Confined nanoparticle solutions for nanotribological applications

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Current advances in micro- and nano-electromechanical devices (MEMS and NEMS), micro and nanofluidic systems, and other nanotechnological areas all involve the tribological issues of friction, wear, and lubrication at the microscale or nanoscale. Under such nanotribological conditions, the lubricant films are molecularly thin and have been shown to possess properties that are significantly different from those of bulk fluids but not desirable for tribological applications. Recent experimental studies using surface force apparatus (SFA), atomic force microscopy (AFM), friction force microscopy (FFM), and quartz crystal microbalance (QCM) have confirmed the significant effects of the confining surfaces on the properties of nanoscopically confined fluid films and further suggested that nanoscale confinement can induce fluid molecules to form layered configurations, causing nanoconfined fluids to have very different properties than those of bulk fluids, where molecules possess no preferred orientation. Explicit evidences at the molecular level have come from computer molecular simulation studies using Monte Carlo (MC) and molecular dynamics (MD) techniques. Other theoretical approaches such as density functional theory and integral equation theory have also been extended to analyze nanoconfined fluids and confirm the formation of fluid layers under confinement.

It has now been well established that when the separation/spacing between the confining surfaces is larger than about ten molecular diameters, confined fluids behave much the same as bulk fluids in many aspects. As the separation decreases, molecular orientation and fluid configuration undergo changes and, more importantly, the isotropy between the perpendicular and parallel directions breaks down. The difference between the perpendicular pressure ($P_\perp$) and the parallel pressure ($P_\parallel$) has been measured as the solvation force (f_s) by the surface force apparatus, where the confined fluid is open to the bulk reservoir under isothermal-isobaric condition and the parallel pressure as a result is taken to be the same as the bulk pressure. Interestingly, when symmetric molecules are confined under a constant bulk/parallel pressure, salvation/surface force oscillates as a function of surface separation with a periodicity that is equivalent to the mean molecular diameter [cf. Fig. 1(a)]. This behavior is not in accord with the expectations from conventional continuum theories but signifies the formation of layered configurations parallel to the confining surfaces by the confined fluid molecules. When a strongly layered confined fluid is sheared, instead of lubricated smooth motion, it exhibits yield stress, stick-slip motion [cf. Fig. 1(b)], and apparent shear viscosity that could be orders of magnitude higher than bulk values. These solid-like responses reflect the solid-like nature of the layered configurations, which could be linked to the peaked, repulsive surface forces, and can cause undesirably large friction and wear and consequently significant material and energy costs. Between two peaked surface forces and during the slip phase, nanoconfined fluids undergo configurational changes to become less layered, thereby exhibiting lubricated smooth motion and reduced friction and wear.

Alkanethiol-capped nanoparticles represent a recent technological breakthrough and have been touted as one of the most important ingredients for nanotechnologies. They are charge-neutral composites with an inorganic crystalline core capped in a dense shell of
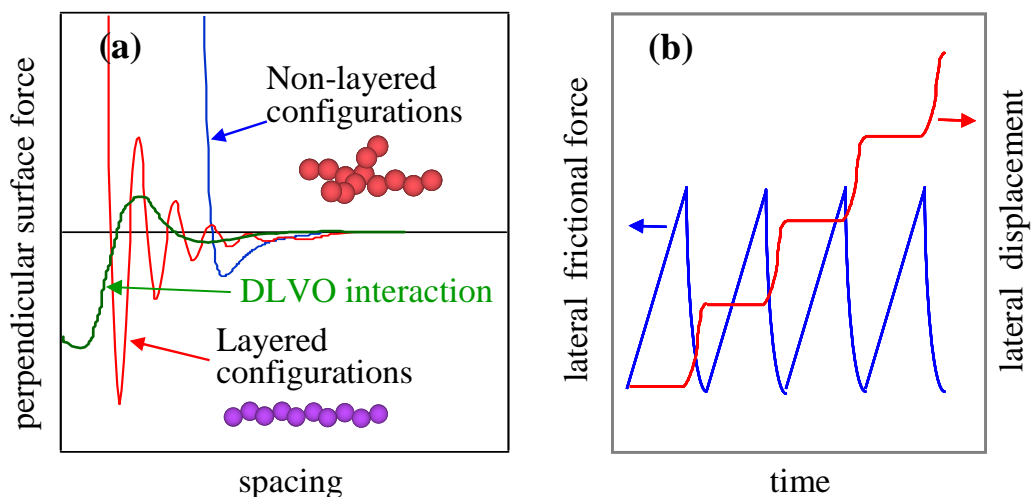
Figure 1. Schematics of (a) solvation/surface force profiles for confined fluids with layered or non-layered configurations and (b) stick-slip motion of confined fluids with layered configurations.

