Theory of surface freezing of alkanes

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A fluctuation-based entropic scenario for the explanation of surface freezing in normal alkanes is proposed. The model is based on the notion that strong fluctuations along the molecular axis of uniaxially ordered stretched chains, can exist in a solid monolayer on top of a liquid phase and provide sufficient entropy to stabilize it against the formation of a bulk rotator phase, in which such fluctuations are suppressed by the presence of neighboring layers. We show that the phenomenon can exist only in a restricted range of molecular weights, and calculate the molecular weight dependences of the temperature range in which it is observed and of the correction to the surface tension of the liquid due to the presence of the solid surface layer. The roughness of solid surface monolayer is also calculated. The results are in agreement with recent experiments. [S1063-651X(97)13701-1]

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I. INTRODUCTION

Extensive experimental and theoretical investigations are devoted to the peculiarities of phase transitions near interfaces. Nevertheless, recent observations of *surface freezing* in normal alkanes gave the first ever example of surface-induced long-range order in a one-component system [1–5]. This behavior is in surprising contrast to the usually observed phenomena of *surface melting* and *roughening phase transition*, both of which are characterized by the suppression of long-range order near the free interface due to the weaker molecular ordering field on the surface.

In normal alkanes, it was found that a solid monolayer is formed on the surface of the liquid, in a small temperature interval above the bulk solid-liquid transition. The monolayer consists of hexagonally ordered, stretched (in an all-*trans* configuration) alkane chains which are oriented normal, or slightly tilted with respect to the normal, to the surface. The density and symmetry of the monolayer correspond to that of a bulk rotator phase [6,7]. Surface freezing occurs only in a finite range of molecular weights which, in alkanes, corresponds to degrees of polymerization from 14 to approximately 50. Only a single solid monolayer exists in the temperature range between the surface and bulk freezing points and there is no gradual growth of the surface ordered phase as the temperature of the bulk transition is approached.

In this paper a theory for surface freezing in normal alkanes is presented. According to the proposed scenario [8], the effect is driven by the free energy gain due to the fluctuations of molecules in the solid surface monolayer, parallel to their axes, which are suppressed by neighboring layers in the bulk solid phase. The plan of the paper is as follows. In Sec. II we derive the general condition for surface freezing

$$\Delta_s - \gamma^{(0)} > 0. \tag{1}$$

Here $\gamma^{(0)}$ is a certain combination of interfacial tensions and Δ_s determines the contribution to the free energy due to the fluctuations of the ordered layer on the top of the liquid. Our estimate of the parameter $\gamma^{(0)}$, which is mostly contributed by van der Waals interactions, shows that it is positive and, therefore, cannot be responsible for surface freezing.

Inspection of inequality (1) shows that this condition can be satisfied if the fluctuation free energy of the solid surface monolayer, Δ_s, is high enough. For low molecular weight substances, however, this cannot be the case. While a liquid can possess significant fluctuational free energy, the amplitude of fluctuations in solids is always much lower than the characteristic size of their constituents (''atoms''). This property is directly related to the empirical Lindemann criterion of the melting of crystalline substances: fluctuations at the transition point are of order of 10% of the period of the lattice.

In the case of long molecules which crystallize into layered structures, the normal-to-plane (longitudinal) periodicity is determined by the length of the molecules. Therefore, fluctuations along the molecular axis can, in principle, exceed the typical monomer size (the amplitude of in-plane fluctuations is limited by the Lindemann criterion to a fraction of the monomer size, just like in small-molecule solids). This means, in particular, that an ordered layer can possess significant entropy due to such fluctuations, which do not affect its stability. The resulting reduction of the free energy may lead to the formation of a stable solid surface monolayer under thermodynamic conditions when the bulk is in the liquid phase. This is the entropic scenario proposed in this work for the explanation of surface freezing in liquids of long chain molecules (e.g., alkanes).

In Sec. III we calculate the free energy gain due to the fluctuations of the ordered monolayer of stretched chain molecules. Our model Hamiltonian contains two contributions, one which accounts for the reduction of the binding energy due to the decreased overlap between the ends of neighboring molecules, caused by their relative displacement (this *end mismatch* contribution will be present even when the molecules are modeled as structureless cylinders), and another due to the *internal mismatch* produced by the relative shift of the internal segments of parallel neighboring molecules (this effect arises due to the deviation of the symmetry of the all-trans molecule from that of a cylinder). The latter effect is expected to be much smaller in a uniaxial rotator

phase than in a fully ordered crystalline phase in which there is perfect registry between neighboring all-trans chains.

In Sec. IV we derive the molecular-weight dependence of the surface freezing temperature and of the modification of the liquid surface tension due to the presence of the solid surface monolayer. Our theory yields the magnitude of the mean square fluctuation amplitude of the molecules in the surface monolayer. These theoretical results are shown to agree with the experimental data.

