PHASE TRANSITIONS OF LONG-CHAIN n-ALKANES AT INTERFACES

by

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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 Yaminsky. 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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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.

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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
Physical Review Letters, **82**, 4667 (1999)

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
Physical Review Letters, **84**, 698 (2000)

A phase transition of n-alkane layers adsorbed on mica
Nobuo Maeda, Mika M. Kohonen and Hugo K. Christenson
Physical Review E, **61**, 7239 (2000)

A method for the calibration of force microscopy cantilevers via hydrodynamic drag
Nobuo Maeda and Tim J. Senden
Langmuir, **16**, 9282 (2000)

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

CONTENTS

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.