SURFACE MELTING

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Abstract. In a brief introduction we consider some evidence for surface melting as an appearance of a surface thin film phase rather than as a surface roughening.

In the main original part, we first present an ellipsometric technique allowing to measure both the thickness and refractive index of a film on a birefringent crystal interface.

In ellipsometric experiments the sample crystal was placed into thermostat, in which the temperature was kept constant with the accuracy of $\approx 0.01$ K.

A noticeable film appears on the basal (001) and pinacoidal (010) biphenyl faces at supercooling $\Delta T \leq 15$ and 25 K below the melting point. At $\Delta T \approx 0.3$ K the film thickness $H$ obeys the law $H_{001} = 73 - 23 \ \text{Å} \ \ln \Delta T$ and $H_{010} = 220 - 65 \ \text{Å} \ \ln \Delta T$, respectively. The film refractive index tends to the one of bulk melt when $\Delta T \to 0$ i.e. $T \to T_m$. Along with the high purity of the crystal used this indicates that the film present the biphenyl melt.

The logarithmic $H(\Delta T)$ dependence follows from a model in which the melt is supposed to be ordered at the crystal interface its free energy minimizing a functional containing a sum of squares of the order parameter and its spacial gradient.

At $\Delta T = \Delta T_c \approx 0.3$ K and 0.4 K for the (001) and the (010) faces, respectively, the background ellipsometric signal intensity achieved under best compensation conditions exhibit a high peak which is a measure of the strong incoherent light scattering. At $\Delta T < \Delta T_c$ the $H \sim \ln \Delta T$ law is replaced by the $H \sim (\Delta T)^{1/p}, \ 2.5 \leq p \leq 3.5$ law.

The data may be understood if the surface melt appears first (at $\Delta T > \Delta T_c$) in a liquid-crystalline (LC) state and at $\Delta T = \Delta T_c$ undergoes a phase transition into isotropic liquid existing within the interval $\Delta T_c > \Delta T > 0$. Since the bulk biphenyl melt does not exhibit LC properties the surface melting via a LC phase may be a general phenomenon and a LC film may cover the interface between the crystal and its isotropic melt.
1. Introduction

1.1 Surface melting and surface roughening

The term "surface melting" means often two interconnected, but physically different phenomena:

1. Two-dimensional phase transition from atomically smooth to atomically rough interface-surface roughening (SR). SR is symbolized by the transfer Fig. 1(a)→Fig. 1(b).

2. Surface melting in its direct sense, consisting in an appearance of liquid or quasiliquid melt phase on a crystal surface (the transfer Fig. 1(a)→Fig. 1(c) or Fig. 1(a)→Fig. 1(d)). Thickness $H$ of the such melt layer is increased unlimittedly when the sample temperature approaches the melting temperature $T_m$ i.e. $H\to\infty$ at $\Delta T\equiv T_m-T\to 0$. The film thickness is determined by temperature dependences of the film phase molecular structure and corresponding thermodynamical properties as well by the crystal surface wetting conditions. Since the film phase properties are similar to the melt properties the crystal-film interface structure can be, generally speaking, either smooth or rough (Fig. 1)—in accordance with the roughening criterion $L/kT=\Delta S/k\geq 2/3$, where $L$ and $\Delta S$ are the heat and entropy of fusion, $k=1.38\times 10^{-16}$ erg/K.\textsuperscript{1}

This paper is dedicated to surface melting in its direct sense.