II. THERMODYNAMICS

Consider a system of long molecules which, at a certain temperature, undergoes a transition from a liquid to a layered ordered solid phase, such as a rotator or a crystalline one. In order to investigate the possibility of surface freezing, we calculate the free energy of the following sandwichlike structure: air (vacuum)—N solid layers—liquid bulk. We find the value of N which minimizes the free energy of the system, and which becomes infinite at the bulk liquid-solid phase transition temperature T^b. Since we are interested only in the equilibrium characteristics of the system, our consideration does not imply any particular mechanism of nucleation of the ordered phase, although, in the case when surface freezing does take place, it is plausible that the crystallization of the bulk solid phase proceeds by surface-induced nucleation. In order to investigate the possibility of surface melting of the solid, we also consider the opposite configuration, i.e., vacuum—liquid layer—solid bulk, below T^b. Since the number of particles in the system is assumed to be fixed, a canonical ensemble is used in the following.

In the case of a free liquid interface, the surface free energy γ is essentially the bare liquid surface tension, γ_l. The creation of a stack of N solid monolayers on the top of the liquid results in two corrections to the surface tension. One of them, $\delta\gamma^{(0)} = \gamma_s + \gamma_{sl} - \gamma_l$, is due to the replacement of the free liquid surface with solid-vapor and solid-liquid interfaces. Another one accounts for the conversion of some amount of liquid into the ordered surface phase. If the free energy per molecule in the solid surface phase was the same as in the bulk, this correction would be $(T - T^b)\delta S_{sl}N/A_0$, where A_0 is the area per molecule in a single monolayer and δS_{sl} is the entropy excess per molecule at the solid-liquid bulk phase transition. The crucial point of our discussion is that we account for an additional correction $-\Delta_s$ to the surface tension due to the deviation of the configurational properties of the surface phase from that of the bulk solid. This correction reflects the difference between the free energy of the stack of solid monolayers on the top of the liquid and that of the same stack embedded in a bulk solid phase due to configurations and fluctuations which are allowed in the former but not in the latter case. The resulting correction to the surface tension of the liquid due to the creation of the surface solid phase is given by

$$\delta\gamma \equiv \gamma - \gamma_l = (T - T^b)\delta S_{sl}N/A_0 + \delta\gamma^{(0)} - \Delta_s. \quad (2)$$

Surface freezing takes place when $\delta\gamma$ is negative at $T = T^b$, i.e., when inequality (1) holds. When condition (1) is satisfied, the minimum of the free energy, Eq. (2), is achieved for $N=1$ (we assume sufficiently weak dependence of Δ_s on N and verify the self-consistency of this assumption

later on). Therefore, one can restrict the investigation to the case of a single monolayer on the top of the liquid. In this case an ordered surface monolayer exists in the temperature range

$$\delta T \equiv T^s - T^b = \frac{A_0(\Delta_s - \delta\gamma^{(0)})}{\delta S_{sl}}. \quad (3)$$

Before proceeding with the analysis of surface freezing, we would like to present a brief discussion of the opposite scenario, i.e., surface melting. The condition for surface melting can be derived by analogy with inequality (1). The free energy per unit surface area of a solid semispace covered with the liquid layer of thickness $L \gg \xi$ (ξ is the correlation length of the bulk liquid) is given by

$$\mathcal{F}(L) = (T^b - T)\delta S_{sl}L_{\rho_l} + (\gamma_l + \gamma_{sl} - \gamma_s) + \frac{\chi_{ls} - \chi_{ll}}{12\pi L^2}, \quad (4)$$

where the free energy is measured with respect to that of a pure solid semispace. The first term accounts for the change of the free energy due to the transfer of $L_{\rho_l}A$ molecules from the solid to the liquid phase, the $\gamma_l + \gamma_{sl} - \gamma_s$ term accounts for the replacement of a solid-vapor with a liquid-vapor interface, and the last term in the free energy, Eq. (4), accounts for finite size corrections to the van der Waals interaction energy, where χ_{ls} and χ_{ll} are the Hamaker constants of the solid-liquid and liquid-liquid interactions, respectively. This term determines the equilibrium thickness of the liquid layer in the case when it exceeds the correlation length in the liquid

$$L = \left(\frac{\chi_{ls} - \chi_{ll}}{6\pi(T^b - T)\delta S_{sl}\rho_l}\right)^{1/3}. \quad (5)$$

Here $\chi_{ls} - \chi_{ll} > 0$, due to the higher density of the solid phase. Note that we do not take into consideration the finite size van der Waals correction in the case of the solid surface layer, because its thickness is quantized in units of stretched chain length and the correction is negligible even for a monolayer.

