Phase transition of *n*-alkane layers adsorbed on mica

Nobuo Maeda, Mika M. Kohonen, and Hugo K. Christenson*

*Department of Applied Mathematics, Research School of Physical Sciences, Australian National University,
Canberra ACT 0200, Australia*

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Thin (thickness $h \approx 3$ nm) films of *n*-octadecane and *n*-hexadecane adsorbed on mica surfaces from vapor close to their bulk melting points (T_m) have been studied in a surface force apparatus. Using data on the growth rate of capillary condensates between the mica surfaces in contact and measurements of h, we have identified a transition in the structure of the adsorbed films a few degrees above T_m. As T decreases the alkane layers appear to undergo a transition to a more ordered structure, akin to the postulated ''surface freezing'' of long-chain liquid *n*-alkanes.

The properties and behavior of *n*-alkanes are important for understanding the physics of systems such as lipids and liquid crystals. In many cases, van der Waals forces between long alkyl chains favor the formation of ordered monolayers, at surfaces or in aggregates, in which the molecules are oriented parallel to one another. By contrast, liquid *n*-alkanes are characterized by great disorder in the bulk, and the melting entropy is large, as for many polymers. For *n*-alkanes with $n \geq 20$, rotator phases are found at temperatures between the liquid and crystalline phases [1]. In these there is rotational freedom about the long axis of the molecules, although the layered structure and positional order of the bulk triclinic (for *n* even) or orthorhombic (*n* odd) crystal structure is preserved. It has also been reported that the interface between vapor and bulk liquid *n*-alkanes for $15 \leq n \leq 50$ exhibits ''surface freezing'' [1–3]. The surface tension of these alkanes shows a maximum a few degrees above T_m, instead of the usual monotonic decrease with T. The formation of an ordered monolayer at the liquid-vapor interface with a structure like that of the bulk rotator phase has been inferred from x-ray reflection studies [3] and reproduced in simulations [4].

n-alkanes at graphite surfaces order parallel to the surfaces, both in vapor [5] and liquid [6]. Measurements of the solvation force between mica surfaces in liquid alkanes for $6 \leq n \leq 16$ have shown that the period of the oscillatory force is close to the mean width of the alkyl chains [7], confirming that the molecules in the liquid state order parallel to smooth, solid surfaces. By contrast, it has been reported that a molecularly thin film of *n*-eicosane (n-C_{20}) on silica thickens and orders more normal to the surface below a transition temperature slightly above the bulk melting point T_m [8].

We are currently studying adsorption from vapor and phase transitions induced by the presence of solid walls with a simplified surface force apparatus (SFA) [9–11]. At isolated surfaces we have measured adsorption isotherms of *n*-pentane and cyclohexane (c-C_6) and with *tert*-butanol (t-BuOH) identified a continuous wetting transition and the related increase in the surface separation (≈ 10–30 nm) at which a capillary-condensation transition occurs [12]. The

condensates of t-BuOH remain liquid down to well below T_m [10]. The reduction in the total interfacial free energy of the system due to wetting by the liquid is large enough to compensate for the free energy increase incurred by keeping a small volume of substance liquid below T_m.

In the case of long-chain alkanes like *n*-octadecane (n-C_{18}), the condensed liquid freezes when the annular condensate becomes a bridge as the mica surfaces are separated from contact [11]. The precise behavior at a given T appears to be a function of the relative areas of the mica-condensate and vapor-condensate interfaces. The mica-liquid interface suppresses freezing, but the liquid-vapor interface appears to facilitate freezing. With t-BuOH and related alcohols freezing is not observed under similar conditions [10,11].

The SFA has also recently been used to study the kinetics of capillary condensation of liquids such as c-C_6, *n*-hexane (n-C_6), and water. The condensation rate is limited by the rate of diffusion of vapor through the very narrow wedge around the contact zone of the mica surfaces, and is slightly slower than that calculated from a Langmuir-type model [13].

By applying such dynamic measurements in capillary condensation experiments with n-C_8 and n-C_{16}, we here report evidence for a structural transition in adsorbed *n*-alkane films above the bulk T_m. A decrease in film thickness and a marked increase in the rate of surface diffusion characterize the transition.

The experimental setup and procedure have been described in detail [9–11,14]. Multiple-beam interferometry [15] is used to measure the separation H between two molecularly smooth mica surfaces mounted in a crossed-cylinder configuration. The refractive index n of the medium between the surfaces can be determined independently, which permits the detection of phase changes in the interlayer. Adsorbed film thicknesses h are determined via a three-layer approximation, or $2h = H(n-1)/(n_f - 1)$, where n_f is the refractive index of the film, usually assumed to be the bulk value. Capillary condensation occurs at small H and the curved mica surfaces ($R \approx 2$ cm) are pulled into contact and flattened under the influence of strongly adhesive forces. Annular condensates then grow in the narrow wedge (angle $\approx 0.1°$) surrounding the contact region (diameter ≈ 50 μm).

