PHYSICAL REVIEW E VOLUME 47, NUMBER 5 MAY 1993

Light-scattering study of a surface-induced phase transition in alkane fluids

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(Received 4 January 1993)

The surfaces of normal liquid alkanes (chain lengths between 15 and 18 carbon atoms) have been studied by light scattering from thermally excited capillary waves. These fluids have recently been reported to exhibit a surface-induced phase transition at temperatures (T_k) near, but distinct from, their melting points. In all cases the propagation of the capillary waves showed abrupt discontinuities at this transition. While the data above T_k are consistent with predictions based on the known properties of the liquids, below this temperature they suggest the presence of a structured surface layer which is viscoelastic in nature. Below T_k both elastic and viscous parts of the surface excess transverse shear modulus are negative, indicating that the surface layer responds more easily to shear normal to the surface plane than does the bulk fluid. The light scattering thus suggests the existence of a surface layer which is much more ordered than the bulk fluid. This is consistent with the negative surface excess entropy density found in the new phase.

PACS number(s): 64.70.Ja, 47.35.+i, 68.10.Et, 78.35.+c

I. INTRODUCTION

The normal alkanes are amongst the most fundamental of molecular series. These simple, flexible molecules are important in a range of scientific and technological fields, forming as they do the basis for an enormous variety of other molecular families. They display a rich variety of phase behavior (reviewed in [1]) and novel transitions continue to be discovered. Recent examples include the observation of a solid phase of mixtures of long-chain alkanes having smectic symmetry [2], and the discovery of domains of intermolecular orientational alignment in thin adsorbed alkane films [3]. This richness of phase behavior has hitherto been confined to the solid state. However, we have recently reported a novel surface-induced phase transition in the fluid phase of normal alkanes between 15 and 18 carbon atoms in length [4]. This paper presents the results of a light-scattering study of the surfaces of these fluids.

Our previous paper [4] concerned the surface tension of the normal alkane fluids as a function of temperature, down to or below their freezing points. Well above the melting points the tension, measured by a Wilhelmy plate, agreed well with literature values. However, on cooling the fluids, the tension underwent a distinct change in behavior at a temperature (T_k) close to, but distinct from, the melting point. Below T_k the tension fell monotonically with decreasing temperature, rather than the more usual rise, as observed above T_k. For such one-component systems as the present fluids the negative of the temperature derivative of the tension is just the surface excess entropy density. This quantity underwent a discontinuous reduction on cooling through T_k, indicating the occurrence of a first-order surface-induced phase transition. The surface excess entropy density was negative below T_k, implying a reduction in molecular degrees of freedom in the surface phase compared to the bulk fluid. Rough arguments suggested that the surface layer of the phase below T_k was of the order of 10 nm thick.

The present paper concentrates on a parallel study, using quasielastic light scattering to study thermally excited capillary waves on the free surface of these alkane fluids. Rather dramatic changes occur at T_k, due to the appearance of surface excess viscoelastic properties in the surface phase below T_k. The details of the interpretation of the light-scattering data fully support the conclusion inferred from the classical tension data. The present work provides further insight into the nature of the surface phase.

II. EXPERIMENTAL METHODS

The surfaces and interfaces of liquids are continually agitated by thermally excited capillary waves. The resulting surface roughness scatters light. The spectrum of the scattered light is just the power spectrum of the thermally excited waves, and carries information on the properties of the system which affect the wave propagation.

There is no need to discuss the experiment in detail [5]. In brief, a beam of light from an Ar^+ laser ($\lambda = 488$ nm) was incident upon the surface of the liquid. Light scattered at a small angle from the specularly reflected beam was selected for detection, being mixed at the photomultiplier with a reference beam at the original laser-beam frequency; the frequency shifts involved are rather small and heterodyne detection of the scattered light is necessary for their measurement. The output of the detector was modulated by the spectrum of the thermally excited capillary waves which scattered the light, the wave number q being set by the experimental geometry. The spectral information was recovered in the time domain by autocorrelation of the detector output. The correlation functions were analyzed by fitting with the form

$$g(\tau) = B + A\cos(\omega_0|\tau| + \phi)\exp(-\Gamma\tau)\exp(-\beta^2\tau^2/4), \tag{1}$$

yielding unbiased estimates of the complex capillary-wave frequency ($\omega \equiv \omega_0 + i\Gamma$) [6]. The phase term ϕ in this objective function largely accounts for the deviations of the exact spectral form from a Lorentzian profile. The final Gaussian term represents instrumental line broadening arising from the finite extent of the laser beam illuminating the liquid surface. Failure to include these instrumental effects leads to overestimation of the capillary-wave damping constant Γ at low q; they can, however, be neglected at higher q [7]. The fitted values of ω_0 and Γ for pure liquids agree within errors with the exact theoretical behavior derived from the dispersion equation for capillary waves [Eq. (2)] using known fluid properties.

The alkanes were of stated purity ~ 99% as supplied (Aldritch Chemicals, and Sigma Chemical). They were further purified by two passages through columns of silver nitrate on alumina [8]; the effects to be reported were not observed for materials not so repurified. Trace amounts of impurities which stained the tops of the columns brown could not be recovered in sufficient quantities for analysis. Spectroscopic analysis of the repurified materials 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. The melting points of our samples agreed with literature values to within the precision of the thermometry ($\pm 0.05\,^\circ$C), confirming the lack of contamination. The question of contamination and its possible influence on the present results will be further discussed below.

The sample under investigation was contained in a watch glass placed in a double-walled thermostatted cell. The temperature was controlled by circulating water from a water bath stable to ± 0.01 K (Colora); the temperature was measured to within ± 0.05 K using a calibrated thermocouple. The sample could be maintained without detectable temperature change over many hours. The double-walled cell reduced acoustic disturbance of the liquid surface and air currents. To minimize evaporation from the sample, paper towels soaked in the appropriate fluid were draped inside the cell.

III. RESULTS

We have studied the free surfaces of four of the homologous series of normal alkanes, from n-pentadecane to n-octadecane. Only these members of the molecular series had melting points accessible with our thermostatting arrangements.

The majority of the basic data of this study are presented in Figs. 1–4, which show the frequencies and