The condition of surface melting follows from the expression for the free energy (4):

$$\gamma_s - \gamma_{sl} - \gamma_l > 0. \quad (6)$$

This condition formally coincides with that for a complete wetting, i.e., surface melting corresponds to the case when the liquid phase completely wets the solid. A similar interpretation can be applied to the condition for surface freezing, Eq. (1). The fluctuation contribution Δ_s should be viewed as a finite size correction, since it vanishes for a sufficiently thick solid layer. The conditions for surface freezing and surface melting are independent and either one or none of the two phenomena may take place in a given material.

We proceed to estimate the parameters which appear in the condition for surface freezing, Eq. (1). The value of γ_{sl} can be related to the surface tensions of the solid and the liquid and to the contact angle in the liquid-solid-vapor system. Indeed, in the case of partial wetting the contact angle of the liquid on the solid surfaces is given by

$$\cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l}. \tag{7}$$

This yields

$$\gamma_{sl} = \gamma_s - \gamma_l \cos\theta. \tag{8}$$

The direct measurement of the contact angle for solid and liquid phases of the same substance is complicated by the fact that only one of the phases is stable under given thermodynamic conditions (outside the coexistence range of the phase diagram). The difficulty can be overcome by performing contact angle measurements on the chains (e.g., alkanes) of two slightly different molecular weights, under conditions where the longer chains are in the equilibrium solid phase while the shorter ones are in the liquid phase (without a surface monolayer).

In order to relate the solid surface tension γ_s to measurable quantities, we use the fact that the surface tension of a substance is proportional to its Hamaker constant χ which, in turn, is proportional to the square of its polarizability. We assume that the polarizability of the reference bulk solid differs from that of the uniform liquid by the ratio of their densities, ρ_s/ρ_l [9,10]. This yields $\gamma_s/\gamma_l \simeq \chi_s/\chi_l \simeq (\rho_s/\rho_l)^2$.

Collecting the above results, one obtains

$$\delta\gamma^{(0)} = \gamma_l \left[2\left(\frac{\rho_s}{\rho_l}\right)^2 - (\cos\theta + 1) \right]. \tag{9}$$

Since the measured value of contact angle for normal alkanes is very close to zero (almost complete wetting) [11], this expression yields $\delta\gamma^{(0)} \simeq 18$ dyn/cm.

III. FLUCTUATION CORRECTION TO FREE ENERGY

Consider the out-of-plane displacements of the monolayer surface $h_{\mathbf{r}}$, where $\mathbf{r}$ parameterizes the center of mass positions of molecules in the monolayer. We assume hexagonal in-layer ordering, with period $a = (2A_0/\sqrt{3})^{1/2}$. Note that, in general, the molecular axes need not be perpendicular to the interface but may be tilted with respect to the normal direction. Indeed, several rotator mesophases, which differ by the molecular tilt and distortion of the in-plane ordering, are observed in bulk alkanes. Moreover, the tilt and distortion of the surface solid monolayer may differ from those of the bulk solid below T^b. For the sake of simplicity, we assume that there is no tilt of the molecular axes and no distortion of the hexagonal lattice both in the surface and the bulk solid phases (such structure corresponds to R_{II} rotator phase [7]). The applicability of our results to other realizations of bulk and surface solid phases is discussed in Sec. IV.

Let l be the length of a single chemical bond (monomer) along the chain. If the chains are uniform along their contour, the energy cost of the *end mismatch* produced by a relative shift h of two parallel neighboring molecules in the surface layer is simply the energy needed to transfer h/l internal monomers to the surface. Upon the transfer of a monomer, the system loses half of the interaction energy between the monomer and the neighboring chain. Consequently, the energy penalty for this relative displacement is $\epsilon h/6l$, where ϵ is the van der Waals binding energy of the solid per monomer (we attribute the binding energy to the
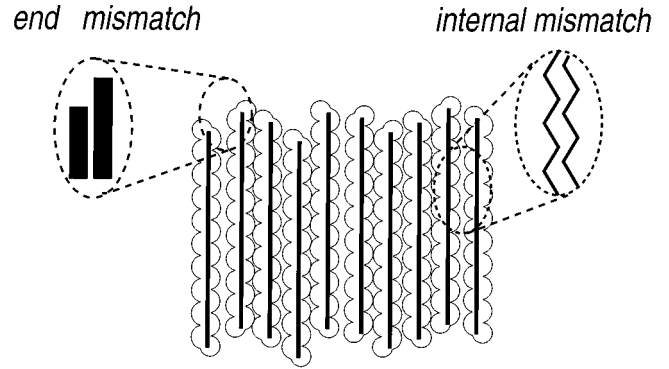

FIG. 1. End and internal mismatch effects in a fluctuating solid layer.

interaction of the monomer with six neighboring chains).