alkanethiol molecules, and have nowadays been routinely synthesized. They have good solubility in common non-polar solvents and are much larger in size than typical solvent molecules. To explore possible advantages resulting from good solubility and size mismatch of alkanethiol-capped nanoparticle, we perform MD simulations to study the nanotribological potential of confined liquid solution containing alkanethiol-capped nanoparticles. The model nanoparticle considered is hexanethiol-capped gold nanoparticle, $Au_{140}(SC_6H_{13})_{62}$, which is modeled as a soft sphere by using the Lennard-Jones (LJ) 12-6 potential. Separate atomistic simulations were performed in order to determine the LJ parameters for the gold-thiol nanoparticle ($\sigma_{gold-thiol} = 29$ Å, $\varepsilon_{gold-thiol} = 10827.08 k_B$). For computational consistency and efficiency, spherical cyclohexane is chosen as the non-polar solvent and its LJ parameters are adopted $\sigma_{cyclohexane} = 5.466$ Å and $\varepsilon_{cyclohexane} = 484 k_B$ from the literature. Since a relatively large portion of the envisioned nanotechnologies involve silicon (Si), we have considered the Si(111) surface as the confining surface, which has the diamond structure and a lattice constant equal to 5.43 Å. Following a standard approach, the Si lattice structure and energy results in $\sigma_{Si} = 3.826$ Å, $\varepsilon_{Si} = 202.45 k_B$ for its LJ potential. Taking hints from SFA, the thermodynamic state of the confined nanoparticle solutions is defined and controlled in our simulations by constraining the temperature and the parallel pressure ($P_{||}$) to prespecified bulk phase values at all times (300 K and 1 atm) via a recently developed *NhPT* MD method, which in effect is a virtual isothermal-isobaric reservoir method. The equations of motion are integrated with the fourth-order Gear predictor-corrector algorithm along with a time step of 5 fs. All confined nanoparticle solutions are first equilibrated at a separation of $h=10$ nm (100 Å) between two confining Si (111) surfaces and under continuous compression by decreasing the separation at a speed of 5 m/s.