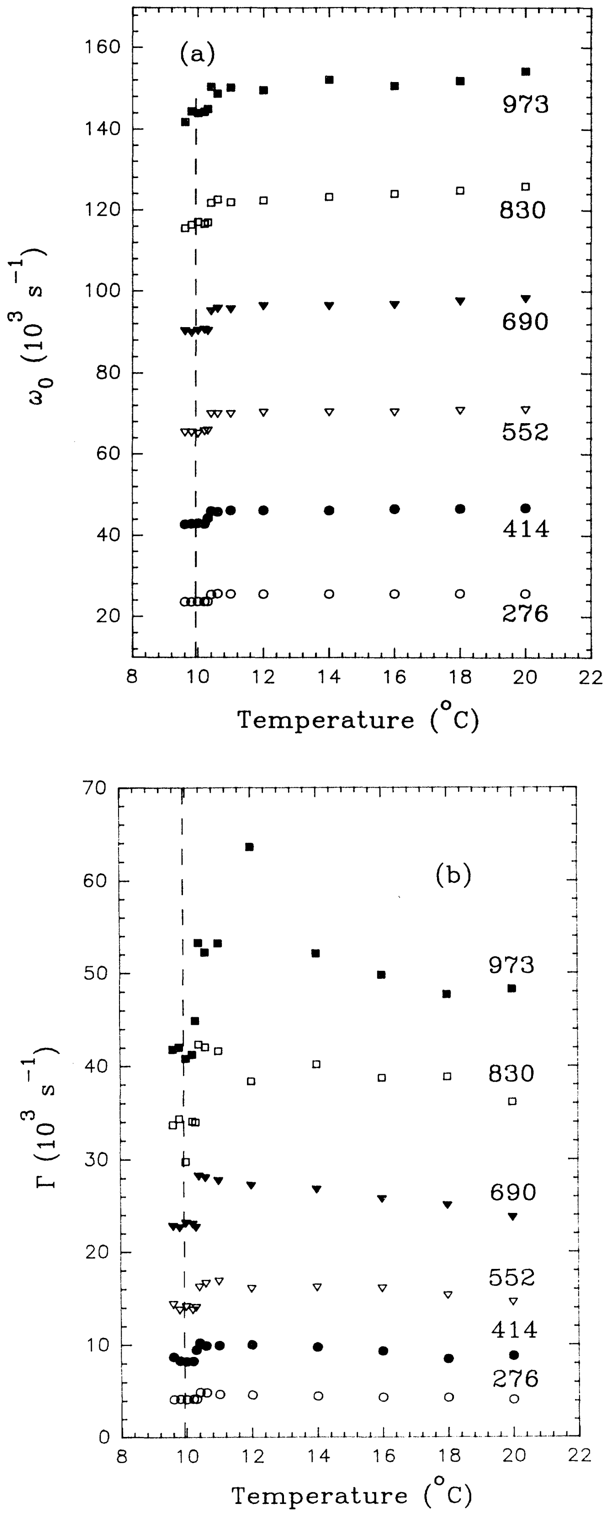

FIG. 1. The frequencies (a) and damping constants (b) of capillary waves of various wave numbers (in cm^{-1}) on the free surface of n-pentadecane as functions of temperature. The vertical dashed lines indicate the melting point (T_m) of the material. Note the discontinuities in both quantities at 10.4 °C. This temperature is designated as T_k. Errors omitted for clarity.

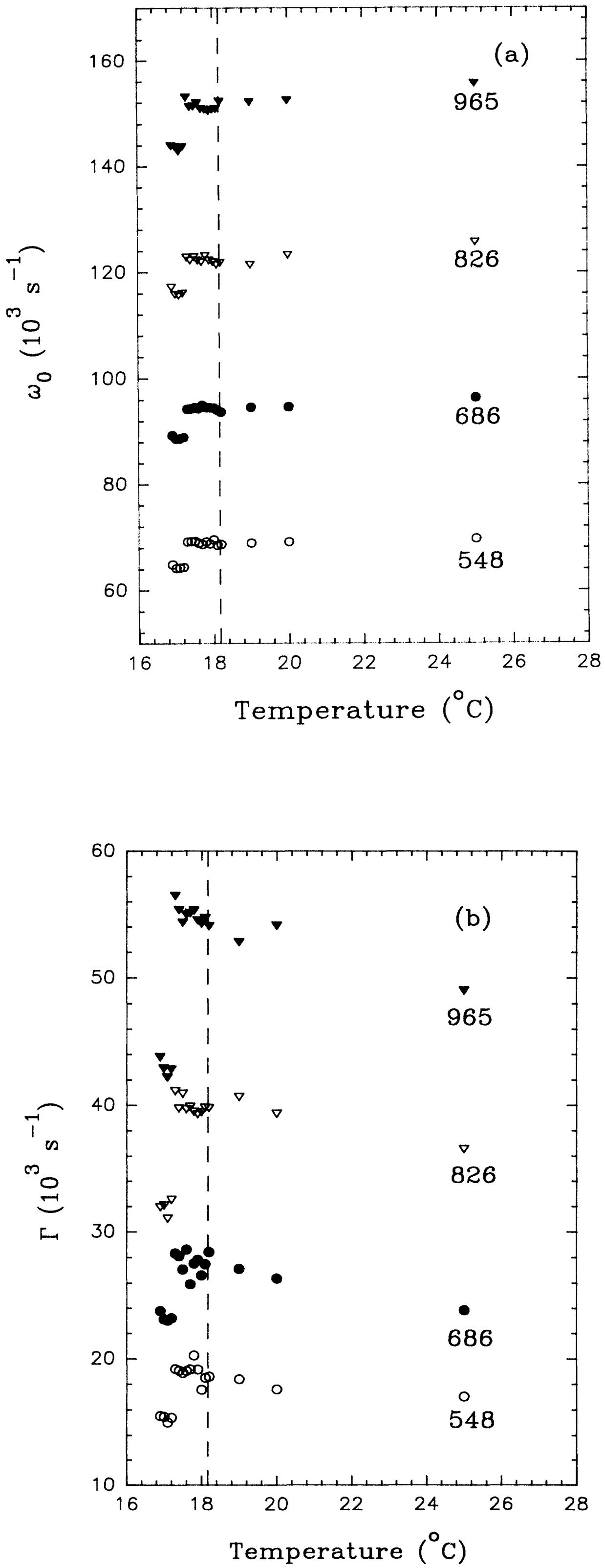

FIG. 2. As in Fig. 1, but for *n*-hexadecane. In this case the discontinuities in the capillary-wave propagation are observed only on supercooling the fluid (i.e., $T_k < T_m$).

damping constants of capillary waves of a range of q values for each of the four materials studied. Data extending the trends evident in these figures to $q \sim 1250$ cm^{-1} are not shown, to avoid confusing overlap of the Γ data at the higher q. The errors on ω_0 and Γ, which were 1% and 4%, respectively, are omitted to avoid confusion. The effects to be discussed here are substantially larger than these errors.

The behavior of all the materials studied was essentially similar. It is simplest to focus on one material: heptadecane provides a convenient example (Fig. 3). At each q studied the capillary-wave dispersion was relatively independent of T, apart from a single discontinuity at a temperature about 2 °C above the melting point (T_m). Both the wave frequency ω_0 and damping Γ decreased significantly on cooling the liquid through this temperature (designated T_k). For $q = 276$ cm^{-1}, for example, the decrease in ω_0 was 7%, while that for Γ was 14%. Above this temperature the capillary-wave propagation was entirely consistent with theoretical predictions based on the accepted properties of the fluid. However, below T_k there were large discrepancies in both frequency and damping, which increased in absolute magnitude with q.

The values of T_k and T_m for the different fluids are summarized in Table I. For hexadecane T_k lies below T_m: supercooling was necessary to produce the present effects.

We first address the question as to whether these discontinuities could be of instrumental origin. The agreement with expectation of the capillary-wave propagation for temperatures above T_k demonstrates the correct functioning of our spectrometer, and argues for the reality of the effects. As the tension and viscosity of the liquid vary with T the viscous damping of the capillary waves will vary relative to the driving forces, so that some artifact might conceivably arise. However, the changes were observed for all q studied, over which range Γ increases by a factor of about 2 relative to ω_0, and the instrumental line broadening drops from a significant to a negligible fraction of Γ. Indeed the correlation functions themselves clearly show changes in frequency and damping: Figure 5 shows two correlation functions for hexadecane, recorded just above and just below T_k. On cooling through T_k the period of the correlation functions indeed increases noticeably, while the damping decreases. In summary, we believe that the changes shown in Figs. 1–4 cannot be ascribed to artifacts in the experiment or data analysis, but reflect real effects within the fluids involved.

Precautions were taken to eliminate the possibility that the discontinuities at T_k could be artifacts from some

TABLE I. Properties of the alkane fluids. Data on melting points from [1], those for T_k and surface excess entropy density from [4].

Material	T_m (°C)	T_k (°C)	S_s ($< T_k$) [10^{-4} (J/m^2)/K]
Pentadecane	9.93	10.4	-3.30 ± 0.10
Hexadecane	18.17	17.25	-5.28 ± 0.34
Heptadecane	21.98	24.0	-7.70 ± 0.07
Octadecane	28.15	29.6	-9.17 ± 0.13

aging of the free surface of the fluids during the experiments. Collection of light-scattering data for all q took about 1 h. Data were taken over arbitrary sequences of q for each temperature, sometimes starting with the highest value studied, sometimes with the lowest. In different experiments samples were cooled or heated through T_k. No differences were ever found between the results of such different experimental protocols. The data of each