The above picture overlooks effects associated with the local structure of the chains (deviations from uniform electron density along the chain contour). In order to account for these contributions we notice that in addition to the previously discussed contribution due to the decrease of the overlap, there is an *internal mismatch* energy penalty for fractional shifts (when h is not an integer multiple of $2l$) due to the deviation of the shape of an all-trans molecule from that of a cylinder. Neglecting chain-end effects which were included in the previous mechanism, the interaction between two parallel all-trans chains is invariant with respect to a shift by an integer multiple of $2l$. The above effects can be modeled by the following Hamiltonian which describes the energy cost of surface fluctuations (Fig. 1)

$$H = \sum_{|\mathbf{r}-\mathbf{r}'|=a} \left\{ \frac{J}{2} |h_{\mathbf{r}} - h_{\mathbf{r}'}| + \frac{wn}{2} \left[1 - \cos\frac{\pi(h_{\mathbf{r}} - h_{\mathbf{r}'})}{l} \right] \right\}. \tag{10}$$

A rough estimate gives $J \simeq \epsilon/6l \simeq 10^{-6}$ dyn for the rotator phase of normal alkanes (we assume $\epsilon \simeq 0.8 \times 10^{-13}$ erg and $l \simeq 1.3$ Å [10,6]). While the reduction of overlap is a chain-end effect, the internal mismatch energy is additive along the chain, and, therefore, the strength of the second, periodic, term in the Hamiltonian is proportional to the degree of polymerization n. Note that the value of the internal mismatch parameter w is apparently much larger in the low-temperature crystalline phase than in the rotator phase, consistent with the higher coherence of the out-of-plane positions of the molecules. Although in the following we use w as a fitting parameter, we find that the final results are only weakly dependent on it.

In order to reduce the calculation of the free energy of the fluctuations to the evaluation of Gaussian integrals, we use a variational procedure [9] with the trial Hamiltonian

$$H_g' = \frac{g}{4} \sum_{|\mathbf{r}-\mathbf{r}'|=a} (h_{\mathbf{r}} - h_{\mathbf{r}'})^2. \tag{11}$$

The free energy which corresponds to the original Hamiltonian, Eq. (10), can be estimated as the minimum (with respect to the variational parameter g) of the expression

$$F[g] = \langle H - H_g' \rangle + F'[H_g']. \tag{12}$$

Here, both the average and the anzatz free energy $F'[H'_g]$ are evaluated with the trial Hamiltonian H'_g. Thus

$$\langle H - H'_g \rangle \equiv \frac{\int D[h_{\mathbf{r}}](H - H'_g)\exp(-H'_g/T)}{\int D[h_{\mathbf{r}}]\exp(-H'_g/T)}, \quad (13)$$

where $D[h_{\mathbf{r}}]$ denotes functional integration over the displacement field $h_{\mathbf{r}}$.

$F'[H'_g]$ is calculated in a standard way by using the Fourier transform of $h_{\mathbf{r}}$

$$h_{\mathbf{r}} = \sum_{\mathbf{q}} h_q \exp(i\mathbf{q} \cdot \mathbf{r}). \quad (14)$$

Here

$$h_{\mathbf{q}} = h^*_{-\mathbf{q}}$$

and $\mathbf{q}$ is in the first Brillouin zone, which in the case of a two-dimensional hexagonal lattice can be approximated by a circle

$$\sum_{\mathbf{q}} \cong \int_{|\mathbf{q}| < q_{max}} \frac{A d\mathbf{q}}{(2\pi)^2}, \quad (15)$$

where A is the total surface area, and $q_{max} = 2\sqrt{\pi/A_0}$ (the total number of independent modes is A/A_0).

The anzatz Hamiltonian, Eq. (11), is diagonal in the Fourier representation

$$H'_g = \frac{Ag}{2A_0} \sum_{\mathbf{q}} h_{\mathbf{q}} h_{-\mathbf{q}} \sum_{\sigma=1}^{6} \left(1 - \cos\left[qa \, \cos\left(\phi_q + \frac{\pi l}{3} \right) \right] \right). \quad (16)$$

The summation over the index σ accounts for the interactions with all the six neighbors of a molecule, and the angle ϕ_q determines the orientation of the wave vector with respect to the crystal lattice. In order to simplify the Hamiltonian we keep only the second order term in its expansion in power series of the parameter qa. The quadratic term gives a reasonable approximation to the Hamiltonian, Eq. (16), throughout the first Brillouin zone. Neglecting the in-plane anisotropy of the hexagonal structure, one can also average the Hamiltonian with respect to the angle ϕ_q

$$H'_g \simeq \frac{A}{A_0} \sum_{\mathbf{q}} h_{\mathbf{q}} h_{-\mathbf{q}} \frac{g(aq)^2}{4} \sum_{\sigma=1}^{6} \cos^2\left(\phi_q + \frac{\pi l}{3} \right)$$

$$\simeq A \sum_{\mathbf{q}} \frac{gq^2}{2} h_{\mathbf{q}} h_{-\mathbf{q}}. \quad (17)$$

Here we have used the relationship between A_0 and a: $a^2/A_0 = 2/\sqrt{3} \simeq 1$.

