscope (SEM) and transmission electron microscopy (TEM) images (Fig. 1b and 1c), the open nanoscale cup geometry as well as its graphitic nature make carbon nanocups a robust nanocontainer which prevent the change in volume and interfacial area during heating. Differently sized Pb nanoparticles were formed inside the nanocontainer by controlling Pb deposition. The free space inside the nanocontainer and the particle size determines the motion of the nanodroplets that form upon heating. For typical figures, as shown in Fig. 1c–1d and 1f–1g, the ratio of the particle volume to free volume ranges from 1.5 to 310 for the large (60 nm) to the small (15 nm) droplets we have observed. Finally, a carbon film (7 nm thickness) was deposited under 10−6 torr pressure to cap the nanocontainer making it a perfectly sealed, closed system.

Observation of nanodroplets by in-situ TEM. In-situ transmission electron microscopy (JEOL-3011 with an accelerating voltage of 300 kV equipped with a heating specimen stage) studies were performed to observe the motion of Pb nanodroplets inside the sealed nanocontainers. The specimen temperature was increased to 630 K for a large Pb nanoparticle (≈60 nm diameter) and 600 K for small Pb nanoparticles (≈15–20 nm diameters), in order to undergo complete phase transition from solid to liquid (confirmed by molecular
dynamic simulations, supplemental text and Fig. S1). Fig. 2 is the sequential TEM images of Pb nanodroplets captured over a period of 1–5 seconds at the elevated temperature. At the early stage of heating, a melted larger Pb nanoparticle starts to fluctuate in both axial and radial directions inside the cylindrical nanocup (Fig. 2a and supplemental movie S1). This fluctuation occurred in random directions due to the limited free space as well as the interfacial forces between the nanocontainer surface and the molten Pb nanodroplet. With time, this motion becomes more along the axial direction of the nanocontainer following the cylindrical empty space that exists in the nanocup container (Fig. 2a and supplemental movie S1). This fluctuation occurred in random directions due to the limited free space as well as the interfacial forces between the nanocontainer surface and the molten Pb nanodroplet. With time, this motion becomes more along the axial direction of the nanocontainer following the cylindrical empty space that exists in the nanocup container (Fig. 2a and supplemental movie S1). During heating and melting of particles, we also observed that irregularly shaped Pb nanoparticles changed the shape to near spherical without the movement reflecting the lowest surface energy/volume ratio at thermodynamic equilibrium for the isotropic molten particle.

Unlike larger confined Pb nanodroplets, smaller Pb nanodroplets showed significantly different dynamic behavior inside the nanocontainer (Fig. 2b–c). Smaller droplets ceaselessly moved inside the nanocontainer as shown in Fig. 2b–c and supplemental movie S2. Individual movement of each nanodroplet appeared random and at a much faster rate than the motion of the larger droplets seen in Fig. 2a.

In addition to the brisk movements of the small nanodroplets we also observed spontaneous evaporation of 1–3 nm sized secondary droplets from the volume of the Pb 15–20 nm droplets, and the coalescence between them; despite the fact that smaller nanodroplets had active movement inside the nanocontainer, collisions and coalescence between two such droplets was only observed rarely.

**Discussion**

To understand the movement of smaller Pb nanodroplets inside nanocontainer, we monitored their position in 2-dimensional space and mean square displacement (MSD) over time as shown in Fig. 3 and supplemental movie S2. Two dimensional projected position changes of the two nanodroplets (Fig. 2b) and the merged droplet (Fig. 2c) are shown in Fig. 3a and b. The positions were marked every 0.1 seconds. The two nanodroplets moved irregularly in the nanospace, frequently changing their direction without overlapping displacements before being merged. This nonoverlapping might be due to the electrostatic charging effect by primary electron absorption from TEM into nanodroplets. Since each of two nanodroplets occupies smaller space than merged, the scaling with particle size is counter-intuitive as one would expect the smaller droplet reaching...
to a much larger asymptotic values. For the smaller droplets (Fig. 2b) and the merged slightly larger one (Fig. 2c), the second temporal evolution is seen as diffusive (Fig. 3c). A linear increase in the MSD is indicative of Brownian dynamics of the droplet. We speculate that upon heating under low pressure, surface atoms in nanodroplets are energetically excited and evaporated from the nanodroplets. Simultaneously these evaporated clusters can be condensed on the wall of nanocontainer. When condensed droplets become bigger than evaporated clusters, the vapor pressure become smaller again but the confined system will be placed in a nonequilibrium state and droplets will evaporate and condense repeatedly. In this case, the nanodroplet motion is influenced by condensation and evaporation of clusters, van der Waals attractive forces with the container, and unlike most systems, is not mediated by a solvent or by gas molecules. Thus we conjecture that the observed irregular motions of nanodroplets are due to the transfer of energy and momentum from the clusters to the nanodroplets through amplified molecular collisions inside of nanoscale confined space. Future study will be necessary to quantitatively understand the dynamics of nanoparticles/droplets in confined systems, which will provide important insight nanoscale influences on melting point, vapor pressure, and heat transfer.