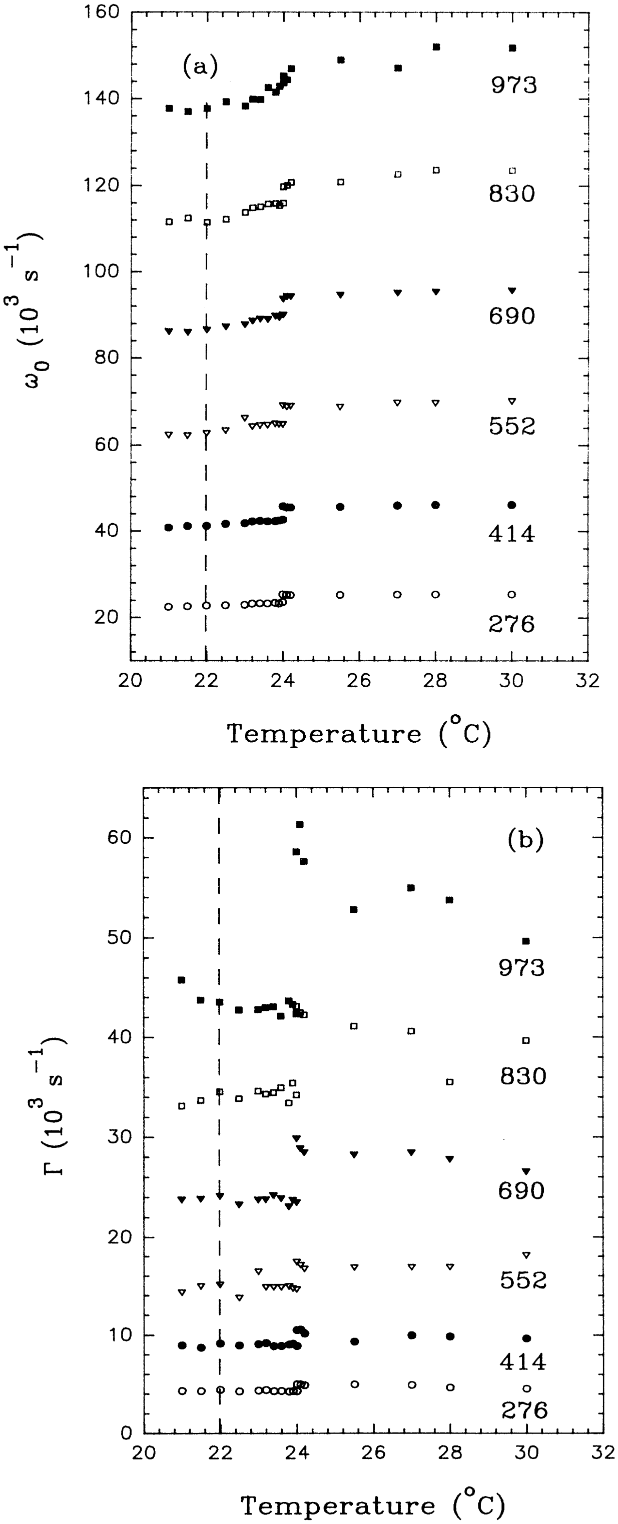

FIG. 3. As in Fig. 1, for n-heptadecane.

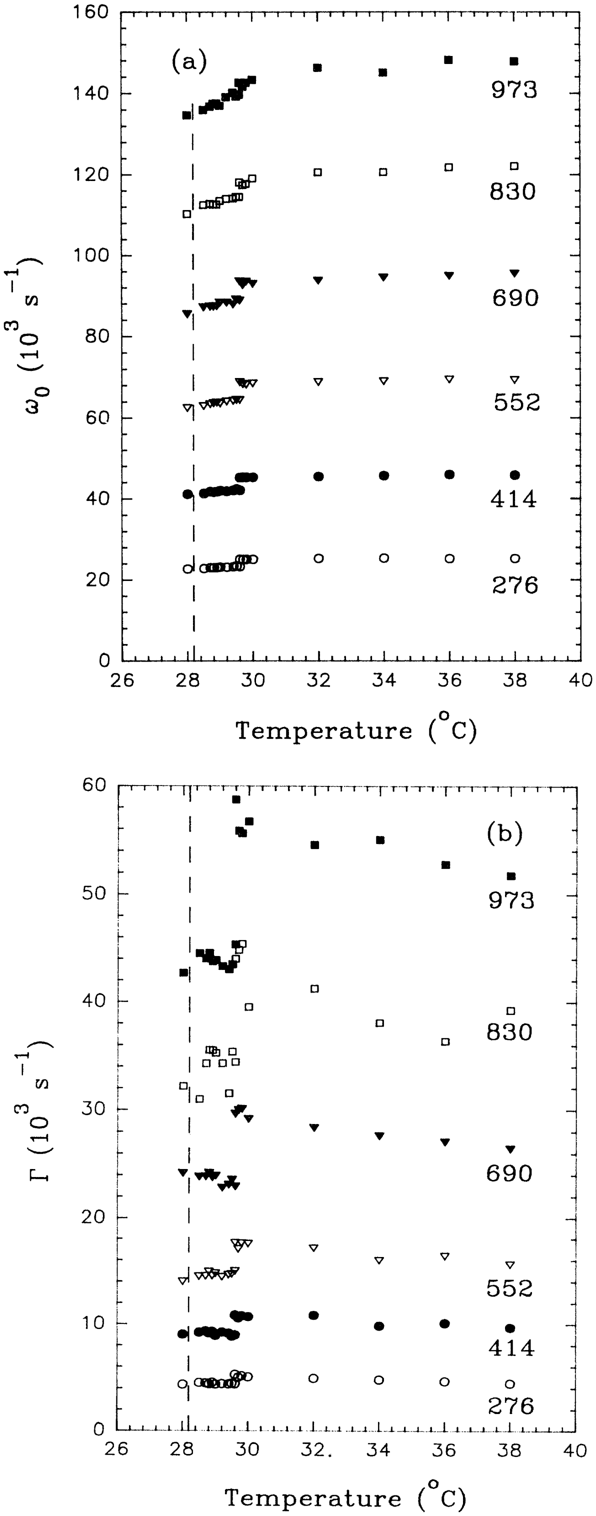

FIG. 4. As in Fig. 1, for n-octadecane.

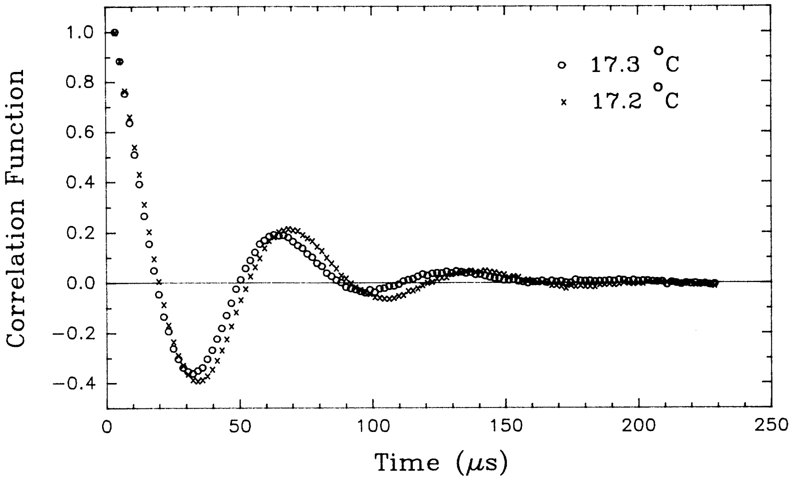

FIG. 5. Two correlation functions measured for hexadecane ($q = 690$ cm^{-1}) at temperatures just above and below T_k. The changes in period and damping are clearly apparent.

of Figs. 1–4 derive from many different samples. A fresh sample was used each day; in some cases materials from different batches were used.

There was no evidence for any hysteresis in the light-scattering data. The changes were entirely reversible, and reproducible: a sample could be repeatedly cycled through T_k, the capillary waves switching from one behavior to the other each time (Fig. 6). The change in the capillary-wave behavior occurred very rapidly, successive correlation functions showing either one behavior or the other (recording a correlation function took typically 10 sec). Intermediate values of ω_0 and Γ were not observed. The rapid changes in the light-scattering response arise from the sharpness of the transition in the surface layers of the fluids.

The different materials show slight differences in the light scattering data (Figs. 1–4). The discontinuities in ω_0^2 and Γ are, as will emerge below, almost the same for all the materials studied. However, below T_k the slope of the temperature variation of ω_0 (in particular) seems to increase with the chain length of the alkane.

