In this Letter, dynamic wetting of water nano-droplets containing non-surfactant gold nanoparticles on a gold substrate is examined via molecular dynamics simulations. The results show that the addition of non-surfactant nanoparticles hinders the nano-second droplet wetting process, attributed to the increases in both surface tension of the nanofluid and friction between nanofluid and substrate. The droplet wetting kinetics decreases with increasing nanoparticle loading and water-particle interaction energy. The observed wetting suppression and the absence of nanoparticle ordering near the contact line of nano-sized droplets differ from the wetting behaviors reported from nanofluid droplets of micron size or larger. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4837717]

Nanofluids, fluids containing suspensions of nanometer-sized particles, are a type of complex fluids designed to enhance thermal properties and/or reduce drag coefficients for applications ranging from electronics cooling to microfluidics, among others.1–3 The suspended nanoparticles can significantly modify the transport properties of the base fluids, and the resulting nanofluids exhibit attractive properties such as high thermal conductivity and boiling heat transfer coefficient.4,5 The wettability of nanofluids is of particular interest to microfluidic systems, in which surface tension plays an important role due to the relative small dimensions and high specific surface areas of these micro-devices.6,7 Additionally, through wetting and particle deposition processes, nanofluids are widely used to functionalize substrates for desired surface morphologies and properties.8

The addition of nanoparticles makes the wetting kinetics of nanofluids more complicated compared with that of the base fluids, due to additional particle-particle, particle-substrate and particle-fluid interactions. The self-assembly of nanoparticles within the bulk liquid, at the solid-liquid and liquid-vapor interfaces, and/or in the vicinity of the contact line region greatly affects the wettability of nanofluids. Wasan and Nikolov9 reported the enhancement of droplet spreading behavior, i.e., super-spreading of nanofluids of 8 nm micellar solution, 1 μm latex suspension, and 20 nm silica suspension. A solid-like ordering structure of nanoparticles was observed near the contact line region using interferometry. This solid-like ordering structure stemming from the settlement and assembly of nanoparticles gives rise to a structural disjoining pressure in the vicinity of the contact line. This excess pressure in turn alters the force balance near the contact line and enhances the spreading of nanofluids.10–13 The super-spreading behavior of nanofluids was also reported in single-wall carbon nanotubes suspended in water14 and aluminum–ethanol nanofluids.15 The self-assembly of nanoparticles and the structural disjoining pressure induced super-spreading behavior of nanofluids were widely used to explain the enhancements in drop-wise evaporation16,17 and critical heat flux of nanofluids.18–21

Although experimental observations9,11 have been obtained for the effects of ordering of nanoparticles inside the micron-sized wedge-film near a contact line on the dynamic wetting of nanofluid droplets, no direct evidence has been provided for the fast spreading of nano-sized droplets containing nanoparticles, a process important to many nanofluidic devices and nanoporous membranes for water purification, for instance. Molecular-level simulations have been recognized as a powerful tool in examining transport phenomena of nanoparticles in a bulk liquid and at interfaces.22–31 Self-assembly of nanoparticles of Lennard-Jones (LJ) type at fluid-fluid interfaces have been examined via molecular dynamics (MD) simulations.22–27 Drazer et al.28,29 and Li et al.30 investigated the mobility of a single nanoparticle transporting in liquid (liquid argon or nitrogen) within a cylindrical nanochannel filled with nitrogen gas. Kim et al.31 simulated the ring-like deposition of nanoparticles from a drying droplet using a Monte Carlo scheme. To date, no MD simulations have been reported for spreading of nanofluids on solid substrates. In addition, most MD simulations focused on nanofluids containing LJ particles in an LJ fluid, a system that is quite different from real nanofluids and is hence impossible to mimic important physical properties (e.g., surface tension, density, and viscosity) of nanofluids during wetting.

