WETTABILITY ON NANOPARTICLE MODIFIED SURFACE: FOR THERMAL ENGINEERING

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DISSERTATION
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ABSTRACT

In many thermal engineering applications, manipulation of the wetting behavior of liquids is used as a heat transfer enhancement strategy. Hydrophilicity, implying better wettability of liquid on solid surface, is preferred in some processes of air-conditioning and power-generation systems, such as dehumidification, evaporative cooled condensers, and pool boiling at high heat flux. Recent research in nanofluid boiling has revealed a manufacturing technique that is promising for air-conditioning and refrigeration applications. Nanofluid boiling on a solid surface induces deposition of the particles on the boiling surface, and these surfaces exhibit enhanced surface wettability. The properties of the deposited nanoporous layer are affected by the nanofluid boiling parameters such as nanoparticle concentration, nanoparticle type and size, solvent liquid type, boiling surface roughness, heat flux, boiling deposition duration and so on. In this thesis, an investigation of the effect of the nanofluid boiling conditions on the resulting wetting behavior of the treated surface is presented. Understanding how the fabrication process influences the wettability enhancement will guide the design of a surface treatment technique to achieve superhydrophilicity. Experimental results show that boiling duration positively affects wettability, but little additional enhancement occurs for durations beyond 10 minutes of NBND. Surface wettability change by NBND is independent of boiling heat flux if the particle concentration is 1 wt.%, while at a low nanoparticle concentration of 0.01 wt.%, heat flux has some random influence. The overall systematic trend observed in the experimental study is that, the higher the nanoparticle concentration, the higher the wettability after NBND process, and at the same time the rougher the surface. The goal is to obtain superhydrophilic surface, which is achieved at high particle concentration (1%wt) NBND. Microscopic analysis gives evidence of particle deposition after NBND. Nanomicro structures were studied using SEM. The images show the growth of “nano-grass” like pseudoboehmite on aluminum surfaces after NBND using alumina nanofluids. Surface
roughness factor was obtained from AFM scan and contact angle measurements independently, but show good agreement. If the coating was to be applied on fins to enhance their wettability, the height of a droplet on the fin surface would be a parameter that would affect the optimization of fin spacing. The higher the wettability, the lower the height of a droplet of fixed volume, so close fin spacing could be for dehumidification. Also, wetting experiments on rough surfaces with a porous coating by NBND at high nanoparticle concentration reveals the involvement of imbibition effect. This suggests the Hemi-wicking mode of wetting. In this thesis, the solid fraction $\phi$ is determined by contact angle data analysis and confirmed by linear fitting of data. Durability of the treated surface under dry conditions was studied by exposure to air. Air-borne contamination reduces surface wettability, but the NBND treated surface remained more hydrophilic than the untreated surfaces. Eventually, the surface treatment loss its ability to enhance wettability. A possible solution is recommendation as a future work. Overall, this study provides an understanding of wettability changes by nanofluid boiling nanoparticle deposition, and provides a guidance to the wettability treatment for thermal engineering applications.
To my parents, for their love and support.
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TABLE OF CONTENTS

LIST OF SYMBOLS ........................................................................................................ viii

1. INTRODUCTION ................................................................................................. 1
   1.1. Background ................................................................................................. 1
   1.2. Literature Review ....................................................................................... 3
       1.2.1 Effect of surface wettability on heat transfer ........................................ 3
       1.2.2 Methods to enhance wettability .............................................................. 4
       1.2.3 Wettability on nanoparticle modified surface ....................................... 7
       1.2.4 Fundamental theory of surface wetting states....................................... 10
       1.2.5 Summary of literature review ................................................................. 19
   1.3. Figures ......................................................................................................... 20

2. EXPERIMENTAL METHODS ............................................................................. 26
   2.1 Introduction .................................................................................................. 26
   2.2 Surface preparation ..................................................................................... 27
       2.2.1 Substrate roughness control .................................................................. 27
       2.2.2 Preparation of nanofluids ...................................................................... 29
       2.2.3 The pool boiling experiment ................................................................. 31
   2.3 Tables ........................................................................................................... 35
   2.4 Figures ......................................................................................................... 37

3. EXPERIMENTAL RESULTS ............................................................................... 45
   3.1 Introduction .................................................................................................. 45
   3.2 The effect of boiling time ............................................................................. 46
   3.3 The effect of boiling heat flux ...................................................................... 47
   3.4 The effect of nanoparticle concentration ...................................................... 48
   3.5 The effect of surface roughness .................................................................. 50
   3.6 The effect of nanoparticle size and material ................................................. 52
   3.7 Figures ........................................................................................................... 54

4. SURFACE ANALYSIS ......................................................................................... 61
   4.1 Introduction .................................................................................................. 61
   4.2 Topography .................................................................................................. 62
       4.2.1 Micro-nano structures on the surface .................................................... 62
       4.2.2 The effect of nucleate boiling on surface morphology ....................... 66
       4.3 The effect of air-borne contamination ...................................................... 69
       4.4 The wetting states ..................................................................................... 70
       4.4.1 Observation of Wenzel’s state of wetting ............................................. 70
       4.4.2 Observation of hemi-wicking state of wetting ..................................... 73
4.4.3 Semi-empirical wettability model for hydrophilic surface.................. 76
4.5 Tables................................................................. 80
4.6 Figures ............................................................. 81

5. CONCLUSIONS AND RECOMMENDATIONS ....................... 100
5.1 Conclusions from current work ........................................ 100
5.2 Recommendations for future work .................................... 103
5.2.1 Future work to study topography .................................. 103
5.2.2 Recommendation on surface chemistry study .................... 105
5.2.3 Future work for thermal engineering application .................. 107

REFERENCES ......................................................................... 109
APPENDIX ............................................................................. 119
LIST OF SYMBOLS

A  Area

F  Helmholtz free energy

h  Heat transfer coefficient

I  Electrical current

k  Thermal conductivity

N  Molecular quantity

n  Number of molecules; number of measurements

P  Pressure

q"  Heat flux

r  Roughness factor

Ra  Arithmetic roughness

S  Entropy

T  Temperature

U  Internal energy; electrical voltage
\( V \) \hspace{1cm} \text{Volume}

\( v \) \hspace{1cm} \text{Specific volume}

**Greek letters**

\( \gamma \) \hspace{1cm} \text{Surface tension}

\( \delta \) \hspace{1cm} \text{Thickness}

\( \theta \) \hspace{1cm} \text{Apparent contact angle}

\( \theta_Y \) \hspace{1cm} \text{Young's contact angle}

\( \mu \) \hspace{1cm} \text{Chemical potential}

\( \phi \) \hspace{1cm} \text{Solid fraction}

**Subscripts**

\( lv \) \hspace{1cm} \text{Liquid-vapor interface}

\( sl \) \hspace{1cm} \text{Solid-liquid interface}

\( sv \) \hspace{1cm} \text{Solid-vapor interface}
1. INTRODUCTION

1.1. Background

For a range of engineering applications, including air conditioning, refrigeration, power generation, electronics cooling, and others, engineers seek to manipulate the wetting behavior of liquids on solids in the presence of a gas, as part of an overall heat transfer enhancement strategy. The desired wetting behavior depends on the physical nature of the process and the requirements in the application. In some circumstances, hydrophilicity, which implies a relatively lower free energy at the solid-liquid interface than the solid-gas interface, is superior. In applications such as dehumidification in air-conditioning systems, and evaporative cooling of condensers in refrigeration, air-conditioning and power-generation systems, hydrophilicity is preferred because better wettability improves the performance of the system. In nuclear power plants, as well as the cooling process of electronic devices, better wettability enhances critical heat flux (CHF) in pool boiling [1], which improves the reliability and performance of these systems [2]–[5]. Another case is the condensation process, where a hydrophilic solid surface possesses lower energy barrier for condensate nucleation and better drainage of the liquid phase, both of which have positive impact on heat and mass transfer [6]–[8]. Other cases are frosting and defrosting. Frost formed on a hydrophilic surface is denser and thus exhibits higher thermal conductivity than that on hydrophobic surfaces [9][10], mitigating a series of problems accompanying with the growth of frost. All of these facts point to the positive effect of hydrophilicity on the performance of the aforementioned thermal processes, which saves energy on a system level of view.

Clean metal surfaces are hydrophilic [11], so metals used in thermal processes are inherently hydrophilic. However, to further enhance surface wettability, certain treatment to
change the solid-liquid interfacial energy is required. Interfacial energy is a function of temperature, pressure, surface chemistry and solid surface topography [12]. In thermal engineering, the temperature, pressure and the type of the fluid are often determined by the working conditions and the needs in applications. Thus, wetting behavior is often manipulated by two means: controlling solid surface chemical composition, and modifying solid surface topography.

Wettability manipulation techniques have been an active area of research, especially over the last two decades. Meanwhile, the development in micro/nano scale manufacturing technology nurtures novel surface wettability manipulation techniques. However, in air-conditioning and refrigeration applications, methods that are more cost effective than typical micro-fabrication are needed. Recent research in nanofluid boiling has revealed a manufacturing technique that might be suitable for air-conditioning and refrigeration applications. Nanofluid boiling on a solid surface induces deposition of the particles on the boiling surface, and these surfaces exhibit enhanced surface wettability. The properties of the deposited nanoporous layer are affected by the nanofluid boiling parameters such as nanoparticle concentration, nanoparticle type and size, solvent liquid type, boiling surface roughness, heat flux, boiling deposition duration and so on. In this research the effect of the boiling conditions on the resulting wetting behavior of the treated metal surface is investigated. The goal is to understand how the fabrication process influences the wettability enhancement, which could guide the design of a surface treatment technique to achieve super-hydrophilicity. Aluminum is used as the substrate material in this study, since it is one of the most commonly used materials for heat transfer in HVAC&R applications.

The following section presents a review of technical literatures on the methods of wettability manipulation. The review focuses on related work on nanoparticle modified surfaces and the effect of wettability on heat transfer processes.
1.2. Literature Review

1.2.1 Effect of surface wettability on heat transfer

Interfacial energy and the force balance at the contact line are important for multiphase heat and mass transfer, especially at submillimeter scale. The spreading of a liquid on a solid surface affects many thermal processes, such as boiling and evaporation, condensation and frosting and defrosting. Hydrophobicity and hydrophilicity have been studied theoretically and experimentally for their impact on heat transfer.

Under certain conditions, better wetting behavior provides enhancement in thermal-hydraulic performance. One of such case is condensation of water on the air-side of a compact heat exchanger. According to literature [6], slit-fin-and-tube heat exchangers that have fin spacing of 1.2 mm, which is smaller than the capillary length of water, were reported to have a significantly lower Fanning friction factor once the fins are treated to be hydrophilic, with no penalty on heat transfer. A similar study was reported by Kim and Webb [13]. They tested hydrophilic fins for multiple wet/dry cycles in a wind tunnel and concluded that the overall performance of superhydrophilic fins is superior to untreated ones, up to 1000 wet/dry cycles. This indicates that hydrophilic treatment of fin surfaces saves fan power without sacrificing the air-side heat transfer. Thus, hydrophilicity can be preferred for its positive influence on thermal-hydraulic performance of a heat exchanger. Another case is the formation of frost. Liquid condensation morphology on solid surface is a strong function of wettability. Hence, the structure of early stage frost, which is the frozen condensate, depends on wettability to a large extent. It has been reported by Hoke and co-workers [10], that frost grown on a hydrophilic surface is denser and thinner in the early stage than on a hydrophobic surface, and it exhibits a higher thermal conductivity even in the mature stage of frost growth. Even though superhydrophobic surfaces can potentially delay frost formation, contamination and longevity are issues have not been satisfactorily resolved. For the case of boiling, hydrophobicity is superior in bubble nucleation while hydrophilicity benefits bubble departure [1] [14]. Spreading of the liquid is critical for boiling at high heat flux. Liquid rewetting on the superheated solid surface can be improved by hydrophilic treatment, which is considered to enhance critical heat flux (CHF) in pool
boiling [1] [2] [15]. Similarly, in evaporative cooling applications, enhanced liquid spreading can potentially help to generate a uniform layer of thin liquid film to alleviate dry-out phenomenon and improves mass transfer. It has been reported by Takata [15] that the evaporating falling fill is stabilized at low Reynolds number by hydrophilic surface treatment. Enhancing liquid wettability on solids, often metals, is an active area of research.

1.2.2 Methods to enhance wettability

Wetting is a physical process in which the overall gas-liquid-solid interfacial energy is minimized. In thermal-fluid science and engineering, the property and state of the working fluid are designed to serve a specific purpose and working condition. As a result, the liquid-gas surface energy is often predetermined, leaving solid surfaces available for manipulation. Thus, solid surface property control has become the focus of research. Various methods have been developed to obtain super-hydrophilic or more generally, super-wetting surfaces.

In order to enhance evaporation or boiling heat transfer, micro-nano-porous structures have been made to obtain better wetting performance on surfaces.

Xiao and coworkers from MIT enhanced liquid wetting for thin film evaporation by utilizing anodized aluminum membranes with nano-size pores on top of micro-size liquid channels [5]. The porous membrane is applied directly on the heat transfer surface, and the capillary force is in parallel to the direction of heat flow. Heat flux as high as 960 kW/m² was achieved using isopropanol. This approach enhances the local capillary driving force for wetting at no cost of viscous resistance in liquid channels, since the two forces are normal to each other and the porous membrane is thin. Even though surface roughness factor is not reported, the idea to utilize capillary force is valuable.
Coso et al. fabricated a biporous structure by lithography and etching on silicon [16]. Micro-scale pin fins are packed between larger sized channels. Such a surface enhances local wicking effect to enhance heat transfer. On a vertical plate, the surface achieved up to 1200 kW/m² heat flux with water evaporation. The authors could control the pin diameter and channel width precisely in a search for the optimum geometry. Even though the author did not report a number for roughness factor nor solid fraction. According to the pillar dimensions given in the paper, the roughness factor ranges from about 10 to 20, and the solid fraction for wicking mode is about 0.06.

The above surface manipulation methods and other similar designs are very effective and can be precisely controlled. They are promising in electronics cooling applications. In many other thermal systems, such as HVAC&R and power generation, the component sizes are much larger, as is the area for heat transfer is huge. A method that is more cost effective than typical MEMS techniques is needed, to mass produce super-wetting surface.

One of the most popular method to chemically enhance wettability of larger surface area is to coat with TiO₂ and irradiate with UV light. TiO₂ is a photocatalyst that can be activated by ultraviolet light to break down organic compounds. At the same time, OH groups are adsorbed onto the surface, making the surface superhydrophilic. Its application for antifogging and self-cleaning was first proposed by Fujishima [17], and it has been widely used as a coating on glass windows. Later Takata introduced such surface treatment to enhance boiling and evaporation heat transfer [15]. The author reported a stabilized liquid film for low Reynolds number falling film evaporation, enhanced critical heat flux of pool boiling, a higher Leidenfrost temperature and a higher heat transfer coefficient for thin film evaporation. However, the superhydrophilic state does not survive long. The contact angle could increase from 0° to 20° during 4 hours of darkness (without UV light). This means that such treatment is not suitable for many thermal components. A coating that does not rely on UV light would offer advantage.

For HVAC engineering, dehumidification process is important. Condensate water drainage behaviour has a big impact on component and system level performance.
In thermal engineering applications, material surfaces are usually not atomic smooth in topography, nor homogeneous in chemistry. This leads to contact angle hysteresis. In other words, the contact angle when liquid drop is in advancing is larger than the contact angle when liquid is receding. When a liquid drop is under gravity or shear force, its tendency to move is hindered by the retention force generated from contact angle hysteresis. Thus, a “smooth” aluminum fin surface often has water droplets hanging vertical.

One way to prevent this problem is to make a surface, where water can form a continues film. An example is the droplets on windows in a rainy day, where a film or a stream of water drains faster than isolated droplets. On an aluminum fin, the water film will be able to drain smoothly towards the bottom or the far edge of the fin, driven by gravity or shear force from airflow. If the surface wettability is high, then water automatically spreads on the surface. Contact angle on such surfaces is nearly zero, and so does the contact angle hysteresis. Thus, hydrophilic fin coatings are used in many HVAC&R systems. Unfortunately, such high energy surface degrades extremely fast in air. If the coating is a very smooth layer, then the coating itself also degrades fast because of the adsorption of contamination. Since the chemistry of a “dirty” surface is complicated, the contact angle hysteresis is often high.

To enhance the performance of HVAC&R components, surfaces where heat transfer with phase change occurs can be treated with optimum plasma zone process (OPZ) [18]. The process requires gas feeding, DC bias of 1kV and vacuumed chamber, in order to generate plasma. The polymer coating has hydrophilic functional groups that chemically enhances wettability, and the coating has 0.1-0.2 micro meter particles that adds roughness to enhance wettability. Coated surfaces show a contact angle of about 20°, and can maintain hydrophilic for at least 500 days if the surface is stored/immersed in water. Kim and coworkers coated copper tubes with the polymer by OPZ [19]. They reported 40% enhancement of overall heat transfer coefficient for plain copper tubes, and up to 26% for
low-finned tubes.

Kim and Webb applied the OPZ surface treatment to coat fin stock for dehumidification applications [13]. They conducted 1000 wet/dry cycles by dipping and drying the surface repeatedly. For every 250 wet/dry cycles, they measured wettability. They found that contact angle stayed at about 20° for 1000 cycles. Also, pressure drop for wetted heat exchangers is reported in the paper for up to 500 wet/dry cycles. At 500 wet/dry cycles, the air-side pressure drop of the coated surface is only 30% higher than for dry conditions, while the untreated one is 90% higher than for dry conditions. Consequently, if the same fan power is applied, the hydrophilic coating helps to increase cooling capacity by about 10%.