1.2 Selected findings in surface melting research

Liquid phase below melting point was microscopically observed by

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**Fig 1.** Scheme of possible surface transformations.
Faraday\(^2\) as a meniscus in ice cracks,\(^3\) as droplets and film on surfaces of \(p\)-toluidine\(^4\) and other crystals\(^5\) growing from vapor or existing in equilibrium with it. SM manifests itself also in: the light emissivity difference between various faces of copper and gold single crystalline spheres just below their melting temperatures,\(^6\)–\(^8\) appearance of a narrow NMR line from highly mobile water protons at \(-20^\circ\)C and higher,\(^9\)–\(^13\) narrow NMR line in highly dispersed mixture of biphenyl with a SiO\(_2\) balls at temperatures by \(\approx30^\circ\) below the biphenyl melting point \(T_m=69.5^\circ\)C,\(^14\) disappearance of a shear modulus between ice and strain gauge frozen at its surface,\(^15\)–\(^17\) proton channeling violation in ice\(^18\)–\(^20\) and lead\(^21\) surface layer, increasing of ellipticity of the light reflected from ice surface at \(T\rightarrow T_m\),\(^22\),\(^23\) SM is also responsible: for the zero growth rate of biphenyl crystal from the vapor at \(T\rightarrow T_m\) in spite of a nonzero supersaturation at this temperatures,\(^4\) for the increase of the movement velocity of a copper ball through naphthalene and stilbene crystals under the action of a fixed mechanical force at premelting temperatures,\(^24\)–\(^26\) for the increase of an isobaric heat capacity of a thin gallium\(^27\) and sodium\(^28\)–\(^30\) samples at \(T\rightarrow T_m\), and also for the change from faceted to rounded shapes of, for example, adamantane crystals growing from the vapor at \(T\rightarrow T_m\).\(^31\) Series of results concerning SM have been reviewed by Nenow.\(^32\)

Theoretical approach includes both the molecular dynamic simulation\(^33\)–\(^35\) and analytical consideration.\(^14\)–\(^42\) In the latter, enhanced amplitude of surface atoms vibrations,\(^38\) van der Waals,\(^41\) phonon\(^14\) and molecular ordering contributions\(^42\) to the thin film chemical potential have been considered.

### 1.3 Statement of the problem

In spite of many experiments indicating to the surface melting and roughening no direct data are available allowing to distinguish SR and SM phenomena. Ellipticity increase in a polarized light reflected from ice prism face at \(T\rightarrow T_m\)\(^22\) does not allow unequivocal conclusion since this face apparently is rough in contact with its own melt.

The film thickness vs undercooling dependence, \(H(\Delta T)\), is determined by the intermolecular interactions within the film and brings therefore a fundamental information. Indeed, let \(\mu(T, H)\), \(\mu_b(T)\) and \(\mu_s(T)\) are the chemical potentials of the melt film, bulk liquid and crystal, \(\Pi(H)\) is the disjoining pressure in the film and \(\omega\)-its specific atomic volume. Then, by definition of \(\Pi(H)\),

\[
\mu(T, H) = \mu_b(T) + \Pi(H)\omega
\]

and the \(H(\Delta T)\) dependence follows from the equilibrium condition
\[ \mu(T, H) = \mu_0(T) \]  \hspace{1cm} (2)

giving

\[ \Pi(H) = L \Delta T / \omega T. \]  \hspace{1cm} (3)

For the van der Waals intermolecular interactions \( \Pi(H) \approx A/\Delta T^3 \) or \( \Pi(H) \approx B/\Delta T^4 \).\(^{41} \) Accordingly, \( H \sim (\Delta T)^{-1/3} \) or \( H \sim (\Delta T)^{-1/4} \). The discreteness of the thin film phonone spectrum leads to \( H \sim (\Delta T)^{-1/2} \), contribution of a molecular ordering to the disjoining pressure results in \( H \sim \ln \Delta T \).\(^{42} \) At present almost all these dependences were observed experimentally along with \( H \sim (\Delta T)^{-1} \) for biphenyl and ice.\(^{14} \) Thus new precise \( H(\Delta T) \) data are needed.

The aim of this work was to quantitatively analyse the \( H(\Delta T) \) dependence and to decide whether the SM and SR are the same or principally different phenomena. To solve the latter problem, one needs to show that the melt film exists even on the crystalline face which remains atomically smooth when in contact with its own melt. In our experiments the basal (001) plane of biphenyl was taken as an example along with the pynacoid (010) face which, on the contrary, is atomically rough when in contact with the melt. As an experimental tool, the ellipsometry was chosen.

2. The Method

2.1 Ellipsometry

Since biphenyl is optically birefringent the ellipsometry was developed able to describe thin isotropic transparent films on uni and biaxial nonabsorbing crystals\(^{43}-^{45} \) (see below).