In this Letter, the dynamic wetting of water nano-droplet with non-surfactant gold nanoparticles on a gold substrate was studied using MD simulations with validated interatomic potentials. The results are compared first with the molecular kinetic theory (MKT).32 The effects of particle volume fraction and particle wettability on the wetting kinetics and contact line mobility of nanofluids are examined. The surface tension of the nanofluids and the friction...
between the nanofluid and substrate are calculated and compared with those of base fluids. The wetting behaviors of the present nano-sized nanofluid droplets are compared with those reported in literature based on nanofluid droplets of micron size or larger.

The cylindrical water droplets (diameter $d = 10 \text{ nm}$, length $l = 1.64 \text{ nm}$, 4500 water molecules) with four gold nanoparticle loading levels (number of nanoparticles $n = 0$, 9, 19, and 27, corresponding to particle volume fraction $\varphi = 0\%, 3.43\%, 6.77\%$, and 9.81\%) spreading on a Au(100) surface ($61.35 \times 1.64 \times 1.64 \text{ nm}^3$ fcc crystal total of 9600 gold atoms) at 300 K were simulated in this study. The gold nanoparticles (0.8 $\times$ 0.8 $\times$ 0.8 nm$^3$, 32 gold atoms per particle) were calibrated at 300 K and then absorbed spontaneously by a water droplet until the nanofluid system reached its minimum energy where the nanoparticles were randomly distributed inside the drop. The newly formed nanofluid droplets then spread on a Au(100) surface until the equilibrium contact angles were achieved. The four-point TIP4P-Ew water model$^{33}$ was used to describe the water-water interactions, where the particle-particle-particle-mesh (PPPM) technique was used to compute the long-range Coulombic forces, and the SHAKE algorithm was applied to keep the water molecules rigid.$^{34}$ The embedded-atom method (EAM)$^{38}$ was applied to describe the gold-gold interactions, which occur among particle-particle, water-water interactions, where the particle-particle-particle self-assembly of nanoparticles, the diffusion time scale of nanoparticles was estimated by the Einstein diffusion theory,$^{38}$ where the diffusion coefficient is defined as $D = k_B T / 6\pi \eta d$. Here, $k_B$ is the Boltzmann constant $1.38 \times 10^{-23} \text{ J/K}$, $T$ is the temperature, $\mu$ is the viscosity of water, and $d$ is the nanoparticle diameter. The diffusion time for one nanoparticle to move from the center of the droplet to the interface is $\tau_d = \pi R^2 / D \approx 160 \text{ ns}$ at 300 K, much longer than the entire spreading process of approximately $10 \text{ ns}$. This implies that not enough time is available for nanoparticles to self-assemble into ordered structures near the contact line region during the spreading process. Consequently, the spreading enhancement of nanofluids due to the presence of structural disjoining pressure as a result of nanoparticle ordering is not valid mechanism in this study. Limited diffusion rate of nanoparticles in the contact line region as nanofluid spreads was also reported when 10 nm silica nanoparticles suspended in a polyethylene glycol solution.$^{39}$ It is noted here, the droplet sizes used in most nanofluid wetting studies were several millimeters in diameter,$^{9,11}$ corresponding to a much longer spreading time during which solid-like ordering structures of nanoparticles may occur.

In a microfluidic system, the dynamic spreading of a droplet is mainly controlled by the viscosity and surface tension of the fluid. To examine the effects of these two properties on dynamic spreading, the dimensionless drop spreading radius, $R' = R/R_0$, as a function of the dimensionless time $t' = \gamma t / \mu_{\text{eff}} R_0$ is plotted in Fig. 2. Here, $R_0$ is the initial drop radius prior to spreading, $\gamma$ is the surface tension of water, and $\mu_{\text{eff}}$ is the effective viscosity of the nanofluid, calculated using $\mu_{\text{eff}} = \mu (1 + 2.5 \varphi)$ to eliminate the effect of viscosity in droplet spreading kinetics. For fluids of equal surface tension, the $R'$ versus $t'$ curves are expected to collapse into one master curve.$^{40}$ However, as shown in Fig. 2, both the dynamics and equilibrium spreading radii decrease with the presence of nanoparticles and further decrease with the increasing nanoparticle volume fraction, indicating a change in surface tension of nanofluids with particle loading.

