

Direct Observation of Capillary Condensation of a Solid

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We describe the direct condensation of a solid from vapor in an annular mica wedge. *Neo*-pentanol initially condenses as a liquid from 8 to 57 °C (the melting point T_m), followed by nucleation of a solid from vapor for $T < 45$ °C. Menthol ($T_m = 42$ °C) gives only liquid condensates down to 12 °C. The adsorbed films of *neo*-pentanol, which unlike those of menthol show layering transitions, and the disordered crystalline phase of bulk *neo*-pentanol appear to facilitate condensation of the solid phase. There is evidence for a change in the nature of the solid *neo*-pentanol condensate with T .

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Freezing and melting transitions in confinement are of key importance in phenomena such as frost heave, flow in porous media, catalysis, and separation processes. To study the properties of solids in confinement, one usually freezes a porous medium filled with liquid by direct imbibition or capillary condensation of liquid from vapor. Such investigations have revealed a temperature depression of T_m [1–4] and of many bulk solid-solid transitions [3,4], structural changes in the confined phases compared to bulk [5,6], and modified dynamic behavior of capillary solids [7,8]. Large hysteresis effects between freezing and melting are often present in porous media and the origin of these has been the subject of much debate [9,10].

We have been investigating freezing and melting in confinement by directly condensing vapor between mica surfaces below T_m [11–14]. This allows the study of conditions in a single pore, and true equilibrium with the vapor phase is easily established. Complications due to pore interconnectivity, pore blockage, and polydispersity of pore size are absent. By contrast, direct condensation of solid from vapor in porous media is not possible due to pore blockage. In previous work with *tert*-butanol, *neo*-pentanol (2,2-dimethylpropanol) [11–13], and long-chain *n*-alkanes *n*- C_m ($m = 14$ – 18 carbon atoms) [14], we have shown how capillary condensation of liquid occurs below T_m , at or slightly off coexistence. The size of the condensates shows the expected inverse relationship with the temperature depression ΔT ($= T_m - T$). With *n*- C_{18} , the condensates freeze for sufficiently large ΔT as the degree of confinement is reduced when the surfaces are separated [14].

In this Letter, we present the first direct study of capillary condensation of a solid from vapor. With *neo*-pentanol, initial condensation of liquid from vapor below T_m is rapidly followed by nucleation of a solid from vapor at lower temperatures ($\Delta T \geq 12$ °C). Similar experiments with menthol at equivalent ΔT give only liquid condensates. We speculate that the state of adsorbed

surface films at the mica surfaces is important for the condensation of a solid phase to occur. The nature of the condensing solid *neo*-pentanol shows a transition at a temperature close to that which has been associated with a bulk phase change.

The experiments were performed using a modified Mark IV Surface Force Apparatus (SFA) [12,15]. The heart of the apparatus is a multiple-beam interferometer formed from two back-silvered mica sheets, mounted as crossed cylinders and sealed in a stainless-steel chamber. White light passes through the surfaces and onto a diffraction grating. The resulting fringes of equal chromatic order (FECO) are recorded with a charge-coupled device camera, stored digitally and used to deduce the thickness of films adsorbed to the mica surfaces, the separation of the surfaces, as well as the refractive index and dimensions of the capillary condensates between the surfaces. Information on multiple-beam interferometry and FECO can be found in the literature [16], and recent work has described the procedure and analysis followed in capillary-condensation experiments [11–14].

After calibration by measuring the mica thickness in dry N_2 , solid *neo*-pentanol ($T_m = 57$ °C) or menthol ($T_m = 42$ °C), both 99% from Aldrich, were introduced into the chamber and 48 h was allowed for equilibration. The surfaces were then brought into contact to observe the formation and growth of capillary condensates. Three hours after the growth appeared to have ceased, the surfaces were separated. After complete evaporation of the condensate, the cycle was repeated until consistent results were obtained. Experiments were carried out over a range of 8–57 °C for *neo*-pentanol and 12–44 °C for menthol. Measurements were made both with increasing and decreasing T . The relative vapor pressure in the chamber was estimated from the Kelvin equation (see below).