In order to calculate the contribution to the free energy due to the surface fluctuations, one must specify the reference system whose free energy is chosen to be zero. In the considered case of a fluctuating free solid surface, the reference system is a solid monolayer in the crystalline bulk. Since the positions of the terminal groups of the monolayer

are strongly coupled to the shape of the interface of the adjoint layer, we assume that each such end group experiences the potential

$$W_{\mathbf{r}}(h) = uh_{\mathbf{r}}^2/2. \quad (18)$$

The parameter u is estimated in the Appendix.

Using the above potential, the reference Hamiltonian can be written in the form

$$H^{(0)} = \sum_{\mathbf{r}} \frac{u}{2} h_{\mathbf{r}}^2 = \frac{Au}{2A_0} \sum_{\mathbf{q}} h_{\mathbf{q}} h_{-\mathbf{q}} \quad (19)$$

and one can calculate the anzatz free energy $F'[H'_g]$

$$F'[H'_g] \equiv -T \ln\left\{ \frac{\int D[h_{\mathbf{q}}]\exp(-H'_g/T)}{\int D[h_{\mathbf{q}}]\exp(-H^{(0)}/T)} \right\}$$

$$= \frac{T}{2} \sum_{\mathbf{q}} \ln\left(\frac{gA_0 q^2}{u} \right) \simeq \frac{AT}{2A_0} \left[\ln\left(\frac{4\pi g}{u} \right) - 1 \right]. \quad (20)$$

From Eqs. (11) and (20), we obtain the following expression for the mean square relative shift of the neighboring molecules:

$$\langle (h_{\mathbf{r}} - h_{\mathbf{r}'})^2 \rangle = \frac{2A_0}{3A} \left(\frac{\partial F'}{\partial g} \right) = \frac{T}{3g}. \quad (21)$$

One can now calculate the averaged Hamiltonians $\langle H \rangle$ and $\langle H'_g \rangle$

$$\langle H'_g \rangle = \frac{3A}{2A_0} g \langle (h_{\mathbf{r}} - h_{\mathbf{r}'})^2 \rangle = \frac{AT}{2A_0}, \quad (22)$$

$$\langle H \rangle = \frac{A}{A_0} \left\{ J\left(\frac{6T}{\pi g} \right)^{1/2} + 3wn\left[1 - \exp\left(-\frac{2\pi^2 T}{3gl^2} \right) \right] \right\}. \quad (23)$$

Finally, we obtain the variational free energy, Eq. (12)

$$F[g] = \frac{A}{A_0} \left\{ J\left(\frac{6T}{\pi g} \right)^{1/2} - T + \frac{T}{2} \ln \frac{4\pi g}{u} \right.$$

$$\left. + 3wn\left[1 - \exp\left(-\frac{2\pi^2 T}{3gl^2} \right) \right] \right\}. \quad (24)$$

The minimization of $F[g]$ with respect to g yields

$$\frac{J}{2g^{3/2}} \left(\frac{6T}{\pi} \right)^{1/2} = \frac{T}{2g} \left(1 - \frac{6wn}{T} X_g e^{-X_g} \right), \quad (25)$$

where

$$X_g = \frac{2\pi^2 T}{3gl^2}. \quad (26)$$

In the case of a rotator phase, the internal mismatch contribution to the original Hamiltonian, Eq. (10), is expected to be small. Assuming $6wn/T \ll 1$ and using Eq. (25) gives

$$\widetilde{g} = \frac{6J^2}{\pi T}. \qquad (27)$$

This yields the following expression for the fluctuation contribution to the free energy:

$$-\Delta_s \equiv \frac{F[\widetilde{g}]}{A} = -\frac{T}{2A_0} \ln\left(\frac{uT}{24J^2} \right) + \frac{3wn}{A_0}. \qquad (28)$$

The first, temperature-dependent term on the right-hand side of Eq. (28) is due to the entropy associated with the longitudinal (normal to the layer) fluctuations. The second term is a correction due to the loss of the longitudinal coherence of neighboring molecules in the surface monolayer, compared to the bulk solid phase. The typical relative displacement of such molecules in the rotator phase is of order of the bond length l

$$\langle (h_\mathbf{r} - h_{\mathbf{r}'})^2 \rangle = \frac{\pi}{18} \left(\frac{T}{J} \right)^2 \sim l^2. \qquad (29)$$

