REPORT DOCUMENTATION PAGE

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE
08/12/2021

2. REPORT TYPE
Final

3. DATES COVERED

START DATE
07/01/2017

END DATE
05/14/2021

4. TITLE AND SUBTITLE
Evaporative Processes and Vapor Nucleation via Molecular simulations and Theory

5a. CONTRACT NUMBER
N000141712767

5b. GRANT NUMBER
N3160-NV-ONR

5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHOR(S)
Keblinski, Pawel and Garde, Shekhar

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Rensselaer Polytechnic Institute
110 8th Street
Troy, NY 12180-3590

8. PERFORMING ORGANIZATION REPORT NUMBER
NA

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
875 NORTH RANDOLPH STREET

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited distribution, all data are available upon a reasonable request

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The report presents the summary of the most important accomplishments of focusing of the two technical areas both involving molecular dynamics simulations and associated thermodynamics-based analysis. Area 1: Molecular simulation study of evaporation-condensation at a liquid vapor interface revealed that so called Schrage theory is very accurate in predicting evaporation rates. Furthermore, we develop closed analytical formula to estimate the degrading role non-condensing gases on the efficiency of the colling process that can be useful for the desig

15. SUBJECT TERMS
molecular simulation, FEM simulations of multi-phase flow, evaporation-condensation, heterogeneous nucleation

16. SECURITY CLASSIFICATION OF:

a. REPORT
U

b. ABSTRACT
U

C. THIS PAGE
U

17. LIMITATION OF ABSTRACT
UU

18. NUMBER OF PAGES

19a. NAME OF RESPONSIBLE PERSON
Keblinski, Pawel

19b. PHONE NUMBER *(Include area code)*
518-526-5438

PREVIOUS EDITION IS OBSOLETE.

STANDARD FORM 298 (REV. 5/2020)
Prescribed by ANSI Std. Z39.18

Evaporative Processes and *Vapor* Nucleation via Molecular simulations and Theory

Final Project Report:

PI: Pawel Keblinski, Materials Science & Engineering Department, Co-PI Shekhar Garde,
Chemical & Biological Engineering Department, Rensselaer Polytechnic Institute, Troy, NY
Senior Researcher, Zhi Liang, Mechanical Engineering Department, California State University, Fresno, CA

Abstract

This report presents a summary of the most important accomplishments within the project's two technical focus areas, both involving molecular dynamics simulations and associated thermodynamics-based analysis**. Area 1: S*imulation study of evaporation-condensation at a liquid vapor interface*** – this study revealed that the so-called Schrage theory is very accurate in predicting evaporation rates. Furthermore, we developed closed analytical formulas to estimate the degrading role of non-condensing gases on the efficiency of the evaporative cooling process that can be useful for the design of heat pipes with nano and micro dimensions. Finally, we developed interfacial constitutive relationships that render continuum simulations capable of accurate description of evaporative rates even in the cases on nanoscale dimensions and ultra-fast processes. **Area 2: *Molecular simulations of heterogeneous bubble nucleation processes***. In these simulations, we found that in the case of a strong wetting interface, regardless of the topology, the interface does not affect nucleation. Only weaker wetting leads to heterogenous nucleation at the interface. In this case, the easiest nucleation occurs when there is a surface defect with a size comparable to that of the critical (homogeneous) bubble nucleation radius. Our findings provide design guidelines for the development of surface grooves that control the generation of vapor bubbles.

Research Area 1: Molecular simulation study of evaporation-condensation at a liquid vapor interface

(a) Molecular dynamics simulations:

The major accomplishment associated with this work was the determination of the net evaporation rate at an interface in terms of local thermodynamics conditions at the interface, i.e., temperature of the liquid, temperature of the vapor, vapor density, and saturated vapor density, as well as the kinetic factor, i.e., mass accommodation coefficient.

