

Nanofluidics: Wetting and spreading phenomena and applications

Darsh Wasan, and Alex Nikolov

Department of Chemical and Biological Engineering
Illinois Institute of Technology
Chicago, IL 60616

ABSTRACT

Suspensions of nanometer-sized particles in liquids (nanofluids) are used in a variety of technological applications and biological systems. For example, their spreading and adhesion behavior on solid surfaces can yield materials with desirable structural and optical properties. The wetting and spreading phenomena of nanofluids have been pursued by us both experimentally and theoretically in recent years (1 - 11). This lecture will review the progress made in the wetting and spreading of nanofluids over solid surfaces with an emphasis on the complex interactions between the particles in the nanofluid and with the solid substrate, as well as the spreading of their nanofluidic films containing nanoparticles on hydrophilic surfaces driven by the structural film tension gradient. In addition, this talk will highlight potential applications including their use as nanofluids comprised of liquid suspensions of environmentally sustainable inorganic nanoparticles or “green cleaners” for cleaning contaminated hard surfaces, and as “smart fluids” for accelerating recovery of hydrocarbon and stimulation of fluids from oil and gas reservoirs.

BACKGROUND

Pure liquids spread over wet surfaces, but wetting and spreading behavior changes if liquids contain nanosized particles. Recent experiments conducted in our laboratory have clearly demonstrated that the

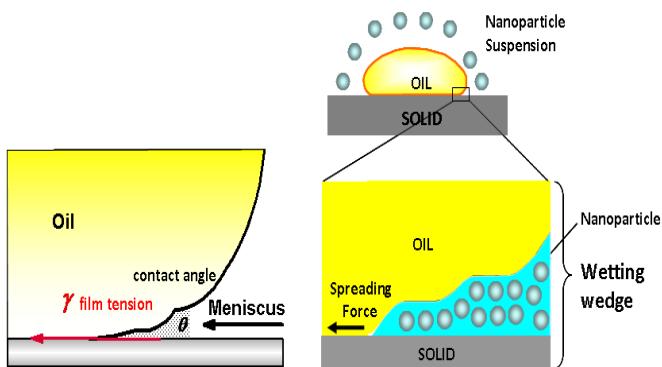


Figure 1. Nanoparticle structuring in the film-meniscus resulting in disjoining pressure gradient/film tension gradient at the wedge tip. [6]

spreading of wetting nanofluids (i.e., nanoparticle solid surface (Fig. 1)). Particles inside the wedge film tend to form more ordered structures (due to the collective interactions) in the confined region than those in the bulk meniscus. Theoretical calculations based on the statistical mechanics approach and Monte Carlo simulations have indicated that the film structural disjoining pressure (i.e., the excess pressure in the film relative to that in the bulk solution) in the wedge film exerted by the particles on the surface has an oscillatory decay (compared to that in the bulk-meniscus) with the increasing film thickness, and a period of oscillation equal to the effective diameter of the nanoparticles (Fig. 2) [1, 10,11]. The structural disjoining pressure dominates on scales larger than the diameter of a nanoparticle, below which other disjoining pressure components, such as van der Waals, electrostatic and solvation forces, are prevalent.

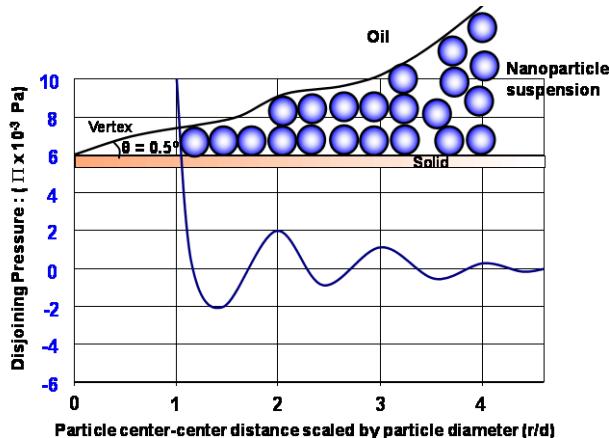


Figure 2. Pressure on the walls of wedge for 0.5° contact angle at the vertex as a function of radial distance. [6]