Such polymer coatings do not maintain hydrophilicity for long in dry air, which is a non-polar environment. Exposing the treated surface to air for as short as a week would result in total loss of hydrophilicity, because the chemically treated surface has the tendency to lower its energy. By dipping the treated surface in distilled water shortly after it gets dry, helps to maintain the hydrophilic state of the coating [13], [18], [19]. Overall, these surface treatments that rely on surface chemistry changes, often experience issues of longevity when in use. The question then arises whether super-hydrophilicity can be achieved in a scalable process by topography manipulation. Recent research [20]–[24] suggests that nanofluid boiling nanoparticle deposition (NBND) is one of the alternatives.

1.2.3 Wettability on nanoparticle modified surface

Over the past decade there has been intensive study of heat transfer enhancement by nanofluids for both pool boiling [20]–[22], [25], [26] and flow boiling [2], [27]–[29]. It has been found that critical heat flux (CHF) can be enhanced by nanofluids, due to the presence of a layer of nanoparticle deposition. According to Kim, Kwark and many other researchers, such a porous layer is responsible for the change of surface wettability [20], [21], [25], [26]. Thus, deposition of nanoparticles from the suspension during the boiling process is potentially a simple way to modify surface wettability.
The literatures includes reports of pool boiling experiments conducted on NiCr wires and stainless steel surface using Al₂O₃, TiO₂, and SiO₂ nanoparticle water suspensions [20], [22], [30]. A dramatically lowered static contact angle of water indicates that such treatment strongly enhances wettability. The mechanisms of such deposition processes have been investigated by Kwark and co-workers. Their experimental results indicate that, in a well dispersed aqueous nanoparticle suspension, nanoparticles can only be deposited effectively when boiling occurs on the substrate. This was considered to be a direct consequence of microlayer evaporation at the base of the vapor bubble during nucleate boiling [26]. More generally, liquid evaporation at the receding contact line is the reason for the deposition process of micro/nano particle suspensions [31]. This phenomenon has been as well observed in a drying droplet [32], [33], and evaporating film at a receding meniscus [34]. Boiling and drying of nanofluids both lead to evaporation-induced particle deposition.

A model for the early stage growth of the deposited layer during nanofluid boiling was proposed by Ganapathy and Sajith [35]. According to their model, the early stage deposition process is a function of the nanofluid boiling parameters such as nanoparticle concentration, particle size, solvent liquid type, boiling surface roughness, heat flux, boiling deposition duration and so on. Experimental results have been reported indicating surface roughness changed after the boiling deposition of nanoparticles. Some reported an increase in roughness, while others reported a decreased or unchanged roughness after boiling a metal substrate in nanofluids [36]. According to Kim and coworkers [21], the initial substrate surface roughness influences the final surface topography after the boiling deposition. Because substrate roughness determines the number of cavities for bubbles to nucleate during boiling, while the bubble growth and departure is the cause of particle deposition, the initial roughness will directly affect the early stage of particle deposition process. Moreover, the scale of the cavities compared to that of the particles or agglomerated groups will lead to either filling of the cavities to make it more smooth or adding roughness on top of the surface during the deposition process.

The nanoparticle layer deposited on to the surface after boiling in nanofluids changes surface wettability, because surface chemical composition and topography are modified. In 2006,
Kim and coworkers reported that boiling of nanofluids enhances critical heat flux due to wettability enhancement [21]. They modeled the wettability enhancement by Wenzel’s wetting theory and validated by surface analysis using AFM. Later in 2007, Kim and Kim proposed an additional effect that influences critical heat flux in nanofluid boiling [20]. They argued that the porous layer of nanoparticle deposition generates capillary wicking effect in the spreading of liquid. They demonstrated that the porous layer of coating also improves the capillary wicking, which enables a superior rewetting ability to prevent the propagation of dry-patches in transition boiling regime. This contributes to the higher CHF of boiling on nanoparticle deposited surface. Rough and porous surface texture causes liquid to wet the surface by both spreading and imbibition, which cannot be characterized by the Wenzel nor Cassie-Baxter model. The wetting mode is described as the hemi-wicking mode, as introduced by Quere to characterize such a regime of wetting [37]. In this regime, liquid would be much more effectively supplied to prevent dry patches. This argument was supported by data of surface wettability and critical heat flux in their paper [20]. Observation from the current experiments, which will be presented later in this thesis, suggests that both Wenzel’s wetting model and the hemi-wicking model (the models will be introduced in section 1.2.4) can be descriptive, depending on the NBND condition.
1.2.4 Fundamental theory of surface wetting states

Surface wettability can be manipulated in many different ways, but the basic concept is the same in terms of physics and chemistry. So the theory of surface wettability is the first thing to be introduced here.

Consider a system where a liquid droplet is in contact with a solid surface and surrounded by a vapor, as shown in Figure 1.1. There are three interfaces in the system, namely the liquid-vapor interface \( lv \), the solid-liquid interface \( sl \) and the solid-vapor interface \( sv \). Assume temperature and volume of the three phases are kept constant and there is no chemical reaction, then the thermodynamic equilibrium of the system is reached when the Helmholtz free energy of the system is minimized with respect to the solid-liquid interfacial area \( A_{sl} \) [12]. Helmholtz free energy \( F \) is defined in Equation (1.1). The total Helmholtz free energy is the sum of the Helmholtz free energy of the bulk liquid, vapor, solid phases and the three interfaces (Equation (1.2)). Differentiating both side of Equation (1.1) results in Equation (1.3) for the bulk phases, and Equation (1.4) for the interfaces, where is the interfacial energy or surface tension and \( A \) represents the area of an interface.

\[
F = U - TS \tag{1.1}
\]

\[
F_{total} = F_l + F_v + F_s + F_{lv} + F_{sl} + F_{sv} \tag{1.2}
\]

\[
dF = -SdT + \mu dN - PdV \tag{1.3}
\]

\[
dF = -SdT + \mu dN - \gamma dA \tag{1.4}
\]

Suppose an infinitely small perturbation causes a reversible change of the system while
keeping the temperature and volume constant. Then the total effect can be expressed by differentiating Equation (1.2), substituting Equation (1.3) and (1.4) into it and applying the fact that $T$ and $V$ are constants, results in Equation (1.5). Conservation of species gives Equation (1.6) meaning that the total number of molecules in the system is constant (no chemical reaction occurs). Substitute Equation (1.6) into Equation (1.5) and consider the fact that at thermodynamic equilibrium, the chemical potential $\mu$ is the same in all parts of the system. We can thus obtain Equation (1.7).

\[
dF = (\mathcal{S}dT + \mu dN - PdV) + (\mathcal{S}dT + \mu dN - PdV)_s
\]
\[
+ (\mathcal{S}dT + \mu dN - \gamma dA)_v + (\mathcal{S}dT + \mu dN - \gamma dA)_w
\]
\[
+ (\mu dN_i + \mu dN_v + \mu dN_w) + (\gamma_{iv} dA_{iv} + \gamma_{iw} dA_{iw} + \gamma_{iv} dA_{iw})
\]  
(1.5)

\[
dN = dN_i + dN_v + dN_s + dN_v + dN_w + dN_i + dN_s + dN_v = 0
\]  
(1.6)

\[
dF = \gamma_{iv} dA_{iv} + \gamma_{iw} dA_{iw} + \gamma_{iv} dA_{iw}
\]  
(1.7)

It is obvious from Figure 1.1 that the advancing of solid-liquid interface results in a receding of the solid-vapor interface for the same amount of area, expressed by Equation (1.8). As stated previously, thermodynamic equilibrium of this system Figure 1.1 corresponds to the minimum of the total Helmholtz free energy with respect to the area of the solid-liquid interface $A_{sl}$. This statement is expressed by Equation (1.9). Substituting Equation 1.8 into it gives Equation (1.10), which is the basis of later discussion.
\[ dA_{sv} = -dA_{sl} \quad (1.8) \]

\[ \frac{\partial F}{\partial A_{sl}} = \frac{\partial}{\partial A_{sl}} (\gamma_{lv} dA_{lv} + \gamma_{sl} dA_{sl} + \gamma_{sv} dA_{sv}) = 0 \quad (1.9) \]

\[ \gamma_{lv} \frac{dA_{lv}}{dA_{sl}} + \gamma_{sv} - \gamma_{sl} = 0 \quad (1.10) \]

If the solid material is ideally smooth and homogeneous, then the area change of the liquid-vapor interface can be expressed in terms of the change of solid-liquid interfacial area by the cosine of the contact angle \( \theta_Y \), as Equation (1.11). The schematics is in Figure 1.2.

\[ dA_{lv} = dA_{sl} \cos(\theta_Y) \quad (1.11) \]

Substituting Equation (1.11) into Equation (1.10) and rearranging gives Equation (1.12), which is called the Young’s Equation. This relates the easily observable geometry to the interfacial energies, which is determined by the physical and chemical nature of the liquid, vapor and solid phases. If \( \theta_Y \) is an acute angle, then the solid material is considered to be hydrophilic (Figure 1.2(a)). If \( \theta_Y \) is an obtuse angle, then the solid material is considered to be hydrophobic by its nature (Figure 1.2(b)).

\[ \cos(\theta_Y) = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (1.12) \]
However, engineering surfaces are not perfectly smooth nor perfectly homogeneous. Roughness and heterogeneity of the solid surface would result in the change of the state at equilibrium for a system as shown in Figure 1.1.

If the surface is homogeneous but rough, then the “trenches” or “valleys” of the rough surface can be invaded with water, as shown in Figure 1.3. The actual solid-liquid interfacial area and the projected area underneath the liquid drop can be related by a roughness factor $r$, defined by Equation (1.13). Consequently, the relationship between liquid-vapor interfacial area $A_{lv}$ and the solid liquid interfacial area $A_{sl}$ is now Equation (1.14). Substituting Equation (1.14) into Equation (1.10) gives Equation (1.15). Using Equation (1.12), the cosine of this actual contact angle $\theta$ on a rough surface can be expressed by the Young’s contact angle $\theta_Y$ (on an smooth surface), as displayed in Equation (1.16). This model was proposed by Wenzel in 1936 [38], and this mode of wetting is often called the Wenzel state of wetting. Note that the roughness factor $r$ is always larger than unity in reality, so the contact angle on a rough surface $\theta$ should be smaller than $\theta_Y$, if $\theta_Y$ is an acute angle, and $\theta$ should be larger than $\theta_Y$, if $\theta_Y$ is an obtuse angle. In other words, the Wenzel’s theory suggests that the naturally hydrophilic solid material would be more wettable by water if the solid is roughened, and vice versa. The roughness factor, $r$, is a parameter directly related to the topography of the solid surface.

$$r = \frac{\text{actual surface area}}{\text{projected surface area}}$$  \hspace{1cm} (1.13)

$$dA_{lv} = \frac{\cos(\theta)}{r} dA_{sl}$$  \hspace{1cm} (1.14)
\[
\frac{\cos(\theta)}{r} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}
\]  
(1.15)

\[
\cos(\theta) = r \cos(\theta_f)
\]  
(1.16)

If the liquid “sees” the surface as planar but chemically heterogeneous, one commonly observed case is that the liquid only wets the asperities of the surface, and the “valleys” have trapped air forming liquid-vapor interface under the liquid cap. This wetting state differs from the prediction of Wenzel’s model. In this case, wetting at the solid-liquid interface is heterogeneous, as shown in Figure 1.4. A parameter that represents the percentage of the wetted area (asperities) out of the total area underneath the liquid cap is introduced. It is often called the solid fraction \( \phi_s \), and is defined by Equation (1.17). Using this parameter, the \( dA_{lv} \) can be expressed in Equation (1.18). In Equation (1.18), is simply the differential of total area underneath the liquid cap. The term \( \cos(\theta) \) accounts for the change of the liquid-vapor interface on the liquid cap, and the term \((1 - \phi_s)\) accounts for the liquid-vapor interface underneath the liquid cap. Substitute Equation (1.18) and Equation (1.12) into Equation (1.10), and rearrange, and we have Equation (1.19). This model was proposed by Cassie and Baxter in 1944 [39]. As a result, this mode of wetting it is often referred to as Cassie-Baxter wetting state. The solid fraction \( \phi_s \) is a parameter related to the topography and is difficult to determine for a randomly rough surface.

\[
\phi_s = \frac{\text{area of the solid–liquid interface}}{\text{total area underneath the liquid cap}}
\]  
(1.17)
In order to determine whether the liquid on the solid surface is in the Cassie-Baxter state or not, a criterion must be evaluated. The thermodynamic criterion can be found by comparing the Helmholtz free energy of the Wenzel state to that of the Cassie-Baxter state. Since the comparison is for identical temperature, volume and shape, the energy in the bulk phases are the same, only the surface energy needs to be compared. Equation (1.20) gives the surface energy of Wenzel’s wetting model, and Equation (1.21) gives that of Cassie-Baxter’s wetting model, where $A_{\text{cap}}$ is the surface area of the liquid cap and $A$ is the total projected area under the liquid cap. For Cassie-Baxter state of wetting to be favorable, $F_{\text{Surface,Cassie}}$ must be less than $F_{\text{Surface,Wenzel}}$. This gives the inequality (1.22). Substitute Equation (1.12) into (1.22) and rearrange, and we have Equation (1.23) as the criteria for Cassie-Baxter state of wetting to be stable thermodynamically. Note that Equation (1.23) involves the Young’s contact angle, which represents the chemical nature of the material, and the roughness factor and solid fraction, representing the topography. It is always true that $\phi_x \leq 1 \leq r$; therefore, thermodynamically stable wetting in Cassie-Baxter state, there must be $\cos(\theta_x) \leq 0$, which means that the solid material must be hydrophobic. For a hydrophilic material such as brass, it is still possible to make a surface texture to obtain Cassie-Baxter state of wetting of water, which has been achieved by researchers [40], but the system is in a metastable state.

\[
F_{\text{Surface,Wenzel}} = \gamma_{lv} A_{\text{cap}} + \gamma_{sl} r A
\]  

(1.20)
\[ F_{\text{Surface, Cassie}} = \gamma_{lv} \left[ A_{\text{cap}} + A(1 - \phi_s) \right] + \gamma_{sl} \phi_s A + \gamma_{sv} (r - \phi_s) A \quad (1.21) \]

\[ \gamma_{lv} \left[ A_{\text{cap}} + A(1 - \phi_s) \right] + \gamma_{sl} \phi_s A + \gamma_{sv} (r - \phi_s) A < \gamma_{lv} A_{\text{cap}} + \gamma_{sl} r A \quad (1.22) \]

\[ \cos(\theta_f) < \frac{\phi_s - 1}{r - \phi_s} \quad (1.23) \]

In another case, the liquid does not only wet the “trenches” and “valleys” of the rough solid surface underneath the liquid cap, but also wets them beyond the area of the cap, as shown in Figure 1.5. It is sometimes referred to as “impregnated Cassie-Baxter” state of wetting, or more intuitively called the hemi-wicking wetting, since both wetting and wicking are involved in this process, as stated in the literature [37]. The fraction of solid-vapor interface that would be replaced by solid-liquid interface if the liquid drop advances is the solid fraction \( \phi_s \). The resulting relationship between \( A_{lv} \) and \( A_{sl} \) is then expressed as Equation (1.24). Substitute Equation (1.24) and Equation (1.12) into Equation (1.10), and rearrange, we have Equation (1.25).

\[ dA_{lv} = \frac{\cos(\theta) - (1 - \phi_s)}{\phi_s} dA_{sl} \quad (1.24) \]

\[ \cos(\theta) = \phi_s \left( \cos(\theta_f) - 1 \right) + 1 \quad (1.25) \]

There is a prerequisite for the hemi-wicking state, that is criterion establishing that a penetrating film of liquid must develop, while keeping the plateaus dry. The criterion for this can be obtained by comparing the energy of a dry solid surface (Figure 1.6(a)), and the
surface energy of a solid with liquid penetrated in its roughness (Figure 1.6(b)). Energy of a dry surface is expressed as Equation (1.26). That of a wetted surface is expressed as Equation (1.27), where A is the total projected area. Thermodynamically, the criterion for the wet case to occur is that \( F_{\text{wet}} < F_{\text{dry}} \). Subtracting Equation (1.27) from Equation (1.26), and substituting Young’s Equation (1.12) gives the inequality (1.28). This implies that the formation of a penetrating liquid film is favorable if the inequality 1.28 is satisfied. This was proposed by Bico, Thiele, and Qur in their paper published in 2002 [37], and it is now taken as the criterion for the transition from Wenzel state to hemi-wicking state of wetting.

\[
F_{\text{dry}} = \gamma_{sv} rA \tag{1.26}
\]

\[
F_{\text{wet}} = [\gamma_{lv} (1 - \phi_s) + \gamma_{sl} (r - \phi_s) + \gamma_s \phi_s] A \tag{1.27}
\]

\[
\cos(\theta_f) > \frac{1 - \phi_s}{r - \phi_s} \tag{1.28}
\]

Shibuichi et al. in 1996 [41] published the experimental data for the three different state of wetting by measuring water static contact angles on fractal surfaces. Bico et al. in 2002 [37] explained the theoretical basis of the hemi-wicking wetting regime to interpret the data and discussed the transition between states. For the current research, the focus is on hydrophilic and superhydrophilic surfaces. The goal is to enhance surface wettability. Therefore, the Wenzel regime, the hemi-wicking regime and the transition between them is to be investigated. Figure 1.7 summarizes these two wetting models and the transition criterion by plotting the relationship between the cosine of the apparent contact angle \( \theta \) on a rough surface, and the cosine of the Young’s contact angle \( \theta_Y \). The plot shows \( \cos(\theta) \) versus \( \cos(\theta_f) \) for different roughness factors and solid fractions. Roughness factor \( r \) is the slope of the Wenzel wetting regime, referring to Equation 1.16. The higher the roughness factor
the steeper the slope, so the more sensitive the value of $\cos(\theta_r)$ (apparent wettability) is to the difference of $\cos(\theta_r)$ (the chemical nature of the material). The value of the solid fraction $\phi$ demonstrates a direct impact on the transition point, “turning point” on the plot. The larger the solid fraction, the earlier the transition into hemi-wicking state. In other words, it is easier for less hydrophilic material to be wet in a hemi-wicking regime, if the solid fraction of the topography is of a larger value. One could imagine that, larger solid fraction would result in a smaller capillary diameter (refer to Figure 1.6), and thus higher capillary force to drive the wicking process. Intuitively, it would be easier for the wicking of the roughness to occur in such case, so the hemi-wicking state of wetting could occur on a less hydrophilic material (smaller $\cos(\theta_r)$ ) if the solid fraction $\phi$ is larger.