Before the surfaces are brought into contact, *neo*-pentanol or menthol adsorb to the isolated mica surfaces. Figure 1 shows the adsorbed film thickness t vs T . With

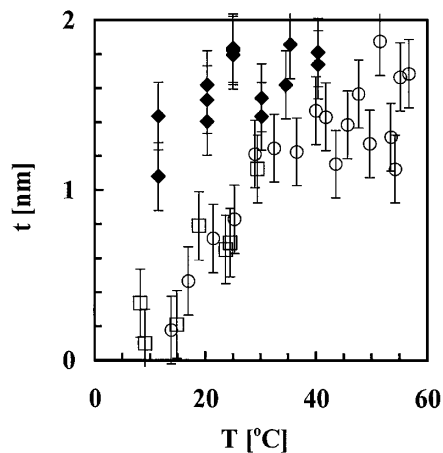


FIG. 1. Thickness t of *neo*-pentanol films (open symbols: circles are runs with increasing T , squares with decreasing T) and menthol (filled symbols) adsorbed on mica vs T .

neo-pentanol (open symbols) one may tentatively identify two steplike layering transitions, where t increases from about 0.4 nm (one layer?) to 0.8 nm (two layers?) at $T = 17$ – 19 °C, and from 0.8 to 1.2 nm (three layers?) at 26 – 29 °C. Above 36 – 39 °C, there is a further, slight increase in t , although the greater scatter (due to increased thermal drift at higher T) precludes us from drawing any firm conclusions. The layering transitions at lower temperatures suggest a solidlike adsorbed film.

There is no indication of layering in the adsorbed menthol film (filled symbols) and the change in t is smaller—about 0.5 nm from 10 to 40 °C. While layering transitions may be present at lower temperatures, the menthol film appears to be more liquidlike for a comparable ΔT . The larger size of the menthol molecule should make the detection of any layering transitions easier.

At a characteristic surface separation H_c , the surfaces jump into contact as capillary condensation occurs. Below about 35 °C, H_c for *neo*-pentanol is constant at 10 ± 1 nm, and increases to 13–14 nm at higher T . For menthol there is an increase from 10–11 nm at 13–25 °C to 12–13 nm at 30–40 °C. These H_c are consistent with previous measurements of H_c for liquids such as cyclohexane, *n*-C₅ [17], and *tert*-butanol [18], where $H_c \approx 12$ nm was found for $t \approx 2$ nm. These H_c have been found to be larger than expected from a model of capillary condensation based on a thickening of adsorbed films due to van der Waals forces between the opposing surfaces. Evidently, we are here seeing the same effect, and it is unclear if the overall increase in H_c with T is due to the increase in t , or if some change in the mechanism of capillary condensation is involved.

Above 45 °C, the capillary condensates of *neo*-pentanol remain liquid. At lower temperatures initial condensation of liquid is followed by condensation and growth of solid *neo*-pentanol outside the liquid condensates [11]. This occurs more readily the lower the temperature. Solid and

liquid condensates are distinguished as follows: (i) A solid condensate connecting the surfaces acts as a glue, and a much greater force must be applied to effect separation, when there is instantaneous rupture of solid-solid contact. On separation with a liquid condensate, this becomes a bridge that thins and breaks at larger separations. (ii) The behavior under compression (i.e., when the surfaces are pushed together under a load) differs—a liquid is squeezed out, whereas the mica surfaces deform around a solid.

In what follows, we refer to the thickness of the condensate at its interface with vapor as the size of the condensate. This size h is measured by determining the surface separation at which there is a discontinuous change in the refractive index n of the medium between the mica surfaces. Since the contact angle θ of both liquids on mica is small, for liquid condensates $h \approx 2r$, where r is the radius of curvature of the condensate-vapor interface. The relationship between h and interface curvature is less clear for the solid condensates due to uncertainties in θ . The maximum value of h , after the growth of the condensate has ceased, is denoted h_{eq} , and this has been plotted as a function of T for the *neo*-pentanol condensates, both liquid (open symbols) and solid (closed symbols), in Fig. 2. For the solid condensates, the change in h_{eq} with T shows two distinct regimes: From 8 °C to ca. 34 °C, h_{eq} increases with increasing T . We refer to this here as the low-temperature (LT) solid regime. From 34 °C to 45 °C, h_{eq} is significantly smaller and shows the opposite behavior with a decrease with increasing T —this is the high-temperature (HT) solid regime. Also, the growth rates of the condensates are different above and below the apparent transition at 34 °C. A liquid condensate is observed from 38–39 °C to T_m and overlaps the HT-solid regime. Below 45 °C, nucleation of solid is liable to occur whenever the system is perturbed. This solid condensate then continues to grow outside the liquid condensate to a much larger h_{eq} , as shown. From