To evaluate the surface tension of nanofluids, two NVT systems, one with a nanofluid film of two free surfaces and the other with only a bulk nanofluid were simulated. The time-averaged excess energy of these two systems, $(E_w - E_{w/o})$, led to the surface tension, $\sigma = (E_w - E_{w/o}) / A_{\text{interface}}$, for pure water and nanofluids with different particle loadings. Here, the subscripts w and w/o denote with and without liquid-vapor interfaces, respectively. In MD simulations, surface tension can also be calculated from pressure based on the Young-Laplace equation,$^{41}$ but is avoided here due to large pressure fluctuations. Table I summarizes the calculated liquid-vapor surface tensions based on the free energy method for pure water and
nанофлюидов с фазами \( \phi = 3.43\% \), 6.77\% и 9.81\%, где погрешности были получены с использованием разных случайных скоростей в качестве инициализации для различных температур.

Для воды на газ-жидкость интерфейсе.

Для воды в газ-жидкость переходе, сила вулканического взрыва, приведенная к остаточному радиусу, определяется силами и механизмами диссипации с помощью выражений."}

**Таблица 1.** Поверхностное натяжение жидкости и водяных-золотых нанофлюидов различных объемных фракций на основе энергетического метода.

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>Pure water</th>
<th>( n = 9 )</th>
<th>( n = 18 )</th>
<th>( n = 27 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle E_\mu \rangle (\text{eV}) )</td>
<td>(-1789.081 \pm 3.343)</td>
<td>(-2841.828 \pm 5.399)</td>
<td>(-3885.474 \pm 8.548)</td>
<td>(-4943.323 \pm 10.875)</td>
</tr>
<tr>
<td>( \langle E_{\text{w/o}} \rangle (\text{eV}) )</td>
<td>(-1796.242 \pm 3.481)</td>
<td>(-2853.841 \pm 5.993)</td>
<td>(-3910.417 \pm 7.820)</td>
<td>(-4969.034 \pm 10.435)</td>
</tr>
<tr>
<td>( \gamma_s (N/m) )</td>
<td>0.0679 \pm 0.0043</td>
<td>0.1002 \pm 0.0065</td>
<td>0.1109 \pm 0.0073</td>
<td>0.1175 \pm 0.0075</td>
</tr>
</tbody>
</table>
and nanofluids of various particle loadings (the standard deviation of 0.258) indicate that the solid-liquid friction coefficient increases with the increasing liquid-vapor surface tension. The MKT assumes that the viscous dissipation in a bulk liquid is negligible while focusing on the local dissipation in the vicinity of contact line so that the friction coefficient, $\zeta$, is affected only by surface tension. A larger surface tension due to a higher non-surfactant nanoparticle volume fraction leads to a larger solid-liquid friction during the dynamic wetting process.

Figure 4 shows the effect of wettability of nanoparticles on the dynamic spreading of nano-droplets of $\varphi = 9.81\%$. Here, the wettability of nanoparticles is modified by changing the particle-water interaction energy $\varepsilon$ (the wettability increases with increasing $\varepsilon$) while keeping $\varepsilon$ of substrate-water the same. As expected, the droplet spreading kinetics slows down when the interaction between particles and water molecules increases, which can be attributed to the increases in both the surface tension and solid-liquid friction.

In conclusion, the dynamic spreading of water nanodroplets containing non-surfactant nanoparticles is examined via molecular dynamics simulations. The addition of non-surfactant nanoparticles hinders rather than enhances the droplet spreading kinetics during the nano-second process. The contact line velocity decreases with increasing nanoparticle volume fraction and particle-water interactions, as a result of increasing surface tension and solid-liquid friction and the absence of nanoparticle ordering in the vicinity of contact line. It is important to note that, in the present study, the diameter of the nano-droplets is only about ten times that of nanoparticles. Future studies will focus on exploring the threshold droplet size where nanoparticle ordering becomes significant and the surface tension is not significantly affected by the presence of nanoparticles.

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