The fundamental theory of wetting models provided in the literatures have been introduced above. Even though there are researchers questioning the Wenzel and Cassie-Baxter models, the apparent contact angle $\theta$ on a rough surface is a function of the Yong’s contact angle $\theta_y$, the roughness factor $r$ and the solid fraction $\phi$. Note that the Yong’s contact angle is only determined by the chemical nature of the three phases, as described by Equation (1.12). The roughness factor $r$ and the solid fraction $\phi$ are directly related to topography of the solid surface. It can be concluded that wetting phenomena is governed by both the surface chemistry and topography. This is buttressed by the fact that combinations of chemistry and topographical modification are the basis of engineering efforts to manipulate wettability on solid surfaces.
1.2.5 Summary of literature review

The merits of hydrophilic and superhydrophilic surfaces have been recognized to benefit heat transfer when phase change occurs. There are many techniques to enhance surface wettability based on modifying surface chemistry, topography or both, in order to benefit component performance in thermal systems. Deposition of nanoparticles by boiling or evaporation of its suspension has been demonstrated to change surface wettability. This method is potentially a more cost effective surface treatment suitable for HVAC&R applications. However, there is limited information about wettability control by such method. Only very limited information can be found on the coupled boiling and deposition process in nanofluids, and even less about the influence of substrate roughness on the treated surface topography and wettability after boiling. There has been no published work to date, reporting a systematic experimental study to understand the role of various nanofluid boiling parameters on the surface properties after such treatment. The parameter space is large, including, nanofluid concentration, solvent liquid type, nanoparticle size and species, surface heat flux and boiling duration, and substrate material and roughness. Other evaporative-induced deposition methods, such as evaporation of volatile solvent liquid by spraying are also subject to investigation.

In this thesis, a comprehensive evaluation of the aforementioned parameters on the surface topography and wettability after nanoparticle deposition by boiling or evaporating its suspension (so-called nanofluid) is presented. Analysis is presented on the wetting behavior of the treated surface using wetting state models. Also presented is the durability of the hydrophilic coating after NBND. Especially the effect of exposure to dry air, since air is typically laden with organic contaminations that would lower the surface energy and reduce wettability, and because exposure to air is universal to HVAC&R applications.

The results of this work leads to a fundamental understanding of the resulting surface wettability after deposition of nanoparticles. Thus, the research informs the design of a surface treatment technique to achieve superydrophilicity, so as to benefit the thermal-hydraulic performance of heat transfer devices.
1.3. Figures

Figure 1.1: Schematics of a system at equilibrium: liquid in contact with a solid surface in a vapor environment.
Figure 1.2: Young-Laplace contact angle of liquid on an ideally smooth homogeneous solid surface: (a) the solid is a hydrophilic material, (b) the solid is a hydrophobic material.
Figure 1.3: Schematics of Wenzel wetting state of liquid on a rough solid surface.

Figure 1.4: Schematics of Cassie-Baxter wetting state of liquid on a rough solid surface.
Figure 1.5: Schematics of Hemi-wicking (impregnated Cassie-Baxter) wetting state of liquid on a rough solid surface.
Figure 1.6: Schematic of a textured surface (cross section view): (a) the surface is dry, (b) the notches are filled with water.
Figure 1.7: Apparent surface static contact angle on a heterogeneous surface versus the Young’s contact angle, plotted by varies roughness factors $r$ and solid fractions $\phi$. 
2. EXPERIMENTAL METHODS

2.1 Introduction

In order to investigate surface wettability change after nanofluid boiling nanoparticle deposition (NBND) process, the role of various parameters needs to be evaluated. According to the literature, the coating process is the result of microlayer evaporation at the bottom of the vapor bubbles during nanofluid boiling [26], [35]. Therefore, boiling parameters such as boiling heat flux and boiling time are potentially factors that could influence the coating, which changes both surface roughness and wettability[21], [24], [36], [42]. Moreover, during the boiling process, the roughness of the hot surface directly effects the number of cavities for bubble nucleation[12], [35], [36]. Surface roughness not only affects the deposition of nanoparticles, but also plays an important role in boiling heat transfer. After the NBND treatment, the measured apparent surface wettability is also affected by roughness [39], [43], [44]. Figure 2.1 demonstrates the relationship of each factor on wettability change by NBND. The complex interplay of surface roughness, nanofluid boiling condition and surface wettability is not well understood, each parameter should be investigated systematically. The parameters are of two categories: one is the material properties, the other is the boiling conditions. For the material properties, there are parameters such as, nanoparticle size, nanoparticle type, nanoparticle shape, nanoparticle concentration, solution fluid type, and substrate material. For the boiling conditions, there are parameters such as boiling heat flux, boiling duration and initial substrate roughness. Based on the application background for this research, the substrate material is aluminum, the nanoparticle materials are alumina and silica, and the solvent liquid is water. The parameters investigated here are nanoparticle size, concentration, substrate roughness and boiling heat flux. After NBND, surface wettability and roughness are measured by conducting contact angle experiment. In this chapter, the experimental method to investigate the role of above parameters on wettability after NBND is described in detail.
2.2 Surface preparation

The surface preparation includes surface roughness control and preparation of nanofluids before boiling, followed by nanofluid pool boiling nanoparticle deposition process.

2.2.1 Substrate roughness control

Since roughness plays an important role in nucleate boiling and thus affects the surface morphology after nanoparticle deposition, surface roughness control is critical. For this study, an isotropic surface with well controlled roughness is required. However, initially, specimen surface as received was observed to be anisotropic, because strips and grooves of certain pattern can be seen by the naked eyes. These patterns could be caused by machining. To confirm this, surface wettability and roughness of an as received sample were measured. Because of its anisotropic nature, contact angle and roughness factor are measured both parallel and perpendicular to the surface pattern. Before surface characterization, each specimen was cleaned by washing in acetone, and then isopropanol, followed by deionized water, and again wash with isopropanol. Nitrogen was used to dry the surface thoroughly. Surface roughness was measured by a Tencor Alpha P-10 profilometer set on a vibration isolated table. The profilometer has a 5 μm radius 60° cone stylus tip, which has a maximum vertical resolution of 0.0012 μm. The surface was scanned over a length of L=1000 μm, at a speed of 5 μm/s, and the sampling rate was 100Hz, which results in a lateral resolution of 0.05 μm. A filter with cutting length of 400 μm (about the diameter of a sessile droplet in the contact angle experiment) was used to cut off the surface waviness. The stylus scanned the surface in both perpendicular and parallel direction to the strip pattern. Figure 2.2 is the surface profile. Obviously, the roughness pattern varies with direction. Quantitative analysis of surface roughness was done by calculating the arithmetic roughness Ra. Its formula is Equation (2.1). For perpendicular scanned profile, Ra=0.9 μm, while for parallel scan profile Ra= 0.2 μm. This means that the surface is far from isotropic.
\[ Ra = \frac{1}{L} \int_{0}^{L} |Z(x)| \, dx \]  

(2.1)

Wettability was also characterized on the as received surfaces. The static contact angle experiment was conducted with 5.5μL water droplets, and measured at three different locations on each surface, namely center, edge and corner. The average contact angle of these three locations is used as the characteristic wettability of the surface. Typical sessile droplet contact angles are shown in Figure 2. When the camera is directed in parallel to the strip pattern, the contact angle is 109° (Figure 2a), while 94° (Figure 2b) was recorded with camera perpendicular to the stripes. It is believed that, such difference in contact angle is caused by the isotropic surface pattern.

In order to have isotropic surface with well controlled roughness, surface sanding/lapping process was performed. The top surface of each specimen was sanded on a flat sanding sheet with soap water for lubrication, and the trace of movement was pattern “8” for 200 times. It was insured that the initial anisotropic surface pattern was fully removed, and the isotropic roughness is only associated with the grit size of the sand paper. 60 grit silicon carbide sanding sheets were used to obtain rough substrates. The abrasive particle size on 60 grit silicon carbide sand paper is large, so that it does not remain on the surface after cleaning by nitrogen. 400 grit alumina sanding sheets were used to obtain smooth surfaces. In order to obtain flat ultra-smooth surfaces, a lapping machine (Lapmaster 12) was used. The lapping slurry was alumina abrasive powder in a water-based fluid. The alumina abrasive particles that are two to three orders of magnitude larger than the nanoparticles. By cleaning the surface with IPA-DI water and Nitrogen. After cleaning, the surfaces were inspected using optical microscope and SEM. Occasionally, an unidentified particle of tens of micrometers could be observed. However, that is not capable to impact the topography such that it makes a significant difference on wettability.
Surface profile of the rough substrates, smooth substrates and ultra-smooth substrates were characterized by the profilometer. Each surface was scanned multiple times in different directions. Typical surface profiles of each type of surface are shown in Figure 2.4. The data of Ra for each scan is listed in Table 1 in the Appendix, as well as the method to estimate uncertainty. The arithmetic roughness factor was found to be $1.2 \pm 0.2 \mu m$ for the rough substrates, $0.27 \pm 0.1 \mu m$ for the smooth substrate and $0.01 \pm 0.01 \mu m$ for the ultra-smooth substrate.

The surface wettability was tested by a static contact angle experiment with 5.5μL water droplet, and measured center, edge and corner. The average is used to characterize the wettability of the surface. Images of surfaces of different roughness types and the photos from contact angle measurements are shown in Figure 2.5. The static contact angle of an ultra-smooth surface was slightly higher than 90 degrees, because of the contaminants adsorbed from air, which is often the case for metal surfaces of thermal devices [45]. These characterized aluminum surfaces are used as the substrate for the next step treatment, namely boiling in pure water or various types of nanofluids.

### 2.2.2 Preparation of nanofluids

The nanofluid was prepared by dispersing dry nanoparticle powder in pure water. Alumina or silica powder was weighed to 0.01 g accuracy using a precision balance (Mettler AE200). A 50 mL Erlenmeyer flask was used to mix the nanoparticle with pure water to make a mixture of high nanoparticle concentration. The flask is then placed into a room-temperature Ultrasonic Bath (Brasonic 1510R), with 30 minute of ultra-sonication at a vibration frequency of 42 kHz. The energy density of ultra-sonication, which aided dispersion, was $7.2 \times 10^4$ kJ/m$^3$, calculated according to NIST [46], which effectively dispersed the hydrophilic alumina particles in DI water. A near uniform dispersion of nanoparticles in water was achieved. Then the fluid was mixed with pure water. The final concentrations of the nanofluids were controlled by the mass ratio of nanoparticle and water.
added. The concentration, size and type of water based nanofluids are listed in Table 2.1. Deposition of nanoparticle was done by pool boiling of the listed nanofluids.

The nominal size of nanoparticles listed in Table 2.1 is the number provided by the vendor: 40-50 nm alumina from Alfa Aesar, 13 nm alumina and 10-20 nm silica from Sigma Aldrich, 300 nm alumina and 60-70 nm silica from US nano. However, particle size in water suspension also need to be studied. This was done in two ways: dynamic light scattering and SEM imaging. During the nanofluid preparation process, the suspension that was observed to be the most stable and well dispersed was 13 nm Al₂O₃, so dilute 13 nm alumina water suspension was the first to be investigated using dynamic light scattering. Anton Paar Litesizer 500 was used to measure the particle size and zeta potential of the suspension. Kalliope Professional software was then used to process the data. Results are shown in Figure 2.6. The peak of the size distribution occurs at 107 nm, which is an order of magnitude higher than the anticipated 13 nm diameter. The results indicate that the particles are agglomerated in the fluid. In order to estimate the actual particle sizes, SEM images of particles were recorded. Nanofluids were made and one drop of each type of nanofluid was placed on clean glass slides. After a while, water evaporated, so the glass slide was coated with nanoparticles by evaporative coating method, similar to the mechanism of NBND. The coated glass slides were then sputtered with gold to make the surface conductive for SEM imaging. The results are shown in Figure 2.7 and Figure 2.8. Detailed information of calculation for particle size estimation from these SEM images is provided in the Appendix. Overall, the sizes estimated from SEM images are close to the nominal sizes advertised by the vendors. The only exception is the 65 nm SiO₂ nanoparticle. Its size is only 24 nm, very close to the 15 nm nominal size SiO₂ nanoparticle. As a result, the nanofluids made from these two kinds of nano-powders are considered as the same type.

Zeta potential of 13nm Al₂O₃ nanoparticle water suspension was measured. The measurement was done in an Omega cuvette cell at temperature of 24 °C. Zeta potential distribution function is shown in the Appendix Figure 5. It was found that both the mean zeta potential and the peak of distribution are about 43 mV, which is commonly seen in
well dispersed $\text{Al}_2\text{O}_3$ colloidal suspension in water, and can be stable for a couple of days. For this study, NBND experiment was conducted immediately after the nanofluid was made using the sonication bath. As a result, the nanofluid for NBND process are well dispersed colloidal suspensions.

2.2.3 The pool boiling experiment

The three liter boiling vessel is shown in Figure 2.9. It has sensors hanging from the top and the specimen inserted through the bottom. The top plate has a vent, cooling coil, a K-type thermocouple and an absolute pressure sensor. Temperature and pressure readings were captured by an NI 9213 module and recorded by LabVIEW. The heater and specimen are located at the bottom center of the vessel. The test specimen is levelled with the top surface of a PTFE block.

Detailed structure of heating section and the specimen is shown in Figure 2.10. The test specimen is a 2 cm $\times$ 2 cm $\times$ 9 cm aluminum block. A 2 cm $\times$ 2 cm $\times$ 0.2 cm square WatLow ULTRAMIC ceramic heater located under the aluminum blocked is used to heat the specimen. The top surface of the heater and the bottom surface of the specimen is firmly in contact with each other, secured by the force of the spring underneath the heater. A K-type thermocouple was used to measure the temperature of the heater to monitor the heating process. Another two K-type thermocouples were inserted into 0.5 $\times$ 5 mm holes in the aluminum specimen, 6.4 mm below the boiling surface, to monitor the temperature of the aluminum. DC current was supplied to the heater by a power supply (Agilent Technologies N5771A). During the boiling process, LabVIEW recorded the current and voltage of the heater, which was then used to calculate the heat flux by Equation (2.2), in which “Area” is 2 cm $\times$ 2 cm. Also recorded were the temperature of the specimen and the boiling pool.

$$q^* = \frac{UI}{\text{Area}} \quad \text{(2.2)}$$
Before starting the boiling deposition process, the pool is heated to degas and later sustain at near saturation temperature by a circular shape auxiliary heater located at the bottom of the vessel (Figure 2.9 (b)). When the temperature reading for the pool is near the saturation temperature and varies within the uncertainty of the thermocouple (0.3 K) over 10 minutes, it is considered as steady state, and the boiling deposition process can start. The DC voltage on the heater is set constant by the power supply during boiling deposition processes, so that a prescribed heat flux at the boiling surface is maintained. The pool boiling deposition process is kept at a constant heat flux for a certain length of time. The specimen temperature was utilized to calculate the boiling surface temperature by Fourier’s law of conduction, as shown in Equation (2.3), where the δ is the distance between the thermocouple hole and top specimen surface (6 mm) and k is the thermal conductivity of AA6061 (16 W/m-K). The heat transfer driving potential ΔT is the difference between pool temperature $T_{pool}$ and the specimen top surface temperature $T_{w}$ (Equation (2.4)). With the above parameters calculated, heat transfer coefficient can be easily found using Equation (2.5).

Uncertainties of measurements are listed in Table 2.2. The heat loss is calculated by a model (using ANSYS) of the heating section. The modeling result is then compared to the measured temperature inside the specimen, and agreed within 0.2 K difference. This is
included in the uncertainty of the heat flux.

Near uniform heat flux was generated to the best effort. It is ensured by the following factors:

1) The heater: a special ceramic heater (ULTRAMIC) was used to heat up the specimen. According to the manufacturer (Watlow), the advanced ceramic heater construction uses aluminum nitride with a uniform grain size, and the circuit layout in the heater is optimized. Because of these, uniform temperature is achieved.

2) Flatness: Surface flatness of the heater is 0.05mm with less than 1.5 um roughness of surface finish. For the aluminum block, the top surface and bottom surface are made to be parallel under a stringent manufacturing process, carried out by the most skilled technician in the machine shop. As a result, uniformity at the heater could propagate to the top surface of the aluminum specimen.

3) Leveling: The top surface is the boiling surface, and its leveling is ensured by the sample holder and the adjustable legs of the pool, in order to ensure a horizontal surface boiling.

4) The pool: The pool is significantly larger than the specimen, and the temperature was kept at near saturation by an auxiliary heater located at the bottom of the pool.

5) The surface: Uniformity roughness and wettability of the original substrate was ensured in the preparation of the substrate, which is described in section 2.1 of the paper.

6) Insulation: The specimen was mounted in a sample holder made of PTFE by silicone. The heater was insulated inside a thick PEEK block. In addition, the whole heating section was insulated by 2in thick EPDM rubber insulation material.
In summary, uniformity was ensured from the heat source and heat conduction path to the boiling surface with minimized heat loss from the side, and the well prepared horizontal specimen surface in the controlled pool environment should lead to a near uniform boiling heat transfer coefficient. As a result, heat flux at the surface should be nearly uniform.

Experimental conditions for NBND process at various heat flux, surface roughness and nanofluid concentrations are shown in Table 2.3. After the nanofluid boiling nanoparticle deposition process, the specimen was removed carefully from the bottom of the pool, ready for wettability characterization.
2.3 Tables

Table 2.1: List of varies concentration of nanofluids made from different size and material of nanoparticles used in this study.