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*Electronic address: hugo.christenson@anu.edu.au FAX: 61-2-6249-0732.
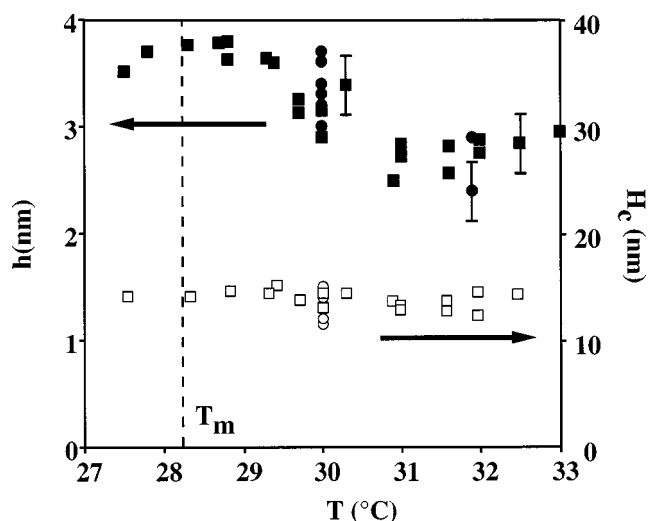
FIG. 1. Film thickness (h; filled symbols) and the critical surface separation (H_c; open symbols) at which capillary condensation occurs as a function of temperature of n-C_{18}. h refers to the left ordinate and H_c refers to the right one. Different symbols are from different experiments. A change in h is observed in the range 29.5–31 °C, and it occurs at a lower temperature on cooling than on heating, which causes a finite width of the transition range. No significant change in H_c over the temperature range studied is detected.

After determining mica-mica contact in nitrogen (with CaH_2 or P_2O_5 as the drying agent), liquid n-C_{16} or n-C_{18} (Sigma or Aldrich, 99+%—used as received or distilled under reduced pressure, with no detectable difference in the results) was introduced into the measuring chamber. Due to the low vapor pressure of n-alkanes (0.9 mtorr at 20 °C for n-C_{16}, 0.3 mtorr at 30 °C for n-C_{18} [16]), one week was allowed for equilibration, at an elevated T of up to 40 °C. The temperature was controlled and monitored to within ± 0.05 °C. The relative vapor pressure p/p_0 of n-alkane was estimated from the measured condensate size using the Kelvin equation [9]

$$\frac{\gamma v_m}{r} = kT \ln(p/p_0). \quad (1)$$

Here v_m is the molecular volume and γ the surface tension of the condensed liquid. As the liquid almost wets the mica, the radius of curvature r is approximately half the surface separation at the vapor-condensate interface (identified by a discontinuity in the refractive index). Due to the very slow condensate growth, we could only put a lower bound on p/p_0 at $\geqslant 0.98$. At least ten hours were allowed to pass after each change in temperature.

Figures 1 (n-C_{18}) and 2 (n-C_{16}) show both h and the critical surface separation (H_c) at which capillary condensation occurs as functions of temperature close to T_m. A change in h for n-C_{18} is observed in the range 29.5–31 °C. The change occurs at a slightly lower temperature on cooling than on heating, which leads to the finite width of the transition as shown. No experimentally significant change in h is observed for n-C_{16}. No change in h at T_m (28.1–28.2 °C for n-C_{18} and 18.1–18.2 °C for n-C_{16}) and no change in H_c over the temperature range studied are detected for either liquid.
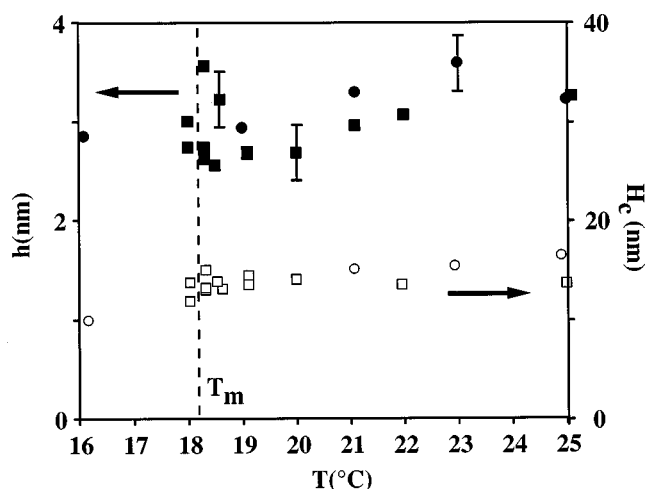

FIG. 2. Similar to Fig. 1 but for n-C_{16}. Unlike for n-C_{18}, no significant change in either h or in H_c is observed over the temperature range studied.

