CONDENSATION ENHANCEMENT WITH MICRO AND NANOSTRUCTURED AMPHIPHILIC SURFACES

P.A. Kottke[1], D.M. Anderson[1,2], and A.G. Fedorov[1,2]
[1]Woodruff School of Mechanical Engineering & [2]Institute of Paper Science & Technology
Georgia Institute of Technology, Atlanta, USA

Abstract: We present a novel strategy for condensation enhancement in which controlled thickness of the condensed film, maintained via autonomous action of engineered surfaces, promotes improved condensation behavior. The surfaces passively remove condensed liquid, thus minimizing the length of the conduction path in the condensed film. The key features shared by the two markedly different surfaces we have developed to enable this approach are interconnected hydrophilic sublayers adjacent to the substrate, and hydrophobic superstructures.

Keywords: Smart surfaces, super hydrophobic

INTRODUCTION

In condensation, the thermal conduction resistance of condensed liquid films becomes the controlling heat transfer resistance when convective heat and mass transfer coefficients in the vapor phase are sufficiently large. Our approach to overcome this limit is to minimize the conduction resistance by developing surfaces which autonomously control the condensate film thickness by passively removing condensed liquid from the heat transfer surface, thus minimizing the length of the conduction path in the condensed film. This stands in contrast to most current research efforts in the field, which explore the use of superhydrophobic surfaces to enhance droplet removal prior to film formation, in an attempt to promote perpetual dropwise condensation [1-2].

The first strategy we present is based on adherent amphiphilic nanowire surfaces integrated with the heat transfer surface. We have previously reported on the fabrication and experimental observation of the condensation behavior of surfaces covered with a close packed array of amphiphilic nanowires [3]. Briefly, the nanowire array consists of ~100-200 nm diameter gold (hydrophilic) wires formed through deposition in a porous alumina template. The template is dissolved, leaving high aspect ratio (>> 100) wires with packing fraction of >80%. Plasma-enhanced chemical vapor deposition (PECVD) of the wires with a fluoropolymer produces hydrophobic caps because of the limited hydrophobic precursor penetration into a dense nanowire array, thus yielding the amphiphilic character of the wires. High speed optical visualization, and high resolution environmental scanning electron microscope imaging indicate that for such surfaces larger droplets serve as a reservoir for excess liquid collection, with droplet coalescence driven by a Laplace pressure imbalance between droplets of differing radii of curvature occurring through liquid sublayer flows. This recently described coalescence phenomenon [3] is the key mechanism for film thickness control by amphiphilic nanowire surfaces.

Herein we present a theoretical description of the underlying mechanisms that govern the observed processes in the condensation behavior of the amphiphilic nanowire surfaces. This description, based on an integral form of equations enforcing mass, momentum and energy conservation, enables improved surface design and yields a better understanding of the process in general. Among the key results of the description is the ability to predict the effect of experimentally controllable parameters on observable quantities such as distance between droplets undergoing Laplace pressure induced coalescence.

The second type of enhanced condensation surface we have investigated is prepared via electrophoretic deposition of a 2-D close packed microsphere array

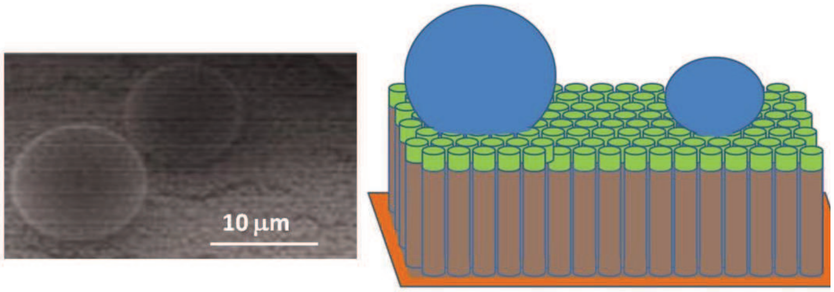

Fig. 1: Environmental SEM image of droplets forming above the hydrophobic superstructure of the nanowire array (left). As depicted schematically, (right) the drops, which rest on the fluorocarbon coated tips (green) of the nanowires, are in hydraulic communication via a liquid sublayer that permeates the hydrophilic (gold) array.