The significance of our results is underscored by the fact that despite over a century of research dating back to pioneering work of Hertz and Knudsen [1], the above issue is still a subject of discussion and dispute. In particular, the predictions of the Hertz-Knudsen (HK) relations developed under an assumption that the velocity distribution of vapor molecules is the Maxwell-Boltzmann (MB) distribution were often found not consistent with experimental data or numerical simulation results. The next key theoretical advance was introduced by Schrage [2] who noticed that the vapor molecules move perpendicularly to the liquid-vapor interface with a nonzero mean (macroscopic) velocity, thus it is more appropriate to assume that the vapor molecules adjacent to the interface have an MB velocity distribution shifted by the mean (macroscopic velocity).

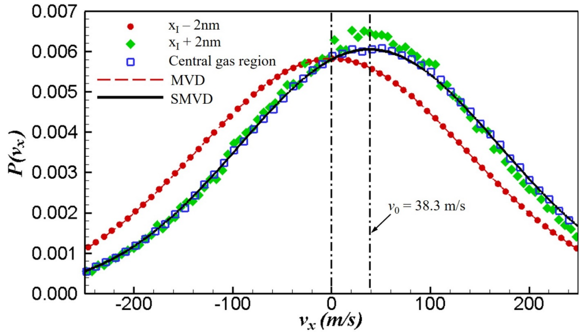

Fig.1. The normal to the liquid-vapor interface component velocity distribution of liquid molecules 2-nm from the interface (red circles), vapor molecules 2-nm from the interface (green diamonds), and vapor molecules in the central vapor region (blue squares). The dashed line is the Maxwell velocity distribution of The solid line is the MD distribution shifted by the macroscopic vapor flow velocity. From Ref [3].

The fact that the validity of Schrage relationships, or for that matter, any other relationships describing evaporation/ condensation rates, remains under discussion, is partially caused by challenges in the experimental quantification of evaporation and condensation processes. To this extent, one needs to measure the temperature at the liquid-vapor interfaces, density in the vapor phase, and the mass accommodation coefficients accurately – direct measurement of these quantities with "interfacial" resolution is still beyond the experimental realm. By contrast, molecular dynamics (MD) simulations are naturally capable of providing all these quantities with high (nanoscopic) spatial resolution and high accuracy. Moreover, the velocity distribution of evaporating/ condensing molecules, which is an important indicator of the validity of Schrage analysis, can also be directly determined from MD simulations (see Fig. 1).

Quite remarkably, we demonstrated that non-linearized Schrage relationships are capable of the accurate prediction of the evaporation and condensation rates even when the driving forces are very large, and even when approaching evaporation to the vacuum. The question why the distribution in the vapor is well represented by a shifted equilibrium MB distribution with such large driving forces remains open - our simulation results are likely to stimulate theoretical efforts by providing highly accurate "numerical experiment" data.

The MD simulation results described above were obtained for a planar heat pipe model system with only working fluid present. In the next simulation effort, we added a non-condensable gas to the system. This is important from the point of view of realistic evaporative processes, such as those occurring at air-water interfaces. We found that the presence of non-condensable gas has a very small effect on the accommodation coefficient of condensable gas. The main role of the non-condensable gas is creating resistance to the heat flow in the vapor phase. In this context, the main accomplishment was the development of analytical formulas [4] allowing estimation of the relative role of heat transfer resistance due to the resistance of the interface and the resistance of the vapor-gas mixture. These formulas are useful in guiding the design of heat pipes in terms of geometrical dimensions and the concentration of non-condensable gas. In this context, we estimated the so-called equivalent interfacial length, L_e, i.e., the length over which the overall resistance to the evaporative mass flow in the gas phase is the same as the resistance of the interface.