The measurements were carried out using conventional ellipsometer (Fig. 2) with monochromatic radiation of the He–Ne laser. The incident beam was converted into the circularly polarized light by the \( \lambda/4 \) plate, into the linearly polarized light by the polarizer \( P \), the light intensity being independent on \( P \) orientation and finally into the elliptically polarized light by compensator

\[ \text{Fig 2. Scheme of the ellipsometric experiment; P: polarizer, A: analyzer, } \lambda/4: \text{ quarterwave plate, D: detector.} \]
C. In practice, the polarizer and the compensator were arranged to get such an ellipticity of the light incidenting on the surface under investigation that the reflection transforms it exactly to the linearly polarized one. Then the analyzer \( A \) was adjusted to determine the reflected light polarization, used to judge on the surface state. The angles between the incidence plane and the polarizes axis \( \gamma_p \), analyzer \( \psi_a \) and the direction of the “fast” compensator axis \( \psi_c \) in an extinguishing position of light outgoing from analyzer (the nulling angles) for various ellipsometric zones were initial values for calculations. The subtle imperfections of the ellipsometer optical elements were also taken into account.\(^45\)

The biphenyl crystal surface with the orientation close to the face under investigation placed so as to make an optical contact with the \( \approx 4 \text{ mm} \) thick glass plate (Fig. 3). The incident light beam diameter was \( \leq 1 \text{ mm} \) so that the beam reflected from the external glass surface was eliminated. The optical parameters of the glass plate and its damaged surface layers were preliminarily determined using the same ellipsometer. At \( \lambda = 6328 \text{ Å} \) (HeNe laser) and \( T = 22^\circ\text{C} \) the glass refractive index \( n_{gl} = 1.533 \), the effective thickness and refractive index of the damaged glass layer being 320 Å and 1.527, correspondingly. The parameters of optical elements of ellipsometer were also preliminarily determined from measurements on isotropic sample.

The film refractive index \( n_f \), the bulk crystal refractive indexes \( n_b, n_p, n_m \), the angle \( \theta \) between the face normal and crystal optical axis \( g \) along with the azimuthal angle \( \phi \) between the incidence plane and projection of the \( g \) axis on the face under investigation, 6 parameters in total, were calculated by a computer minimization procedure (CMP) making use of the complex normalized Jones matrix and taking into account the glass plate and the glass damaged layers. The film transparency allowed to arrange the procedure in a such manner that film thickness \( H \) was determined without increasing the numbers of parameters which are found from this CMP. The Jones matrix was found from 4 pairs \( (j = 1, \ldots, 4) \) of the measured nulling angles \( \gamma_p^{(j)} \) and \( \psi_a^{(j)} \) of polarizer and analyzer, respectively, at two fixed and symmetrical to

\[ \begin{align*}
\lambda & \quad \gamma_p & \quad \psi_c & \quad n_{gf}^{(1)} & \quad c_{gf}^{(1)} \\
1 & \quad 2 & \quad 3 & \quad n_{gf}^{(2)} & \quad c_{gf}^{(2)} \\
4 & \quad n_{\theta}, n_{\psi_p}, \theta, \omega & \quad n_{gf}, c_{gf} & \quad n_{gf}, c_{gf} & \quad n_{gf}, c_{gf}
\end{align*} \]

Fig 3. Scheme of the sample; 1: damaged glass layers, 2: glass, 3: surface quasiliquid film, 4: crystal \( n \)-refractive index, \( n_b, n_m, n_p \)-three refractive indices of the crystal \( d \)-thickness, \( g \)-glass, \( f \)-film, \( \theta, \omega \)-angles determining the crystal orientation.
incidence plane compensator orientations $\psi_c = 30^\circ$, making use another CMP and taking into account the imperfections of the ellipsometer optical elements. The compensator orientation $\psi_c = 30^\circ$ was chosen to avoid identity in an incidence and reflected light polarization states in various ellipsometric zones.

2.2 Samples and thermostat

The biphenyl plates were cut out of a meltgrown single crystal and dry-polished. Spectral-luminescent analysis of the crystals showed that bulk part of the most typical impurities—antracene, acenaphthene, naphthalene was $<10^{-4}\%$. The plate orientation was determined preliminarily under polarization microscope and finally by the ellipsometer. The glass plates were carefully annealed to avoid a stress birefringence. Surface of the glass plates was cleaned from organic impurities with a heated acid and repeated washing in a double distilled water.