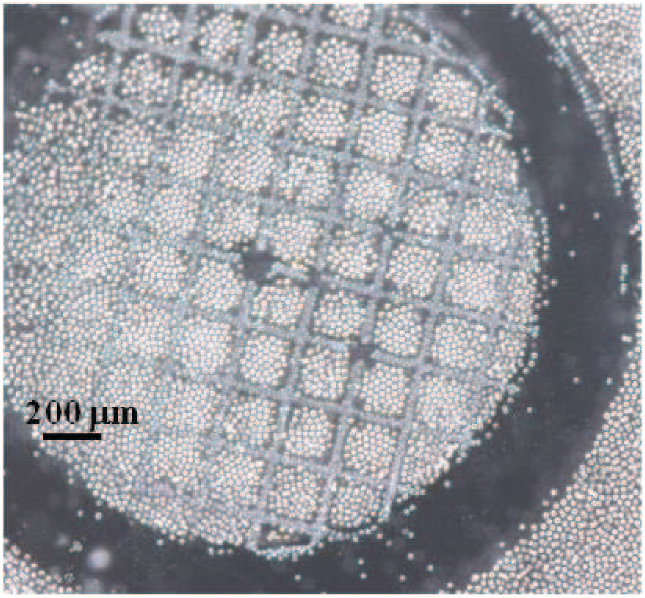

Fig. 2: Optical micrograph of electrophoretically deposited 20 μm diameter polystyrene microspheres. The patterning is due to a spatially varying current density during the deposition processes. The current density variation is a consequence of a patterned gold coating over the indium tin oxide substrate.

on a hydrophilic substrate (Figs. 2 & 3). Although this sort of monolayer assembly has been previously reported for use in soft lithography [4], its use as a heat transfer surface is novel. The microsphere superstructure can be made of inherently hydrophobic (e.g., polystyrene), or hydrophilic (e.g., silica) microspheres. The latter can be modified in a manner similar to that reported for the amphiphilic nanowires, which would yield a hydrophobic top, while the shaded undersides of the spheres and protected substrate could retain their wettability. By covering only selected portions of the heat transfer surface with the amphiphilic microstructure, liquid is passively pumped to “collection lanes” in between for rapid removal via gravity drainage or alternative mechanisms (Fig. 3). We have developed a theoretical model describing the condensation process on these surfaces, which enables prediction of effects of surface energy and feature geometries on obtainable condensation rates.

MODELS

For both surface types, the underlying physics for the models are the same. Condensation occurs at a spatially and temporally varying rate predicted using the assumption that the condensation is limited by the ability of the liquid layer to conduct thermal energy from the liquid/vapor interface to the actively cooled liquid/solid interface. Mass conservation requires that all liquid added through condensation either increases the rate of lateral flow in the liquid layer, or produces a local increase in the thickness of the liquid layer. Capillary and viscous forces dominate the flow of liquid through the micro/ nanostructured. Momentum conservation is imposed using a homogenized form of the Navier Stokes equations, i.e., Darcy’s law. Capillary forces impose a spatially varying pressure field over the liquid that depends on the superstructure geometry, surface properties, and the local thickness of the liquid layer.

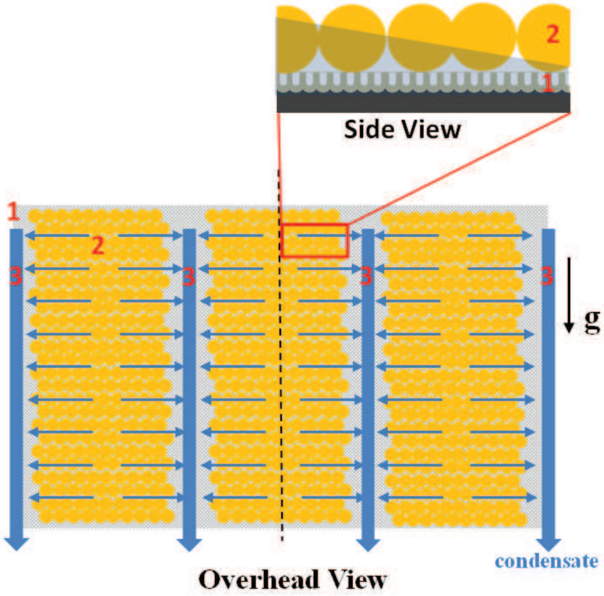

Fig. 3: Schematic depiction of the strategy of patterned microstructured amphiphilic surfaces for condensation enhancement. The strategy is based on surfaces that have (1) an underlying hydrophilic substrate with low energy barrier for nucleation and high roughness, (2) a hydrophobic or amphiphilic superstructure consisting of tightly packed spheres, and (3) regularly spaced reservoirs for liquid collection and removal. Due to the curved superstructure, a Laplace pressure gradient is created that causes the condensed liquid sublayer to flow away from areas of highest condensation rate.

Amphiphilic Nanowires

The model for the droplet coalescence behavior is best understood in the context of the conceptual description of condensation on the amphiphilic nanowire surfaces, following reduction of the substrate surface temperature below the saturation temperature of the vapor to be condensed:

- Film growth through condensation: liquid layer growth occurs at constant (saturation) pressure until the top of the liquid layer reaches the height on the nanowires where the fluorocarbon coating has rendered the surface hydrophobic.