The propagation of capillary waves on the free surface of a pure fluid is given by the well-known dispersion equation [9]

$$\left(i\omega + 2\frac{\eta q^2}{\rho}\right)^2 + gq + \frac{\gamma q^3}{\rho} = 4\frac{\eta^2 q^3 m}{\rho^2}, \qquad (2)$$

where

$$m = \sqrt{q^2 - \frac{i\omega\rho}{\eta}}, \quad \mathrm{Re}(m) > 0 \qquad (3)$$

and γ, η, and ρ are, respectively, the surface tension, viscosity, and density of the liquid. The first-order approximations to the roots of this equation in the capillary regime,

$$\omega_0 = \sqrt{\frac{\gamma q^3}{\rho}}, \qquad (4)$$

$$\Gamma = \frac{2\eta q^2}{\rho}, \qquad (5)$$

will prove useful below. More accurate predictions of the frequency and damping of waves of given q can be derived by numerical solution of Eq. (2). Alternatively, given experimental data for the wave propagation, this equation can be solved to yield estimates of the fluid tension and viscosity as perceived by the capillary waves (assuming ρ has its accepted value).

The data for heptadecane (Fig. 3) extends furthest below T_k, and so provides a useful subject for this exercise.

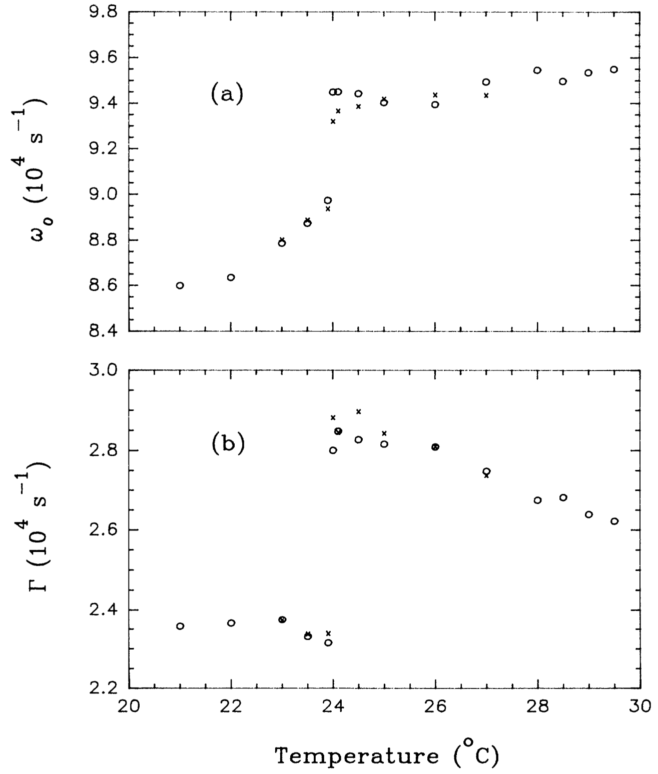

FIG. 6. Data for heptadecane ($q = 690$ cm^{-1}) taken for successive cooling (○) and heating (×) runs. No hysteresis is evident. Errors omitted for clarity.

The other materials entirely support the picture which emerges. Values for the apparent γ and η, determined from ω_0 and Γ as described, are shown in Fig. 7. The values plotted are averages over all q; no significant q dependence of the apparent fluid properties was evident at any T.

Above T_k the agreement with the literature variations is rather good, but this is not the case at lower T. Reliable literature data for the properties of alkane fluids tend to be tabulated only at 5 or 10 °C intervals above the melting point [1], so we measured γ and η by conventional techniques for more detailed comparisons. The viscosity thus determined showed no discontinuity at any temperature above the melting point, and accorded well with the accepted behavior. Our Wilhelmy plate tensions, indicated by the lines of Fig. 7, displayed a change of gradient at just that temperature (T_k) associated with the discontinuities of the light-scattering data [4]. However, the classical γ showed no step such as is apparent in Fig. 7 for the light-scattering data.

Consideration of the first-order approximations for ω_0 and Γ [Eqs. (4) and (5)] shows that the decreases in both quantities which lead to the changes in the apparent tension and viscosity below T_k could alternatively arise from an increase in the fluid density at that temperature. However, the results of such an interpretation of the data are not consistent: the apparent drops in γ and η (Fig. 7) would require changes in density $\sim 16\%$ and $\sim 24\%$, respectively. Direct measurements of the density of one material—heptadecane—confirmed that it varied smoothly above T_m (as established for longer alkanes [1]).

We emphasize that the light-scattering data of Fig. 7 are *apparent* fluid properties. The discontinuities of γ and η are not real; they simply represent an alternative view of the capillary-wave-propagation data of Fig. 3. We do *not* believe that, for example, the real fluid viscosity drops discontinuously; the drop of the apparent η is indicative of changes in other fluid properties which affect the capillary waves on the liquid surface.

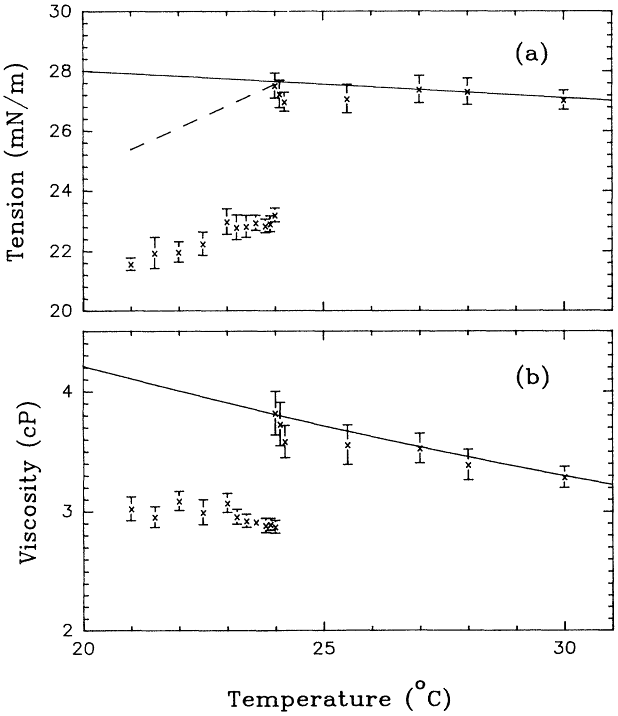

FIG. 7. Temperature variations of the apparent tension and viscosity of heptadecane inferred from the propagation of capillary waves. The solid lines indicate the corresponding literature variations [1], extrapolated as necessary. The dashed line for tension indicates the behavior found below T_k using a Wilhelmy plate; above T_k these values agreed with the literature data [4].

IV. DISCUSSION

The discussion is structured as follows: firstly we note certain evidence tending to support the reality of the present effects, then we briefly review the previous work on the classically measured surface tensions, which motivates an approach to the present results in terms of those surface excess properties of the fluids which affect the capillary waves. Following a brief discussion of the likely nature of the surface phase, we review two alternative (but untenable) explanations of the data.

A. Fluid densities

The densities of the alkane fluids at T_k are remarkably constant, much more so than at T_m. Figure 8 shows these values of ρ, interpolated from literature tabulations [1]: they vary only trivially (2 parts in 7750). The scatter of the points is within the precision of interpolation; direct measurement of the density of heptadecane (Paar densitometer) indicates that the errors of interpolation are of the order of magnitude of this scatter. This constancy of ρ at T_k was quite unexpected, and immediately

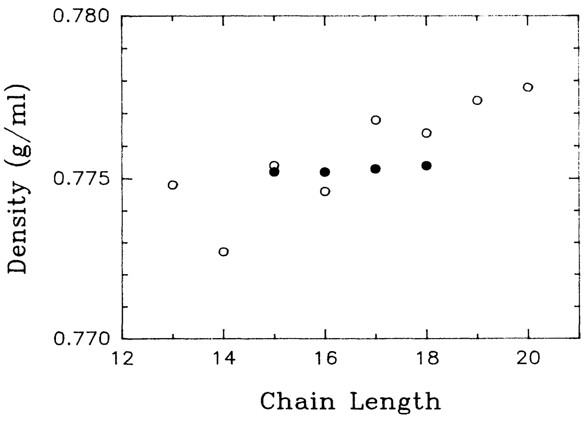

FIG. 8. The densities of alkane fluids at T_m (○) and T_k (●), interpolated from literature tabulations [1]. The densities at T_k are very constant (note the expanded scale) despite a range of almost 20 °C in T_k, and do not show the odd-even effects evident for those at T_m.

suggests the reality of the present results: it seems very unlikely that the extreme constancy of $\rho(T_k)$ could arise accidentally. This density is, of course, that of the bulk fluids rather than of the surface layer. However, it indicates that the surface field can only induce cooperative changes in the surface layer of alkane molecules when the molecular separation reaches some critical value.