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material density [g/mL]</td>
<td>3.97</td>
<td>2.4</td>
</tr>
<tr>
<td>Size [nm]</td>
<td>13 50 50 50 300</td>
<td>15 65</td>
</tr>
<tr>
<td>Weight Percentage %</td>
<td>1.0 1.0 0.1 0.01 1.0</td>
<td>0.6 0.6</td>
</tr>
<tr>
<td>Number density per mL</td>
<td>2×10¹⁵ 4×10¹³ 4×10¹¹ 4E+11 2×10¹¹</td>
<td>1×10¹⁵ 2×10¹³</td>
</tr>
<tr>
<td>Volumetric concentration %</td>
<td>0.25 0.25 0.025 0.0025 0.25</td>
<td>0.25 0.25</td>
</tr>
</tbody>
</table>

Table 2.2: Uncertainty of measurements

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling heat flux [kW/m²]</td>
<td>±10 %</td>
</tr>
<tr>
<td>Nanoparticle concentration [wt.%)</td>
<td>±0.001</td>
</tr>
<tr>
<td>Contact angle [Degree]</td>
<td>±0.5 ~ ±4</td>
</tr>
<tr>
<td>Arithmetic roughness factor Ra [µm]</td>
<td>Rough substrate ±0.1</td>
</tr>
<tr>
<td></td>
<td>Smooth substrate ±0.05</td>
</tr>
<tr>
<td></td>
<td>Ultra-smooth substrate ±0.01</td>
</tr>
</tbody>
</table>
Table 2.3: Deposition of 50 nm Al₂O₃ on different substrates, by boiling aqueous nanofluid of various concentration over a range of heat flux.

<table>
<thead>
<tr>
<th>heat flux (kW/m²)</th>
<th>0.01 wt% (0.0025 vol%)</th>
<th>0.1 wt% (0.025 vol%)</th>
<th>1 wt% (0.25 vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>Smooth substrate</td>
<td>\</td>
<td>Smooth substrate</td>
</tr>
<tr>
<td>100</td>
<td>Smooth substrate</td>
<td>\</td>
<td>Smooth substrate</td>
</tr>
<tr>
<td></td>
<td>Rough substrate</td>
<td>Rough substrate</td>
<td>Rough substrate</td>
</tr>
<tr>
<td>150</td>
<td>Smooth smooth</td>
<td>ultra-smooth</td>
<td>ultra-smooth</td>
</tr>
<tr>
<td>200</td>
<td>Smooth substrate</td>
<td>\</td>
<td>Smooth substrate</td>
</tr>
<tr>
<td>300</td>
<td>Smooth substrate</td>
<td>\</td>
<td>Smooth substrate</td>
</tr>
</tbody>
</table>
2.4 Figures

Figure 2.1: The complex interplay between boiling heat transfer, surface roughness, surface wettability and the NBND process.

Figure 2.2: Surface-profile of both perpendicular and parallel scan of the specimen as received from machine shop.
(a) As received specimen, CA=109°. Camera parallel to the direction of trenches.

(b) As received specimen, CA=94°. Camera perpendicular to the direction of trenches.

Figure 2.3: Contact angle experiment on a surface as received after machining.
Figure 2.4: Surface profile of specimens: rough, smooth and ultra-smooth surfaces.

(a) Ultra-smooth substrate  (b) Smooth substrate  (c) Rough substrate

Figure 2.5: Microscopic images and the static contact angle of water on substrate of varies roughness: (a) Ra=0.01 µm, (b) Ra=0.27 µm, (c) Ra=1 µm.
Figure 2.6: Particle size distribution obtained by dynamic light scattering (DLS) of 13 nm alumina water based nanofluid.
(a) 13 nm nominal size Al₂O₃ particle. SEM image indicates an average particle size of 21 nm

(b) 40-50 nm nominal size Al₂O₃ particle. SEM image indicates an average particle size of 71 nm

(c) 300 nm nominal size Al₂O₃ particle. SEM image indicates an average particle size of 577 nm.

Figure 2.7: SEM image of different size alumina nanoparticles on glass slides.
(a) 15nm nominal size SiO$_2$ particles. SEM image indicates an average particle size of 18 nm.

(b) 65nm nominal size SiO$_2$ particles. SEM image indicates an average particle size of 24 nm.

Figure 2.8: SEM image of different size silica nanoparticles on glass slides.
Figure 2.9: The boiling pool with instrumentation: (a)schematic of the side view showing instrumentations, (b) photo of the vessel showing the black circular auxiliary heater at the bottom of the vessel
Figure 2.10: Heating section and the specimen: (a) 2D side view with instrumentation, (b) 3D assembly in ANSYS model.
3. EXPERIMENTAL RESULTS

3.1 Introduction

As stated in the previous chapter, the parameters studied here that could impact the surface wettability after nanofluid boiling nanoparticle deposition (NBND) are: the boiling duration, boiling heat flux, surface original roughness, the nanoparticle concentration in the suspension, particle size and type.

Experiments have been conducted using the method described in the previous chapter. During the experiment, the aforementioned parameters could have complex interaction with each other together with boiling heat transfer, as demonstrated previously in Figure 2.1. In order to investigate the role of each parameter, experiments have been done changing the parameters one at a time with the rest controlled. For instance, in order to study the role of nanofluid boiling heat flux on surface wettability, experiments have been conducted at heat flux ranging from 50 kW/m$^2$ to 300 kW/m$^2$, while all other parameters are controlled to be the same by using 50 nm Al$_2$O$_3$ nanofluid of 0.01 wt.% particle concentration and boiled for 10 minutes on smooth surface for any heat flux investigated. The resulting surface wettability for each set of parameters was characterized and plotted against the varying parameter. In this way, the significance of each parameter can be found. Based on such method, the effects of these parameters on surface wettability and their interaction with the nanofluid boiling nanoparticle deposition process are discussed one by one in this chapter.
3.2 The effect of boiling time

According to the literature [26][35], deposition of particles happens near the three phase contact line of micro-layer evaporation process when a bubble nucleates. The nano-porous layer grows faster when the particle concentration is high. In order to study the effect of boiling duration, a low concentration suspension of 0.001 wt.% (0.00025 vol.%) was used. The boiling heat flux was $140 \pm 5 \text{kW/m}^2$. At this heat flux, the boiling process was within nucleate boiling regime, far above the onset of nucleate boiling and far below the film boiling regime. The aluminum substrates were polished to ultra-smooth finish before they were treated by boiling deposition process. Figure 3.1 shows the water static contact angles and the cosines of contact angles on aluminum surfaces. The data show the wettability of aluminum surfaces boiled in pure water, as well as that of the aluminum surfaces boiled in nanofluid for 10 minutes and 30 minute. These data are compared to surface wettability before boiling. The decrease in water static contact angle indicates that the wettability was enhanced after boiling in pure water. This is the result of pseudoboehmite grown on the aluminum surface when in contact with hot water [46]. The contact angle decreased even after boiling the surface in very low concentration nanofluid for 10 minutes, and longer boiling time seems to have a positive effect on wetting behavior. However, this trend is very weak in comparing the 30 minutes case with the 10 minute case. This result agrees with the reported wettability change in literature [47]. Park and coworkers used NiCr wires to study the nanoparticle deposition by boiling 50 nm alumina nanofluids and found that wettability was independent of time after 500 seconds or about 8 minutes of boiling. The current study shows that the effect of boiling time on wettability for wires and plane surfaces has been confirmed to be steady in less than about 10 minutes of boiling, regardless of the huge difference in shape of the surfaces. A possible explanation is that, after 10 minutes of NBND, the substrate surface is already fully covered by nanoparticle deposition, so more deposition on top of the porous layer does not further alter changing the surface wettability. This effect strongly depends on the concentration of particle in the suspension [35]. In fact, the surface treated by 30 minutes of NBND do not appear to be very different from that treated by 10 minutes of NBND. The work done by Huitink and coworkers [48] inspires one other aspect of possible explanation to this. During the
vigorous boiling process, the liquid shear force acts on the porous nanoparticle deposition layer, and may remove loosely deposited particles. This effect is dictated by fluid dynamics, and would have little to do with the particle concentration of the nanofluid.

In the following sections, the concentrations used in NBND processes were 10 to 1000 times larger than here. As a result, even on rougher substrates, little change on wettability could happened beyond 10 minutes of NBND. Moreover, the growth of nanoporous layer by NBND is faster at higher concentration [35]. Since 10 minutes is enough for this low concentration case of 0.001 wt%, it is more than sufficient for 0.01 wt%, 0.1 wt% and 1 wt% cases. It is concluded that the first 10 minutes of boiling deposition process contributes the most of surface modification. As a result, in the investigation of other parameters in section 3.3 to section 3.6, the boiling process was limited to 10 minutes.

3.3 The effect of boiling heat flux

The bubble departure frequency is related to the heat flux, nucleation site density, and the regime of the boiling process. As stated previously, these parameters are considered to influence the deposition of nanoparticles during nanofluid boiling process. Consequently, varying the heat flux of the boiling process will change the morphology of the coated layer after deposition of particles, and hence influence the wetting behavior of the surface after such treatment. Figure 3.2 presents the cosine of the water static contact angle versus the heat flux during the nanofluid boiling process. The boiling was on sheet aluminium which has a roughness factor similar to that of a smooth substrate in the previous experiments. At relatively high nanoparticle concentration, there were always enough particles deposited onto the surface no matter what heat flux during the nanofluid boiling process. Consequently, all of the surfaces became superhydrophilic. However, it is demonstrated that at low nanoparticle concentration of 0.01 wt%, heat flux has some influence on the wettability. The general trend is that, for boiling heat flux higher than 100 kW/m², increasing the heat flux enhances wettability. At low heat flux, the bubbles sometimes stayed on the surface and did
not depart, or even collapsed during the experiment, due to a small degree of liquid subcooling. This leads to continuous deposition of particles at the three phase contact line of the bubble, while very little deposition on other spots. The resulting surface topography is highly heterogeneous, with a thick layer of porous coating in some region, and hardly any coating in others. The droplet size used in the static contact angle experiment was 5 µL, which exceeds the size of the heterogeneous morphology.

Overall, for the range of heat flux studies in this experiment (in the nucleate boiling regime), heat flux of NBND has some random influence on the resulting wettability if the concentration of nanofluid is low. And heat flux does not have significant impact on the resulting wettability after NBND if the concentration of nanofluid is high.

### 3.4 The effect of nanoparticle concentration

An interesting result was observed from boiling heat transfer analysis. Figure 3.3 shows the result for varies nanoparticle concentrations of 50 nm Al₂O₃ aqueous nanofluid, and the data are grouped by substrate roughness. The horizontal axis in log scale, represents nanoparticle concentration by weight percentage, and the left end of the axis represents pure water boiling cases. It is known that roughness has an impact on the boiling process because of its direct relationship to cavities and nucleation. The rough surface has higher heat transfer coefficient, because it has more surface area and active cavities in this study. Interesting to notice is that, there is a relationship between the nanoparticle concentration and the boiling heat transfer coefficient. Heat transfer tends to be enhanced by low or medium concentration nanofluids, while higher concentration of nanoparticle in the fluid has a deterious effect on heat transfer. This trend is general for all roughness types of substrates (initial boiling surfaces). The phenomenon has to do with the tradeoff between the positive aspects of nanofluid boiling nanoparticle deposition: creation of some active nucleation cavities and the enhanced surface wettability; and the negative aspects of nanofluid boiling nanoparticle deposition: filling up of some active cavities and the added
conductive heat transfer resistance by the accumulation of the particle deposition. Such effects are complicated and not very well understood. The investigation of surface wettability after nanofluid boiling in a range of nanoparticle concentration, and the change of surface roughness for different types of substrates could give some insight into this problem. In this section, the effect of nanoparticle concentration on surface wettability after NBND is discussed.

Nanofluids for a range of particle concentrations have been used to modify aluminum surface. After NBND surface wettability was characterized to reveal the effect of nanoparticle concentration. In this section, nanoparticle concentration is represented by weight percentage. The method to control nanoparticle particle concentration during nanofluid preparation method has been described in section 2.2.2 Preparation of nanofluids. For each category of substrate roughness, NBND experiments have been conducted at a heat flux of 140 ± 5 kW/m² for 10 minutes, using 50 nm Al₂O₃ nanoparticle to prepare nanofluids of a range of concentrations, namely 0 wt.% (pure water), 0.01 wt.%, 0.1 wt.% and 1 wt.%. The resulting wettability is compared to that of the specimens before boiling (baseline). Data are plotted in Figure 3.4 and grouped by substrate roughness: ultra-smooth in green, smooth in blue, rough in black. The straight lines represent wettability of each type of substrate before any surface treatment. Cosine of water static contact angles for each type of substrate have been plotted against the nanofluid concentration of NBND. Contact angle in degrees are shown by the data label. The percentage of nanoparticle concentration is plotted on logarithm scale. It is impossible to have a zero point on the logarithm scale. However, for the purpose of comparison only, the data points for pure water cases, which have 0 wt.% of nanoparticle concentration, are placed on the left edge of the chart.

It was observed that, for a surface that is originally ultra-smooth, the water contact angle dropped to 47° after boiling in pure water (green circle on the left edge of the chart). This is the result of chemical reaction between hot water and the aluminum substrate, which forms pseudoboehmite [46]. It is a type of aluminum oxide hydroxide, which thus contains hydroxyl groups that enhances the affinity to water molecules. On macro scale, it exhibits
as enhancement of water wettability. When boiled in 0.01 wt% nanofluid, the water static contact angle decreased to 31° after boiling, indicating an enhancement in wettability. As the concentration of nanoparticle in suspension goes up to 0.1 wt% and 1 wt%, wettability is enhanced even more, showing that the water static contact angle decreases to 27° and 22°, respectively. This implies that enhancement of surface wettability is induced by nanoparticle deposition. The higher the nanoparticle concentration in the suspension the stronger the enhancement after boiling deposition treatment. Similar trend of wettability change can be observed on smooth (blue squares) and rough (black triangles) substrates treated by NBND process. For the cases when the smooth and rough aluminium surfaces are treated by 1 wt.% nanofluid NBND, their data almost overlap at \( \cos(\theta) \) approaching unity, which indicates superhydrophilic state of wetting.

Comparing the three series of data plotted in Figure 3.4, it is clear that, the original roughness of the substrate itself plays a role in the final wettability of the surface after nanoparticle deposition. This motivates the investigation into topography. A straightforward way is to study surface roughness

### 3.5 The effect of surface roughness

Topography can be modified by particle sedimentation during nanofluid boiling. Surface roughness of each specimen was measured after NBND process using profilometry described in the Chapter 2 section 2.2.1 Substrate roughness control. Shown in Figure 3.5 are the surface roughness Ra before and after boiling treatment in nanofluids of various concentrations. Data are grouped by the substrate type: the initially ultra-smooth substrate, initially smooth substrate and the rough substrate. Apparent from Figure 3.5 is a systematic trend that, surface roughness increases as nanoparticle concentration increases. This behavior results from a rapid creation of a heterogeneous coating during nucleate boiling of a nanofluid, which roughened the surface. The higher the particle concentration, the more effective the build-up of the rough layer. This trend is general, except for the very rough surfaces boiled in 1 wt.% nanofluids. A possible explanation may be that, during
NBND process on a very rough surface, some of the particles were filling the trenches by particle deposition, making it smoother, while the others added on top of its roughness making it rougher. The overall outcome appears to be no significant change of roughness after NBND.

Also apparent from Figure 3.5 is that, substrate type is playing a role. In this experiment, the original substrate topography significantly affects the roughness after boiling. For instance, after boiling a smooth surface in 1 wt.% nanofluid (shown as triangle), its surface roughness is the maximum in its series of data. However, its roughness Ra is still less than that of a rough substrate (black dashed line in Figure 3.5). This explains the data in Figure 3.6, which are discussed in the following paragraph.

It has been explained in Chapter 1 section 1.2.4, that surface wettability strongly depends on the topography. In Wenzel’s model, it is the roughness factor r. In the Cassie-Baxter and the hemi-wicking models, it is the solid fraction ϕ. In these models, the cosine of the apparent static contact angle is expressed as a function of the factors r or ϕ. Therefore, even though surface roughness data are the arithmetic roughness Ra, it is still interesting to plot the wettability data against Ra. Cosine of water static contact angle on boiling treated surfaces were plotted against the arithmetic roughness Ra in Figure 3.6. This gives an idea of how the surface wettability is related to roughness. The plot demonstrates that surface wettability and roughness are positively related. Data are grouped by the substrate type. It is found that the group of rough substrate data shifts to the right in comparison to the smooth and ultra-smooth cases. This is because on the rough substrate is the dominating factor in determining the surface roughness even after boiling treatment, as has been explained by the discussion of Figure 3.5 on the significant role of substrate roughness. Nevertheless, the general trend in Figure 3.6 is consistent: the rougher the surface the higher the wettability, which agrees with the wetting models for hydrophilic surface [37], [43], [44]. As described in Equation (1.16) and (1.25), topography plays an important role in the determination of the apparent contact angle. The figure shows that for both the smooth and rough substrates after NBND, topography was modified to an extent that made a highly wetting surface with cos(θ) approaching unity.
3.6 The effect of nanoparticle size and material

For section 3.2 to 3.6, results have been shown on the wettability of surfaces after NBND using nanofluids made from one type of nanoparticle, Al₂O₃ particles of nominal size 50 nm, so that other parameters can be studied. In this section the size and material of nanoparticles are discussed. In order to study the effect of particle size on the resulting wettability after NBND, alumina particles of different sizes have been studied. Nominal sizes of the particles are: 300 nm, 50 nm and 13 nm. A detailed size study of these particles was described in Chapter 2 section 2.2.2 Preparation of nanofluids, Figure 2.7, Figure 2.8 and the Appendix. Even though there are some discrepancies between the sizes measured under SEM and the size claimed by the vendors, the discrepancy is small compared to the size difference between different types of particles. As a result, the convention is used that particles are labeled by the nominal sizes claimed by the vendors.