The sample made of the glass plate placed on the polished crystal face was heated in a special thermostat used also as a measurements camera which allowed to maintain the sample temperature with an accuracy of 0.007°C relative to reference ice in a range of 40°C $\pm$ 70°C, the temperature change step being 0.014°C. When the sample temperature approached the biphenyl melting point a liquid layer was formed on the interface between the glass and the crystal producing their optical contact. Because of a slightly salient form of the polished crystal surface the melt appeared at $T \rightarrow T_m$ pushed the air bubbles to a periphery when a pressure was applied to the sample. The prepared sample was characterized by the low degree of incoherent light scattering.

3. Experimental Results

3.1 Thickness of quasiliquid layer

The sample was placed into thermostat which was carefully adjusted on the optical stage. Nulling angles of polarizer and analyzer were measured in four zones at fixed compensator azimuth $\pm 30^\circ$, at fixed azimuthal crystal orientation for various temperatures of the sample. Angle of incidence was 60°. Experimental temperature dependences of $(\gamma_p^{(1)}, \psi_s^{(1)})$ and $(\gamma_p^{(2)}, \psi_s^{(2)})$ for the (001) face are shown in Fig. 4.

Temperature dependences of refractive index $n$ and thickness $H$ for the films on the (001) and (010) faces are shown in Figs. 5 and 6. With the accuracy $\pm 5$ Å the $H(\Delta T)$ dependence is described by

$$H(001) = 73 \text{ Å} - 28 \text{ Å ln}\Delta T$$

for the basal (001) face at $T < T_c^{(001)} = 69.15^\circ$ C. For the less close packed
Fig 4. Polarizer $\gamma_p^{(1,2)}$ and analyzer $\gamma_a^{(1,2)}$ nulling angles vs. temperature $T$.

Fig 5. The film thickness $H$ and refractive index $n_f$ dependences on temperature $T$, (001) face.

Pinacoid (010) face up to $T_c^{[010]}=69.0^\circ$C we obtain with the same accuracy

$$H(010) = 220 \text{ Å} - 65 \text{ Å ln} \Delta T.$$  \hspace{1cm} (4')

The logarithmic function $H(\Delta T)$ transfers to exponent $H \sim (\Delta T)^{1/p}$ with $2.5\leq p \leq 3.5$ within the range $T_c < T < T_m$ for both faces.

The ellipsometrically measured refractive index of the film tends at $T \rightarrow T_m$ to the one of bulk biphenyl melt, $n_r = 1.590$ (see insertion in Figs. 5 and 6) for both faces. The bulk value was determined independently by Abba refractometer at 70$^\circ$C. Ellipsometrically found temperature dependences of
Fig 6. The film thickness $H$ and refractive index $n_t$ dependence on temperature $T$. (010) face. (---): extrapolation of the logarithmic $H(\Delta T)$ dependence.

Fig 7. Main refractive indexes $n_g, n_p, n_m$ of the crystal vs. temperature $T$ dependence.

the main values of refractive indexes $n_g, n_p, n_m$ for bulk crystal are shown in Fig. 7. These values changed fast at $T\rightarrow T_m$, became drastically steep at $T\geqslant 69.0^\circ$C and tended to $n_v$ within the $69.0^\circ$C $< T < T_m$ interval.
3.2 Light scattering

The light scattering is known to be important method to investigate phase transitions, including surfaces and thin films. In our experiments, the scattered incoherent light intensity $J_{sc}$ is determined as the minimal detected signal corresponding to the best extinguishing of the reflected beam. An important feature found in the experiments was the scattering intensity peak presented in Fig. 8. The scattering was observed on both the (001) and (010) biphenyl faces with peak top just at $T_c$ and reveals a hysteresis to heating and cooling of the sample.

4. Discussion

4.1 Film thickness

The existence of the quasiliquid layer in a contact with a rough glass surface and its $H(\Delta T)$ dependence might be determined by the size spectrum of the glass surface cavities—because of the Gibbs-Thomson effect. Since, however, there is no liquid film at room temperature, we had a possibility to find the effective optical parameters of a damaged glass surface layer contacting with biphenyl and thus the amount of biphenyl penetrated into the cavities. The measurements have shown that effective thickness of the layer remained the same and gave 1.527 and 1.529 for its effective refractive indices for the glass-air and glass-crystal interface layers, respectively. This negligible difference proves that the melting point depression by surface energy is not responsible for SM.