The volume per molecule (V) at T_k deduced from these densities varies linearly with chain length, ranging from 455 to 545 Å^3 as n, the number of C atoms in the molecule, varied from 15 to 18. V is the total average volume occupied by each molecule and is greater than that in the solid phase (406 to 454 Å^3 [1]). A useful way to analyze the data is by plotting V/n vs $1/n$. The intercept, corresponding to an "infinite" chain alkane, is the volume per $-\mathrm{CH_2}-$ group and the value at $1/n = 0.5$, corresponding to ethane, that for the $-\mathrm{CH_3}$ group. The volume per $-\mathrm{CH_2}-$ group at T_k thus found is 29.98±0.01 Å^3, and for a terminal methyl group is 32.51±0.08 Å^3. These values may be compared with those for T_m: 29.7 Å^3 and 34.6 Å^3 [averaging the values for odd (33.6 Å^3) and even (35.6 Å^3) chain alkanes], respectively [1]. The volume of the two $-\mathrm{CH_3}$ groups, representing the total excess free volume per molecule, is lower at T_k than at T_m. It seems likely that conformational changes of the alkane chains are somewhat inhibited at T_k.

B. Classical tension data

The temperature dependence of the Wilhelmy plate tension values [4], indicated by the lines in Fig. 7, forms the best starting point for discussion of the light-scattering data. These values were significantly more precise than those derived from light scattering. The principal point of present interest is that while the Wilhelmy plate tensions concurred with the accepted variation above T_k, the temperature derivative of the tension became positive at $T < T_k$ rather than the more usual negative value above T_k. For a single component fluid, such as pure alkanes, this derivative of the equilibrium surface tension is just the surface excess entropy density [10],

$$S_s = -\frac{d\gamma}{dT}. \tag{6}$$

As surface excesses will be important in what follows, we interpolate a brief summary. The surface excess of any density of the fluid is the difference between the integrals of the variation of that density from $z = -\infty$ to $+\infty$ through the surface and of a hypothetical variation corresponding to a sharp surface (c.f. Fig. 9). Such a surface excess may be positive or negative, although the actual density is always strictly positive. The location of the idealized surface plane is a matter of definition: the Gibbs convention places it so that the surface excess matter density is zero [10].

The surface excess of the entropy density undergoes a discontinuous change at T_k, indicating that a first-order surface-induced transition occurs in these alkane fluids at that temperature. For $T > T_k$ the temperature gradients found were in good accord with the accepted values [1]: the positive S_s there is as for a normal fluid, in which the surface permits greater freedom for molecular motion or conformational change. However, for $T < T_k$ the negative surface excess entropies (Table I) indicate some reduction in the molecular degrees of freedom.

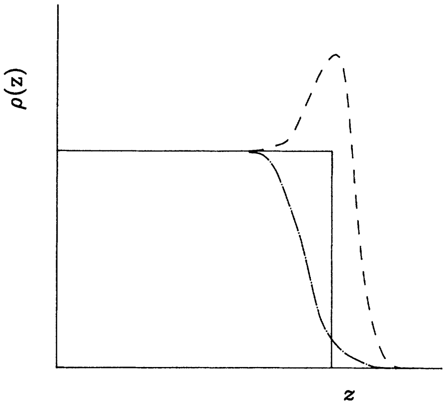

FIG. 9. Schematic variations of an arbitrary density ρ compared to an idealized fluid for which the bulk fluid density extends to the surface and there drops sharply to zero. The surface excess of the density ρ may be positive (dashed line) or negative (chain line).

The Wilhelmy plate data indicated no discontinuous drop in γ at T_k, such as is evident in the apparent tensions from light scattering (Fig. 7). However, the temperature gradients of the latter data, both above and below T_k, are entirely compatible with those found for the Wilhelmy plate data. While hysteresis might be expected for the first-order transition at T_k indicated by the surface excess entropy density, it was never observed using either technique. This may be because the surface acts to nucleate the transition in the surface layer.

For alkane fluids in the bulk, the conformational entropy density per $-\mathrm{CH_2}-$ group is about $0.82R$ [11], where R is the gas constant. This constitutes about 12.5% of the total entropy density (S) for all the materials studied here [12]. A crude estimate of ~ 60 Å for the thickness of the surface film for the case of heptadecane was derived [4] on the assumption that S decreases in the surface layer by about 10%. The rough coincidence with the conformational part of S is entirely fortuitous, but does, however, serve to indicate that the loss of all or part of the conformational entropy in that layer would not be inconsistent with the present data. The different values of S_s for the different alkanes (Table I) indicate that the surface suppresses the molecular freedom of longer alkane chains more effectively.

C. Viscoelastic surface waves

The above considerations motivate an approach to the present phenomena in terms of surface waves on a viscoelastic fluid supporting a structured surface layer

[13]. The full theory encompasses a wider range than is presently necessary. Firstly, the bulk fluids in the present case do not seem to display any viscoelasticity: to the highest frequencies studied they appear as viscous fluids. Secondly, the surface structure leads to a variety of surface excess viscoelastic moduli, only one of which appears germane to the present case.

Before summarizing those features of the theory which are relevant, we briefly mention the different possible surface excesses. Tejero and Baus [13] find three different surface excess viscoelastic moduli: one governing shear in the surface plane, one compression in that plane and the third shear normal to that plane. For an isotropic surface the in-plane shear does not couple to capillary waves [14]. The capillary waves, governed by the transverse shear, do couple to the compression modes [13,14]. However, the effects of the compression modulus upon the capillary waves are mainly upon their damping, the wave frequencies being hardly affected [15]. It is difficult to see how the observed reductions in ω_0 could arise from the effects of this modulus. We thus concentrate upon the transverse shear modulus which directly affects the capillary waves [14,16].

Given the simplifications just outlined, the theory of capillary waves on a fluid with a structured surface layer which possesses surface excess viscoelasticity [13] reduces to that for a clean liquid, with the tension supplemented by a surface excess transverse shear modulus. In particular, the modified dispersion equation of the capillary waves reduces to Eq. (2) with the following substitution:

$$\gamma \longrightarrow \gamma_{\rm eq} + \gamma_s(\omega) + i\omega\gamma'(\omega). \tag{7}$$

Here $\gamma_{\rm eq}$ is the equilibrium value of the tension, while $\gamma_s(\omega)$ is the elastic and $\gamma'(\omega)$ the viscous part of the surface excess transverse shear modulus. The latter two quantities do *not* comprise the surface excess of the shear viscoelastic properties for the bulk fluid: they derive from the usual interpolation between the low-frequency surface excess viscous properties of the fluid and the high-frequency surface excess elastic response [13]. We may think in terms of the usual Maxwell formula [17]

$$\gamma(\omega) = \gamma_{\rm eq} + \frac{-\omega\eta_s(\gamma - \gamma_{\rm eq})}{\gamma - \gamma_{\rm eq} - i\omega\eta_s}, \tag{8}$$

where we now use γ to indicate the total transverse shear elastic modulus at a frequency ω, and η_s the surface excess transverse shear viscosity in the limit $\omega \longrightarrow 0$.

The discontinuities in the capillary-wave propagation at T_k suggest that the surface-induced phase transition leads to the appearance at $T < T_k$ of a surface layer having nonzero surface excess viscoelastic properties. Both ω_0 and Γ decrease on cooling of the alkane fluids through T_k. Evidently both γ_s and γ' must be negative, like the surface excess entropy density S_s. The negative surface excess viscoelastic properties suggest that the structuring in the surface layer is such that the fluid is easier to shear normal to surface than is the bulk material. This seems consistent with the reduced chain flexibility assumed to underlie the negative surface excess entropy density [4]: a fluid comprising relatively rigid rodlike molecules should flow more easily than one consisting of a tangle of flexible molecules.

