

Surface-induced phase transition in normal alkane fluids

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(Received 18 June 1992)

The surface tension of normal liquid alkanes (chain lengths between 15 and 18 carbon atoms) has been measured as a function of temperature. In all cases the tension exhibits a well-defined change in behavior at a temperature close to, but distinct from, the melting point. The phenomena are consistent with a surface-induced phase transition in which the conformational degrees of freedom of molecules close to the surface are inhibited. Various properties of the transition vary smoothly with alkane chain length.

PACS number(s): 64.70.Ja, 68.10.Cr

The normal alkanes are among the most fundamental series of molecules, being important in technological and scientific (organic, polymeric, and biological) fields. These molecules exhibit a rich variety of phase transitions [1], which continues to yield novelties [2]. These transitions strongly affect the behavior of molecules incorporating alkane moieties, and thus have a wide significance. Most of the observed complexity of phases is confined to states below the melting points [1], where the materials are in the solid state. We have found a new phase transition in the fluid state for normal alkanes of moderate chain lengths, which manifests itself in hitherto unobserved behavior of the tension of the free liquid surface. It appears to involve a surface-induced reduction in molecular degrees of freedom. As the temperature is lowered the tension departs from the accepted steady increase, changing instead to a monotonic decrease close to the freezing point. The transition has been observed for paraffins between 15 and 18 carbon atoms in length.

Normal alkanes, such as heptadecane $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_3$, are simple flexible chain molecules, some 4 Å in thickness and roughly 20 Å in length (for lengths from 15 to 18 carbon atoms). We have studied the tension of the liquid-air interface for several alkane

fluids. Figure 1 shows the results for heptadecane, the accepted melting point (T_m) of which is close to 22 °C [3]. Well above T_m the measured tension (γ) agreed quantitatively with both the accepted value and its temperature variation [3]. However, on cooling below 24.0 °C, γ departed from the accepted variation and fell steadily with decreasing temperature. This behavior was reversible and entirely reproducible. The change of behavior at 24.0 °C was only found for material that had been purified by passage through a column of silver nitrate on alumina [4]. The sample was allowed to attain thermal equilibrium over a period of 5–10 min at each temperature. No hysteresis was observed in the transitions for any of the materials examined. Similar phenomena were observed for normal alkanes from pentadecane to octadecane, the only members of the homologous series whose melting points were easily accessible with our apparatus. The variations of γ were quantitatively confirmed by surface light scattering (to be published), which provides an independent, noninvasive probe of surface tension [5].

We believe that these phenomena are intrinsic to the alkane fluids. They were only observed for purified materials. The melting points of our samples agreed with literature values to within the precision of the thermometry (± 0.05 °C), confirming the lack of contamination. Spectroscopic analysis by capillary gas chromatography (with mass spectrometry) showed no evidence of branched homologues; any contaminants (present in trace quantities, $\ll 0.1\%$) appear to be other normal alkanes of chain lengths comparable to the main constituents. If the effect were due to tiny traces of surface-active contamination, emerging from bulk solution at some temperature, one would expect γ to undergo a step change, rather than a change of slope. The reversibility of the isotherms also seems incompatible with effects of contamination. It is difficult to see how contamination would lead to the observed systematic dependences of various features upon alkane chain length (see below).

Now, for one-component systems, such as the present one, the tension is the surface excess free energy [6], so that changes in its temperature dependence indicate a change of phase affecting the surface layers. The data thus indicate a new phase transition in the fluid phase of these alkanes. Within the precision of our thermometry

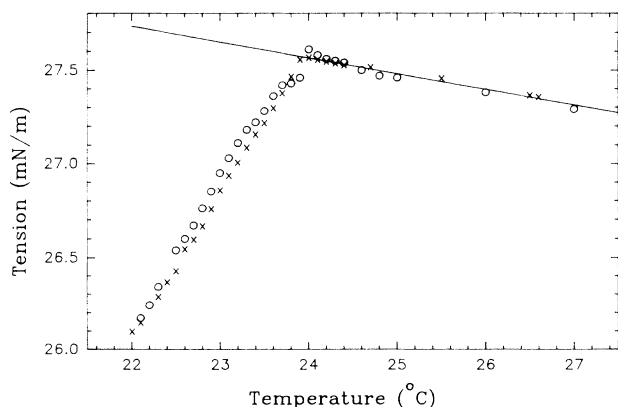


FIG. 1. Temperature dependence of the surface tension of *n*-heptadecane (×, cooling; o, heating), measured by Wilhelmy plate. The line indicates the accepted variation [3], extrapolated to the freezing point of 22.0 °C.