High purity of the biphenyl crystals used, along with the reproducibility of the $H(\Delta T)$ values after several melting-and-freezing cycles make the

![Image of Fig 8](image_url)

**Fig 8.** Light scattering intensity $J_{sc}$ as a function of temperature $T$; (010) face; $T_c$ is the surface phase transition temperature.
melting point depression by impurities also improbable. We should thus conclude that the SM is a real fundamental surface phenomena rather than an artifact.

The SM in our experiments was found on the close packed basal (001) face which remains atomically smooth in contact with the own melt,\textsuperscript{47} the film refractive index approaching the bulk melt refractive index at $T\to T_m$. Consequently, the data obtained may not be ascribed to the SR transition and corresponding interface diffuse thickening. On the opposite, the data should be interpreted as an appearance of the surface film phase, i.e. the SM in a direct sense.

It is possible to treat the logarithmic $H(\Delta T)$ dependence as a result of a mutual repulsion between partly ordered quasiliuid layers adjusted to both the crystal and glass interfaces. Let us clarify the physical sense of the parameters in (4, 4') within the framework of this well-known model. Consider a liquid of long asymmetric molecules each characterized by a director $\mathbf{n}=[n_x, n_y, n_z]$, the order parameter being $\eta=(\langle n_x^2 \rangle + \langle n_y^2 \rangle + \langle n_z^2 \rangle)^{1/2}$ with the averaging extended to a physically infinitely small volume. Choose the coordinate axis $z$ along the normal both to the crystal and glass surfaces so that $\eta=\eta(z)$. Let the indices 1, 2, 3 be assigned to the crystal, liquid and glass, correspondingly. A free energy of the crystal-melt (12) or melt-glass (23) interface may be divided into: 1) a short range part, $\alpha_{12}^0$ or $\alpha_{23}^0$ determined by interaction between first solid and liquid monomolecular boundary layers and 2) an integral contribution from the ordering in another liquid layers. Then the appearance of the melt film on the crystal-glass interface changes the system free energy by

$$
\Delta f = H\mu_k - \mu_c) + \alpha_{12}^0 + \alpha_{23}^0 - \alpha_{13} + \omega^{-1} \int_0^z \left( c\eta^2 + g \left( \frac{d\eta}{dz} \right)^2 \right) dz.
$$

(5)

Here $\alpha_{13}$ is the crystal-glass surface free energy and $\mu_k > \mu_c$ at $T < T_m$. Coefficients in the ordering functional have the following dimensions: $[c]=\text{erg}$, $[g]=\text{erg-cm}^2$. In a bulk liquid at $z\to\infty \eta=0$, $d\eta/dz=0$. Since $\eta$ is a measure of the system ordering, it should be expected that $c \sim T$ within the order of magnitude. The gradient term in the functional in Eq. (5) has a sense of a deformation energy. Its magnitude is determined by intermolecular interactions. In the molecular scale, $\omega^{1/3}$, the crystal shear modulus might be a measure of the interaction. In the scale of short-range ordering regions (the cluster), the grain boundary energy might be taken as a typical g-value. For systems of electrically polar molecules the electrostatic interaction should be added. The numerical estimates for $g$ and $c$ will be given below.

The equilibrium structure of the quasiliuid film should provide a minimum of the ordering functional from (5) with respect to $\eta(z)$ variations:
\[
\delta \int_0^H \left[ c \eta^2 + g \left( \frac{d\eta}{dz} \right)^2 \right] \, dz = 0
\]

(6)

and with the boundary conditions

\[
\eta(0) = \eta_{12}, \quad \eta(H) = \eta_{23}. \tag{7}
\]

The Eqs. (6) and (7) are satisfied by

\[
\eta(z) = \left[ \eta_{12} \text{sh}(h - \zeta) + \eta_{23} \text{sh}\zeta \right] \text{sh}^{-1}h, \quad \zeta \equiv z/\zeta_0, \quad h \equiv H/\zeta_0 \tag{8}
\]

where the characteristic length \( \zeta_0 = \sqrt{g/c} \) is introduced. Substituting Eq. (8) into Eq. (5) and applying the equilibrium condition \( \partial \Delta f/\partial H = 0 \) one gets the \( H(\Delta \mu) \) dependence in the form:

\[
\text{sh}^{-2}h[-(\eta_{12}^2 + \eta_{23}^2) + 2\eta_{12}\eta_{23}\text{ch}h] + \Delta \mu/c = 0. \tag{9}
\]

