

Light scattering during surface melting of diphenyl; possible formation of a surface liquid-crystal phase

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Light scattering has been discovered in a molten film which is becoming thicker on the surface of a crystal as the melting point of the crystal is approached from below. The scattering by (001) and (010) faces of diphenyl is at a maximum for supercoolings $\Delta T \approx \Delta T_c$, where the dependence of the film thickness on the supercooling changes from logarithmic to power-law. It is suggested that although a bulk melt is isotropic, a film is a liquid crystal at $\Delta T > \Delta T_c$ and undergoes a phase transition at $\Delta T = \Delta T_c$.

Solid surfaces are capable of causing an ordering in adjacent layers of liquids. This effect is seen clearly in the case of liquid crystals, but isotropic liquids require more-subtle experiments. In particular, evidence for an ordering of isotropic liquids comes from the oscillatory dependence of the disjoining pressure in a film on the thickness of the film at the molecular scale¹ and also the logarithmic dependence on the supercooling ΔT of the thicknesses of molten films which appear on crystals as the melting point T_m is approached, i.e., during surface melting.^{2,3}

In the present experiments we used an ellipsometric method to study the surface melting of the diphenyl (001) and (010) faces in optical contact with glass in a constant-temperature chamber with a temperature regulation better than 10^{-2} K (Ref. 3). The thicknesses of the molten films, H , are measured within ± 5 Å on both faces; the results are shown in the coordinates $H - \ln \Delta T$ and $\ln H - \ln \Delta T$ in Fig. 1. For the closest-packed face, the (001) face, which is atomically smooth in contact with the bulk melt at $T < T_{c(001)} = 69.15$ °C, we have $H_{(001)} (\text{Å}) = 73 - 28 \ln \Delta T (\text{K})$. For the less closely packed (010) face at $T < T_{c(010)} = 69.0$ °C we have $H_{(010)} (\text{Å}) = 220 -$

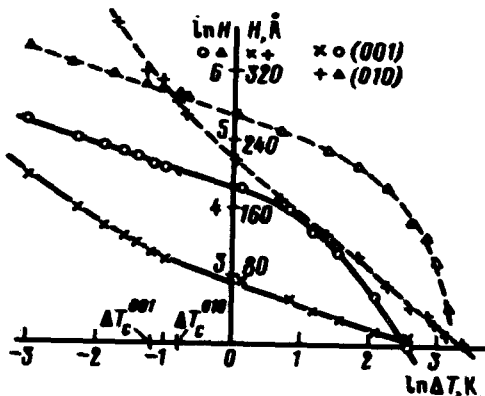


FIG. 1. The thickness of the film phase, H , versus the supercooling, ΔT , in rectifying coordinates.

$65 \ln \Delta T (\text{K})$. At supercoolings $\Delta T < \Delta T_c$, the behavior becomes a power law in each of these cases: $H \sim (\Delta T)^{-1/p}$, where $2.5 < p < 3.5$.

In ellipsometric measurements, only the polarized part of the light reflected from the sample is quenched; the laser noise and the light depolarized upon reflection enter the measuring photomultiplier. Consequently, the minimum signal from the photomultiplier when the quenching is at its best proportional to the intensity of the depolarized part of the scattered light, which furnishes information on phase transitions. The scattering intensity J measured in this manner for the (010) face of diphenyl is shown in Fig. 2 in units of the average scattering background far from T_m , at $T < T_m$. The scattering peaks are reached at $\Delta T_{c(001)} = 0.3 \text{ K}$ and $\Delta T_{c(010)} = 0.45 \text{ K}$. We observe no visual changes either in the interior of the crystal or near the contact with the glass on these occasions. As the temperature is lowered after T_c is crossed in the upward direction, we observe a hysteresis in the scattering and in the ellipsometric angles determining the thickness of the film. At $T < T_c$ there is no hysteresis.