Note that any corrections for anisotropy in n of the films would reduce h by less than the experimental error.

Because of the uncertainty in p/p_0 we cannot obtain an equilibrium adsorption isotherm to compare with theoretical expectations. We note, however, that the relationship between h and H_c is similar to what has been previously found with c-C_6, n-C_5, and t-BuOH [9]. There is no change in behavior across the range of temperatures studied, and we conclude that in this regard these alkanes behave like the previously studied liquids. When the surfaces come into contact after capillary condensation $H \approx 1$ nm, suggesting that two or three layers of molecules parallel to the surfaces are trapped, as found in experiments on solvation forces [7].

The decrease in h found for n-C_{18} just above T_m suggests some change in the structure of the adsorbed layer. Unfortunately, any similar decrease with n-C_{16} is not borne out by the results. However, measurements of the condensate growth rate for both alkanes provide clear evidence that a change in film structure occurs slightly above T_m. Figures 3 (n-C_{18}) and 4 (n-C_{16}) show the condensate volume V ($\approx 4\pi R r^2$) [11] as a function of time for various temperatures. There is a dramatic change in growth rate in the range 29.5–31 °C for n-C_{18} and 18.5–20 °C for n-C_{16}—by an order of magnitude. This transition occurs for both n-alkanes at a slightly lower temperature on cooling than on heating.

The dashed lines in Figs. 3 and 4 show that the condensate growth rates for n-C_{16} and n-C_{18} below this transition temperature T_t are close to those predicted by the Langmuir-type model, in accordance with previous results with other liquids at room temperature (far above their T_m) [13]. The rate of diffusion through vapor would not be expected to change markedly over a few degrees, as the concentration in the vapor phase is nearly constant. This suggests that in the case of n-C_{16} and n-C_{18} another mechanism of condensate growth is operating above T_t. The only other possible method of material transfer into the condensate is by surface diffusion, along the large area of mica exposed to vapor.

A crude prediction of the rate of increase of the volume of the condensate due to drainage of surface films can be obtained from thin film hydrodynamics [17]. Neglecting curvature effects, the pressure in the film P_f is given by
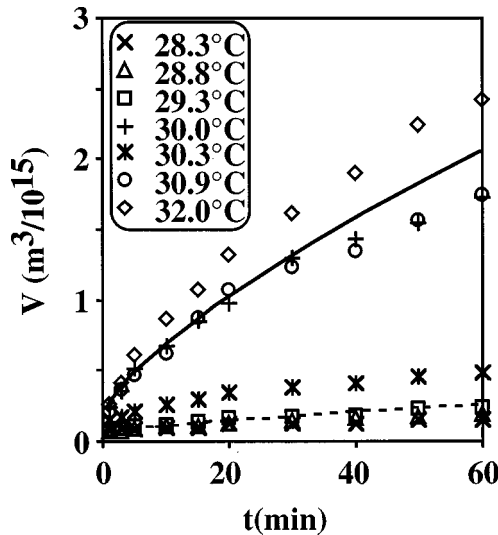
FIG. 3. n-C_{18} condensate growth rate for various temperatures. Condensed volume is plotted against the time the surfaces are kept in contact for each temperature. There is a dramatic change in growth rate in the range 29.5–31 °C. As for the change in h, it occurs at a slightly lower temperature on cooling than on heating. The lines are the theoretical predictions of diffusion-limited condensate growth from vapor [13] (dashed) and surface diffusion only (solid—see text), with $\eta = 4.2$ mPa s, $h_0 = 3$ nm, $A = 1.2 \times 10^{-20}$ J. Note that for the vapor, the growth calculation $p/p_0 = 0.995$ was used. On the scale of the plot, the curves for all $p/p_0 \geq 0.98$ are indistinguishable.

$$P_f = P - \frac{A}{6\pi h^3}, \qquad (2)$$

where P is the external pressure and the second term is the disjoining pressure of the film, with A being the Hamaker constant [17]. Variations in h give rise to pressure gradients that result in the flow of liquid. For small perturbations in h the evolution equation for the profile of an axially symmetric film of initial (uniform) thickness h_0 is [18]

$$\frac{\partial h}{\partial t} = \frac{A}{6\pi\eta h_0} \frac{1}{\rho} \frac{\partial}{\partial \rho}\left(\rho \frac{\partial h}{\partial \rho}\right), \qquad (3)$$

where η is the viscosity of the liquid and ρ is the radial coordinate.