As further validation of the origin of the collective diffusive behavior of the confined nanodroplet, we have characterized the nanodroplet behavior after the capping layer is punctured. Carbon nanocounters have strong C-C bonds and multi-layered graphitic structure, while the cap of nanocups was created by depositing amorphous carbon, which can be cracked by an external force. Fig. 4 and supplemental movie S3 shows the shape changes of a liquid Pb nanodroplet after the cap of the nanocontainer is punctured. The stationary liquid Pb droplet at thermodynamic equilibrium abruptly moved toward the end (sealing) of the nanocontainer after 0.03 seconds (Fig. 4a and b and supplement movie S4). This phenomenon is due to the pressure difference of inside and outside (under $10^{-7}$ torr in TEM chamber) of the nanocup container. The thermal energy is used to transform a given quantity of a substance from a liquid into a gas at a given pressure. The pressure and temperature within the nanocontainer rapidly equilibrates to the ambient conditions inside the vacuum column of the TEM. Under these conditions the vapor pressure of the metal changes abruptly. 2D characterization of the nanodroplet at several temperatures above the melting point shows that static nanodroplets wet the nanocontainer sidewalls with well-defined contact angles. Increasing temperature results in enhanced evaporation and the droplet reduces in size. The evaporation kinetics is discontinuous due to the heterogeneous nature of the defective sidewalls of the container. At larger volumes, the nanodroplet develops a meniscus as it wets multiple sidewalls. Below a critical droplet size, the volume becomes low enough such that the droplet is forced to wet a single sidewall and as a result, the droplet surface curvature changes sign. Supplemental movie S3 of the evaporation kinetics indicates a transition between pinned and moving contact.
by thermal evaporation and by being annealed at 500 °C inside nanocontainers was controlled by adjusting the thickness of a Pb film deposited in the nanocarriers to control and separate nanocontainer structures. The size of Pb nanoparticles in the carbon nanocup film structure were synthesized by using a chemical vapor deposition method.

Methods

Formations of nanodroplet inside nanocontainer. Nanoporous alumina template was prepared using a standard electrochemical anodization process to fabricate highly organized short nanochannels of 120 nm in length. The connected arrays of carbon nanocup film structure were synthesized by using a chemical vapor deposition process, and the Pb film was deposited on the inner surface of the nanocarriers. Pb and Pt nanoparticles were fabricated by heating a Pb- and Pt-loaded alumina template in a vacuum chamber at 780 Torr. The Pb film was deposited on the inner surface of the nanocarriers by a vacuum deposition method. The Pb film was then annealed at 500 °C to form the Pb nanoparticles inside the carbon nanocarriers. The Pb nanoparticles were synthesized by adjusting the thickness of the Pb film deposited on the inner surface of the nanocarriers by thermal evaporation and annealing at 500 °C.

In-situ TEM. In-situ TEM studies of the Pb nanoparticles behavior inside the carbon nanocarriers were carried out in a JEOL-3011 with an accelerating voltage of 300 kV equipped with a heating specimen stage. Double tilt heating holder was used for placing sample and it was tilted by 30° in x-axis during imaging for all line regimes. This is also evident in Figure 4j, which shows the evaporation tendency of the instantaneous area of cross-section of the droplet at spontaneously increased temperatures. The rate increases rapidly between 770 and 820 K where its shape is changed concave to convex.