Nanofluids made from each size of alumina particles have been used in the NBND process to coat the ultra-smooth (mirror like finish) substrate. The concentration of the nanofluids was 1.0 wt.%. Boiling was imposed using a heat flux of about 145 kW/m² and the duration was 10 min for all cases. After the boiling treatment, the surfaces were dried, and water static contact angles on coated surfaces were measured immediately. The results are displayed in Figure 3.7. The horizontal axis represents the nominal size of the particles, and is in logarithm scale. The vertical axis shows the cosine of apparent contact angles to represent surface wettability. For the purpose of comparison, wettability on surfaces treated by boiling in pure water is placed on the left edge of the chart. The pure water case may be interpreted as an extreme case of “nanofluid” with particles of size 0 nm. Figure 3.7 suggests that the larger the particle size used for NBND, the higher the resulting surface wettability. When it comes to the case where 300 nm nanoparticles are used, \( \cos(\theta) \) is almost equal to one, indicating superhydrophilic state of wetting. This suggest that, even an ultra-smooth substrate can be modified by NBND process to become supper wettable.
Also studied here are nanoparticles of another type of material. The material itself should be hydrophilic, so silica nanoparticles are used. The nominal size of the particle is 15 nm, and size study using SEM shows a size about 20 nm (Section 2.2.2 Preparation of nanofluids, Figure 2.8). By convention, the vendors’ claim of particle size 15 nm is adopted.

The SiO\(_2\) nanofluid had a concentration of 0.6 wt%, so that the volumetric concentration is the same as that of 1.0 wt% Al\(_2\)O\(_3\) nanofluid. The boiling heat flux was 145 kW/m\(^2\) and boiling duration was 10 minutes, to be consistent with the conditions used for alumina nanofluid boiling. Also, the substrate was ultra-smooth, so that the resulting wettability can be compared with that of the 13 nm Al\(_2\)O\(_3\) particle NBND. Wettability was measured with the same procedure as before. It was observed that the SiO\(_2\) coated surface became superhydrophilic, showing an apparent contact angle of nearly zero degrees, very difficult to be measured using the goniometer. This is a significant wettability enhancement compared to the surface treated by 13 nm alumina nanofluid boiling, which gives an apparent contact angle of 25°. During the contact angle experiment, it was observed that the SiO\(_2\) nanofluid treated surface showed a more obvious wicking process during the spread of water. Transient contact angles measured in the first second of liquid spreading process are shown in Figure 3.8. The navy circle is data series for surface treated by 13 nm Al\(_2\)O\(_3\) nanofluid; the green diamond is data series for surface treated by 15 nm SiO\(_2\) nanofluid. The photos are views from the goniometer camera during contact angle experiments, at the time of 0 second, 0.3 second, 0.5 second and 1 second. It can be found that the liquid on surface modified by 15 nm SiO\(_2\) nanofluid is not only of a lower contact angle in the beginning, but also seems to be spreading for a longer time comparing to the 13 nm Al\(_2\)O\(_3\) case. This opens up the question of the hemi-wicking state of wetting, which will be discussed in the following chapter.
3.7 Figures

![Figure 3.1](image1.png)

Figure 3.1: Water static contact angles (right vertical axis) and their cosines (left vertical axis) on different surfaces: before boiling, after boiling in pure water, boiled in 0.001 wt.% (0.00025 vol.%) alumina nanofluid for 10 minutes and 30 minutes.

![Figure 3.2](image2.png)

Figure 3.2: Surface wettability versus the heat flux of NBND process, for 1 wt.% and 0.01 wt.% nanofluids.
Figure 3.3: Heat transfer coefficient versus nanoparticle concentration during nanofluid boiling on ultra-smooth, smooth and rough aluminum surfaces. The nanoparticle in the fluid is 50 nm Al₂O₃.
Figure 3.4: Water wettability versus nanoparticle concentration in the suspension. Data are grouped by substrate roughness: ultra-smooth in green, smooth in blue, rough in black. Data for pure water boiling cases are plotted on the left frame of the figure. The straight lines show wettability of each substrate before boiling. The numbers are static contact angles in degrees.
Figure 3.5: Roughness versus nanoparticle concentrations. Straight lines indicate original substrate roughness. Data for pure water boiling cases are plotted on the left frame of the figure. Ra represents arithmetic roughness factor obtained by profilometry.
Figure 3.6: Wettability (cosine of static contact angle) versus roughness for each type of substrate after boiling treatment.
Figure 3.7: Wettability of surfaces boiled in alumina nanofluid made from different size of particles. Pure water boiling case is plotted on the left frame of the figure.
Figure 3.8: Transient liquid wetting behavior in the first second of contact angle experiment. The navy circle is data series for surface treated by 13 nm Al$_2$O$_3$ nanofluid; the green diamond is data series for surface treated by 15 nm SiO$_2$ nanofluid. The photos are views from the goniometer camera during contact angle experiments, at the time of 0 second, 0.3 second, 0.5 second and 1 second.
4. SURFACE ANALYSIS

4.1 Introduction

It is reported in the literature that the nanoparticle sedimentation during nanofluid boiling changes the topography of the specimen [21], [24], [26], [35], [36], [47]. According to Bico [37], [44], both a Wenzel wetting mode and hemi-wicking (also called impregnated Cassie-Baxter) would show an apparent contact angle that depends on topography. After boiling, specimens could be in the hemi-wicking mode, where imbibition come into play. Such phenomena on nanoparticle deposited surfaces have also been reported by Kim and coworkers [20]. The water droplet on rough substrate surface are mainly in Wenzel wetting mode after boiled in pure water or low concentration nanofluids. Some reports proposed that the wetting could be in a Wenzel and Cassie-Baxter hybrid mode, when the nanoscale roughness is significant in topography [49]–[51]. Nanoscale texture introduced by nanoparticles could lead to this hybrid mode, especially when particle concentration is low during nanofluid boiling nanoparticle deposition (NBND) process. However, at concentration of 1 wt%, the particles eventually cover the surface to an extent that some of the surfaces are in hemi-wicking mode of its wetting process to help make the surface “super-wetting”[37]. When exposed to organic contamination, these highly wettable surfaces tend to adsorb the contaminating compounds that lowers their surface energy. This leads to the degradation of hydrophilicity over time, when the surfaces are exposed to air.

In this chapter, in depth investigation on topography, the application of the wetting state models, and the effect of contamination are discussed.
4.2 Topography

4.2.1 Micro-nano structures on the surface

As stated in the previous chapters, surface topography plays a very important role in determining the wettability. NBND process has been proven to change the surface roughness, but no in-depth understanding of the roughness change has been discussed. In order to have a better understanding of the boiling deposition process, scanning electron microscope (SEM) was used. To reveal the micro and even nano scale surface structures. Surfaces for SEM investigation were sputter with a very thin layer of gold, so as to improve the image quality, without changing the topography. The instrument was a Hitachi S-4800 field emission scanning electron microscope with a maximum resolution of 1.0 nm.

A sample of ultra-smooth surface boiled in 1 wt% was investigated using SEM and compared to that of an original bare aluminium substrate at 400 times of magnification. Shown in Figure 4.1 are the original substrate (a) and the boiled surfaces (b ~ f). Before boiling, the substrate appeared smooth even under 50k of magnification. After boiling in pure water (Figure 4.1(b) and (c)), a ‘grass-like’ nano-structure can be observed. This is pseudoboehmite – formed by a reaction between aluminium and hot water [46]. According to Vedder and Vermilyea [46], a layer of aluminum oxide forms on the surface of aluminum, which is hydrolyzed in water and then dissolved. Its precipitation is aluminum oxy-hydroxide, which takes the form of fine crystals, but its structure is “poorly crystallized” [52]. For this reason, it is called pseudoboehmite. In the water based Al$_2$O$_3$ nanofluid, plenty of surface area of aluminum oxide is exposed to water. During nanofluid boiling, water temperature is high. This enables fast hydroxylation of large surface area of Al$_2$O$_3$, and high dissolution rate. Precipitation of the solute forms nanoscale pseudoboehmite crystals on solid aluminum oxide surfaces. On surfaces where nucleate boiling occurs, bubble formation and departure results in the nonuniform transient surface temperature profile, which facilitates the precipitation of aluminum oxy-hydroxide. During the precipitation process, heterogeneous nucleation of pseudoboehmite crystals at the solid
liquid interface is preferred because of a lower energy barrier. The nucleation of pseudoboehmite crystals not only happens on the boiling surface of the aluminum specimen, but also occurs on the surface of alumina nanoparticles suspending in water. During the formation of pseudoboehmite, as the precipitated layer grow thicker, transportation of HO\(^-\) to the aluminum oxide surface is hindered. Consequently, the size of the pseudoboehmite crystal is limited at tens of nanometers in boiling water. Pseudoboehmite has a chemical composition of Al\(_2\)O\(_3\)·nH\(_2\)O, where 1 < n < 2. Thus, after boiling in water and aqueous Al\(_2\)O\(_3\) nanofluids, there is a change in both the chemistry and the topography of the surface that collaborates in enhancing surface wettability. Bare aluminium surfaces show a lower contact angle after boiling in water, as demonstrated here in Figure 4.1 (b), and previously in Figure 3.1 and Figure 3.4. Comparing Figure 4.1 (b) and (d), it is obvious that the wettability is further enhanced by the nanoparticles deposited onto the surface. As shown in Figure 4.1 (d-f), the boiling deposition process adds topographical structures effectively at both nano and micro scale onto the pseudoboehmite surface. In some regions (darker under SEM, image (d)), there are the spherical nanoparticles inserted into the pseudoboehmite (Figure 4.1 (e)), while in the others (lighter under SEM, image (d)), the NBND process introduced micro-scale structures, shown at higher magnification in Figure 4.1 (f). A magnified image for the lighter regions reveals a cluster of fluffy spheres. The generation of this structure is not very well understood; however, a possible explanation is that, some alumina particles might have grown pseudoboehmite in the hot water and thus formed the fluffy structure, while it agglomerated and settled onto the substrate. Such a structure enhances surface wettability, and it is caused by topographical change only in comparison to that of pure water cases.

Figure 4.2 shows the nano and micro structures introduced by boiling in 1 wt% 13 nm alumina nanofluid. From Figure 4.2 (a), it can be observed that under five thousand times of magnification, the coating appears to be nonuniform at micro scale. Some places, are lighter in the SEM image, while other places are darker. This could indicate a nonuniform thickness of coating, and a different material. To understand this, magnification of fifty thousand times was used to examine into the “darker” region, and an SEM image is shown in Figure 4.2 (b). The image reveals that the surface has “nano grass” and “nano-flakes” in
this region. This indicates the existence of pseudoboehmite as a result of aluminum and hot water reaction [46], similar to the case of 50 nm alumina nanofluid NBND. Figure 4.2 (c) is the SEM image of one hundred and ten thousand time of magnification for the “lighter regions”. The nanoparticles that were deposited on to the surface can be clearly seen. This coating also makes the surface nano-porous, which could affect liquid wetting process on this surface. Unlike those shown in Figure 4.1 (d), here no pseudoboemite has been observed to have grown on these nano-particles.

Ultra-smooth aluminum surface after boiling in 1 wt% 300 nm Al₂O₃ nanofluid also has a layer of particles deposited, as shown in Figure 4.3. It appears under SEM, that the coating has microscale roughness, and it is porous (Figure 4.3 (a)). There are more densely packed regions, and there are also spots that have holes. Magnifying fifty thousand times on a “densely packed” region gives a clear image of the nanoparticles on the surface, which is shown in Figure 4.3 (b). Even in this region, nanoscale porosity exists. If we look into the “holes” shown in Figure 4.3 (a), with larger magnification (Figure 4.3 (c)), then the structures inside a hole can be observed. Figure 4.3 (c) exhibits the existence of pseudoboemite inside the holes and on the walls. It is not very clear from this image, whether pseudoboemite can grow on the alumina particles as shown before in Figure 4.1. To answer this question, another SEM image that demonstrates pseudoboemite grown on alumina particle is shown in Figure 4.3 (d). It is now clear that pseudoboemite can grow on the surface of these particles. Not only does the porosity introduced by deposition of nanoparticles helps to enhance wettability, but also the pseudoboemite grown on these surfaces could help to enhance the capillary force during the spreading of liquid on the treated surfaces. This suggests advantages when using alumina nanoparticles.

Surface treated by NBND of 0.6 wt% (0.25 vol%) silica nanofluid was also studied using SEM. As shown in Figure 4.4 (a), the originally ultra-smooth substrate is now covered with a porous layer. The coating is nonuniform at microscale, which introduces microscale roughness. In contrast with NBND using alumina nanofluid, where pseudoboehmite can be observed, taking a closer look at a less coated region of this silica NBND treated surface at eighteen thousand times of magnification (Figure 4.4 (b)) does not show any evidence
of pseudoboehmite. According to the mechanism of aluminum water reaction and silica water reaction reported in literature [46][53], a possible reason could be the dissolution of silica in hot water and the effect of PH on the inhibition of precipitation of aluminum hydroxide. In the region with thicker coating, magnified image Figure 4.4 (d) reveals the nano-size silica particles.

From Figure 4.1 to Figure 4.4, it can be observed that, nanoparticles are deposited onto the substrate after boiling of the nanofluid, and the porous coating is nonuniform at microscale, which introduces microscale roughness. The reaction of hot water with alumina results in the growth a nano-porous grass like structure (pseudoboehmite), which could grow on the surface of alumina nanoparticles themselves for the case of 50 nm and 300 nm alumina NBND. By contrast, for the 13 nm alumina NBND case, pseudoboehmite was not observed on the surface of these nanoparticles. The reason for this is not clear, but probably should be associated with the size of the particle and maybe the surface curvature. For water alumina NBND, the nanoporous structures are the consequence of the deposited nanoparticles and the growth of pseudoboemite, while for water based silica NBND on aluminum substrate, the only observable nanoporous structures are built by the deposition silica nanoparticles. In either cases, there is a change of chemistry simultaneously with the modification of topography. These should contribute to the change of liquid wetting behavior on such surfaces at macro scale.

These observations also suggest the bonding mechanism of the coating to the surface as well as that between the particles. By its chemical nature, alumina is hydrophilic, so the nanoparticle and the substrate are both hydrophilic. Hydrogen bonds could form at contact. The hydrogen bond is generally about 0.2 eV/bond, which is much stronger than van der Waals adhesion (typically about 0.04 eV/bond)[54]. However, hydrogen bond has very short intramolecular distance (0.176 nm) [55], it will not form unless the particle and the substrate are closely in contact. As a result, hydrogen bonding is much less significant if the surface is rough and if the particles are rigid, which is the case in this study. In the current work, another added complexity is the growth of pseudoboehmite on the alumina surface. Pseudoboemite is a type of crystalized aluminum oxide hydroxide, it increases
surface roughness and changes chemistry of alumina surface. The needle/grass like crystal pseudoboemite can grow on the aluminum substrate as well as on the larger size alumina particles (nominal 50 nm and 300 nm), as shown in Figure 4.1, Figure 4.2 and Figure 4.3. Such structure provides mechanical interlocks that hold the particles to the surface. The pseudoboehmite grown on the particles also helps to hold the particles with each other. This brings about another mechanism of bonding. Overall, the growth of pseudoboehmite during water based alumina nanofluid NBND contributes to the mechanical stability of the coating. In contrast, for the case of NBND using silica nanofluid, no pseudoboehmite was grown (Figure 4.4), so in dry air, the deposited particles were loosely adsorbed on to the substrate mainly by Van der Waals force, and the coating can be easily removed from the substrate. Figure 4.5 shows one of the “scars” of the silica coating caused by accidental wiping. For the case of silica treated surface, the lack of mechanical interlocking significantly reduces the mechanical stability of the coating. The functionality of the surface after NBND treatment relies on the coating, so the vulnerable silica coating by NBND is not suggested for thermal engineering applications, unless additional treatments were applied to strengthen its bonding. Consequently, the stronger bonded alumina coating by NBND is considered to be more suitable for thermal engineering applications such as HVAC&R.

4.2.2 The effect of nucleate boiling on surface morphology

In the previous subsection, a study of topography was mainly in the range of tens of microns to nano scale. In this subsection, surface morphology at meso scale ranging from a few millimeters to hundreds of micrometers is presented.

Shown in Figure 4.6 is a millimeter scale image of the surface after nucleate boiling of silica nanofluid. It is an interesting observation is the “donut shaped” morphology of the coating. Demonstrated in Figure 4.6 (a) is that, the “donuts” could be next to each other and effect the shape of each other. Tilting the sample stage in SEM and taking an image of twice of magnification gives Figure 4.6 (b). Defects of coating at the center of a “donut”
can be clearly observed. Taking a closer look at the cracks in the defect reveals an adsorbed layer of porous coating underneath the thicker one (Figure 4.6 (c)). The thicker layer of coating at the center part is estimated to be about 40 µm thick. As has been stated in Chapter 1 the coating is formed by nanofluid boiling nanoparticle deposition, during which, particles are coated onto the surface by microlayer evaporation underneath the vapor bubbles. It is intuitive to relate these “donut” shape morphology of coating to the formation and departure of vapor bubbles during the boiling process. If that is the case, then a similar phenomenon should also appear on surfaces treated by NBND using other types of nanofluid, and boiling on a substrate of different surface texture.

NBND has also been conducted on an aluminum sheet as received. The aluminum sheet has a surface texture showing the evidence of rolling process during its manufacturing. Very fine stripes can be observed from a bare aluminum sheet. Figure 4.7 (a) shows the pattern of such texture under 400 times of magnification. In order to know the result of NBND wettability change on such surface, a sample sheet was coated with nanoparticle by boiling 1 wt% of 50 nm Al₂O₃ nanofluid. After boiling, the surface was removed immediately without rinsing, so that the surface kept its topographical character at its last moment of boiling. It was dried in air and characterized with goniometer for its wettability and with SEM for surface morphology. Surface wettability was dramatically enhanced, giving a static contact angle of less than 5°. Shown in Figure 4.7 are original substrate (a) and the boiled surface (b-g). The circle shown in Figure 4.7 (b) is considered to be the consequence of the shear force acting on the porous layer that strips away loosely deposited particles when bubbles depart [48]. It can be observed from Figure 4.7 (b) and (c) that the edge of the outer circle has a relatively thicker deposition, and near the nucleation site, there are concentric circles with varying thickness. According to the literature [31]–[33], this phenomenon may be due to the advancing [31] and receding [33] contact line during the drying and rewetting cycles in nanofluid boiling process. These structures roughen the surface and introduce porosity, which in turn help water to wet the surface.