Another significant accomplishment associated with liquid-vapor MD simulations was the determination of the mass accommodation coefficient at a liquid-vapor interface moving rapidly towards the vapor phase. This mimics the situation where vapor bubbles nucleated e.g., by mechanical agitation, exhibit rapid collapse. We demonstrated [5] that even for interfacial velocities much larger than thermal velocities, the vapor accommodation coefficient is very large and consequently the density buildup the front of the liquid-vapor interfaces is much smaller than when one assumes low condensation rate. The latter assumption is often employed in the continuum-level modeling of collapsing vapor cavities. Therefore, our results have significant conceptual implications for the understanding of vapor bubble collapse and other processes involving high-velocity, vapor-liquid collisions.

While the MD simulations reported above involved a steady state configuration, our transient evaporation and condensation simulations also demonstrated good agreement with the predictions from the Schrage relationships [6]. Furthermore, our analyses show that at the nanoscale, the kinetics of the transient heat and mass transfer between the evaporating and the condensing surfaces in the nanochannel are mainly controlled by heat and mass diffusion in the vapor rather than by convection. The simulation results also indicate that the Schrage relationships are capable of accurately describing the transient evaporation/condensation processes and their rates even under a high-frequency oscillatory driving force condition. This allows for and justifies the quantitative analysis of the recent experimental observations of transient laser heating induced evaporation [7].

Finally, we simulated evaporation of molecular water. The results show that in the limit of low evaporation rates, the Schrage theory predicts the rates within 10-15% percent accuracy, and that the accuracy improves significantly at higher rates. [8] In comparison, our prior results on monoatomic fluid show that the deviations from Schrage predictions were extremely small (< 3%) at all driving conditions [3]. However, molecular non-polar fluids such as n-dodecane [9] showed larger deviations for smaller driving forces akin to that we observe for water. This indicates that the rotational motion of the molecules has some effect on the evaporation process, however, the effect is not very significant. In literature, based in the experimental studies, the observed behavior often deviates from the Schrage theory by up to orders of magnitude. As compared to these observations, our results indicate that the discrepancy between theory and observed fluxes is relatively small. While our results show overall good agreement with the theory, discrepancies of ~ 10-15% for molecular liquids appears to be systematic rather than statistical. The apparent reduction of discrepancies at higher fluxes might be due to the cancellation of systematic errors: one being the inaccuracy of Schrage relations and the other arising from non-linear effects that can be present in highly driven systems which are far away from equilibrium

1 (b) Development of continuum framework for evaporative multi-phase flow

Continuum numerical methods modeling liquid-vapor phase change processes typically assume a local thermal equilibrium at the liquid-vapor interface, the continuity of temperature at phase interfaces and a relation between interfacial saturation pressure and temperature based on phase co-existence curves. Several standard macroscopic problems have been solved accurately by adhering to this assumption. However, at the micro-scale and certain non-standard macro-scale applications, significant jumps in temperature are observed at liquid-vapor interfaces during phase change, and vapor pressure can be far from equilibrium values. To relax the above assumptions, we developed a locally discontinuous arbitrary Lagrangian Eulerian finite element formulation with temperature discontinuities at interfaces between two phases [10]. With the use of a kinetic-theory-based Schrage relationship tested by our molecular simulations, we applied our methodology to solve the problem of flowing vapor in a planar heat pipe geometry and demonstrated an excellent agreement with our MD mics simulation results of the same problem [3]. Interestingly, accounting for temperature discontinuities leads to only a slight improvement in the prediction of mass fluxes as compared to the case when temperature continuity is assumed. This contrasts with the large improvement in the prediction of temperature profiles and is a consequence of the weak dependence of the evaporation/condensation rates on the vapor temperature.

We expanded our continuum capabilities to model highly transient evaporation processes [11]. As shown in Fig. 2, the continuum formulation is capable of very accurately modeling our MD results [6] despite the extremely small time and length scales involved. This is an interesting fact considering that continuum methods are efficient in modeling multi-phase flow at large time and length scales, and their applicability to nanoscale systems and processes is questionable. When the mean free path and the average time between atomic collisions is comparable to the characteristic length and time scales of interest, the continuum hypothesis approaches its spatial and temporal limit. Our results [10, 11] indicate that continuum conservation laws can correctly represent the dynamics of the specific problem of interest at nanoscale, provided that appropriate constitutive relations are used at liquid- vapor interfaces.