Equation (2), using the substitution of Eq. (7), can as usual be solved numerically to estimate the frequency and damping of capillary waves on the surface of a fluid supporting a viscoelastic structured surface layer. Figure 10 shows the results for a hexadecane surface with and without such a layer (the viscoelastic properties were chosen for their relevance to the present data). In considering the effects shown, modified first-order approximations for the capillary-wave frequency and damping [13],

$$\omega_0 \approx \sqrt{\frac{[\gamma_{\rm eq} + \gamma_s(\omega)]q^3}{\rho}}, \tag{9}$$

$$\Gamma \approx 2\frac{\eta q^2}{\rho} + i\frac{\gamma'(\omega)q^3}{2\rho}, \tag{10}$$

which may be compared with the more conventional Eqs. (4) and (5), provide useful guides to the eye. Clearly the principal effect of a negative value of γ' is to decrease the wave damping, the effect rising with increasing q. However, the steady decrease in Γ as q rises induces a slight increase in ω_0, which tends to offset the decrease in that parameter due to the negative γ_s.

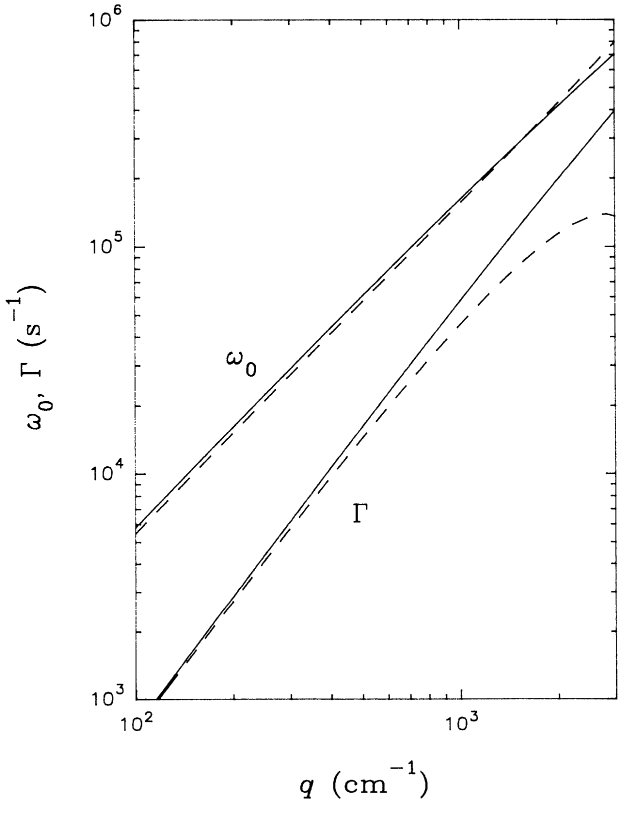

FIG. 10. Capillary-wave dispersion evaluated from Eq. (2) for the cases of the free surface of hexadecane (solid lines) and the same fluid supporting a structured, viscoelastic surface layer (dashed lines: $\gamma_s = -3$ mN/m, $\gamma' = -2\times10^{-5}$ mN s/m).

Comparison of Eqs. (9) and (10) with Eqs. (4) and (5) shows that, for constant surface excess quantities, the changes in ω_0^2 [defined as $\Delta\omega_0^2 = \omega_0^2(T_k^+) - \omega_0^2(T_k^-)$] and Γ [$\Delta\Gamma = \Gamma(T_k^+) - \Gamma(T_k^-)$] as the alkane fluids are cooled through T_k should scale as q^3; they also depend directly upon the surface excess quantities $\gamma_s(\omega)$ and $\gamma'(\omega)$. These approximate conclusions are somewhat modified when the exact numerical solutions of the two dispersion relations are compared. In what follows it will be these exact $\Delta\omega_0^2$ and $\Delta\Gamma$ which are discussed.

The differences between the observed values of ω_0^2 and Γ just above and just below T_k were determined. Above T_k the observed frequency and damping agree with the solutions of the usual dispersion equation [Eq. (2)], and so to minimize the errors on the experimental $\Delta\omega_0^2$ and $\Delta\Gamma$ the values of ω_0^2 and Γ were taken to be those predicted for the accepted properties of the fluids at T_k^+. The differences between these values and the observed data at that temperature just below T_k are plotted in Fig. 11 for all materials studied.

The experimental values of $\Delta\omega_0^2$ and $\Delta\Gamma$ do not scale exactly as q^3: the exponents, for each material individually, over the q range shown are compatible with 2.4 in the former case and 2.3 in the latter. However, the q^3 behavior is only expected from the first-order approximations; the exact predicted behavior departs somewhat from it. Also if γ_s and γ' were to vary because of viscoelastic relaxation this would alter the expected scaling behavior.

The experimental values were compared with the exact theoretical predictions. Evaluation of the theoretical q dependences of $\Delta\omega_0^2$ and $\Delta\Gamma$ requires estimates of the surface excess viscoelastic properties appropriate to the fluids below T_k. These were determined as follows. For each q value the modified dispersion equation was solved for a range of negative values of both γ_s and γ', together with the accepted properties of the bulk alkanes at T_k (the values used were those for hexadecane: any differences due to differences in γ and η for the other materials would be of second order only). Comparison of ω_0^2 and Γ thus found with the results from Eq. (2) for the fluid at T_k^+ provided a grid of values of $\Delta\omega_0^2$ and $\Delta\Gamma$. The experimental values for each material (Fig. 11) were then compared with this grid to determine the corresponding magnitudes of the surface excess viscoelastic properties. At each q studied the values thus found were extremely similar for all materials. It appears that the surface excess viscoelastic properties, as they affect the capillary waves, are rather independent of the material. At each q we can thus average the values of γ_s and γ' for all the materials.

Initially the global averages (over all q) of γ_s (−3.2 mN/m) and γ' (-2.6×10^{-5} mN s/m) were used to evaluate the modified dispersion behavior. This procedure yielded predicted variations which were in general accord with the trends of the data of Fig. 11. Rather than showing this comparison, the lines of Fig. 11 represent predicted behaviors based on certain other averages of the surface viscoelastic properties (to be discussed below). The general trends of the data clearly accord rea-