Taking \( \Delta \mu = \Delta S \Delta T \) and assuming \( h > 1 \) we get approximately

\[
H = -\zeta_0 \ln(\Delta \mu/4c\eta_{12}\eta_{23}) = \zeta_0 \ln(4c\eta_{12}\eta_{23}/\Delta S) - \zeta_0 \ln \Delta T. \tag{10}
\]

The biphenyl fusion entropy \( \Delta S = 13 \text{ cal/K} \), its molecular volume \( \omega = 2.1 \times 10^{-22} \text{ cm}^3 \). Assuming sign \( \eta_{12} = -\text{sign } \eta_{23}, c = T(\text{erg}) \) we obtain from comparison of Eq. (4), (4') and Eq. (10)

\[
\eta^*_{(001)} = 0.064, \quad g_{(001)} = 3.6 \times 10^{-27} \text{ erg } \times \text{ cm}^2
\]

for the (001) face and

\[
\eta^*_{(010)} = 0.139, \quad g_{(010)} = 1.9 \times 10^{-26} \text{ erg } \times \text{ cm}^2
\]

for the (010) face with \( \eta^* = \sqrt{-\eta_{12}\eta_{23}}. \) The shear modulus of crystalline biphenyl \( G \approx 3 \times 10^{10} \text{ erg/cm}^2 \) and thus \( g = G\omega^{5/3} \approx 2.3 \times 10^{-26} \text{ erg } \times \text{ cm}^2. \) An alternative estimate for \( g \) appear if the gradient term \( g(d\eta/dz)^2 = g\omega^{-4/3} \) is accepted to be comparable with the grain boundary energy, say \( \approx 1 \text{ erg/cm}^2. \) In this case \( g \approx 10^{-29} \text{ erg } \times \text{ cm}^2. \) Thus the experimental values of \( g_{(001)}, g_{(010)} \) are within the obtained limits and therefore should be considered as physically reasonable. The better accuracy may not be expected from the rough phenomenological model.

4.2 Orientational melting

Heating of molecular crystals often leads to their orientational disordering\(^{49}\) during which molecules rotate in directions corresponding to the
lowest potential barriers. For biphenyl and naphthalene, the polarized Davydov’s splitting components in the IR spectra indicates that at $T \rightarrow T_m$ the optical indicatrix transfers to elliptic shape from the one described by the cosinesquare law; for a melt, the indicatrix is a sphere. This transfer in biphenyl becomes noticeable at $\approx 15$ K below $T_m$ and is ascribed to a change in molecule configuration: two phenyl rings of which the biphenyl molecule it made are complanar in the crystal, are mutually turned around the C–C bond by $23^\circ$ in the melt and by $45^\circ$ in the gas phase. The mutual rotation of the rings at the premelting temperatures might become possible because of strong anharmonicity. The phenyl rings misorientation in crystal is supported also by Mandelstam-Brillouin scattering which is especially strong at $\sim 0.3$ K below $T_m$.

In our experiments (Fig. 7) a steep change in biphenyl refractive indices at $\approx 7^\circ$ C below $T_m$ is replaced by even steeper change at $\Delta T=0.3$ K, all three refractive indices tending to refractive index of the bulk melt at $T \rightarrow T_m$. These changes may result from the orientational melting described above.