Our solution of the Laplace-Young equation augmented with the contribution due to the structural component of the disjoining pressure for the meniscus profile [2, 3] shows that the fluid wedge film deforms under the action of the structural disjoining pressure (Figs. 1, 2). As the film thickness decreases towards the wedge vertex, the structural disjoining pressure increases. This suggests that the driving force for the spreading of the nanofluid is the structural disjoining pressure gradient (i.e., the film tension gradient). The film tension gradient (i.e., the integrated value of the disjoining pressure over the thickness of the wedge) is directed towards the wedge from the bulk solution and is high near the vertex because of the nanoparticle structuring in the wedge confinement. As the film tension increases towards the vertex of the wedge, it drives the nanofluid to spread out at the wedge tip (the three-phase contact line moves), thereby enhancing the dynamic spreading behavior of the nanofluid (Fig. 1).

The classical concepts of wetting and spreading of simple liquids do not apply to nano and complex fluids (1,6,12). In one set of experiments, when a drop of nanofluid was placed on a glass surface immersed in hexadecane, it displaced the oil phase, and the nanofluid drop contact diameter increased with time. A dramatic increase in the spreading of the nanofluid was seen as the nanoparticle volume fraction increased. However, the viscosity of the nanofluid also increased with an increase in the nanoparticle volume fraction. The measurement of the spreading velocity showed an unexpected enhancement with the increasing nanoparticle concentration rather than a slow down. All well-accepted theories for the spreading behavior of simple liquids on solids indicate that the spreading velocity is inversely proportional to the viscosity of

the liquid. Therefore, our experimental results on the effect of nanoparticles on the spreading of nanofluids clearly demonstrate that the well-established concepts concerning the spreading of simple liquids do not apply to nanofluids.

The complex nature of the interactions between the particles in the nanofluid and with the solid substrate greatly alters the spreading dynamics under the action of the disjoining pressure gradient (6). Nikolov et. Al (4) employed an experimental setup using combined differential and common light interferometry for directly observing the phenomenon of nanoparticle self-structuring within a wedge film, and also the effect of the film size (i.e., drop size) on the film thickness stability on a solid surface. This technique was used in conjunction with a specially designed glass cell to study the oil-solid interactions when a drop of canola oil ($\sim 200\mu\text{m}$) dispersed in a silica nanoparticle aqueous suspension (with an effective particle diameter of 40 nm) approaches an optically smooth glass surface. There is a microscopic transition between the nanofluid liquid film and the meniscus; the nanofluid film changes its thickness in steps. Figure 3 shows a photomicrograph depicting four different particle structural thickness transitions inside a wedge film with a film diameter of 100 μm .

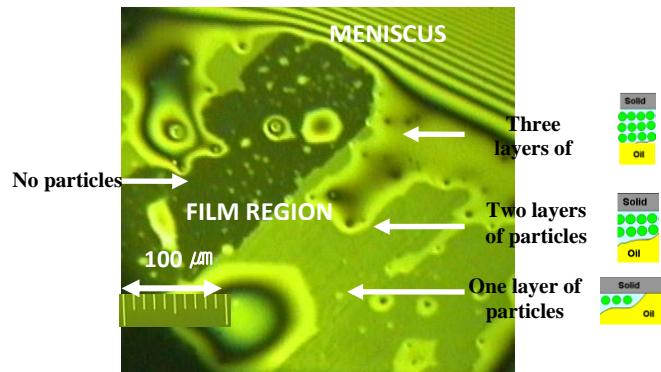


Figure 3. Photomicrograph depicting nanoparticle structural transitions inside a nanofluid film on a solid surface (10 vol% nanofluid). [6]

Both experiments and therefore analyses were carried out by us on the spreading and wetting of nanofluids composed of various concentrations of silica suspensions of 20 nm particles [5]. The foremost predictions from our statics (equilibrium) analysis is