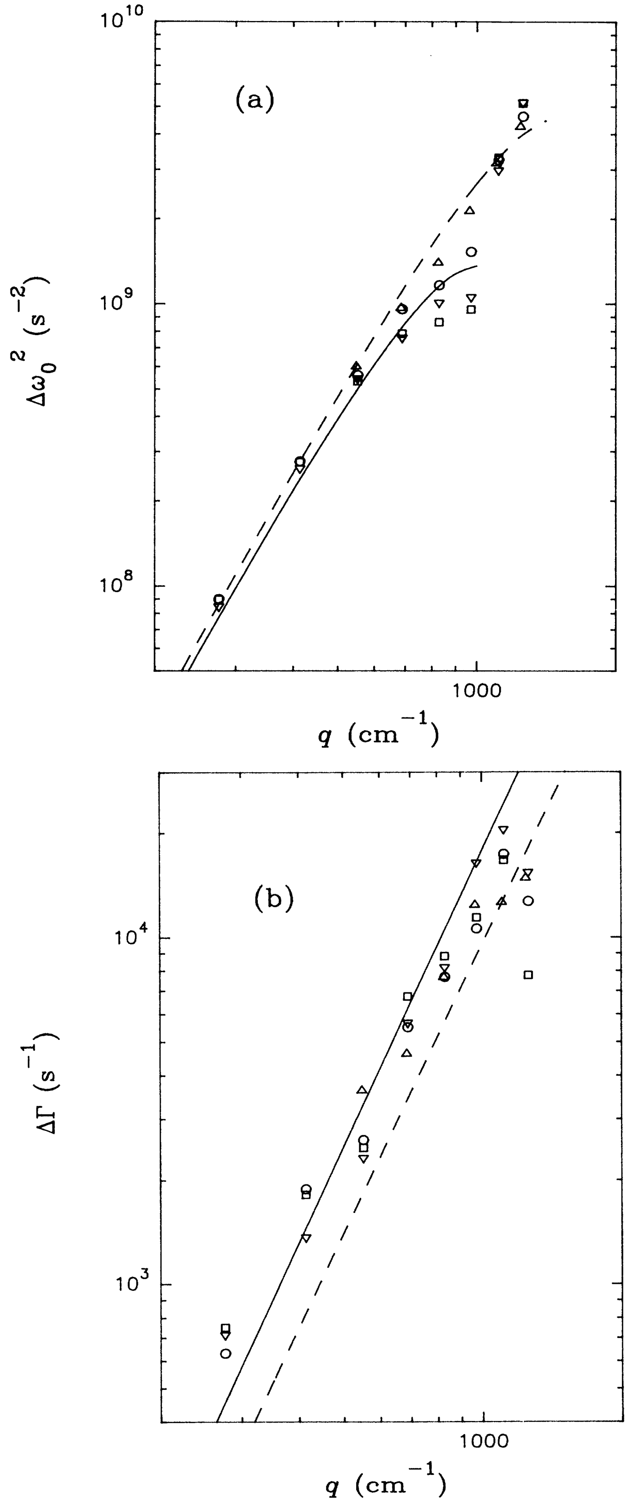

FIG. 11. Values of (a) $\Delta\omega_0^2$ and (b) $\Delta\Gamma$ for all four alkane fluids: ○, pentadecane; △, hexadecane; ▽, heptadecane; □, octadecane. Errors are omitted for clarity. The lines indicate the variations predicted for two different possible sets of surface viscoelastic properties, as discussed in the text: $\gamma_s = -3.15$ mN/m and $\gamma' = -3 \times 10^{-5}$ mN s/m (solid lines) and $\gamma_s = -3.4$ mN/m and $\gamma' = -1.5 \times 10^{-5}$ mN s/m (dashed lines).

sonably with these lines.

$\Delta\omega_0^2$ and $\Delta\Gamma$ at the highest values of q appear to depart somewhat from the trends of the data at lower q. It seems unlikely that this arises from problems at the extremes of the functioning of our apparatus as we have used the same system to study capillary waves to $q \sim 3000$ cm^{-1} for water [18]. These departures may indicate a real frequency dependence of the surface excess viscoelastic properties, as suggested by Eq. (8). We thus explore this possibility.

The values of γ_s and γ' averaged over all materials tended to be rather noisy, but a trend was apparent: both seemed to vary with q. $\gamma_s(\omega)$ rose somewhat at the highest q, while $\gamma'(\omega)$ tended to fall as q increased. These trends were most marked for $q > 1000$ cm^{-1}. The values were not precise enough to determine the frequency dependence of the surface excess properties. However, the compatibility of this suggestion with the observations can be illustrated by computing the modified dispersion behavior using two sets of surface excess properties: those derived by averaging the values for $q < 1000$ cm^{-1} and those found above that q. The results of this procedure are shown in Fig. 11. The solid lines represent predictions based on $\gamma_s(\omega)$ and $\gamma'(\omega)$ at the lower q, the dashed lines those for the higher q. Smaller γ' not only lowers $\Delta\Gamma$ but also reduces the tendency for $\Delta\omega_0^2$ to fall away from the q^3 variation as q rises. These effects can be related to the dispersion behaviors shown in Fig. 10 where, as the two variations of ω_0 converge, those for Γ separate. The higher γ_s increases $\Delta\omega_0^2$, the roll-off of that quantity at high q being somewhat postponed.

Comparing these predictions with the experimental data, the dashed lines are clearly close to the experimental $\Delta\omega_0^2$ and $\Delta\Gamma$ at high q, while the solid ones show trends similar to the low-q results. In particular, the systematic departures of $\Delta\omega_0^2$ from smooth scaling behavior could be accounted for provided $\gamma_s(\omega)$ and $\gamma'(\omega)$ varied as suggested. Clearly theoretical predictions based on some continuous frequency dependence of the surface excess quantities could be brought to agree very well with the experimental values. Further analysis would seem rather speculative.

The relaxation described by Eq. (8) shows that the surface excess viscosity should fall as ω increases, while the surface excess elastic modulus should rise. The nonzero γ_s for the present data implies that relaxation has, indeed, occurred by the experimental frequencies (taking the capillary-wave frequency ω_0 for ω). The rough constancy of γ_s, at least for $q < 1000$ cm^{-1}, suggests that the time constant for relaxation must be $\gg 1/\omega_0$. However, at frequencies far above the inverse of the relaxation time of a Maxwellian process the viscous component, here $\gamma'(\omega)$, should fall as ω^{-2}. Recalling that $\omega_0 \propto q^{3/2}$ [Eq. (4)], Eq. (10) shows that $\Delta\Gamma$ should then be roughly constant. Clearly this is not the case for the present data (Fig. 11). This suggests that at least two relaxation processes must occur in the present viscoelastic surface layers. This is schematically indicated in Fig. 12: $\gamma'(\omega)$ is approximately constant for $\omega \gg 1/\tau_1$ and $\omega < 1/\tau_2$. The strength of the relaxation [$\gamma - \gamma_{\text{eq}}$ in Eq. (8)] must be negative for both relaxation processes. One of the two time constants of the relaxation in the surface phase of alkane fluid is clearly $\gg 1/\omega_0$, as the surface excess elastic modulus is nonzero for all the present data. The second may be of the order of 10^{-5} s; as we have just discussed, further relaxation of $\gamma'(\omega)$ into $\gamma_s(\omega)$ may be occurring about $q = 1000$ cm^{-1}, for which $\omega_0 \sim 10^5$ s^{-1}.

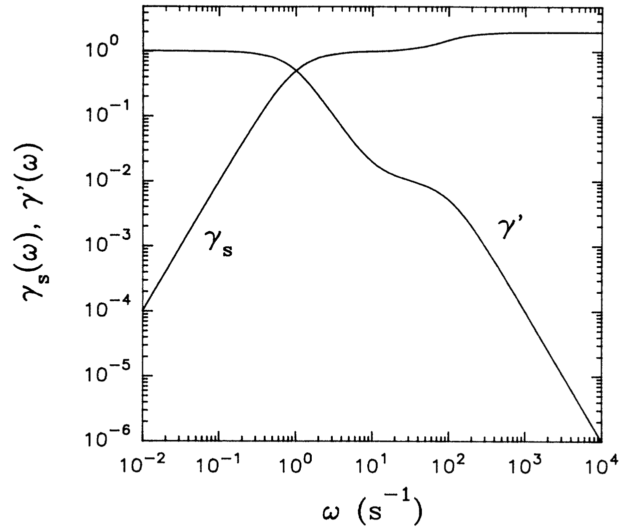

FIG. 12. Schematic variations of the surface excess viscoelastic properties with two relaxation processes present in the system. Each relaxation is of strength 1 mN/m, and the relaxation times were taken to be 1 s and 10^{-2} s. Note the plateaus in both $\gamma_s(\omega)$ and $\gamma'(\omega)$ for $1/\tau_1 \ll \omega < 1/\tau_2$.

It may be that there is some dependence of the strength and time scale of the relaxation upon the materials studied, as shown by the apparent systematic trend with chain length of $\Delta\omega_0^2$ around and just below $q = 1000$ cm^{-1}. However, this evidence is not strong enough to warrant detailed analysis. More precise data are needed.

Like the surface excess entropy density ($d\gamma/dT$ constant) [4], the surface excess viscoelastic properties seem to be independent of T below T_k. At these temperatures the measured $d\omega_0/dT$ and $d\Gamma/dT$ (Figs. 1–4) are consistent with those expected for the known temperature derivatives of γ_{eq} and η. There thus seems no requirement that either $\gamma_s(\omega)$ or $\gamma'(\omega)$ vary with T.

The tensions and viscosities deduced from the capillary-wave propagation (Fig. 7) are, as noted, only apparent values. In particular, the tensions below T_k are affected, via the dispersion equation [Eq. (2)], by the low-η values inferred there. The true variation of the tension affecting the capillary waves studied in this work is shown in Fig. 13. This effective tension will be higher for lower-q capillary waves and must continue to fall for higher frequency waves, as $\gamma'(\omega)$ relaxes into $\gamma_s(\omega)$. Thus experimental investigations of capillary waves of much lower or much higher frequencies than the present would infer different values of $\gamma_{\text{eq}} + \gamma_s(\omega)$.