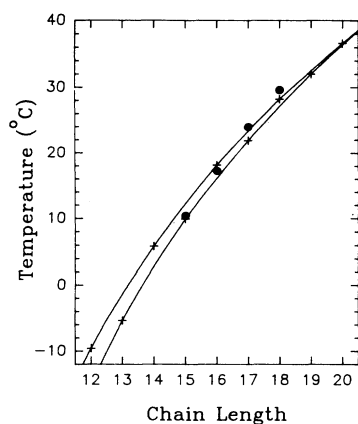


FIG. 2. Temperatures at which the new transition occurred (T_k , \bullet) for alkanes of different chain lengths. The lines indicate separately the variations of the melting points (+) of alkanes of even and odd chain lengths [3].

the transition appeared to occur at a single temperature, which we designate T_k . For such one-component systems $-d\gamma/dT$ is the surface excess entropy density, S_s [6]. The present data suggest that S_s , while constant above and below T_k , undergoes a discontinuous change at that temperature, indicating that the transition is first order in nature.

For the data of Fig. 1, S_s changed from 8.6×10^{-5} (J/m^2)/K above T_k (in accord with literature data [3]) to -7.7×10^{-4} (J/m^2)/K below it (this negative entropy density is of course only the surface excess part). The positive value above T_k , as for most pure fluids, indicates that the surface normally permits somewhat greater molecular freedom than in the bulk [6]. However, the greater magnitude of the negative S_s below T_k indicates a marked reduction in the available degrees of freedom in the surface layers. Below T_k the surface apparently tends to restrict molecular freedom, a situation resembling certain liquid-crystalline systems in which the free surface exerts an orienting field [7, 8]. We thus believe that the transition is surface induced in nature, and we associate it with a cooperative reduction in the internal molecular degrees of freedom. The surface light-scattering data mentioned above support this conclusion. Observation with a polarizing microscope revealed no optical anisotropy at temperatures above T_m . The bulk material remains fluid to T_m ; the viscosity follows the accepted variation with no observable change at T_k .

This new transition occurs at different temperatures for the different alkanes examined. The observed values of T_k vary systematically with the chain length (n) of the alkane fluid, falling significantly faster than T_m as n decreases (Fig. 2). They show no evidence of the well-known odd-even effect apparent in the melting points [9]. For hexadecane some degree of supercooling of the fluid is required, the change in the behavior of γ occurring about 0.9°C below T_m . This is probably simply a consequence of the established higher T_m for molecules of even n [9] combined with the rapid decrease of T_k .

For longer alkane chains the magnitude of the negative surface excess entropy density below the transition

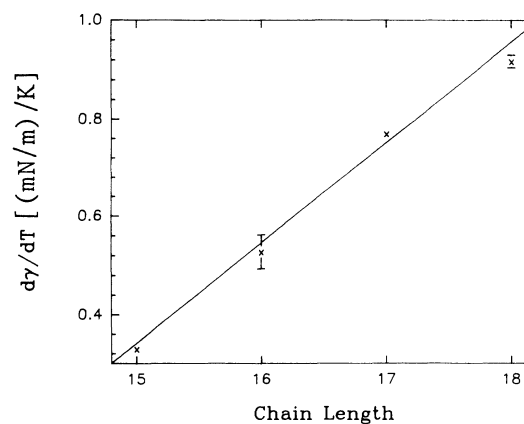


FIG. 3. Gradient of the temperature dependence of transition below T_k , for different chain lengths. These data represent $-S_s$ for the new phase; above T_k the surface excess entropy density is independent of chain length [3], corresponding to -0.086 (mN/m)/K on this plot. Also shown is the best-fit straight line, of slope 0.205 ± 0.015 (mN/m)/K per $-\text{CH}_2-$ group. The surface excess entropy density becomes progressively more negative as the chain length increases.

increases systematically (Fig. 3). Longer molecules thus seem more susceptible to the influence of the surface field. This agrees with naive intuition; shorter molecules would require a greater restraining influence to inhibit flexing and other internal motions. In fact, S_s for $T < T_k$ seems to vary linearly with n . Extrapolated, the linear fit shown intercepts the constant value found above T_k [$S_s = 8.6 \times 10^{-5}$ (J/m^2)/K] between $n = 13$ and 14. This suggests that the new, surface-induced transition might not occur for $n < 14$. This is supported by extrapolation of the trends of Fig. 2, indicating that T_k would be rather far below T_m (and hence involve considerable supercooling) for alkanes of $n < 14$. Unfortunately the melting points of these paraffins are inaccessible with our present thermostating arrangements.

A crude estimate of the thickness of the interfacial layer affected by this surface field can be made from S_s , given an assumed variation of the entropy density (S) through the surface layer. To illustrate the point, above the transition we would estimate a surface layer about 0.7 \AA thick from the surface excess entropy density of 8.6×10^{-5} (J/m^2)/K, given that S for bulk heptadecane is 2.6 (MJ/m^3)/K (at 25°C) [10] and assuming that in the surface layer S rises some 50% above the bulk value. This value is comparable with the accepted order of thickness of a surface diffuse layer [11]. Now $|S_s|$ below T_k is an order of magnitude greater than the value above T_k , suggesting a proportionately thicker surface layer. However, it seems reasonable to assume a rather smaller reduction for S in the surface layer in this case. Assuming a reduction of 10%, the thickness would be some 60 \AA . Smaller reductions of S in the surface layer would increase this estimate. However, it seems likely that the surface layer involved in the new transition is only a few molecules thick.

One of us (C.J.H.) thanks the AFRC and Unilever Research for support.

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