Figure 4.7 (e) and (f) are magnifications for the center part of the nucleation site. That the nanoporous layer consists of spherical nanoparticles of less than100 nm diameter is
obvious. Figure 4.7 (g) is an image of a region outside the evidence of the last nucleation sites. Figure 4.7 (f) and (g) are both of 120k times of magnification and look identical. According to Huitink and co-workers [48], the dynamic process of depositing and wiping during NBND leaves only the sites of nucleation at the end of the boiling experiment to be observable afterward. If this is true, then identical nanoporous structures in (f) and (g) are expected. Such a nanoporous layer of various thicknesses is a direct cause of the enhanced surface wettability. The deposition of nanoparticles it is very likely to provide the topography required for hemi-wicking state of wetting, in this case.
4.3 The effect of air-borne contamination

As introduced in Chapter 1, the goal of using NBND to modify surface wettability is to enhance the performance of thermal systems and components. Significant amount of research has been done to create hydrophilic and even superhydrophilic surface. The most applicable surface treatment method was the optimum plasma zone process (OPZ) [18], [19]. The surface shows remarkable durability of its hydrophilic nature when stored in pure water or kept wet with water. However, such a polymer coating does not maintain hydrophlicity for long in dry air. Exposing the treated surface in air for as short as a week would result in total loss of hydrophilicity, because the chemically treated surface has the tendency to lower its energy. In engineering applications, the surface could be dry and is expose to air for long periods time. For instance, if the coating is applied on the fins of an evaporator in an air-conditioner, then the idling time or shut down period of the system is unpredictable. If the surface lost its hydrophilicity easily in less than a week, then the performance of the air-conditioner could drop at the time when it is started again. Since the study of NBND to modify surface wettability is motivated by the engineering of HVAC&R and other thermal systems, it is very important to understand its durability when exposed to air. As a result, the specimen surfaces were naturally dried in air and they were kept in an office environment. All the samples were stored together to ensure that they were exposed to the same surrounding air. Water wettability on the surface was characterized every few days to monitor its change. The static contact angle change with time is illustrated in Figure 4.1. Contact angle on surfaces treated by different methods, namely oxygen plasma, boiling water, and NBND of different nanofluids, are compared over time. Initially, all the surfaces have contact angles lower than the one treated with boiling water. The plasma cleaned ultra-smooth aluminum surface performed the best, showing fast spontaneous wetting. After about week of exposure to air-borne contamination, the contact angle of the high energy plasma cleaned surface quickly grows to the highest amongst the surfaces, indicating a significant degradation of wettability. After about two months, the nanofluid treated surfaces is superior to the boil water treated pseudoboehmite surface and the plasma clean surfaces. This can be explained by the previously introduced hemiwicking model. After about three months, the 300 nm alumina NBND treated surface
demonstrated an acceleration of contact angle increase. And when its air-borne contamination test gets to over 100 days, the surface became hydrophobic, showing a static contact angle of 120°. This indicates the transition to Cassie-Baxter state of wetting. Such an abrupt transition happens because the air-borne organic contamination can be continuously absorbed by the porous coating, and transform the roughened surface into Cassie-Baxter’s wetting regime once the coverage of the adsorbed contamination goes across the transition point. The roughness itself then becomes an amplifier to the hydrophobicity, and the porous topography turns into a factor that sustains the “air-pockets” underneath the sessile droplet. Such a transition from hydrophilic to hydrophobic or even from superhydrophilic to superhydrophobic when exposed to air-borne contamination, is general on metal and metal oxide surfaces with enhanced micro/nano scale roughness[56]. This phenomenon is exaggerated by the growth of pseudoboehmite and the existence of hydroxyl group. The pseudoboemite surface increases surface energy, and the hydroxyl group is where the organic contaminations anchor, according to literature[57], [58].

4.4 The wetting states

4.4.1 Observation of Wenzel’s state of wetting

For quantitative topography analysis, the surface was investigated using atomic force microscopy (AFM, Asylum Research Cypher), shown in Figure 4.9. This can be used to estimate the roughness factor r, which is an important description of topography and a direct link to wettability of Wenzel’s model (Equation (1.16)). The AFM is of high resolution, but at the expense of the measurement range, so ultra-smooth substrate case is studied here.

On one hand, the roughness factor r can be decided simply by Equation (4.1) according to
its definition: the ratio of total surface area to the projected area. With the surface area reduced from AFM scan, the roughness factor is approximated by the ratio of the actual AFM scan area (12.2 µm²) and the projected area (9 µm²), which gives \( r = 1.356 \).

\[
 r = \frac{\text{Actual surface area}}{\text{Projected area}} \tag{4.1}
\]

On the other hand, according to Wenzel’s wetting theory (Equation (1.16)), the roughness factor can be reduced from surface contact angle analysis, Equation (4.2). Boiling in nanofluids enhances the wettability by the additional topographical change on top of the pseudoboehmite surfaces (pure water boiled surfaces). The roughness factor can be reduced from the cosine of their static contact angle.

\[
r_{NBND} = \frac{\cos \theta_{NBND}}{\cos \theta_{PW}} \tag{4.2}
\]

As shown previously in Chapter 3, the cosine of the static contact angle on ultra-smooth aluminium substrate boiled in pure water is \( \cos(\theta_{PW}) = 0.682 \), and that of surface boiled in 1.0 wt.% alumina nanofluid is \( \cos(\theta_{NBND}) = 0.927 \). This gives a roughness factor \( r_{NBND} = 1.36 \) from equation (4). This result matches well with the AFM analysis that gives \( r = 1.356 \).

AFM can give higher resolution, however, at the expense of its range of measurement. The AFM used in here was Asylum Cypher, which can achieve lattice resolution, but has a limited Z direction measurement of less than 5 µm. The height difference from Peak to Valley on a surface must be well within that limit for the AFM to work properly. Rough surfaces, especially after NBND, are challenging. For instance, after NBND in 300 nm Al₂O₃ nanofluid, AFM probe scan on the surface hit its Z direction limit, and could not
trace the surface profile properly. Consequently, it did not give a reasonable result on surface roughness. Figure 4.10 is the AFM result for surface treated by 300 nm Al₂O₃ nanofluid NBND. The red circles show the area where faulty scan result appears on the 3-D surface profile. Similar problems happen on specimens that have rough substrates. Consequently, the surface profilometer was used to characterize the surface roughness. It has sufficient range in Z direction, but much lower resolution, limited by the tip radius of the stylus. Also, the arithmetic roughness factor \( Ra \), reported in Chapter 3, is not directly related to the roughness factor \( r \) in Wenzel’s wetting model. An approach to estimate the roughness factor \( r \) from the 1-D profile of surface profilometry is to calculate the total length of the profile, which is shown in Appendix Table 1, 2 and 3, where \( Lo \) is the overall length of the 1-D profile of the scan result. Factor \( r \) for 1-D is estimated by the ratio of \( Lo \) and the scan length \( L \). The dimension of a surface should be 2. If the surface is fractal, then the fractal geometry dimension \( D \), of a solid surface, should be \( 2 < D < 3 \), since the surface has some roughness [59]. In order to estimate the real roughness factor \( r_{1-D} \) of the specimen surface, \( r_{1-D}^2 \) and \( r_{1-D}^3 \) have also been calculated by taking the square and cubic of the \( r_{1-D} \) value. Data are listed in Appendix Table 1, 2 and 3. However, these estimated \( r \) values are too small comparing to the roughness change needed to provide the wettability enhancement observed on these specimens by contact angle experiment. For instance, the surface that gives \( r = 1.36 \) from AFM analysis shows 1.027, 1.055 and 1.084 for \( r_{1-D} \), \( r_{1-D}^2 \) and \( r_{1-D}^3 \) respectively. This is the consequence of the limited resolution of using a stylus profilometer, which did not capture nanoscale roughness properly. One might think that the problem can be solved by measuring surface profile over several decades of scales at a range of resolution by utilizing topography characterization instruments with increasing resolution or magnification, so that the real fractal dimension can be found to provide a precise estimation of surface roughness. The prerequisite of such method to succeed is that the topography is self-affine [59]. In other words, the detail of roughness under high magnification is similar to the original profile observed under low magnification, so the features of the roughness are scale dependent. However, the features that contribute to surface roughness consist of grass-like pseudoboehmite of tens of nanometers, round or rectangular shape nanoparticles of certain sizes, and the intentionally controlled roughness of the substrate. None of these surface features is scale independent. As a result, fractal
geometry is not suitable for the specimens studied here. Roughness factor $r$ for Wenzel wetting model can be estimated using Equation (4.2).

For the 300 nm NBND treated surface and the 13 nm NBND treated surface, values calculated from $\cos \theta_{ref}$ is the wettability of the ultra-smooth surface boiled in water. Data that show a similar value of $\cos \theta/\cos \theta_{ref}$ are highlighted in bold. These values indicate the roughness factor $r$. According to the data in Table 4.1, for 300 nm NBND surface, $r$ is about 1.8; For 13 nm NBND surface, $r$ is about 1.5. Figure 4.11 shows the linear fittings of wettability data in the Wenzel wetting regime. The intersection is forced to be at the (0,0) point. Thus, the slope of the linear fittings are estimations of roughness factor $r$ of Wenzel model. Here it is identified that $r$=1.9 and 1.5 for 300 nm and 13 nm NBND treated surfaces, respectively. In this way, the roughness factor of the NBND treated surface can be found based on Wenzel wetting model.

However, looking at all the wettability data for the hydrophilic specimen surfaces (Figure 4.11), there are data points that do not sit in line with Wenzel model. Those data points showing much lower $\cos \theta$ than Wenzel model prediction, may be in between Wenzel and Cassie-Baxter mode. At this stage of transition point, contact angle experiment at one location show high wettability, while at another location a low wettability, which is why these data have high uncertainty (long error bar). For those data showing high wettability near $\cos \theta=1$, wicking behavior was observed during contact angle experiments. Hemi-wicking state of wetting is probably involved. This is explained in detail in the next subsection.

4.4.2 Observation of hemi-wicking state of wetting

The aforementioned Wenzel’s wetting model is illustrated in Figure 4.12 and Equation (1.16). This model indicates that, at thermodynamic equilibrium, the wettability of a rough surface should be proportional to its roughness “$r$”. However, that is assuming
the water can only wet the solid surface underneath the droplet cap. If the rough surface is somewhat porous, such that the liquid invades the trenches beyond the droplet cap, then a different mechanism should be considered. Figure 4.13 shows the transition point between the two wetting states is determined by the roughness factor $r$, and the solid fraction $\varphi$. Both parameters are associated with topography. Consequently, if the solid surface topography is properly modified, liquid should more easily spread on the solid. Combining the hemi-wicking regime and Wenzel regime of wetting gives a full picture of the wetting states on a hydrophilic surface. Changing $r$ and $\varphi$ will shift the transition point, and influence the apparent wettability of a surface. While the Young’s contact angle $\theta_Y$ is only effected by chemistry, both $r$ and $\varphi$ are associated with topography. Given the same surface chemistry, if the solid surface topography is properly modified, liquid could spread on the solid surface in hemi-wicking mode. This can be done by NBND.

The change in topography by NBND significantly improves surface wettability. On such surfaces, the spreading of water is not only the wetting process, but also involves the imbibition process. This relies on capillary force to assist the liquid spreading; thus its wetting state is called the hemi-wicking state. Considering the wicking mechanism, introduces the hemi-wicking model of wetting (Figure 4.14). In this model, the cosine of the apparent contact angle is a function of $\varphi$, which is the fraction of solid gas interface area projected.

For the 300 nm NBND treated surface and the 13 nm NBND treated surface, values calculated from $\frac{\cos \theta - 1}{\cos \theta_{\text{ref}} - 1}$ for all wettability data overtime are listed in Table 4.1, where $\cos \theta_{\text{ref}}$ is the wettability of the ultra-smooth surface boiled in water. Data that show a similar value of $\frac{\cos \theta - 1}{\cos \theta_{\text{ref}} - 1}$ are highlighted in bold. These values indicate the solid fraction $\varphi$. The smaller the value of $\varphi$, the higher the portion of solid surface is wetted in the liquid wicked area beyond the liquid cap [37].
According to the data in Table 4.1, for 300 nm NBND surface, \( \varphi \) is 0.01; for 13 nm NBND surface, \( \varphi \) is about 0.5.

Figure 4.15 shows the linear fittings of wettability data in the hemi-wicking regime of wetting. The (1,1) point is forced to be on the line. Thus, the slope of the linear fittings is an estimation of solid fraction \( \varphi \) of hemi-wicking model. From the figure, it can be found that \( \varphi =0.01 \) and 0.5 for 300 nm and 13 nm NBND treated surfaces, respectively. Not much change, since the solid fraction \( \varphi \) is a parameter that is only associated with the concept of interfacial area between different phases. It is defined as the fraction of solid-gas interface area over the sum of solid-gas and liquid-gas interfacial area. The bulk volume of each phase does not influence the factor \( \varphi \). For NBND method, as long as the surface has been covered by nanoparticle, the solid fraction \( \varphi \) should not change significantly, no matter how thick the layer grows.

The hemi-wicking model agrees with the observation in the contact angle experiment, where water spreaded like wicking, and water spreaded much better on the 300 nm \( \text{Al}_2\text{O}_3 \) nanofluid NBND treated surface than on the 13 nm \( \text{Al}_2\text{O}_3 \) nanofluid NBND treated surface. The wicking effect of water on such surfaces is the reason that NBND treated surface can stay hydrophilic longer under exposure to air-borne contamination. When the coverage of organic contamination adsorbed on the NBND treated surface got large, wettability drops abruptly, since in certain locations, air-pockets maintain underneath the liquid cap. Cassie-Baxter wetting state starts to come into play. In Table 4.1, data obtained 85 days after NBND in 300 nm \( \text{Al}_2\text{O}_3 \) nanofluid show that the values of \( \cos \theta / \cos \theta_{ref} \) is less than 1 and the values of \( (\cos \theta -1)/(\cos \theta_{ref} -1) \) higher than 1. Both values are unrealistic according to their definitions. In contrast, values of \( (\cos \theta +1)/(\cos \theta_{ref} +1) \) is between
0 and 1. Thus, implying Cassie-Baxter state of wetting. For the 13 nm case, 105 days after NBND, both the value of \( \frac{\cos \theta}{\cos \theta_{\text{ref}}} \) and \( \frac{(\cos \theta + 1)}{(\cos \theta_{\text{ref}} + 1)} \) are close to unity, implying that the wetting state is on the edge of transitioning to Cassie-Baxter state. The sessile droplet may have filled most part of the rough textures under its liquid cap, but may also left some sharp valleys with air-pockets.

**4.4.3 Semi-empirical wettability model for hydrophilic surface**

The transition from Wenzel to hemi-wicking state is not necessarily a sharp one as that shown in Figure 4.13. In reality, the wetting state can be a combination of the ideal Wenzel and hemi-wicking state. This means that, the wicking effect may not have wetted everywhere in its territory. There could be distribution of micro-scale dry patches, its wetting should be predicted by Wenzel model. Overall, the apparent wettability could be described as a combination of Wenzel and hemi-wicking model. When liquid wets such surface, the change of Helmholtz free energy \( dF \) is the combination of two parts: \( dF_W \) for \( \omega_W \) portion of dry patches where Wenzel’s wetting occurs, and \( dF_H \) for the wicked area of portion \( \omega_H \) where hemi-wicking takes place. This is demonstrated in Equation (4.1). From this, Equation (4.2) can be derived. Detailed proof is presented in the Appendix Equation (4.1a) through Equation (4.1).

\[
dF_{\text{comb}} = dF_W \omega_W + dF_H \omega_H
\]  

(4.1)

\[
\cos \theta_{\text{comb}} = \cos \theta_W \omega_W + \cos \theta_H \omega_H
\]  

(4.2)

Expressed in Equation (4.3) is a mathematical general expression of apparent wettability modeled by weighted average of various wetting modes, such as Wenzel, Hemi-wicking and Cassie-Baxter. In this thesis, investigation is focused on hydrophilic surfaces, so the
wetting modes involves Wenzel and Hemi-wicking, and thus \( N = 2 \).

\[
\cos \theta_{\text{apparent}} = \frac{\sum_{i=1}^{N} \cos \theta_{\text{mode},i} w_i^n}{\sum_{i=1}^{N} w_i^n} \tag{4.3}
\]

The weighing factor \( W \) for each wetting mode should be based on surface chemistry and topography. The physical constrains are, that the apparent wettability \( \cos \theta \) should approach unity when \( \cos \theta \) approaches unity, and the predicted \( \cos \theta \) can never be higher than one. Also, the proposed method should reflect the role of the transition criteria between different wetting states, and the combination scheme using such weighing factors should be as simple as possible.