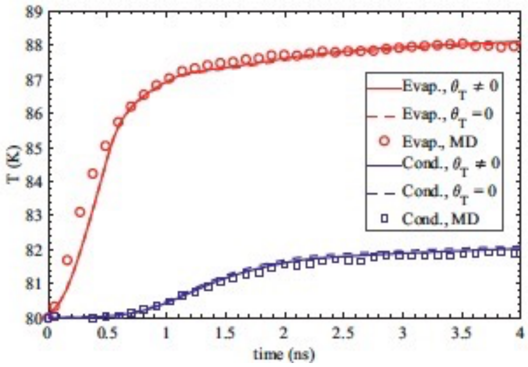

Fig.2. Temperatures of the hot (red) and cold (blue) ends of the nano heat pipe in a highly transient evaporation process. Solid lines represent continuum predictions and the symbols MD results.

Area 2: Molecular simulations of heterogeneous bubble nucleation processes.

Using molecular dynamics simulations, we investigated heterogeneous bubble nucleation processes in molecular water systems under tension. [12] In these simulations, the maximum negative pressure (nucleation pressure) sustained by the system was used a as measure of the system's propensity to nucleate a bubble. We found that in the presence of a planar solid substrate, or a substrate involving defects, such as grooves, when strong interaction exists between the solid and water, nucleation pressure is essentially the same as in the case of homogeneous nucleation. In the weaker solid-liquid integrations, a lowering of the of nucleation pressure is observed. Reduction in nucleation pressure with decreasing gold-water surface interaction strength obtained from our simulations shows good qualitative agreement with classical heterogeneous nucleation theory. As compared to planar surfaces, surfaces with grooves show a further reduction in the nucleation barrier only for weak interfacial interactions. Furthermore, the groove dimensions also influence nucleation, with the easiest nucleation occurring when the length scale of the defect is comparable to that of the critical (homogeneous) bubble nucleation radius (see Fig. 3).

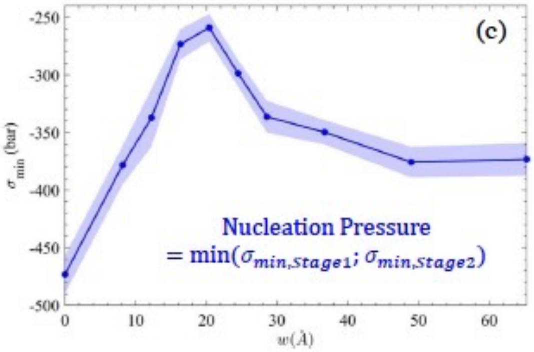

Fig.2. Required negative pressure to nucleate nanoscale vapor bubble as a function of surface groove size. When the groove size is comparable with the critical nucleus size the nucleation is the easiest.

Our findings provide design guidelines of surface grooves for the controllable generation of vapor bubbles. For example, in the case of wetting surfaces, the topology does not affect the nucleation, as the nucleation occurs in the bulk of the liquid and is simply equivalent to homogenous nucleation. In the case when spatially control of vapor bubble nucleation is desired, our results indicated that one should create no-wetting surface heterogeneities with a size comparable to the critical nucleus size – in case of water at normal conditions, this size is of the order of one micron.

Dissemination, recognition, workforce training.

This project led to 8 already published articles in peer-review journals and one submission still under review. In the longer term, perhaps the most influential outcome of this research will be our first publication on the validity of Schrage relationships [3]. The reviewers of this publication said: Reviewer # 1: "This work represents the first actual test of the Schrage theory and is an outstanding contribution to the field of evaporation and condensation" Reviewer # 2: "I have to say this is one of the best phase-change papers I read. It is an important benchmark which has been needed for years." So far, this work was cited almost 50 times and might became a classic.