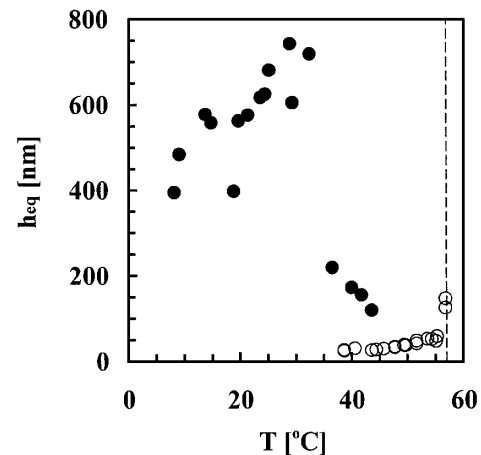


FIG. 2. The equilibrium size h_{eq} of *neo*-pentanol condensates vs T . The filled symbols are solid condensates (see text) and the open ones are liquid condensates. T_m is indicated by the dashed vertical line.

45 °C to T_m , only liquid condensates are observed, with h_{eq} increasing with T .

The menthol condensates remain liquid at all T over the studied range. On separation, the liquid bridge is seen to snap at large distances and two liquid droplets spread over the surfaces and evaporate.

h_{eq} of the liquid capillary condensates of both menthol and *neo*-pentanol decreases with decreasing T . This is shown as a plot of $1/h_{eq}$ vs ΔT in Fig. 3. A relationship between $1/h_{eq}$ and ΔT can be derived for the surface geometry in the SFA [11,12], and, with the assumption that the liquid wets the mica surface in the presence of the solid, one has

$$\frac{1}{h_{eq}} = \frac{\Delta T \Delta H_f}{4V_m T_m \gamma_{sl}}, \quad (1)$$

where ΔH_f is the heat of fusion, V_m is the molar volume of the condensing substance, and γ_{sl} is the interfacial energy between liquid and solid. γ_{sl} may thus be estimated from the slopes of the fits in Fig. 3 and, with literature values for ΔH_f [19], one obtains 25 mN/m for menthol and 14 mN/m for *neo*-pentanol. The *neo*-pentanol condensate sizes in Ref. [11] were obtained for larger ΔT (17–25 °C), before the onset of solid condensation, and recalculation of the slope with the correct ΔH_f gives 12 mN/m for those results. Here, the intercepts give finite condensate sizes at T_m , and p/p_0 can be estimated from the Kelvin equation; $p/p_0 \approx 0.99$ for menthol and $p/p_0 \approx 0.98$ for *neo*-pentanol.

The nature of the deformation of the mica surfaces as the load on these is increased in the presence of the solid *neo*-pentanol condensates changes with T . Figure 4 shows the fringe patterns and appearance of the surfaces deduced therefrom when the surfaces are forced together at 30 °C [4(a) and 4(b)] and at 42 °C [4(c) and 4(d)]. Under compression, the LT solid [4(a) and 4(b)] shows the most significant deformation near the edge, suggesting a less

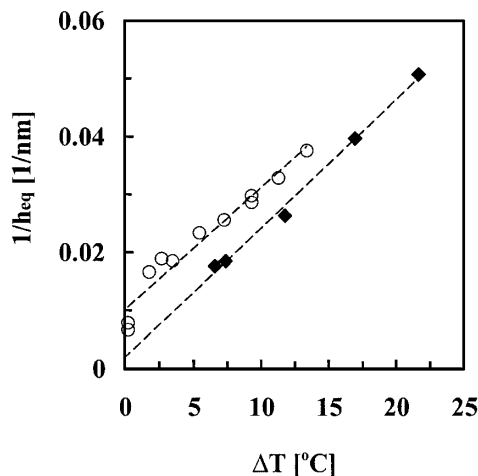


FIG. 3. The inverse condensate size $1/h_{eq}$ vs temperature depression ΔT below T_m for *neo*-pentanol (open symbols) and menthol (filled symbols).

compressible solid. The HT solid is more readily extruded under the same force, suggesting different yield strengths for the two solids.

Furthermore, the refractive indices n of the two solids are significantly different: i.e., LT solid, 1.463 ± 0.002 (30 °C); HT solid, 1.430 ± 0.003 (42 °C) and liquid 1.388 ± 0.003 (57 °C). Literature values are 1.4230 ± 0.0005 (solid at 56 °C) and 1.388 ± 0.003 (liquid at 56 °C) [20]. Liquid menthol at 30 °C gave 1.452 ± 0.003 (literature value 1.460 at 22 °C [21]).