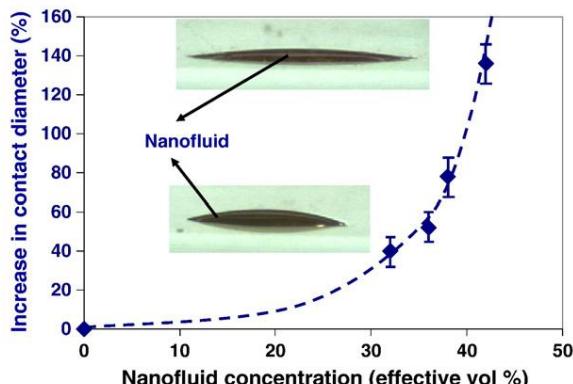


Figure 4. Variation of nanofluid contact diameter with nanofluid concentration in deoiling experiments. [6]

that a suitable compilation of drop size, nanofluid concentration, nanoparticle size and contact angle would result in enhanced spreading of the nanofluid on the solid surface. Experiments revealed that the nanofluids spread forming a thin nanofluid film (inner contact line) between the oil drop and the solid surface. The speed of the inner contact line is seen to increase with an increase in the nanoparticle concentration and the formation of the inner contact line is not seen in pure liquids.

APPLICATIONS

The present talk would explore the technical concept of the nanoparticle structuring in the wedge film with regards to its applications to the oily soil removal phenomena [9]. Specifically, we would discuss using the nanofluids for enhancing oil and gas recovery from petroleum reservoirs, cleansing of oil soils, and removal of bacterial contamination from food contact surfaces.

REFERENCES

- [1] D.T. Wasan and A.D. Nikolov, "Spreading of Nanofluids on Solids" *Nature* **423**, 156-159 (2003).
- [2] A. Chengara, A.D. Nikolov, D.T. Wasan, A. Trokhymchuk and D. Henderson, "Spreading of Nanofluids Driven by the Structural Disjoining Pressure Gradient," *J. Colloid Interface Sci.*, **280**, 192-201 (2004).
- [3] A.V. Chengara, A.D. Nikolov, D.T. Wasan, "New Paradigms for Spreading of Colloidal Fluids on Solid Surfaces," *Advances in Polymer Science*

Vol. 218, Narayanan, R. and Berg J. Eds., Springer-Verlag 117-142 (2008).

- [4] A.D. Nikolov, K. Kondiparty, D.T. Wasan, "Nanoparticle Self-structuring in a Nanofluid Film Spreading on a Solid Surface", *Langmuir* **26**, 7665-7670 (2010).
- [5] K. Kondiparty, A.D. Nikolov, S. Wu, D.T. Wasan, "Wetting and Spreading of Nanofluids on Solid Surfaces Driven by the Structural Disjoining Pressure: Statics Analysis and Experiments", *Langmuir* **27**, 3324-3335 (2011).
- [6] D.T. Wasan, A.D. Nikolov, K. Kondiparty, "The wetting and spreading of nanofluids on solids: Role of the structural disjoining pressure", *Current Opinion in Colloid and Interface Science* **16**, 334-349 (2011).
- [7] K. Kondiparty, A.D. Nikolov, D.T. Wasan, and K. Liu, "Dynamic Spreading of Nanofluids on Solids Part I: Experimental", *Langmuir* **28**, 14618-14623, (2012).
- [8] K. Liu, K. Kondiparty, A.D. Nikolov, and D.T. Wasan, "Dynamic Spreading of Nanofluids on Solids Part II: Modeling", *Langmuir*, **28(47)**, 16274-16284, (2012).
- [9] S. Wu, A.D. Nikolov, and D.T. Wasan, "Cleaning Dynamics of Oily Soil Using Nanofluids", *J. Coll. Interface Sci.* **396**, 293-306, (2013).
- [10] A. Trokhymchuk, D. Henderson, A. Nikolov, and D. T. Wasan, "A Simple Calculation of Structural and Depletion Forces for Fluids/Suspensions Confined in a Film," *Langmuir*, **17**, 16, 4940-4947 (2001).
- [11] D. Boda, K-Y. Chan, D. Henderson, D.T. Wasan and A.D. Nikolov, "Structure and Pressure of a Hard Sphere Fluid in a Wedge-Shaped Cell or Meniscus," *Langmuir* **15**, 13, 4311-4313 (1999).
- [12] M.K. Chaudhury, "Spread the Word About Nanofluids", *Nature*, **923**, 131-132, (2003).