- Pressure increase: The surface energy inhomogeneity pins the contact line, and further condensation creates more positive interface curvatures and therefore higher liquid pressure.
- Initial droplet formation: The curvature reaches a maximum achievable value based on the local geometry and equilibrium contact angle on the fluorocarbon and further increase in meniscus height yields a reduction in curvature.
- Droplet growth: Continued growth results in lower Laplace pressure in the droplet. Liquid from the surrounding region which has higher pressure due to higher local curvatures flows into the droplet, enhancing its rate of growth above that due to condensation. The size of the domain of influence (region of reduced pressure feeding droplet) grows with the droplet.
- Multiple droplet formation: Minor variations in nanowire spacing and fluoropolymer coating depth dictate locations and timing of additional droplets appearing. All droplets grow through combined mechanisms of condensation and influx from surrounding condensed film.
- Coalescence: Simultaneous growth of multiple droplets results in a transient, spatially varying pressure field throughout the condensate layer, with local pressure minima beneath the droplets. Because of different formation times and growth rates, these minima are not equal, and eventually there is a monotonic pressure drop between two droplets. At this point, coalescence of the droplets occurs, with the contents of the smaller (more highly curved) droplet flowing into the larger drop.
- Cascade: Because coalescence leads to a rapid increase in droplet size, it also significantly lowers the pressure in the large post-coalescence droplet and in a rapid manner, which increases the likelihood of additional coalescence events, potentially leading to multiple coalescences occurring nearly simultaneously.

The mathematical model of the surface does not capture the entire process described above. Instead, it is focused on enabling prediction of individual droplet growth rates, and thus is centered on a single droplet (Fig. 4). The model is based on several simplifying assumptions and approaches, including

- Axisymmetry: we consider only growth prior to interaction with other droplets;
- Quasi-steady state growth;
- Droplet is at mechanical equilibrium;
- The liquid film adopts the curvature required to satisfy mass and momentum conservation;
- Darcy Flow Approximation: differential momentum equation integrated across film thickness with permeability of cylinder array found using CFD based simulations;
- Heat flux is uniform outside droplet base, where it becomes negligible (valid for droplet radii much greater than film thickness).

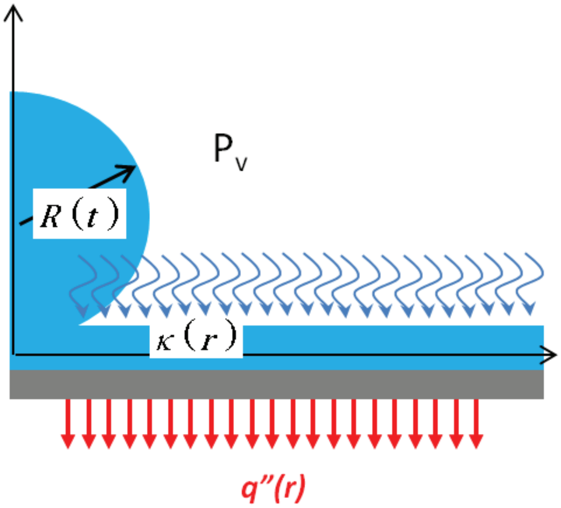

Fig. 4: Axisymmetric droplet growth model geometry.

Hydrophobic Microspheres

The behavior of the surfaces with areas of hydrophobic or amphiphilic microspheres adjacent to liquid “collection lanes” is inherently different than that of the homogeneous amphiphilic nanowire surfaces, as a steady state behavior can be envisaged (due to the presumed ability to remove liquid from the collection lanes), and the effect of liquid layer height on local liquid pressure is quantitatively and qualitatively different. The underlying conservation principles embodied by the model are different, with specific differences being primarily the lack of a transient pressure boundary condition (due to replacement of a growing droplet with a liquid reservoir lane), and a spatially varying liquid layer thickness, with permeability and capillary pressure

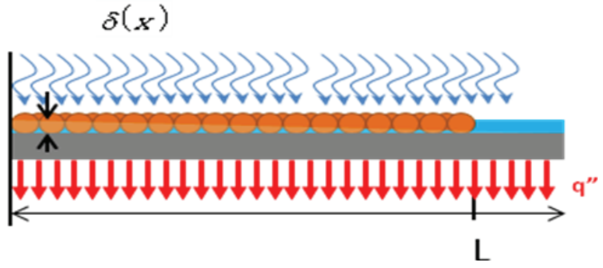

Fig. 5: Model geometry for analysis of behavior of enhanced condensation of the system depicted in Fig. 3.

both functions of local liquid/ vapor interface position (Fig. 5).