4.3 Hypothesis: surface melting via liquid crystal

The reversible increase in the light scattering intensity at $T=T_c$ testifies to phase transition in the surface layer at this temperature. We may thus think of a transition between the liquid crystalline (LC) phase and conventional melt when the film thickness and temperature rises. This possibility is in a general agreement with the previously discussed (See Subsection 4.2) role of liquid ordering in the interface vicinity. This ordering may even provide a liquid crystalline state in the film (for analytic description of this possibility, an $\eta^4$ or other terms with higher power of $\eta$ should be added to functional in (5)). The probable nitrobenzene LC appearance at the glass interface along with many other experiments showing that LC are ordered by solid surfaces also supports the hypothesis of SM via LC phase. Namely, we suppose that a LC phase, not revealed in an ordinary three-dimensional melt, is formed at $T<T_c$. At the $T_c^{(001)}=69.15^\circ$ C for the (001) face and at $T_c^{(010)}=69.00^\circ$ C for the (010) face (Figs. 8 and 9) this LC film transfers to an isotropic melt film (Fig. 9). Within the framework of this hypothesis the observed peak of incoherent light scattering should be attributed to enhanced director orientation fluctuations responsible for strong light scattering in LC and during their phase transitions. This phase transition in the surface liquid film may also explain the change in $H(\Delta T)$ dependence at $T_c$. Indeed, at the temperatures $T \approx T_c$ the logarithmic dependence (4) coming from liquid ordering at $T<T_c$ is replaced by the power dependence $H \sim (\Delta T)^{1/p}$ $(2.5 \leq p \leq 3.5)$ determined probably by long-range forces (e.g. van der Waals, phonones, Sec. I) at $T_c<T<T_m$. Thus, the biphenyl melting, its SM including, may follow the scheme in Fig. 9.
5. Conclusion

The results of our investigation may be summarized as follows. The surface melting is principally different from surface roughening and consists in appearance of a quasiliquid film phase with thickness up to tens or even hundreds of molecular layers depending on supercooling and crystal interface index. Such a surface phase may arise not only on atomically rough interface, but also on the face remaining atomically smooth when in contact with its own melt. It appears that the SM is accompanied by orientational premelting in the crystal bulk. The observed peak in the incoherent light scattering intensity from the surface film phase at $T = T_c = T_m - 0.3 \div 0.5$ K allows to suppose that this surface phase is in a liquid crystalline state at $T < T_c$ and transforms to the isotropic liquid at $T = T_c$.

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*Note added in proofs*

The logarithmic \( H(\Delta T) \) dependence follows also from the experimental attenuation of the density waves existing in a liquid in the vicinity of a solid or of a crystalline wall.\(^7\) In addition to the electromagnetic (photon) Van der Waals interaction resulting in \( \Pi(H) = A/H^3 \) there exists also the acoustic
(phonon) universal interaction. It provides the same $\Pi(H)$ law, with the constant $A$ possessing the opposite sign,\(^{38}\) i.e. causing the film to become thinner and preventing the SM. The complete SM theory should include these contributions.

**DISCUSSION**

**Chernov**

1. The fact that $\gamma$ does not become zero means only that there is no roughening at crystal-gas interface. This does violate Kossel model and does not exclude formation of a quasi-liquid layer (surface melting in direct sense) as it is shown in our work (see page 20 of abstracts).

2. To have surface melting, the Nature uses, in particular, but not necessarily, anisotropic (organic) molecules.

**Bennema**

How does the structure of the substrate (001) and (010) show up in the experiments and in the theoretical model. In this connection I want to mention that (001) has a very strong connected net and (010) a much weaker. Also I want to mention that it follows from our work that the “cell structure” of the substrate “propagates” as it were in the melt (or solution).

**A:** How it's followed from our experiments film is thicker on the (010) face than on the most close packed (001) face. For example at $\Delta T=1\, K$ $H=220\, \text{Å}$ for (010), and 73 $\text{Å}$ for (001) face. In our theoretical model the boundary conditions may be determined by face index. But we did not explicitly take this into account.

**Rodriguez**

Do the ordered anisotropic nature of the melt film over the crystal, indicate that, in the reversal process (growth), the molecules are already ordered in the adsorption layer before they arrive at the crystal surface?

**A:** Our experiments were carried out under equilibrium conditions and on surface with optical contact with glass. However, we believe that the ordering of the liquid is a kind of the interface delocalization and thus may cause an increase in the interface mobility both for growth and dissolution.

**Kuroda**

In your opinion, there are 2 kinds of surface melting, i.e., positional melting and orientational melting. Is the refractive index of the surface layer where positional melting occurs different from that of the surface where orientational melting occurs.
A: We observed orientational melting only of bulk crystal. I think, that it’s impossible to determine surface film thin structure, which is connected with types of melting, using ellipsometry only.