If we assume local equilibrium between the pressure in the growing meniscus (with radius of curvature r) and that in the film, then the film thickness at the edge of the meniscus, h_r, can be calculated by equating the Laplace pressure γ/r with the disjoining pressure. For a condensate with annular radius $\rho = \alpha$, the volume flux (per film) may be found by solving Eq. (3) subject to the boundary conditions $h(\rho,0) = h_0$, $\rho \geq \alpha$, and $h(\alpha,t) = h_r$, $t > 0$, where h_0 is the measured initial film thickness. Equation (3) is formally equivalent to the diffusion equation, with the diffusion coefficient $D = A/6\pi\eta h_0$ and can be solved using standard techniques [19]. The rate of increase of the condensate volume is then

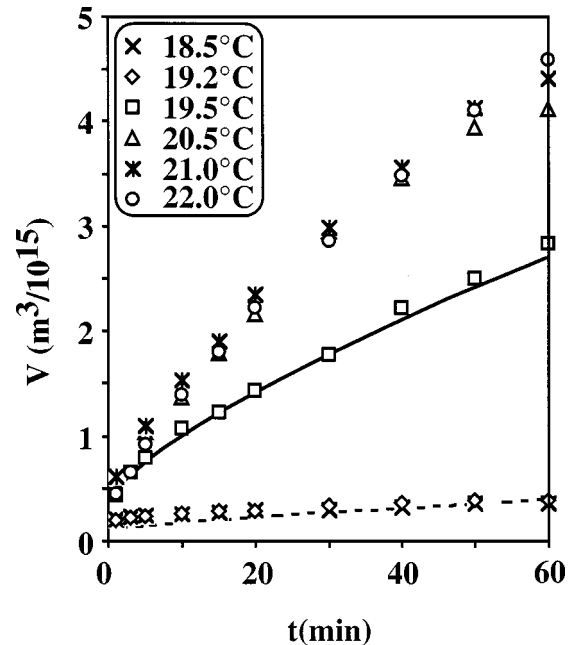$$\frac{dV}{dt} = \frac{16(h_r - h_0)D}{\pi} I(t;D,\alpha), \qquad (4)$$

FIG. 4. Similar to Fig. 3 but for n-C_{16}. The change in growth rate occurs at 18.5–20 °C, at a slightly lower temperature on cooling than on heating. The lines are the theoretical predictions of diffusion-limited condensate growth from vapor with $p/p_0 = 0.995$ (dashed) and of surface diffusion only (solid—see text), with $\eta = 3.0$ mPa s, $h_0 = 3$ nm, $A = 1.2 \times 10^{-20}$ J.

where $V = 4\pi R r^2$ and $I(t;D,\alpha)$ is an integral, the numerical values of which have been tabulated [20].

Equation (4) gives the volume flux into a condensate with fixed annular radius α and fixed boundary film thickness h_r. For the case of a growing condensate, we assume that Eq. (4) remains valid when h_r and α are functions of time. This should be a good approximation as both h_r and α vary slowly with time, and α is small in comparison to the distance over which the film is perturbed.

The results have been plotted as solid lines in Figs. 3 and 4. It is clear that the model is able to account at least semiquantitatively for the observed growth rates for $T > T_t$. Note that the (nonadditive) contribution from vapor diffusion would slightly increase the total growth rates. For $T < T_t$, as in previous experiments [13], the effect of surface flow appears to be comparatively minor.

The significant increase in the rate of surface diffusion indicates a structural change in the films. Taken together with the thickness change found for n-C_{18}, it suggests the adsorbed alkane films undergo a surface phase transition at T_t, slightly above T_m. As T is reduced, the films thicken (at least for n-C_{18}), presumably as the alkyl chains assume a more normal orientation just above T_m. For n-C_{18} the h measured below T_t is larger than the length of an extended molecule. Perhaps a layer or two of molecules of parallel orientation are next to the surface, with an outer layer of normal orientation. As the alkyl chains become more ordered, the lateral mobility of the molecules decreases significantly. The hysteresis in the transition temperature (30.3 ± 0.7 °C for n-C_{18} and at 19.1 ± 0.9 °C for n-C_{16}—see Figs. 1, 3, and 4) indicates a first-order transition, as found with surface freezing of bulk n-alkanes [21]. Few nucleation sites

are expected on the mica surfaces, so the disordered adsorbed films are easily supercooled.

Alkane films adsorbed from vapor to mica thus show a similar surface ordering transition to that found at the bulk alkane-vapor interface. As with alkanes adsorbed on silica [8], however, this transition is occurring in an essentially monomolecular film on a solid substrate. In contrast to previous work, we have relied mainly on experiments that probe the mobility of molecules in the film to identify the transition.

The interactions of the ordered alkane molecules with the underlying mica substrate are expected to be quite different from those with the disordered bulk liquid. The fact that similar transitions are occurring in both systems shows that the strength of lateral interactions dominates the behavior of molecules with long alkyl chains at interfaces.

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