The simulation studies of continuous compression of confined solutions containing 0, 1, 3, 5, and 10 nanoparticles were performed. As can be seen from Fig. 2 where the results from the case of 5 nanoparticles are shown, the employed *NhPT* method controls the parallel pressure well except when at the smallest separations the confined fluid is unphysically forced
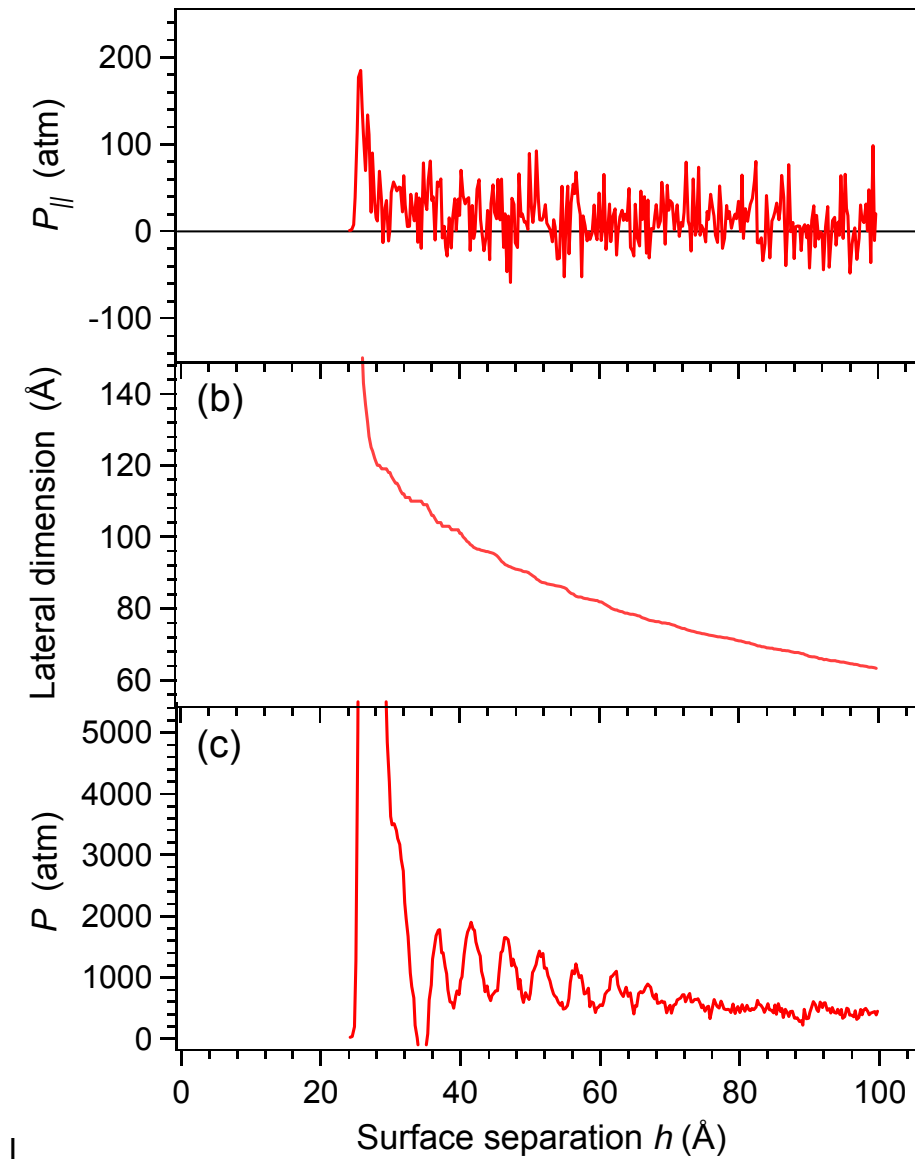
Figure 2. Instantaneous (a) parallel pressure, (b) lateral dimension, and (c) perpendicular pressure as a function surface separation during continuous compression.

to break apart by the imposed compression. Figure 3 shows the simulation results from continuous compression of different nanoparticles solutions. The data are instantaneous properties calculated and recorded every 1000 Δt's. Exhibiting the strongest force oscillations [cf. Fig. 3 (b)] is the pure cyclohexane fluid in nanoconfinement that can be understood to be most layered among all solutions studied. A closer examination of the force oscillations reveals that the periodicity is about the same as the cyclohexane molecular diameter, 5.466 Å. The connection between the surface force and the fluid configuration can be analyzed by comparing Figures 3 (a) and (b) together. It can be easily seen that the lateral dimension of the confined cyclohexane under continuous compression undergoes step-like expansion and the width of the steps is the same as the periodicity of the force oscillations. More specifically,

minimum surface forces occur at separations that correspond to completion of step-like expansion and more disordered, less layered configurations. When compression continues, the less layered confined fluid are squeezed to become more layered and the surface force builds up again until the confined fluid could not sustain the strong pressure any more and sudden expansion occurs in the lateral directions.