Studies of wetting and capillary condensation of *tert*-butanol between mica surfaces for $\Delta T \leq 12$ °C showed no condensation of solid [13]. On reduction of T after the liquid condensates had reached h_{eq} , the condensates would evaporate until the reduced h_{eq} at the lower T had been reached. Only with *n*-C₁₈ ($T_m = 28.2$ °C) has very slow (due to the low vapor pressure) growth of crystals from the liquid-vapor interface been observed, for $\Delta T \approx 11$ °C [14].

Presumably, the structure of the films adsorbed at the mica surface and/or the structure of the liquid condensate-vapor interface dictate the mechanism of condensation and further growth of crystal outside the liquid condensates. Crystal growth with *n*-C₁₈ is probably related to the ability of the alkane-vapor interface to nucleate solid, due to surface ordering or surface freezing at this interface. It seems less likely that the liquid-vapor

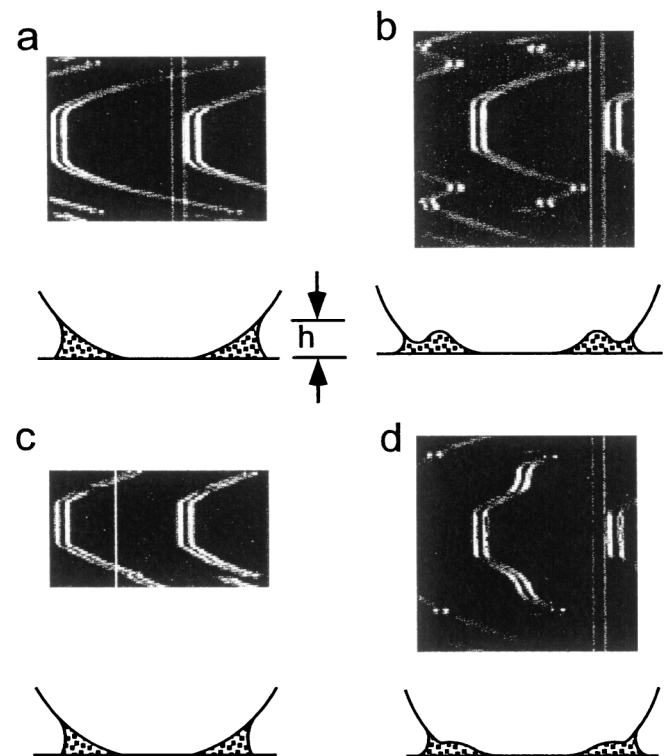


FIG. 4. Fringe patterns with the appearance of the condensates and mica surfaces for LT solid (a), LT solid under compression (b), HT solid (c), and HT solid under compression (d). The “condensate size” h is shown in (a) only.

interface would play a direct role in the nucleation of bulk solid *neo*-pentanol. The solidlike structure of the adsorbed films of *neo*-pentanol at lower T might lead to nucleation and growth of solid below 38–39 °C, as observed. Nucleation at isolated mica surfaces was never observed and would not be expected as the system is slightly off bulk solid-vapor coexistence. The fact that the bulk phases of *neo*-pentanol are disordered (plastic) crystalline phases [22,23] may also contribute by reducing lattice mismatch between the adsorbed film and the bulk crystal. On the other hand, if the film disorders (roughens) at higher temperatures, closer to T_m , as the t values perhaps suggest, condensation of solid would not occur as readily, in agreement with our observations.

The reason for the apparent change in h_{eq} (and growth rate) at about 34 °C may be related to a change in the adsorbed film structure, or to the increasing fraction of liquidlike solid said to be present at temperatures close to T_m . An NMR relaxation-time study has shown the coexistence of two disordered solid phases of bulk *neo*-pentanol, with a phase of a more liquidlike structure increasing in relative concentration from about 45 °C up to T_m [24]. Perhaps there is a difference in the equilibrium vapor pressure over the LT solid and HT solid. The extent to which differences in interface curvature and polycrystallinity might play a role is also open to question.

In conclusion, we have for the first time observed directly capillary condensation of a solid from vapor. The apparent change in properties of the solid condensates with temperature has been discussed with reference to structural transitions in the bulk materials and the films adsorbed at the mica surface. Our results show how the SFA may be used to study solids in nanoscale pores via capillary-condensation experiments.

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