

PHASE CHANGE HEAT TRANSFER – A PERSPECTIVE FOR THE FUTURE:

RESPONSE TO PROFESSOR VIJAY K. DHIR

by

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INTRODUCTION

Phase change heat transfer, specifically the liquid-to-vapor transition, has commanded a great deal of interest in the last 50 years, fueled by applications of enormous technological importance. The applications have evolved over time to include design of efficient heat exchangers, prediction of nuclear reactor accidents, design of cooling systems for microelectronic equipment, and developing commercial ink-jet printer technology. Boiling in particular is the most efficient yet least understood phase change process. It is a subject in which Professor Rohsenow and his colleagues in the Heat Transfer Laboratory at MIT have made pioneering advances. As such, it is an appropriate topic by Professor Dhir to illustrate the future of phase change processes as we celebrate the contributions of Professor Rohsenow in this area.

Two broad themes are discussed by Professor Dhir: the emerging power of computational tools to solve problems in phase change heat transfer; and the role of processes at the molecular level. Professor Dhir uses bubble growth in a quiescent bulk pool (i.e., pool boiling) as a paradigm of phase change. It is a pleasure to have the opportunity to amplify on some of these two themes mentioned by Professor Dhir.

NUCLEATE BOILING

The difficulty of developing a computational capability for nucleate boiling heat transfer is due to the great complexity of the coupled processes of nucleating bubbles at a heated surface, tracking their growth, and accounting for bubble detachment and transport through the bulk liquid. Added to this is the fact that the number of nucleation sites tend to be dependent on surface topology, that the bulk liquid can be moving and may contain impurities, and that the bubble shapes evolve as they grow, detach and move through the bulk.

Advances in our understanding of boiling have relied primarily on carefully designed experiments and what might be termed phenomenological models of various sub-processes of the complete boiling picture. These include liquid spread on surfaces to trap gases in imperfections of different geometries [1,2][§] bubble growth at surfaces [3-5], bubble departure [6,7], nucleate boiling heat flux [8-11], critical heat flux [12,13], and film boiling [14].

To this body of knowledge we now add the successful efforts of Professor Dhir to bring the power of direct numerical simulations (DNS) to the problem of bubble growth and detachment at a surface. The surface has specific nucleation sites where the bubbles are forced to grow, as contrasted to commercial surfaces with their associated random array of active sites and the bulk liquid pool is stagnant. For this idealized system, Dhir simulates the growth, spread, and departure cycle of single isolated bubbles and simple arrays of bubbles in close proximity to other bubbles – arrays of 2, 3 and 5 bubbles. The full complement of transport equations with boundary conditions is solved for the first time to track the evolving bubble shapes. The achievement is considerable and the agreement of the simulations with experimentally observed bubble shapes remarkable.

These are the first DNS of bubble growth and departure. This capability is important for a number of reasons. The ability to predict bubble growth dynamics without invoking any assumptions of the process beyond what is included in the governing transport equations and boundary conditions is in the trend of DNS that has had a significant impact on other branches of engineering, most notably computational fluid dynamics as applied to turbulence and the simulation of free liquid boundaries with time-evolving shapes such as liquid jet or droplet impingement on solid surfaces [16]. With DNS of nucleate

[§]The citations listed are not intended to be an exhaustive compilation.

boiling comes the prospect of even developing numerically-generated correlations that are more faithful to the physics of the process (e.g., for bubble departure diameter) than those based on assumptions. A validated DNS can provide greater certainty about the contributing mechanisms.

In Dhir's clean and careful experiments the nucleation sites are fabricated into the surface. A real surface, however, has randomly distributed sites. Developing a general theory for active site density is a difficult problem and there may be no solution. Interestingly, surface condition does not factor into some long-standing (and successful) theories of certain boiling regimes, such as the critical heat flux which is based on hydrodynamic instability theory ([13] building on work of [15] and others); and film boiling with analogy to boundary layer theory [14]. A simulation will only be as good as the physics which are included in the governing equations. This challenge is underscored by the insights that new metrological tools are bringing to the problem by their ability to probe the nature of the liquid/solid boundary on the smallest scale.