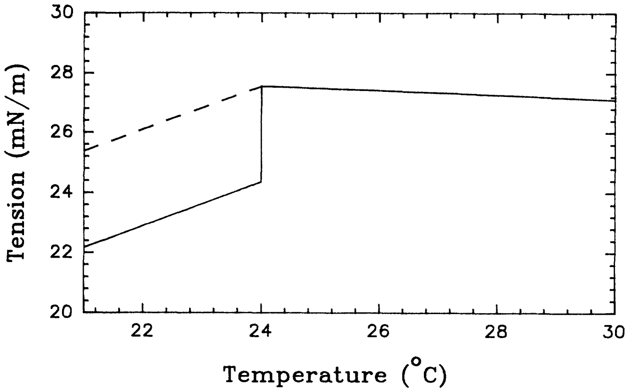

FIG. 13. The temperature dependence of the surface tension as measured by the Wilhelmy plate (dashed line) and as perceived by the capillary waves (solid line). The latter apparent tension, $\gamma_{\mathrm{eq}} + \gamma_s(\omega)$, must be frequency dependent; the variation plotted is that averaged over all surface wave numbers studied.

Unlike many properties of alkane fluids at their melting points, there is no odd-even effect to be discerned in the present values of T_k (Table I) or ρ at that temperature (Fig. 8), or in S_s (Table I) or any of the other surface excess quantities. This is as expected. The observed odd-even effects at T_m arise from the fact that different alkanes melt from different crystalline structures [1]. But here we are concerned purely with fluid phases, so that the different natures of the solids just below T_m are irrelevant.

D. Nature of the surface-induced phase

The negative surface excess entropy density and viscoelastic properties below T_k both tend to suggest that the surface-induced phase is more ordered than the bulk fluid. It seems plausible that this ordering primarily arises from a restriction of the conformational degrees of freedom in the alkane molecules. The van der Waals mean-field approach to fluid interfaces suggests that in a c component system there will be, at the interface, $c+1$ independent densities, as at an interface the energy and matter densities are not necessarily related to each other as in the bulk [10]; for the present one-component systems there can then only be two independent densities. The variations through the interface of all other densities must then follow one or other of these two. Let us take the matter and entropy as defining the two independent densities, and follow the Gibbs convention of placing the interface plane so that the surface excess matter density is always zero. Then below T_k all other surface excess densities must be zero or negative for our alkane fluids, depending on whether they follow the variation of ρ or S. The negative values of the surface excess viscosity and of the elastic modulus γ_s into which γ' relaxes are thus entirely expected.

The molecular orientation in the surface phase is unknown, as is the variation of the order in the phase as we pass from the surface to the bulk. The ordered structure in the surface phase cannot be that of the solid state, or it would nucleate solidification of the entire sample at T_k. Indeed all four materials studied could be supercooled below T_m. It seems likely that the alkane molecules are conformationally relatively well ordered and probably orientationally correlated but their centers of mass are arranged irregularly. The surface phase does not seem to form a liquid crystal. Inspection of a sample of octadecane with a polarizing microscope showed no structure above 28 °C (T_m), at which point optically active crystals appeared. It may be that the surface film is so thin that it influences the polarization of the light insignificantly.

E. Possible alternative explanations

If the surface phase were to form a wetting layer at the fluid surface this might appear to provide an alternative explanation of the present data. Lipowsky [19] has treated the effects of such a layer upon the capillary-wave propagation, assuming that complete wetting involves critical effects. In particular, ξ, the correlation length of the surface fluctuations induced by the wetting layer, should diverge as the wetting transition is approached; ω_0 changes to $\omega_0 \sim \sqrt{\gamma q(q^2+\xi^{-2})/\rho}$. The capillary-wave frequency should reduce smoothly to that of the free surface as $T \to T_w^-$, and for a wetting layer $\Delta\omega_0^2$ should scale as q. No predictions are available for the effects upon Γ. Clearly these predictions are in complete disaccord with the present data: ω_0 increases stepwise rather than gradually as T increases through T_k and $\Delta\omega_0^2$ clearly does not scale linearly with q. We thus reject this possible explanation.

Only when the alkane fluids were repurified were discontinuities of the capillary-wave propagation apparent at T_k. The simplest explanation is that, as received, the fluids contained some contaminant which inhibited the surface-induced transition. However, we consider the alternative possibility, that the attempts to purify the alkanes using an alumina column packed with silver nitrate introduced some contamination, despite the fact that this is a standard method to purify alkanes [8].

Any impurities would have to be surface-active to produce an apparently surface-induced phase transition. However, above T_k the surface wave behavior is entirely compatible with the free surface of pure alkane fluids; any contamination must be restricted to the bulk fluid at $T > T_k$. The reduction in the Wilhelmy plate γ below T_k suggests that the surface concentration of the hypothesized contaminant must depend only on temperature, and not on the system's history. The discontinuous drop in the light-scattering values of tension is not easily explained via this model, as a molecular film on a liquid surface should affect both light-scattering and equilibrium tensions similarly, although $\gamma(\omega)$ has been found to *exceed* the Wilhelmy plate value for certain insoluble monolayers due to viscoelastic relaxation [20].

The theoretical spectrum of light scattered by thermally excited capillary waves on a monolayer-covered liquid surface is established [21], and can be used to extract estimates of the surface viscoelastic properties from observed correlation functions [15]. When applied to light scattered from insoluble monolayers such estimates are self-consistent over different q [20,22]. This was not the case for the present data. Above T_k such fitting yielded surface tensions in accord with accepted data, and returned values for the other surface viscoelastic properties consistent with zero. Below T_k the quality of such fits, judged by the size and the correlation coefficient of the residuals [15], was consistently very poor indeed, and the values of the viscoelastic properties fluctuated randomly from wave number to wave number.

In summary, the present data are inconsistent with the hypotheses of either a wetting layer or a monolayer of surfactant molecules.

V. CONCLUSIONS

Surface light scattering from the free surfaces of the fluid phase of normal alkanes between 15 and 18 C atoms in length shows remarkable and unprecedented effects at a temperature, designated as T_k, which is chain-length dependent. The phenomena support and extend the recent observation of a surface-induced phase transition at these temperatures [4]. The decreases in the capillary-wave frequency and damping which occur as the temperature is lowered through T_k are compatible with the appearance of nonzero surface excess viscoelastic properties.

These observations establish a surface-induced phase transition in fluids of simple flexible molecules. Previous examples have been found in liquid crystals [23], the molecules of which have rigid backbones which seem to render them more susceptible to the effective field of the surface.

Above T_k the surface excess entropy density is positive, as for normal fluids, and there appear to be no surface excess viscoelastic properties. Below T_k both the surface excess entropy density [4] and the surface excess viscoelastic properties are negative. The entire set of data is consistent with the appearance below T_k of a surface layer of fluid in which the molecular freedom is reduced. The hypothesis that the negative surface excess entropy density is associated with a reduction in the conformational degrees of freedom [4] rather naturally explains all of the negative surface excess quantities.

We note that, unlike the surface excess entropy density, the surface excess viscoelastic properties do not seem to vary for the different materials studied. The apparent tension perceived by the capillary waves, $\gamma_{\mathrm{eq}}+\gamma_s(\omega)$, is some 3 mN/m lower than the equilibrium value, significantly different from that inferred using the dispersion equation for a free liquid surface (see Fig. 7). The surface excess transverse shear viscosity is about -3×10^{-5} mN s/m, and appears to show some relaxation over the range of frequencies probed in this work.

We have presented observations of the effects upon fluid surface waves of a viscoelastic surface layer for a pure fluid [13]. Somewhat similar viscoelastic properties (positive, rather than negative) have been found for fluid surfaces supporting a molecular fluid (e.g., [20,22,21]).

Note added in proof. Since the submission of this paper, it has been reported that the structured surface film proposed here is a single-crystalline layer of alkane molecules oriented normal to the surface [X.Z. Wu, E.B. Sirota, S.K. Sinha, B.M. Ocko, and M. Deutsch, Phys. Rev. Lett. **70**, 958 (1993)]. Such a layer seems entirely compatible with the present data and the conclusions drawn from them.

ACKNOWLEDGMENTS

One of us (C.J.H.) wishes to thank DENI and Unilever Research for financial support. We are grateful to Mr. E. Pelan for assistance with viscometry and Dr. B. J. Carroll with density measurements.

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