The method proposed here is to use a weighted average, as expressed in Equation (4.4). The two components on the right hand side of this equation are the wettability predicted by Wenzel model \( \cos \theta_W \) and hemi-wicking model \( \cos \theta_H \), and the weighing factors are \( W_w \) and \( W_H \) respectively. It has been introduced in Chapter 1 section 1.2.4 Equation (1.26), (1.27) and (1.28), that the transition criterion is \( \cos \theta_r > \frac{1 - \varphi}{r - \varphi} \). Notice that, in this criterion, \( \cos \theta_r \) is only a function of surface chemistry, and \( \frac{1 - \varphi}{r - \varphi} \) represents topography. These two parameters are independent factors. For a fixed surface topography, The higher the \( \cos \theta_r \), the better the affinity to water, and the easier for hemi-wicking state to dominant the wetting mechanism. For a certain surface chemistry, the larger the value of \( \frac{1 - \varphi}{r - \varphi} \), the more the tendency for the surface to remain in Wenzel state of wetting. It is obvious, that a higher factor \( r \), which indicates a rougher surface, would results in a smaller value of
\( \frac{1 - \varphi}{r - \varphi} \), that contributes to the role of Wenzel wetting model. In contrast, the higher the \( \cos \theta_f \) would diminish the influence of Wenzel wetting mechanism by making the hemi-wicking mode more dominant. All of these mechanisms can be imbedded in the weighing factor by using \( \cos \theta_f \) and \( \frac{1 - \varphi}{r - \varphi} \) as the two elements to determine the significance of Wenzel mode and hemi-wicking mode. The weighing factors should predict values that asymptotically approaches the Wenzel model for \( \cos \theta_f \rightarrow 0 \), and asymptotically approaches the hemi-wicking model for \( \cos \theta_f \rightarrow 1 \). And when \( r \rightarrow 1 \), the influence of topography factor \( \frac{1 - \varphi}{r - \varphi} \) should vanish, and the only element that make an impact is \( \cos \theta_f \).

The method proposed here is shown in Equations (4.5), which satisfies all the aforementioned requirements. When \( \cos \theta_f > \frac{1 - \varphi}{r - \varphi} \), the weighing factors \( w_w < 1 \) and \( w_H > 1 \), so the hemi-wicking mode dominants, or the probability of the apparent wettability to be in hemi-wicking state is dominating. At the point there \( \cos \theta_f = \frac{1 - \varphi}{r - \varphi} \), the both Wenzel and hemi-wicking state stand 50% of chance, so the local wetting state can be either, and overall appearing to be at a mixed state, which is also the reason that the measuring uncertainty is high for data close to the transition point. The Figure 4.16 shows that the proposed modeling method captures a smooth transition region between the Wenzel and hemi-wicking regime of wetting. The power \( n \) in the weighing factors determines the shape of the model in Figure 4.16. The higher the power, the closer the proposed model fits both the Wenzel and hemi-wicking model. Here, this power is determined to be \( n=2 \), to fit with the data obtained by contact angle experiments. Figure 4.17 shows the combined Wenzel and hemi-wicking model for \( n=2 \), which agrees well with data.
$$\cos \theta_{\text{philic}} = \frac{\cos \theta_{w} w_{w} + \cos \theta_{H} w_{H}}{w_{w} + w_{H}} \quad (4.4)$$

$$w_{w} = \left[ \left( \frac{1 - \varphi}{r - \varphi} \right) \cos \theta_{y}^{-1} \right]^{n}, \quad \text{and} \quad w_{H} = \left[ \left( \frac{1 - \varphi}{r - \varphi} \right) \cos \theta_{y}^{-1} \right]^{n} \quad (4.5)$$

The proposed model provides a method to combine the Wenzel wetting mechanism with hemi-wicking mechanism, which introduces a transition region. In reality, there will not be a sharp transition from absolute Wenzel wetting mode to absolute hemi-wicking mode. Instead, there should be a region that Wenzel mode and hemi-wicking mode are both probable. The so called “transition” is only a matter of moving from Wenzel dominant mixed wetting states to hemi-wicking dominant mixed wetting states, and the transition is smoother. This method predicts the wetting state on hydrophilic surfaces more realistically.

It is preferred that the superhydrophilic coating has a good longevity. This means that the topography should lead to a surface which wettability is insensitive to contamination. In other words, the surface should sustain superhydrophilic property even for a surface chemistry that has a relatively low solid-vapor interfacial energy. Based on the combined hydrophilic model, such surface should have a topography with high roughness factor $r$, which means high surface area, and low solid fraction $\phi$, which indicates a high porosity. Shown in the Figure 4.18 is the combined hydrophilic surface wetting model for varies $r$ and $\phi$. An example for the outcome from a desired surface topography is shown as the green dashed line in the figure below, which is $r=8$ and $\phi=0.1$. For such surface topography, the model predicts that, even for a surface with chemical nature that gives $\cos \theta_{y}=0.12$ (equivalent to Young’s contact angle of $83^\circ$), the surface wettability would show $\cos \theta=0.93$ (equivalent to apparent contact angle of $21^\circ$).
4.5 Tables

Table 4.1: Data of $r$ for Wenzel model, $\phi$ for hemi-wicking model and Cassie-Baxter model are highlighted in bold for each specimen.

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<th>13 nm Al$_2$O$_3$ NBND</th>
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<td><strong>0.34</strong></td>
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</tr>
</tbody>
</table>
4.6 Figures

Figure 4.1 (a)

Figure 4.1 (b)

Figure 4.1 (c)
Figure 4.1: SEM images of specimen surfaces: (a) Bare ultra-smooth aluminium surface ×50k; (b) after boiling in pure water ×2.5k, (c) ×50k; (d) after boiling in 1 wt% 50nm alumina nanofluid ×2.5k, (e) darker region ×50k, (f) lighter region micro structure ×50k.
Figure 4.2: SEM images of surface after NBND of 1wt% 13 nm Al$_2$O$_3$ nanofluid:
(a) ×5k showing the dark and light regions; (b) darker region ×50k shows pseudoboehmite, (c) lighter region ×110k showing nanoparticles.
Figure 4.3 (a)

Figure 4.3 (b)

Figure 4.3 (c)
Figure 4.3 (d)

Figure 4.3: SEM images of surface after NBND of 1wt% 300 nm Al$_2$O$_3$ nanofluid: (a) 801 times of magnification, showing the rough and porous coating; (b) ×50k showing the particles deposited on the surface pseudoboehmite, (c) ×50k looking into a “hole”, showing the pseudoboehmite grown inside, (d) ×50k showing pseudoboehmite grown on and at the corners between particles.
Figure 4.4: SEM images of surface after NBND of 0.6wt% 15 nm SiO$_2$ nanofluid: (a) $\times$2k showing the coating on the surface; (b) $\times$18k, (c) $\times$120k showing the nanoparticles.
Figure 4.5: Silica coating on an aluminum substrate was wiped away by accident.
Figure 4.6: SEM images of surface after boiling in SiO$_2$ nanofluid: (b) $\times35$ shows evidence of NBND nucleation sites, (c) $\times70$ and tilted 30° showing defects, (d) $\times450$ showing the adsorbed layer of coating underneath,
Figure 4.7: SEM images of: (a) aluminum sheet without treatment, (b) evidence of NBND nucleation site from boiling in 1 wt.% 50 nm Al₂O₃ nanofluid, (c) the edge of the site, (d) center of the site ×2.2k, (e) ×35.0k, and (f) ×120k times of magnification. (g) outside of the site ×120k times of magnification.
Figure 4.8: Wettability change of the surfaces after exposure in air for days.
Figure 4.9: Image showing the result from AFM scan of an ultra-smooth surface boiled in 50 nm Al₂O₃ nanofluid.

Figure 4.10: Image showing the result from AFM scan of an ultra-smooth surface boiled in 300 nm Al₂O₃ nanofluid. The red circles show area with unreal spikes, since the probe has went beyond its measuring range in the Z direction.
Figure 4.11: Linear fittings of wettability data in the Wenzel wetting regime. The intersection is forced to be at the (0,0) point. Thus, the slope of the linear fittings are estimations of roughness factor \( r \) of Wenzel model. Here it is identified that \( r = 1.9 \) and 1.5 for 300 nm and 13 nm NBND treated surfaces, respectively. All data listed in Table 4.1 are referred to this chart. Several data points are outside the Wenzel mode.
Figure 4.12: Wenzel’s wetting model, where the roughness factor $r$ is the slope of the line.

Figure 4.13: The transition point from Wenzel’s wetting regime to the hemi-wicking (impregnated Cassie-Baxter) wetting regime.
Figure 4.14: Hemi-wicking model (impregnated Cassie-Baxter), where $\phi$ is the fraction of solid gas interface area projected.

Figure 4.15: Linear fittings of data in the hemi-wicking regime. The point (1,1) is forced, so the slope of the lines are estimations of solid fraction $\phi$. Here $\phi = 0.01$ and 0.5 for 300 nm and 13 nm NBND treated surfaces, respectively.
Figure 4.16: Combined model for n=1,2 and 3, which predicts the smooth transition region between Wenzel regime and hemi-wicking regime. The higher the power n, the closer the prediction of the combined model to the Wenzel model and hemi-wicking model.
Figure 4.17: Short dashed line is the combined model with $n=2$, which fits well with the data.
Figure 4.18: The combined model for varies roughness factor $r$ and solid fraction $\phi$, if $n=2$. 
5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions from current work

Aiming at enhancing the performance of thermal systems, research has been completed to explore a new way to modify surface wettability. Among methods that have been reported in literature, nanofluid boiling nanoparticle deposition (NBND) is promising as a surface treatment method for HVAC&R, because it is an effective way to modify wettability, and it might be scalable to mass production. The nanoparticle deposition process has been applied on a piece of fin for a plain-fin heat exchanger.

Initially on the fin, there were the contaminations and oil residue. The apparent contact angle was 95° (Error! Reference source not found.), indicating the surface is hydrophobic. Also, there were certain texture formed during its manufacturing process. After the deposition of nanoparticles, wettability is significantly enhanced, showing a contact angle of only 28°, and the surface became less anisotropic.

A systematic experimental investigation of wettability change by NBND has been conducted by varying deposition time, heat flux, substrate roughness, nanofluid concentration, nanoparticle size and material. In comparison to pure water cases, wettability is enhanced by boiling nanofluids. Data show that boiling duration positively affects wettability, but little enhancement occurs for boiling time longer than about 10 minutes. Surface wettability change by NBND is independent of boiling heat flux if the nanofluid concentration is 1 wt.%, but at low concentration of 0.01 wt.%, heat flux has some sophisticated influence. This does not undermine the significance of the systematic trend that, the higher the nanoparticle concentration, the higher the wettability after NBND, and at the same time the higher the surface roughness. The goal is to obtain a superhydrophilic surface, which is achieved by high particle concentration (1%wt) NBND treatment.
Magnified images of the nanoporous layer help to reveal the modification of the surfaces, and provides a better understanding of the mechanism of the enhanced wettability. Nano-micro structures were observed under SEM. The NBND treatment not only introduces both micro and nano scale roughness and porosity to the surface, but also changes surface chemistry. All surfaces treated by water based Al₂O₃ nanofluid produced pseudoboehmite, which contributes to an enhanced surface wettability. Deposition of silica particles also changes the chemical nature of the aluminum substrate. Microscopic analysis of the nanoporous layer gives evidence of bubble nucleation site coupled with particle deposition process. The rings around the nucleation sites introduce relatively larger scale topography changes. Overall, the topography changed brought by NBND process, ranges from scales of the size $10^{-3}$ m to $10^{-8}$ m:

- Reaction with hot water produced pseudoboehmite, which is a $10^{-8}$ m “grass” or “needle” like structure.
- The nanoparticles contribute to topography change at $10^{-5}$ m to $10^{-8}$ m scale, depending on the size and surface property of the particles.
- The formation and departure of bubbles during nucleate boiling of nanofluid results in a $10^{-4}$ m to $10^{-3}$ m scale “donut” shape morphology on the coating.

AFM was used to quantify this added surface roughness by nanoparticle deposition. A surface treated by boiling in pure water and an ultra-smooth substrate treated with 50 nm Al₂O₃ NBND were investigated. The surface roughness factor was obtained from AFM scan and contact angle measurements were obtained independently. Their good agreement reveals the physics of wettability enhancement for this case, in comparison to that boiled in pure water. The wetting state of some of the NBND treated surfaces are in the hemi-wicking wetting regime. This was also observable during the sessile droplet experiments, where water spreads through wicking. For those cases, data of surface wettability can be modeled by the hemi-wicking model very well. And the wicking effect of water on such surfaces is the reason that NBND treated surface can stay hydrophilic longer under exposure to air-borne contamination. Because of its special topography, the transition from superhydrophilic to hydrophobic is also abrupt. After three months, the initially superhydrophilic 300 nm NBND treated surface became very hydrophobic. These is
expected to be a general trend for NBND treated surface exposed to air-borne contamination when the surface is dry, since the surface hydroxyl group promotes the adsorption of organic contaminants in air. The 15 nm silica NBND treated surface seems to sustain its hydrophilic nature better, however, the particles are very loosely attached to the surface, so more vulnerable to physical removal of coating.

The functionality of the surface after NBND treatment relies on the coating, so the vulnerable silica coating by NBND is not suggested for thermal engineering applications, unless further treatments is done to strengthen its bonding. The stronger bonded alumina coating by NBND is considered to be more suitable for thermal engineering applications such as HVAC&R.

However, the complex problem of adhesion force for irregular shape, agglomerated particle coating on rough substrate with pseudoboemite grown on the surface should worth an in-depth study in the future.

Nevertheless, the surfaces treated by NBND show dramatically enhancement in wettability. Even though the treated surface cannot resist the trend to reduce surface energy by adsorbing contaminants from the air, they sustain high on wettability much longer than other method proposed in the literature [13], [18], [19]. The coating generated by OPZ treatment degrades quickly in a week, if stored in air [18], the coating is still reported by literature as a “permanent hydrophilic surface” for thermal engineering applications [19]. For heat exchanger fins treated by OPZ method, its coating can remain functional up to 1,000 wet and dry cycles [4], because its hydrophilicity is preserved well if the surface is kept wet or stored in water to isolate from air-borne contamination [19] [18]. In view of this, the NBND treated surface, which does not degrade in air until two months later, its coating could be promising to keep functional for more than 1,000 wet and dry cycles, or even 10,000 wet and dry cycles for industry applications.

However, the ideal coating for industry application would be the one that does not get contaminated at all. How to better address this issue remains as a question for future work.
Adding a layer of polymer brush coating on top of the NBND treated surface could potentially be a solution. The NBND treatment provides the necessary topography while the polymer brush provides the surface chemistry to functionalize and protect the surface. How to better address this issue remains as a question for future work.

5.2 Recommendations for future work

5.2.1 Future work to study topography

Unlike those surfaces treated by 50 nm and 300 nm NBND, here no pseudoboemite has been observed to have grown on the surface of these 13 nm nano-particles. This reveals the fact that, the size or surface curvature of Al₂O₃ particles can determine whether pseudoboehmite can grow or not, since the size and surface curvature could affect the transport of the soluble species and the energy barrier of heterogeneous nucleation of pseudoboehmite. However, no information is available from literature to explain the mechanism of this phenomenon. Future work may involve an in-depth study on the physical-chemistry of the nucleation and the reaction kinetics during the growth of pseudoboehmite on nanoparticles.

The NBND coating is developed for thermal engineering applications. Further investigation is needed to estimate how much the thermal resistance is the coating. Porosity and permeability are also important parameters. These parameters will help to understand the dynamics during the spreading of liquid by capillary force. Thickness and porosity would also determine the thermal resistance added by the coating. The higher the porosity (on the vertical plane), the lower the thermal conductivity of the coating. The thicker the coating the higher the overall thermal resistance.

Adsorption method such as BET, could be used in the future to estimate the porosity. It
could also provide total surface area of the porous coating. The method would not directly suggest a number for \( r \) or \( \phi \), because the surface area that adsorb the gas is not necessarily wetted by liquid. However, it certainly will provide an idea of the upper limit of the total solid surface area that could potentially become a solid-liquid interface. Therefore, future work on NBND coated surface should involve total surface area measurement using adsorption process.

Further understand the topography of the NBND treated surface, to promote its engineering application. Quantitative data for roughness can be found by calculating the power spectral density (Fourier Transform of height) function of surfaces before and after particle deposition will be helpful, if a proper surface profile investigation instrument is available to measure microscale roughness and capture nanoscale structures. Even if no such instrument is available conveniently, a combination of surface investigation at varies scales could be used. Surface profile data can be utilized for Fourier transform of height and Fourier transform of length, which will provide a quantitative understanding of the topography. This method is very valuable as a future work to quantitatively study the topography of NBND treated surfaces.

Also, the NBND treated surface can be coated with a layer of hydrophilic functional groups such as hydroxyl -OH, carboxyl -COOH and amino -NH\(_2\) groups. By comparing the contact angle of an ultra-smooth surface with those functional groups and the contact angle of NBND treated surface with the same functional group, the solid fraction \( \phi \) can be calculated by \((\cos \theta - 1) / (\cos \theta_y - 1)\). This should be adopted as a standard way to find the solid fraction \( \phi \) in future investigation of NBND treated surfaces.
5.2.2 Recommendation on surface chemistry study

To apply NBND treatment in industry, another important aspect is the impact of air-borne contamination. In the current work, the specimen surfaces were naturally dried in air and they were kept in an office environment. All the samples were stored together to ensure that they were exposed to the same surrounding air. Water wettability on the surface was characterized every few days to monitor its change. According to the hemi-wicking model, 

$$\cos(\theta) = \phi \left( \cos(\theta_c) - 1 \right) + 1,$$

the apparent contact angle will be 0° only if the Young’s contact angle is 0°. Here, the surface after NBND is not protected from air-borne contamination, so the chemistry of the surface determines that the contact angle on such surface is higher than zero.

According to literature, the contamination could contain organic species of HCOOR, CH3COOR, H2C=CH-COOR, CH3CH(OH)COOR [56], [60]. Ageing the hydroxylated surface in ambient air would result in the adsorption of these organic species [56], [61]. The organic species will react with the hydroxyl groups on the hydroxylated surface and form covalent bonding [58], [61]. In order to understand the mechanism of air-borne contamination changing surface wettability, information of the chemical composition, percentage of each species and the coverage of organic contamination are important. It is suggested for future research that, surface inspection techniques such as XPS, FTIR and TOF SIMS can be utilized to obtain that detailed information of the organic contamination on hydrophilic surface coatings.

