PHASE TRANSITIONS OF LONG-CHAIN n-ALKANES AT INTERFACES

by

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A thesis submitted for the degree of Doctor of Philosophy

of

The Australian National University

January 2001
PREFACE

This thesis is an account of research carried out at the Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Australian National University, between July 1997 and January 2001.

This thesis is a product of a number of fruitful collaborations. The study described in Chapters 3 and 4 were carried out under supervision of Hugo Christenson and that in Chapter 5 under supervision of Vassili Yaminisky. Modeling and numerical calculation of the rate of condensate growth in Chapter 4 were carried out by Mika Kohonen. Distillation of some of the samples used in the study Chapters 3 through 5 were carried out by Jack Derlacki. The figures 2.1, 2.2 and 2.6 were kindly donated by Mika Kohonen.

The work described in this thesis has not previously been submitted for a degree or diploma in any other institution.

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ACKNOWLEDGEMENTS

The great policy created by Barry Ninham is that each student in the department of Applied Mathematics is encouraged to approach any member of the academic staff for collaboration. The policy and the free, relaxed atmosphere of the department have certainly been maintained during my stay, providing each student an invaluable opportunity to broaden his or her base. I have benefited a lot from this excellent environment, working with top scientists in the field, each of whom has different viewpoint, idea, and philosophy toward science.

First of all, I thank Barry Ninham for introducing me to my supervisors, Hugo Christenson and Vassili Yaminsky and for his advice and encouragement as one of my supervisors. I thank both Barry and Stephen Hyde for their various kinds of support during my Ph.D. program as Heads of Department.

Secondly, I thank Hugo Christenson and Vassili Yaminsky for their supervision and advice. Both Hugo and Vassili gave me a lot of freedom and their good scientific instincts and judgements no doubt helped me to complete my Ph.D. projects within three and a half years. I also learned a lot from their scientific presentation and writing styles.

Thirdly, I thank my collaborators, Tim Senden, Vince Craig, Stjepan Marcelja, David Williams, Chiara Neto and Mika Kohonen. I was very lucky to meet you and have an opportunity to work with you. You all kindly assisted me in different types of projects, though you didn’t have obligations or responsibilities to do so. I particularly owe a lot to my fellow student, Mika, not only for his vast knowledge and deep understanding in the subject, which always impressed me, but also for a wide range of outside activities. On this regard, I thank all my friends who shared fun with me.

Fourthly, I thank our senior technical officers Anthony Hyde, Tim Sawkins and Jack Derlacki and our departmental administrator Diana Wallace. Without their help this thesis would not have been completed. I thank Tim in particular, not only for his technical support but also for being my mentor in the University Toastmasters club. There is no doubt that I owe a lot to all the members of the club for improvement of my seminar presentation skills.
Finally, I thank the Australian National University for offering me the ANU Ph.D. Scholarship and the Department of Applied Mathematics for offering me the Tuition Fee Scholarship.
**ABSTRACT**

An experimental study of phase transitions of long-chain \( n \)-alkanes induced by the effect of interfaces is described.

The phase behaviour of long-chain \( n \)-alkanes (carbon number 14, 16, 17, 18) adsorbed at isolated mica surfaces and confined between two mica surfaces has been studied in the vicinity of and down to several degrees below the bulk melting points, \( T_m \). Using the Surface Force Apparatus we have measured the thickness of alkane films adsorbed from vapour \((0.97 \leq p/p_0 \leq 0.997)\), studied capillary condensation transition, subsequent growth of capillary condensates between two surfaces, and phase transitions in both the adsorbed films and the condensates. By measuring the growth rate of the capillary condensates we have identified a transition in the lateral mobility of molecules in the adsorbed films on isolated mica surfaces. This transition to greater mobility occurs slightly above \( T_m \) for \( n \)-hexadecane, \( n \)-heptadecane and \( n \)-octadecane but several degrees below \( T_m \) for \( n \)-tetradecane, and is accompanied by a change in wetting behaviour and a measurable decrease in adsorbed film thickness for \( n \)-heptadecane and \( n \)-octadecane. Capillary condensates that form below \( T_m \) remain liquid, but may freeze if the degree of confinement is reduced by separation of the mica surfaces. An increase in the area of the liquid-vapour interface relative to that of the liquid-mica interface facilitates freezing in the case of the long-chain alkanes, which show surface freezing at the liquid-vapour interface.

Although thermodynamic properties of the surface freezing transition have been rather well documented, the kinetics involved in formation of such ordered monolayers has so far received very little attention. We studied the surface tension of \( n \)-octadecane as a function of temperature in the vicinity of \( T_m \), using the static Wilhelmy plate and the dynamic maximum bubble pressure methods. The two methods give different results on cooling paths, where nucleation of the surface ordered phase is involved, but agree on heating paths, where both methods measure properties of the equilibrium surface phase. On cooling paths, the surface of bubbles may supercool below the equilibrium surface freezing temperature. The onset of surface freezing is marked by a sharp drop in the surface tension. The transition is accompanied by an increased stability of the films resulting in longer bubble lifetimes at the liquid surface, which suggests that the mechanical properties of the surfaces change from liquid-like to solid-like. Our results suggest occurrence of supercooling of the monolayer itself.
PUBLICATIONS

The kinetics of capillary condensation in a nanoscale pore  
Mika M. Kohonen, Nobuo Maeda and Hugo K. Christenson  

Direct observation of surface effects on the freezing and melting of an n-alkane  
Nobuo Maeda and Hugo K. Christenson  
*Colloids and Surfaces A*, **159**, 135 (1999)

Surface supercooling and stability of n-alkane films  
Nobuo Maeda and Vassili V. Yaminsky  

A phase transition of n-alkane layers adsorbed on mica  
Nobuo Maeda, Mika M. Kohonen and Hugo K. Christenson  

A method for the calibration of force microscopy cantilevers via hydrodynamic drag  
Nobuo Maeda and Tim J. Senden  

Phase behaviour of long-chain n-alkanes at one and between two mica surfaces  
Nobuo Maeda, Mika M. Kohonen and Hugo K. Christenson  
*Journal of Physical Chemistry B*, submitted

Formation of vesicular tubes from the extension of fused phospholipid bilayers  
Nobuo Maeda, Tim J. Senden and Jean-Marc diMeglio  
*Physical Review Letters*, submitted

Condensed phase transitions induced by interfaces I  
Vassili V. Yaminsky and Nobuo Maeda  
Review article invited from *International Journal of Modern Physics B*

Condensed phase transitions induced by interfaces II  
Nobuo Maeda and Vassili V. Yaminsky  
Review article invited from *International Journal of Modern Physics B*

The kinetics of capillary condensation  
Mika M. Kohonen and Nobuo Maeda  
In preparation

Capillary condensation of liquid perfluorocyclohexane below the sublimation temperature  
Hugo K. Christenson and Nobuo Maeda  
In preparation
Whoever comes are the right people.

Whenever it starts is the right time.

Whatever happens is the only thing that could.

When it is over it is over.