MOLECULAR-LEVEL PROCESSES IN PHASE CHANGE

Nucleate boiling is traditionally analyzed from a macroscopic viewpoint. On the other hand, the physics of molecular interactions are central to one of the earliest theoretical modeling efforts of phase transitions, namely those which occur by homogeneous nucleation of liquid droplets in supersaturated vapors or vapor bubbles in superheated liquids [17]. The theoretical analysis of these processes are traced to the early efforts of Gibbs [18] on the energetics of phase change. The kinetics of the growth to the stable or metastable phase is governed by various schemes for tracking the rate at which individual molecules 'evaporate' or 'condense' into the nuclei of the emerging phase. The predicted size of thermodynamically stable nuclei (vapor bubble in superheated liquid or liquid droplet in supersaturated vapor) are of nanometer dimensions. A review of the field is given in reference 19.

The success of classical homogeneous nucleation theory is the excellent agreement it often shows with measured thermodynamic states when the bulk boiling process is explosive in nature (similar to a 'vapor explosion'). However, few practical phase change processes occur this way because of the extremes of heating rate (constant pressure) or decompression rate (constant temperature) required to hold off nucleation of trapped gases in surface irregularities (for example, ink-jet printer technology [20,21]). Taking water as an example in contact with a solid surface, homogeneous nucleation is an operative mechanism if the water is heated at about a quarter billion degrees per second and to temperatures close to 300C at atmospheric pressure

[20] whereas water's boiling point at this pressure is only 100C. Otherwise, bubble nucleation will occur in the traditionally viewed way of gas emergence out of the mouth of cavities which trap vapor.

Nucleate boiling does not enjoy the same level of theoretical rigor as homogeneous nucleation. Part of the reason is that nucleate boiling evolves from a microscopic process early on (wetting and bubble nucleation) into a macroscopic process later (growth and departure) which poses considerable challenges of bridging disparate length scales as noted by Dhir. Homogeneous nucleation, on the other hand, concerns only the birth of stable vapor nuclei and not its subsequent growth. For this reason, homogeneous nucleation can be considered as an initial condition to the bubble growth problem when fluid conditions make homogeneous nucleation a viable mechanism to trigger a bulk phase transition.

Another concern with modeling nucleate boiling is that the process is intimately dependent on the nature of the liquid/solid interface – notions of contact angle, surface wettability and active site density as mentioned previously – but the physics of these processes are not as well developed as originally envisioned. For example, applying atomic force microscopy in the 'tapping' mode, Tyrell and Attard [22] discovered the presence of a vapor layer separating bulk water from a glass surface. Figure 1 below shows some of their images.

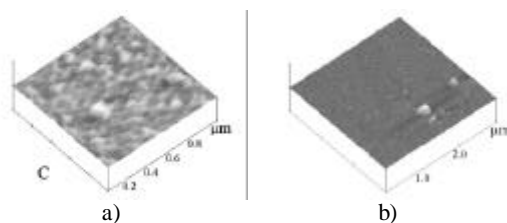


Figure 1: a) AFM tapping mode images of a $1\mu\text{m}$ square glass surface immersed in water (vertical scale is 30nm); b) bare glass surface. From reference 22.

The bubbles are apparently not spherical but rather have a pancake shape with much larger radius of curvature which resolves the question of how they could exist without completely dissolving. The mechanism for forming nanobubbles is unclear and their influence on nucleation is unknown. They apparently only exist on hydrophobic surfaces. One idea is that the hydrophobic surface with nanobubbles is acting as a nucleation site for air in supersaturated water. Supersaturation might occur during submersion of the glass substrate in water by entrainment of gases during flow of the water over the surface, or even by localized heating from the instrumentation used to make the measurements.

Molecular dynamics (MD) simulations of liquids have also been used to numerically predict the liquid/solid interface structure, contact angle, and bubble formation and liquid droplet nucleation in supersaturated vapors at solid

surfaces. In this approach, every molecule is tracked with the equations of motion which can require enormous computational time. This task has been made more feasible for the large systems of boiling by significant advances in computing power and development of efficient numerical algorithms. An example of MD simulations for a water droplet spreading on a platinum surface is shown in figure 2 [23,24]. Computed density profiles are shown in figure 2b.