Even though the NBND treated surface cannot resist the trend to reduce surface energy by adsorbing contaminants from the air, they sustain high on wettability much longer than other method proposed in the literature [13], [18], [19].

However, the ideal coating for industry application would be the one that does not get contaminated at all. How to better address this issue remains as a question for future work. Adding a layer of polymer brush coating on top of the NBND treated surface could potentially be a solution. The NBND treatment provides the necessary topography while
the polymer brush provides the surface chemistry to functionalize and protect the surface.

For air-conditioning systems, for instance, the problem with most hydrophilic fins is that, they have high surface energy that tends to promote contamination from air [56], especially when a HVAC unit is idling. This challenges the longevity and the application of hydrophilic fins. In contrast, a hydrophobic surface which has low surface energy, is much less likely to adsorb organic contaminations in the air. However, the thermal-hydraulic performance of hydrophobic fins is not satisfying [6]. It would be a better solution if there exists a coating that is hydrophilic during dehumidification but hydrophobic during system idling. If this is to be applied on heat exchangers, then it would be very convenient if the wettability of this coating could be modulated by temperature. Fortunately, this is in fact the property of many polymer brushes. The polymer chains changes from hydrophilic to hydrophobic at a temperature threshold. The critical temperature is called lower critical solution temperature (LCST). The coated surface is hydrophilic at higher temperature, and hydrophobic at lower temperature. This change between hydrophilicity and hydrophobicity is the nature of the polymer driven by thermodynamics [62]. With this, both the merits of hydrophilic and hydrophobic surfaces can be integrated into the design.

Usually, polymer coatings are considered as adding thermal resistance because of the low thermal conductivity of bulk polymers. However, the polymer coating used here is nano-size single chain polymer brushes that are covalently bonded to the metal surface at one end, but free at the other, as shown in Error! Reference source not found.. The polymers are nanometers long, so thermal resistance of the polymer brush layer is negligible. Also, researchers claim that a single polymer chain has thermal conductivity much higher than its bulk polymer. This has to do with the direction of phonon propagation on a single chain [63]. It is reported that the thermal conductivity can be higher than 100 W/m-K [64]. Therefore, the polymer brush coatings are expected to have negligible thermal resistance to the fins. The pseudoboehmhte could also contribute to the grafting of polymer brushes, because it is a very good source of hydroxyl groups. Surface roughness helps to exaggerate the transition, and may cause a transition from superhydrophilic to superhydrophobic. The topography of NBND, thus could work with the grafted polymer brushes to enhance each other’s performance. The cooperation of these two treatments is an interesting topic for
future investigation.

5.2.3 Future work for thermal engineering application

Condensation heat transfer can not be directly enhanced by applying NBND coating. However, the drainage of condensate water can be enhanced, which reduces pressure drop and thus benefits the overall thermal-hydraulic performance. Due to the limitation of the pool boiling facility in the lab, NBND treatment was not applied on a heat exchanger, but was applied on a piece of aluminum sheet cut from fin stock. It has been found that, NBND treatment enhanced wettability. There are two major driven force of water drainage on fins: gravity, and shear force from air flow [6], [40]. The hemi-wicking wetting mechanism enhances surface wettability and reduces contact angle hysteresis, so that the drainage behaviour on the hydrophilic fins is enhanced. However, once the surface coating is flooded, the enhancement of wettability to help condensate water drainage is diminished. According to the definition of the solid fraction $\phi$ for hemi-wicking model, the $\phi$ becomes meaningless, because the flooded surface does not have solid-gas interface. The hemi-wicking model cannot be true when the prerequisite $0<\phi<1$ is not satisfied. Experiment should be conducted in the future to test such coating under flooded conditions.

It is recommended that, an experimental setup can be built to do NBND on larger aluminum sheet to make fins, so that a heat exchanger can be made for testing. One way to do so, is to heat up the aluminum sheet or an already made heat exchanger to a high temperature about 600 °C, which is the about the brazing temperature of heat exchangers, but below the melting temperature of aluminum. Then quench it in a pool of nanofluid (the pool has been preheated to near 100 °C). This method may be closer to the procedure that could be applied in industry mass production, but is not very suitable for study in laboratory. A method that provides a good control over temperature and boiling time is needed. Therefore, a better idea would be to run hot liquid (temperature sufficiently higher than the boiling point of water) through the tubes of the heat exchanger, and place the heat exchanger in a large pool of several gallons of nanofluid with controlled temperature (kept at 100 °C). In this way, the fins would boil the nanofluid to have nanoparticles deposited onto the surface. The process than be controlled by the temperature and flow rate of tube-side working fluid.
If the exact same procedure as in the lab is carried out in mass production, the cost for NBND process could be high (1 minute of NBND cost about 2.5 kW-h/cm² of coating, or about 0.3 dollars/cm²). However, instead of a well-controlled pool boiling process using Joule heating, in industry mass production, waste heat from previous processes such as brazing, could be utilized to quench the surface in nanofluid to make the coating. Other convention industry coating processes such as thermal spray could also be utilized to reduce the cost. For future investigation. Plasma spray, which is a type of thermal spray coating method, is a promising method for mass production. Following this route of thinking, other recently developed thermal spray methods, such as cold spray, suspension thermal spray and solution precursor thermal spray processes, which are better in maintaining the shape of nanoparticles, could be methods to deposit nanoparticles onto metal substrates [66]. The investigation into the application of various types of thermal spray process to deposit a coating with a similar topography to the NBND method, is subject to future work.
REFERENCES


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APPENDIX

Uncertainty of the measured roughness and contact angle are calculated for Student-t distribution 90% confidence interval. Data for roughness from profilometry are listed in Table 1 to Table 3. Contact angles are listed in Table 4 to Table 6.

Because only limited number of measurements could be done, the Student-t distribution is used as the method to estimate the accuracy of the averaged value. The true mean should be lying within the interval shown in Equation (1), where $\bar{x}_n$ is the average value calculated from $n$ measurements, and the variance is $s_n = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x}_n)^2}$. If the confidence of the true mean to be lying in such interval is 90%, then Equation (2) express the case. An equivalent expression is Equation (3), and introducing $t = \frac{x_n - \mu}{s_n / \sqrt{n}}$, we have Equation (4). This means we need to find $F_{(A)} - F_{(-A)} = 0.9$, according to Equation (5), where $F_{(t)}$ is the cumulative distribution function (Equation (6)), calculated by integrating the probability density function of Student’s t-distribution, which is expressed as Equation (7). $\Gamma$ is the gamma function. In Equation (7), the degree of freedom is calculated as $\nu = n - 1$.

$$\left(\bar{x}_n - A \frac{s_n}{\sqrt{n}}, \bar{x}_n + A \frac{s_n}{\sqrt{n}}\right)$$

$$\Pr\left(\bar{x}_n - A \frac{s_n}{\sqrt{n}} < \mu < \bar{x}_n + A \frac{s_n}{\sqrt{n}}\right) = 0.9$$
\[
\Pr \left( -A < \frac{\overline{x}_n - \mu}{s_n / \sqrt{n}} < A \right) = 0.9
\]  
(3)

\[
\Pr(-A < t < A) = 0.9
\]  
(4)

\[
\Pr(-A < t < A) = F_A(t) - F_{-A}(t)
\]  
(5)

\[
F(t) = \int_{-\infty}^{t} f(u) du
\]  
(6)

\[
f(t) = \frac{1}{\sqrt{v\pi}} \frac{\Gamma\left(\frac{v+1}{2}\right)}{\Gamma\left(\frac{v}{2}\right)} \left(1 + \frac{t^2}{v}\right)^{-\frac{v+1}{2}}
\]  
(7)
Roughness factors obtained from profilometry are expressed by Equation (8) through (11). The “peak” and “valley” are represented by $R_p$ and $R_v$, respectively. $L_0$ is the overall length of the 1-D profile of the scan result. Factor $r_{1-D}$ is estimated by the $L_0$ and the scan length, expressed by Equation (12). The true topological dimension of the surface should be higher than 2-D and smaller than 3-D. In order to estimate the real roughness factor $r$ of the specimen surface, $r_{2-D}$ and $r_{3-D}$ have also been calculated by taking the square and cubic of the $r_{1-D}$ value. However, these estimated $r$ values are too small comparing to the roughness change needed to provide the wettability enhancement observed on these specimens by contact angle experiment. Data are listed in Table (1) to Table (3).

\[
Ra = \frac{1}{L_o} \int_{L_o}^{L_o} |Z(x)| dx
\]  

(8)

\[
Rq = \sqrt{\frac{1}{L_o} \int_{L_o}^{L_o} Z^2(x) dx}
\]  

(9)

\[
Rsk = \frac{1}{Rq} \frac{1}{L_o} \int_{L_o}^{L_o} Z^3(x) dx
\]  

(10)

\[
Rsk = \frac{1}{Rq} \frac{1}{L_o} \int_{L_o}^{L_o} Z^3(x) dx
\]  

(11)

\[
r_{1-D} = \frac{L_0}{L_{\text{scan}}}
\]  

(122)
Table A. 1. Roughness of the rough substrate, boiled in pure water and after NBND using 50 nm alumina nanofluid:

<table>
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<th>Surface type</th>
<th>Scan number</th>
<th>Ra [µm]</th>
<th>Rq [µm]</th>
<th>Rsk [-]</th>
<th>Rp [µm]</th>
<th>Rv [µm]</th>
<th>Lo [mm]</th>
<th>r 1-D [-]</th>
<th>r 2-D [-]</th>
<th>r 3-D [-]</th>
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<td>1.10</td>
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<td>1.03</td>
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Table A. 2: Roughness of the smooth substrate, boiled in pure water and after

NBND using 50 nm alumina nanofluid:

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<th>Rv [µm]</th>
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Table A. 3: Roughness of the ultra-smooth substrate, boiled in pure water and after NBND using 50 nm alumina nanofluid:

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<th>Rsk [µm]</th>
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<tr>
<td></td>
<td>scan 2</td>
<td>0.23</td>
<td>0.46</td>
<td>4.07</td>
<td>3.12</td>
<td>-0.40</td>
<td>1.016</td>
<td>1.016</td>
<td>1.032</td>
<td>1.049</td>
</tr>
<tr>
<td></td>
<td>scan 3</td>
<td>1.05</td>
<td>1.81</td>
<td>3.29</td>
<td>10.61</td>
<td>-0.99</td>
<td>1.055</td>
<td>1.055</td>
<td>1.114</td>
<td>1.176</td>
</tr>
<tr>
<td></td>
<td>scan 4</td>
<td>0.43</td>
<td>0.69</td>
<td>3.10</td>
<td>3.98</td>
<td>-0.65</td>
<td>1.020</td>
<td>1.020</td>
<td>1.041</td>
<td>1.062</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.53</td>
<td>0.95</td>
<td>3.91</td>
<td>6.11</td>
<td>-0.64</td>
<td>1.027</td>
<td>1.027</td>
<td>1.055</td>
<td>1.084</td>
</tr>
<tr>
<td></td>
<td>Uncertainty</td>
<td>0.48</td>
<td>0.73</td>
<td>1.13</td>
<td>3.98</td>
<td>0.37</td>
<td>0.000</td>
<td>0.022</td>
<td>0.045</td>
<td>0.070</td>
</tr>
</tbody>
</table>
Water static contact angles are measured multiple times on a specimen surface, and each time at a different location. Data for the measurements at varies locations are listed in Table (4) to Table (6).

Table A. 4: Water contact angle of the ultra-smooth substrate, boiled in pure water and after NBND using 50 nm alumina nanofluid:

<table>
<thead>
<tr>
<th></th>
<th>N12</th>
<th>1%</th>
<th>0.10%</th>
<th>0.01%</th>
<th>pure water</th>
<th>before boiling</th>
</tr>
</thead>
<tbody>
<tr>
<td>location 1</td>
<td>19</td>
<td>26</td>
<td>22</td>
<td>36</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>location 2</td>
<td>27</td>
<td>32</td>
<td>33</td>
<td>54</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>location 3</td>
<td>24</td>
<td>23</td>
<td>40</td>
<td>53</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>location 4</td>
<td>17</td>
<td>25</td>
<td>27</td>
<td>33</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>location 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>location 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>22</td>
<td>27</td>
<td>31</td>
<td>47</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Uncertainty</td>
<td>5</td>
<td>5</td>
<td>9</td>
<td>10</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Table A. 5: Water contact of the smooth substrate, boiled in pure water and after NBND using 50 nm alumina nanofluid:

<table>
<thead>
<tr>
<th></th>
<th>N400</th>
<th>1%</th>
<th>0.10%</th>
<th>0.01%</th>
<th>pure water</th>
<th>before boiling</th>
</tr>
</thead>
<tbody>
<tr>
<td>location 1</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>17</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>location 2</td>
<td>7</td>
<td>13</td>
<td>10</td>
<td>24</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>location 3</td>
<td>6</td>
<td>13</td>
<td>16</td>
<td>27</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>location 4</td>
<td>6</td>
<td>12</td>
<td>20</td>
<td>17</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>6</td>
<td>12</td>
<td>17</td>
<td>21</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Uncertainty</td>
<td>1</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>
Table A. 6: Water contact of the rough substrate, boiled in pure water and after NBND using 50 nm alumina nanofluid:

<table>
<thead>
<tr>
<th></th>
<th>N60</th>
<th>1%</th>
<th>0.10%</th>
<th>0.01%</th>
<th>pure water</th>
<th>before boiling</th>
</tr>
</thead>
<tbody>
<tr>
<td>location 1</td>
<td>6</td>
<td>36</td>
<td>38</td>
<td>39</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>location 2</td>
<td>8</td>
<td>36</td>
<td>36</td>
<td>45</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>location 3</td>
<td>6</td>
<td>38</td>
<td>37</td>
<td>43</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>location 4</td>
<td>6</td>
<td>38</td>
<td>35</td>
<td>36</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>location 5</td>
<td></td>
<td></td>
<td></td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>location 6</td>
<td></td>
<td></td>
<td></td>
<td>45</td>
<td></td>
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</tr>
<tr>
<td>location 7</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>7</td>
<td>36</td>
<td>37</td>
<td>39</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Uncertainty</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>
The histogram for the number density of particle size distribution analysis are shown in Figure A.1 to Figure A.5. Data comes from SEM image analysis. Size measurement of one hundred different particles in the images where recorded and scaled by the scale bar in each image of Figure 2.7 and Figure 2.8.

Figure A.1: Histogram of particle sizes of nominal 13 nm Al₂O₃ nanoparticles.
Figure A. 2: Histogram of particle sizes of nominal 50 nm Al$_2$O$_3$ nanoparticles.

Figure A. 3: Histogram of particle sizes of nominal 300 nm Al$_2$O$_3$ nanoparticles.
Figure A. 4: Histogram of particle sizes of nominal 65 nm SiO$_2$ nanoparticles.

Figure A. 5: Histogram of particle sizes of nominal 15 nm SiO$_2$ nanoparticles.
Figure A. 6: Zeta potential distribution function of 13 nm Al₂O₃ nanofluid.
Proof of Equation (4.2):

\[ dF_{comb} = dF_W \omega_W + dF_H \omega_H \]  
(4.1)

\[ \omega_W = \frac{A_{proj,W}}{A_{proj,comb}}, \text{ and } \omega_H = \frac{A_{proj,H}}{A_{proj,comb}} \]  
(4.1a)

\[ dF_{comb} = \gamma_W dA_{v,comb} + \gamma_s dA_{sl,comb} + \gamma_s dA_{sv,comb} \]  
(4.1b)

\[ dA_{v,comb} = dA_{proj,comb} \cos \theta - (1 - \varphi_v) dA_{proj,H} \]  
(4.1c)

\[ dA_{sv,comb} = -dA_{sl,comb} \]  
(4.1d)

\[ dF_{comb} = \gamma_W \left[ dA_{proj,comb} \cos \theta - (1 - \varphi_v) dA_{proj,H} \right] + \gamma_s dA_{sl,comb} - \gamma_s dA_{sv,comb} \]  
(4.1e)

\[ \frac{dF_{comb}}{dA_{sl,comb}} = 0 \]  
(4.1f)

\[ \gamma_W \left[ \cos \theta \frac{dA_{proj,comb}}{dA_{sl,comb}} - (1 - \varphi_v) \frac{dA_{proj,H}}{dA_{proj,comb}} \right] + (\gamma_s - \gamma_v) = 0 \]  
(4.1f)

\[ \frac{dA_{sl,comb}}{dA_{proj,comb}} = \frac{dA_{sl,W}}{dA_{proj,W}} \frac{dA_{proj,W}}{dA_{proj,comb}} + \frac{dA_{sl,H}}{dA_{proj,H}} \frac{dA_{proj,H}}{dA_{proj,comb}} \]  
(4.1g)
\[
\frac{dA_{j,W}}{dA_{proj,W}} = r, \\
\frac{dA_{j,H}}{dA_{proj,H}} = \varphi_{sv} 
\]

(4.1h)

\[
\gamma_{lv} \left[ \frac{\cos \theta}{r \omega_w + \varphi_{sv} \omega_H} - \left(1 - \varphi_{sv}\right) \frac{\omega_H}{r \omega_w + \varphi_{sv} \omega_H} \right] + \left(\gamma_{sl} - \gamma_{sv}\right) = 0 
\]

(4.1i)

\[
\cos \theta - \left(1 - \varphi_{sv}\right) \omega_H = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \\
\cos \theta - \left(1 - \varphi_{sv}\right) \omega_H = \cos \theta_r \left(r \omega_w + \varphi_{sv} \omega_H \right) 
\]

(4.1j)

\[
\cos \theta = (\cos \theta_r r) \omega_w + \left[ \cos \theta_r \varphi_{sv} + (1 - \varphi_{sv}) \right] \omega_H 
\]

(4.1k)

\[
\cos \theta_w = r \cos \theta_r, \text{ and } \cos \theta_H = \varphi_{sv} (\cos \theta_r - 1) + 1 
\]

(4.1l)

\[
\cos \theta = \cos \theta_w \omega_w + \cos \theta_H \omega_H 
\]

(4.2)