At a temperature $\sim 7 \text{ K}$ below T_m , the refractive indices of diphenyl, n_p , n_m , and n_g , begin to change sharply with increasing temperature; at a point 0.3–0.4 K below the melting point, the dependence $n_{p,m,g}(T)$ becomes even steeper. As $T \rightarrow T_m$, all three of these indices tend toward the index of the bulk melt. In the immediate vicinity of T_m ($\Delta T < 0.07 \text{ K}$) the readings of the ellipsometer are essentially independent of the azimuthal orientation of the face. They are at the values calculated for reflection from the interface of molten diphenyl with glass.

The scattering peak near ΔT_c , the simultaneous change in $H(\Delta T)$ from logarithmic to power-law, and the hysteresis are all evidence of a phase transition in a molten surface layer. The logarithmic nature $H(\Delta T)$ at low temperatures $T < T_c$, is evidence of an ordering of a molten film; this order may be of the nature of a surface liquid-crystal phase. As the temperature increases, this phase converts into either another liquid-crystal phase or an isotropic melt, explaining the light scattering. Because of the low energies of the interfaces in a liquid crystal ($\sim 10^{-2} \text{ erg/cm}^2$), pronounced fluctuations in the order parameter and a scattering of light occur in them upon phase transitions. A scattering peak due to similar factors in the interior of a liquid phase has been observed in an MBBA film $40 \mu\text{m}$ between glass plates.⁴

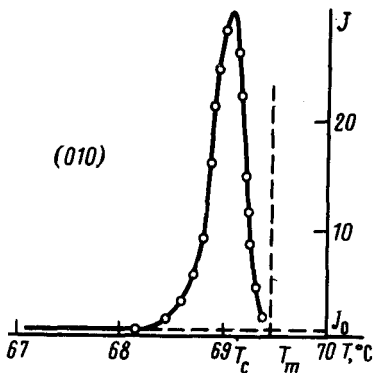


FIG. 2. Temperature dependence of the intensity of the light scattered by the surface of the crystal.

Transitions in a surface films may occur not only because of the temperature rise itself but also, and more probably, because of a rapid thickening of the film as $\Delta T \rightarrow 0$, a weakening of the effect of the walls on the structure of the film, and a transition to the situation described by the theory of surface-induced transitions.⁴ Furthermore, as the film becomes thicker, the fluctuations in the interface between the ordered surface layer, with a thickness of a few molecular sizes, and the remainder of the liquid of the film become "unshackled," and the thickness dependence of the free energy correspondingly changes.

A surface liquid-crystal state is apparently induced by the surface of the crystal, not by the glass. Specifically, an ellipsometric study of the adsorption of diphenyl vapor on glass in our chamber revealed no scattering of the light either as the temperature was raised from 20 to 75 °C or during the subsequent supercooling of an adsorbed film, 1050 Å thick, during heating to $T = 60$ °C, i.e., by $\Delta T = 10$ K.

The integrated (over the temperature) average value $\eta^* = \sqrt{-\eta_{cl}\eta_{lm}}$ of the order parameters at the interfaces of the film with the crystal, η_{cl} , and with the medium (the glass), η_{lm} , can be calculated by comparing the experimental curves of $H(\Delta T)$ with theoretical predictions.³ These values are $\eta_{(001)}^* = 0.064$ and $\eta_{(010)}^* = 0.139$, respectively, for films on the (001) and (010) faces.

Finally, a conversion in the film may be influenced by an orientational melting in the diphenyl, which begins at $\Delta T = 15$ K, according to data from IR spectroscopy⁶ and which is particularly noticeable in Brillouin scattering at⁷ $\Delta T = 0.3$ K. The driving force for the orientational melting is the tendency of the two phenyl rings of the diphenyl molecule to become mutually parallel in the crystal, rotating 23° with respect to each other (this is the equilibrium angle for the melt⁸; in the vapor, this angle would be 45°).

The possibility that a surface liquid-crystal phase forms in an isotropic melt does not contradict the two-stage nature of the surface melting of lead,¹⁰ the viscosity jumps in naphthalene at⁹ $\Delta T = 0.35$ K, and the scattering of light by the crystallization fronts of salol¹¹ and water.¹²

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