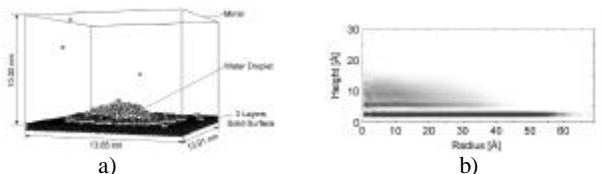


Figure 2: density distribution of a water droplet on platinum [24] at 350K. a) shows a snapshot of the MD simulation; b) illustrates an equilibrium droplet with underlying monolayer.

The simulations include the interaction of platinum molecules beneath the water molecules in the monolayer which forms at the surface. The simulations show a monolayer advancing beneath the bulk water droplet. Disregarding this monolayer results in a predicted contact angle of about 20° . MD simulations of bubble nucleation at heated surfaces [25] have also been carried out. Figure 3 shows a snapshot of a vapor bubble between parallel plates represented by 3 molecular layers of an fcc solid of an insulating material.



Figure 3: MD simulation of Argon bubble nucleation between parallel plates at 100K [25]. The bubble is the void region.

The void or 'bubble' formed 2100ps after the plates were slowly expanded to lower pressure. The resolution of the simulations makes the concept of contact angle questionable at this level, a point also anticipated by Dhir.

When molecular-level processes dominate triggering a phase transition as for homogeneous bubble nucleation, the standard way to probe the nature of the solid/liquid interface is indirectly through sensitive but macroscopic measurement of some form of 'signature' variable. Measurement of the evolution of surface temperature of a pulse-heated material can be used for this purpose if the surface is heated at a fast enough rate to trigger a phase transition by homogeneous nucleation

and if data can be acquired at a high enough frequency to capture the evolution of the process. An inflection point in the evolution of temperature would then result when a bubble forms at the surface [20,21]. A recent study by Thomas et al. [26] used this idea to investigate the influence of chemical functionality of a solid surface on bubble nucleation temperature as a signature for molecular binding on the surface. The figure below from their study shows the average surface temperature of a thin film gold line that was pulse-heated electrically in water to trigger bubble nucleation.

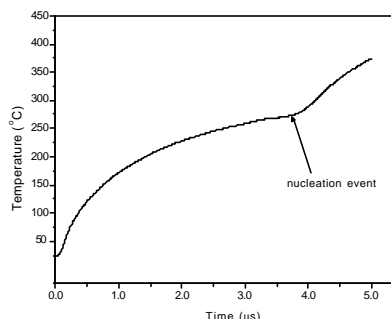


Figure 4: Evolution of surface temperature of a gold thin film coated with a hydrophilic self-assembled monolayer and pulse-heated in water [26].

The targeted application is biochemical sensing through detection of changes to the interfacial water structure. The molecular structure of a thin film gold surface immersed in distilled water was altered by growing hydrophilic or hydrophobic self-assembled monolayers (SAMs) of alkanethiols ($\text{HO}(\text{CH}_2)_n\text{SH}$ or $\text{CH}_3(\text{CH}_2)_n\text{SH}$ where $n=6, 11,$ or 16 for hydrophilic and $6, 11,$ or 15 for hydrophobic SAMs). Rapidly heating the SAM-covered gold films showed that bubble nucleation was very sensitive to the interfacial structure of the water/SAM bonding. Distinct differences in nucleation temperatures (i.e., the inflection point in the evolution of surface temperature) were measured between the hydrophobic SAMs and the hydrophilic SAMs. This established a direct connection between the chemical bond structure at the SAM/water interface and bubble nucleation temperature. Whether this difference was due to the apparent propensity of hydrophobic surfaces to form nanobubbles or it was due to differences in contact angle for hydrophilic or hydrophobic SAMs remains to be answered

CONCLUDING REMARKS

The next challenge for nucleate boiling will lie in advancements in numerical simulation. The robust simulations demonstrated by Professor Dhir are a significant step. We continue to learn new things about the nature of the solid/liquid interface as the discovery of nanobubbles on

hydrophobic surfaces shows. As Dhir notes, the current state of simulations has not yet accomplished the coupling or bridging between molecular and macro transport processes for phase change. While we wait for this achievement, the reliance on clever application of existing experimental designs and development of new techniques will be necessary to maintain the pace of advancement and contribute to new knowledge.

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