When nanoparticles are added to the confined alkane fluid, they significantly reduce the magnitudes of the step-like expansion and force oscillations. In addition, nanoparticles bigger in size can now resist compression and strong perpendicular pressure at larger separations that are about the same as the size of the nanoparticles [cf. Fig. 3(a)]. These behaviors signify better nanotribological properties that could be provided by the presence of alkanethiol-capped nanoparticles in alkane/oil solutions.
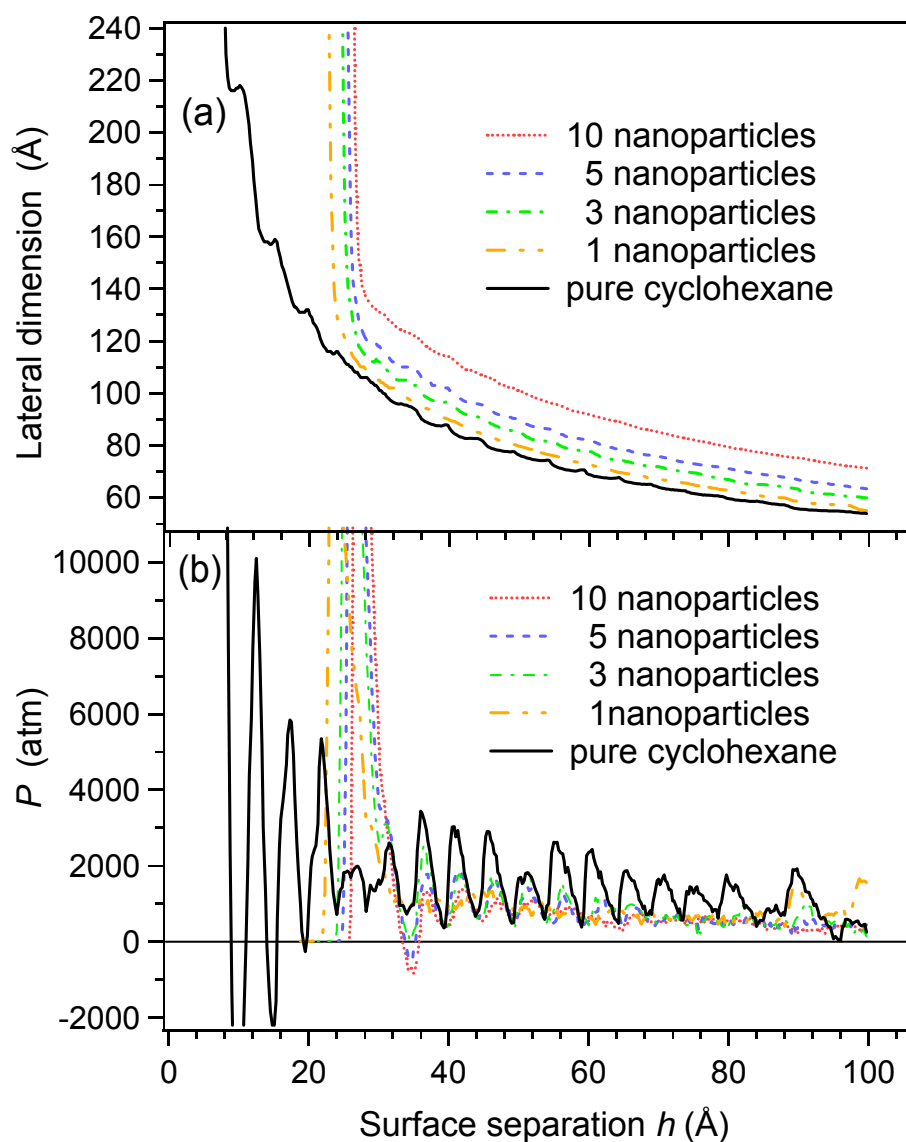

Figure 3. Instantaneous (a) lateral dimension and (b) perpendicular pressure as a function surface separation during continuous compression for different solutions.