In a perfect crystal the periodic potential is strong (all the degrees of freedom of the neighboring molecules are strongly correlated) and the opposite limit, $6wn/T \gg 1$, holds. In this case Eq. (25) yields

$$\widetilde{g} = \frac{4\pi^2 wn}{l^2}. \qquad (30)$$

Since the fluctuations are strongly suppressed by the internal mismatch effect, the typical relative displacement of neighboring molecules is much smaller than the bond length l

$$\langle (h_\mathbf{r} - h_{\mathbf{r}'})^2 \rangle = \frac{Tl^2}{3\pi^2 wn} \ll l^2.$$

IV. RESULTS AND DISCUSSION

Collecting the results obtained in the previous sections, the condition for surface freezing, inequality (1), becomes

$$\frac{T_n^b}{2A_0} \ln\left(\frac{T_n^b}{T_0} \right) - \frac{3wn}{A_0} - \delta\gamma^{(0)} > 0, \qquad (31)$$

where $T_0 \equiv 24J^2/u \simeq 25$ K. The bulk freezing temperature T_n^b (which depends on the molecular weight) and the area per molecule A_0 are experimentally observable parameters. The other parameters (J and u) in inequality (31) were estimated above for the rotator phase in normal alkanes. Although these estimates are quite crude, the final results depend only weakly (logarithmically) on the parameters u and J.

Using inequality (31), one can find the minimal melting temperature at which the surface freezing will be observed

$$T^b(n_{\min}) \simeq 280 \text{ K}. \qquad (32)$$

This temperature corresponds to the chain length $n_{\min} \simeq 15$, which is in agreement with experimental data.

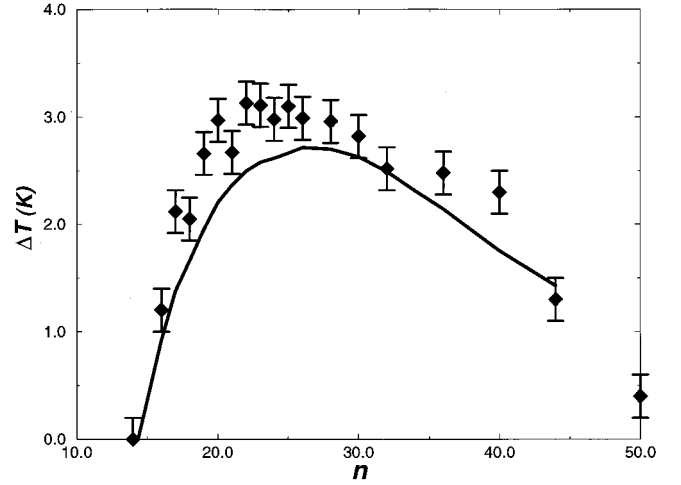The surface monolayer exists in the temperature range

FIG. 2. Molecular weight dependence of the temperature shift of surface freezing with respect to the bulk transition point T^b (in degrees Kelvin). The experimental points are given by diamonds (error bars are shown) and the theoretical curve by the solid line.

$$\delta T \equiv T^s - T^b = \frac{1}{\delta S_{sl}^n} \left[\frac{T_n^b}{2} \ln\left(\frac{T_n^b}{T_0} \right) - 3wn - A_0 \delta\gamma^{(0)} \right]. \qquad (33)$$

The difference between the surface tension of a free liquid and that of a liquid covered by a solid monolayer in the vicinity of bulk phase transition, is

$$\Delta\gamma \equiv \gamma(T^s) - \gamma(T^b) = \frac{T_n^b}{2A_0} \ln\left(\frac{T_n^b}{T_0} \right) - \frac{3wn}{A_0} - \delta\gamma^{(0)}. \qquad (34)$$

The molecular weight dependencies of ΔT and $\Delta\gamma$ are shown in Figs. 2 and 3, respectively. The best fit to the experiment is achieved for $w = 1.2 \times 10^{-16}$ erg.

All the above results are obtained within the assumption of the no-tilt R_{II}-type structure of both the surface and the bulk solid phases. Hence, the theory strictly applies to the range of molecular weight, $20 < n < 26$, in which such a bulk R_{II} rotator phase is observed in alkanes [7]. Nevertheless, the principal thermodynamic parameters, such as entropy and free energy, of the observed surface and bulk rotator phases (up to $n \simeq 40$) turn out to be very close to those of the "reference" R_{II} phase [7,3]. A qualitative change of behavior takes place at $n \simeq 40$ where a strong first-order phase transition accompanied by a sharp decrease of entropy is observed in the surface monolayer ([3]). Moreover, bulk alkanes with more than 40 carbon units do not form stable rotator mesophase ([6]). Therefore, the proposed theory can be applied to normal alkanes of length up to $n = 40$.