The PI presented 20 invited talks at universities and research labs in the USA and multiple European countries. Additionally, graduate students conducted numerous conference presentations. Two students supported by this project received their PhDs and continue to develop successful research careers that contribute to US information and technology leadership. The first student, Jihui Nie (a woman), works at Google, while the second, Anirban Chandra, is a postdoctoral researcher at Argonne National Laboratory. In the course of the project, Anirban Chandra was awarded two competitive IBM summer fellowships, while Jihui Nie was awarded 1-year research fellowship in the Polish Academy of Sciences.

During this project, the PI, (Keblinski) was awarded Marie Sklodowska-Curie Fellowship (Poland-European Union, 2018) and became Materials Research Society Fellow. The fellowship's citation reads: "For influential contributions to the development of computational methods leading to fundamental understanding of thermal transport in materials on nanometer length-scales" (2020).

References:

*indicates publications resulted from this project support

[1] M. Knudsen, Kinetic Theory of Gases, 3rd ed. (London Methuene: London, 1950).

[2] R. W. Schrage, A Theoretical Study of Interphase Mass Transfer (Columbia University Press: New York, 1953).

*[3] *Molecular Simulations of Steady-state Evaporation: Validity of the Schrage Relationships*, Z. Liang. B. Thierry and P. Keblinski, Inter. J. Heat and Mass Transfer **114**, 105–114 (2017).

*[4] *Molecular Simulation of Steady-state Evaporation and Condensation in the Presence of a Non-condensable Gas*, Z. Liang. and P. Keblinski, J. Chem. Physics **148**, 064708 (2018)

*[5] *Mass Accommodation at a High-velocity Water Liquid-vapor Interface:* J. Nie, A. Chandra, Z. Liang and P. Keblinski, submitted to the Journal of Chemical Physics, 2018.

*[6] *A Molecular Dynamics Study of Transient Evaporation and Condensation*, Z. Liang, A. Chandra, E. Bird, and P. Keblinski, Inter. J. Heat and Mass Transfer 149, article # 119152. (2020).

[7] *Plasmonic Sensing of Ultrafast Evaporation and Condensation* J. Park, X. Xie, D. Li, and D. G. Cahill, Nano., Micro. Therm. Eng. 21, 70 (2017).

*[8] *Investigating the validity of Schrage relationships for water using molecular dynamics simulations*, A. Chandra and P. Keblinski, J. Chem. Phys. **153**, article # 124505 (2020).

[9] *Thermal transport across the interface between liquid n-dodecane and its own vapor: A molecular dynamics study,* E. Bird, J. Gutierrez Plascencia, Z. Liang, , The Journal of Chemical Physics 152, article # 184701(2020).

*[10] *A continuum framework for modeling liquid-vapor interfaces out of local thermal equilibrium*, A. Chandra, P. Keblinski, O. Sahni, & A. A. Oberai,. International Journal of Heat and Mass Transfer, 144, article # 118597 (2019).

*[11] *On the applicability of continuum scale models for ultrafast nanoscale liquid-vapor phase change*, A. Chandra, Z. Liang, A. A Oberai, O. Sahni , and P. Keblinski, Inter. J. Multiphase Flow, 135, article # 103508 (2021).

*[12] *Multi-stage heterogeneous bubble nucleation under negative pressures*, A. Chandra, S. Garde, and P. Keblinski, submitted to JCP (2021).

*[13] *Gibbs Adsorption Impact on a Nanodroplet Shape: Modification of Young−Laplace Equation*, M. Isaiev, S. Burian, L. Bulavin, W. Chaze, M. Gradeck,G. Castanet, S. Merabia, P. Keblinski, and K. Termentzidis. J. Phys. Chem. B **122**, 3176 (2018).