In conclusion, we have observed the differences in the mobility of nanodroplets of molten metal trapped inside closed nanospaces and found dramatic differences between the mobility and diffusive nature of these particles as a function of particle size, wetting and confinement. The particles remain active only within closed environments and once open to the environment remains vulnerable to quick evaporation. Although transferable energy of incident electrons in TEM can contribute to droplet motion (shown in the supplemental text, Fig. S4 and movie S5), the dominant factor contributing to the motion is thermal activation that is causative of continuous collisions of the clusters onto the nanodroplets. The results show that under confinement, nanodroplets remain extremely mobile and undergo Brownian movements in the confined space. This could be potentially important in the understanding of the effect of confinement in the activity of small liquid droplets in environments such as porous media.

In-situ TEM. In-situ TEM studies of the Pb nanoparticles behavior inside the carbon nanocarriers were carried out in a JEOL-3011 with an accelerating voltage of 300 kV equipped with a heating specimen stage. Double tilt heating holder was used for placing sample and it was tilted by 30° in x-axis during imaging for all

![Figure 3](image-url) Position trace and the mean square displacement of the center-of-mass of the lead nanodroplet. Two dimensional projected position changes of the two nanodroplets (a) and the merged droplet (b). The positions were marked every 0.1 seconds. The two nanodroplets move irregularly without overlapping displacements before being merged. (c) Temporal evolution of the mean square displacement of the center-of-mass of the two lead nanodroplets (upper and lower one in Fig. 2(b)) and of the eventual merged droplet (Fig. 2c) over second time resolution. The linear behaviors indicate Brownian dynamics of the particle.

![Figure 4](image-url) The behavior of Pb nanodroplet in the open nanocontainer. The size of Pb nanodroplet gradually decreases due to evaporation through the open space. (a) Images at 640 K. The motion of liquid Pb nanodroplet stopped and shape of liquid droplet became spherical. (b) After 0.03 seconds, this stationary liquid Pb droplet moved toward the end (scaling) of the nanocontainer (temperature is 640 K). (c) and (d) Image at 670 K and 770 K, respectively. The shape of liquid Pb changed to a hollow, concave shape. (e)–(i) Images at 820 K, 825 K, 830 K, 835 K and 840 K, respectively. (j) The evaporation tendency of the instantaneous area of cross-section of the droplet at spontaneously increased temperatures. The size of liquid Pb nanodroplet slowly decreased due to evaporation with increasing temperature through the open space. The rate increased rapidly between 770 and 820 K and its shape eventually changed concave to spherical. Scale bars are 20 nm. experiments. All specimens were placed on holey carbon coated molybdenum grid contacted to the heating stage having the electric heater and heated to experimental temperature.

Computational method. To describe the thermodynamic properties of Pb nanoclusters as well as the bulk Pb structure, we performed molecular dynamics (MD) simulations within canonical ensemble using the first-principles DFT. We solved the classical equation of motion with the force acting on each atom, which was calculated using the Hellmann-Feynman force theorem. To prepare the canonical ensemble, we controlled the equilibrium temperature.

We used the Perdew-Zunger form of the Ceperley-Alder exchange-correlation functional in the local-density approximation to DFT, as implemented in the SIESTA code. The behavior of valence electrons was described by norm-conserving Troullier-Martins pseudopotentials in the Kleinman-Bylander factorized form including the scalar-relativistic effect. An atomic orbital basis with a double-$\zeta$ polarization was used to expand the electronic wave functions. The charge density and potentials were determined on a real-space grid with a mesh cutoff energy of 200 Ry. We used a confinement energy shift of 0.01 eV, which defines the cutoff radii of the atomic orbitals. For the bulk Pb structure, the cubic supercell of 32 atoms was constructed in face-centered cubic (fcc) structure with a periodic boundary condition. We constructed Pb nanoparticles with 55 and 13 lead atoms. For the investigation of the phase transition, we calculated the response of a canonical ensemble of Pb nanoparticles and fcc bulk structure to gradually increasing heat bath temperatures using Nosé thermostat and these simulations were carried out for 10 ps with a chosen time step of 1 fs.

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