The mean square fluctuation of the monolayer surface can be evaluated from our model. A straightforward calculation gives

$$\langle h_\mathbf{r}^2 \rangle = \sum_\mathbf{q} \frac{T}{A\widetilde{g}q^2} = \frac{T^2}{24J^2} \ln\frac{A}{A_0}. \qquad (35)$$

The unusual scaling of this expression with temperature is related to the nonanalytic form of the original Hamiltonian
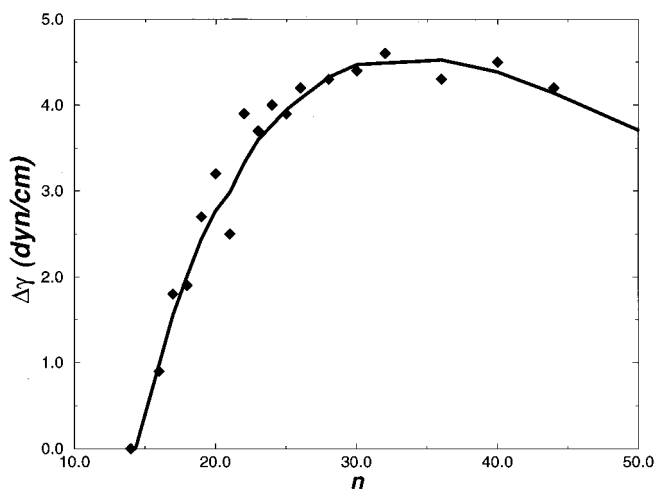
FIG. 3. Correction to liquid surface tension (in dyn/cm) due to the existence of the ordered monolayer at temperature T^b, vs degree of polymerization n. The experimental points are given by diamonds and the theoretical curve by the solid line.

(in the usual case of a Gaussian fluctuation Hamiltonian, the temperature dependence would be linear rather than quadratic). The temperature dependence predicted by Eq. (35) agrees with the experimental data on the surface roughness, as shown in Fig. 4. The best fit is achieved for $J \simeq 0.8 \times 10^{-6}$ dyn, which is close to our estimate of this parameter. Strictly speaking, our results for the surface roughness apply only to alkanes which form the R_{II} surface phase, i.e., for degrees of polymerization in the range $14 < n < 30$. Nevertheless, comparison with the available experimental data suggests that the theory works quite well up to $n \simeq 40$. The fluctuational mechanism of surface freezing proposed in this paper, is supported by the observation that the abrupt decrease of the surface roughness after the surface phase transition at $n \simeq 40$, correlates with the strong suppression of surface freezing.
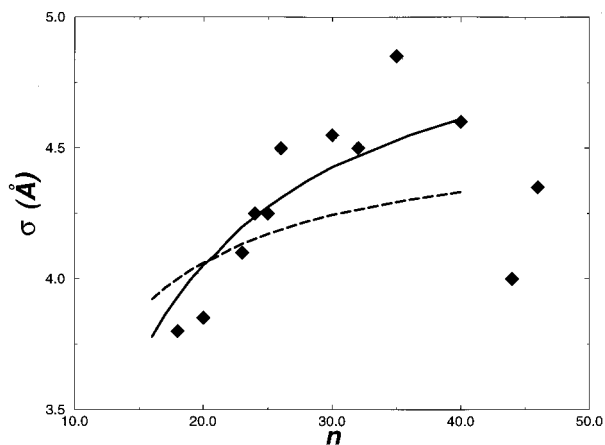
Note that the observed amplitude of surface fluctuations

FIG. 4. Root mean square amplitude of surface roughness of the solid monolayer, σ, vs degree of polymerization n. The experimental points are given by diamonds and the solid line is the result of our calculations (for $J = 0.8 \times 10^{-6}$ dyn). Note that the anomalous linear temperature dependence of the roughness (solid line) fits the experiment much better than the conventional square root dependence typical for capillary waves (dashed line).

should also contain the usual contribution of capillary waves. This effect, however, is significant only on large scales since, below a certain cutoff wavelength, such liquidlike fluctuations are suppressed due to the bending elasticity of the monolayer and, therefore, only the intrinsic roughness given by Eq. (35) contributes to the observed amplitude of surface fluctuations.