RESULTS AND DISCUSSION

The theoretical descriptions of the two amphiphilic micro/ nano-structured surfaces for enhanced condensation serve as a basis for physics based models. The models are then useful in that they can be used to predict the impact of experimentally controllable parameters on observable performance characteristics. For instance, the model of droplet growth on the amphiphilic nanowire surface can be used to predict droplet growth rate as a function of wire density for a given combination of substrate temperature/ water vapor pressure (Fig. 6).

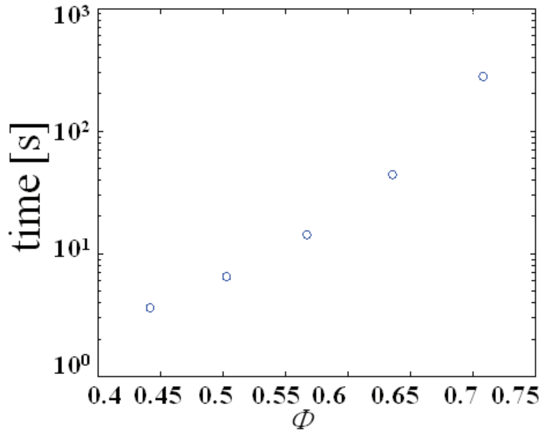

Fig. 6: Using 200 nm diameter nanowires and substrate cooling of 10 K, the model is used to predict the time for a droplet to grow to 50 micron diameter as a function of fractional surface area coverage (Φ).

Similarly, the model for the amphiphilic microsphere monolayer covered surface can be used to predict the impact of sphere size on maximum inter-reservoir spacing, and also to predict the resulting thermal resistance. The results (Fig. 7) indicate that as microsphere size increases, although maximum capillary pressure drops, the flow resistance decreases more rapidly, enabling larger spacing between the “collection lanes”. This spacing increase allows a higher fraction of the surface to be used for active heat transfer, however the film thermal resistance also increases with microsphere size, and thus a tradeoff exits.

CONCLUSION

The approach presented in this work benefits from resting on a clearly understood physical basis, which makes it amenable to theoretical description and thus rational approach to design and optimization.

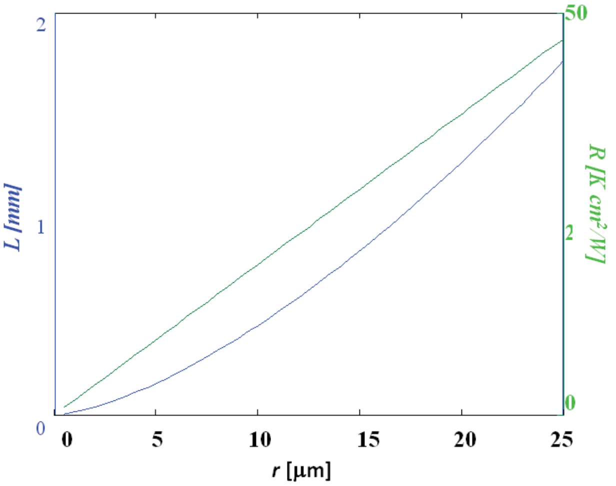

Fig. 7: Model solved for case of mildly hydrophobic uniform microspheres. Reduced thermal resistance, R (green curve), i.e., higher heat transfer coefficient, is obtained with smaller microspheres, but the inter-lane spacing, L (blue curve), must then be reduced as well.

ACKNOWLDEGMENTS: AFOSR BIONIC Center (Award No. FA9550-09-1-0162) provided financial support for this work. DMA was also partially supported by the Paper Science & Engineering (PSE) Fellowship.

REFERENCES

[1] Chen C. H., Cai Q. J., Tsai C. L., Chen C. L., Xiong G. Y., Yu Y., Ren Z. F. 2007 Dropwise condensation on superhydrophobic surfaces with two-tier roughness *Applied Physics Letters* **90** 173108-1 - 173108-3

[2] Miljkovic N., Enright R., Wang E. N. 2012 Effect of Droplet Morphology on Growth Dynamics and Heat Transfer during Condensation on Superhydrophobic Nanostructured Surfaces *ACS Nano* **6** 1776-1785

[3] Anderson D. M., Gupta M. K., Voevodin A. A., Hunter C. N., Putnam S. A., Tsukruk V. V., Fedorov A. G. 2012 Using Amphiphilic Nanostructures To Enable Long-Range Ensemble Coalescence and Surface Rejuvenation in Dropwise Condensation *ACS Nano* **6** 3262-3268

[4] Hayward R. C., Saville D. A., Aksay I. A. 2000 Electrophoretic assembly of colloidal crystals with optically tunable micropatterns *Nature* **404** 56-59