The proposed mechanism of surface freezing presumes that the bulk ordered phase possesses a high degree of long-range positional order with strongly suppressed fluctuations. One should contrast this with the case of the liquid-crystalline systems (such as smectic liquid crystals), in which the nematic to smectic bulk transition is of *weak-crystallization* type, so that strong fluctuations exist in the reference ordered bulk phase near the transition point. The presence of the free surface tends to suppress the normal-to-surface fluctuations in such systems rather than to enhance them. As a result, the qualitatively different modification of surface ordering, viz. parallel-to-the-interface layering with liquidlike in-plane structure is observed in some liquid crystals above the bulk transition point [12,13]. Due to the weak crystalline order in such systems the corresponding correlation length can exceed the spacing between smectic layers and considerably increases while approaching the bulk transition point, leading to the observed growth of the number of surface layers.

The entropic mechanism is not the only scenario which may lead to surface freezing. Recently, it was shown that similar phenomena occur in systems of chain molecules with strong chemical difference between internal and end parts of the chain, in which surface freezing can be attributed to the ''surfactant''-type effects [14]. Such a mechanism is not expected in normal alkanes, because it would require an unphysically large difference between the surface affinity parameters of CH_3 and CH_2 units. Furthermore, although according to this ''chemical'' explanation the surface freezing phenomenon should be very sensitive to the chemical nature of the head group, no such dependence was observed in recent experiments on brominated alkanes [11]. Nevertheless, in general, surface freezing may arise as the result of the interplay between our entropic and other, energy-driven mechanisms.

V. CONCLUSIONS

In this work we developed the theory of surface freezing of liquid normal alkanes. The proposed mechanism is based on the stabilization of the surface ordered phase against bulk freezing due to the entropy associated with the normal-to-the-plane fluctuations of the molecules in the surface monolayer. This effect can be attributed to the increase of the free energy of the bulk solid phase (compared to that of noninteracting solid layers) due to entropic repulsion between adjoint solid layers, which is an analog of the Helfrich interaction between lyotropic membranes [15].

The theoretical results for the chain-length dependence of the surface freezing temperature shift with respect to the bulk transition point and the corresponding surface tension correction are in good agreement with the experimental data. The calculated mean square longitudinal fluctuations of the molecules in the surface monolayer also agree with the data on

surface roughness. In particular, the experimental data can be fitted by the predicted anomalous linear temperature dependence of the roughness rather than by the usual square root one.

The entropic mechanism is suppressed for short chains, because of the decrease of the freezing temperature with molecular weight and the subsequent decrease of the entropic contribution to the free energy. Indirectly, this is related to the fact that, according to the Lindemann criterion, a hypothetical solid surface phase in systems of small molecules would be destroyed by any (including those along the molecular axis) significant thermal fluctuations. In the limit of long molecules the energy penalty due to the internal mismatch of the chains becomes too large and suppresses the fluctuations of the surface layer. In the range of molecular weights in which surface freezing is predicted to take place, the solid surface phase is expected to be of the rotator type since, in the case of perfect crystalline ordering, fluctuations along all directions would be suppressed. Due to the phase transition, which takes place in the surface monolayer at $n \simeq 40$, surface freezing disappears in the long-chain limit even faster than follows from the theory. This suggests that the long-chain surface phase is characterized by stronger coupling between neighboring molecules in the solid monolayer. This conjecture is consistent with the considerable drop of entropy and surface roughness for chains with $n > 40$.

The entropic mechanism presented in this paper for the origin of surface freezing in normal alkanes has the advantage of being universal and applicable to a wide class of simple chain molecules of intermediate length. This is in agreement with recent observations of similar phenomena in mixtures of alkanes [16], thiols, 1,2-diols [11], and alcohols [17].

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APPENDIX: THE REFERENCE HAMILTONIAN OF THE SOLID LAYER FLUCTUATIONS

The parameter u in Eq. (18) can be estimated by assuming Lenard-Jones interactions between the adjoined atoms of the neighboring layers

$$U(r) = \epsilon' \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right]. \tag{A1}$$

Here ϵ' is the binding energy of two head groups in contact. If every such group had a single nearest neighbor in the adjoint layer; the fluctuations of their relative separation about its equilibrium value r_0 would be described by the following potential:

$$W(h) = \frac{h^2}{2} \left(\frac{\partial^2 U}{\partial r^2} \right)_{r=a} = \frac{72\epsilon'}{r_0^2} \frac{h^2}{2}. \tag{A2}$$

This picture can be corrected by assuming that every terminal group has three nearest neighbors in the adjoint layer (this is the case in the R_{II} rotator phase). A simple geometrical consideration of this situation results in an additional factor 2 in the above potential. Taking the optimal center-to-center distance $r_0 \simeq 4$ Å and the binding energy of two head groups in close contact $\epsilon' \simeq 8 \times 10^{-14}$ erg, we estimate the parameter u in the Hamiltonian (18) as

$$u \simeq \frac{140\epsilon'}{r_0^2} \simeq 7 \times 10^3 \text{ dyn/cm}. \tag{A3}$$

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