

Fluctuation-Stabilized Surface Freezing of Chain Molecules

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We propose a fluctuation-based entropic scenario for the explanation of surface freezing in alkanes and other liquids of chain molecules. Our 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. 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.

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Recently, it was discovered that liquid normal alkanes, as well as other chain molecules, form a stable solid surface monolayer, in a small temperature interval above the bulk solid-liquid phase transition [1–3]. 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 [4,5]. Although related phenomena such as wetting and roughness transitions [6] and surface *melting* are widely known, this is the first observation of surface *freezing* in a one-component system. The appearance of surface freezing is quite surprising, as one expects the temperature of the ordering transition to be lower in two-dimensional than in three-dimensional systems, because of the stronger molecular ordering field in three dimensions. The effect has been attributed to a higher surface affinity of the end group (CH_3), as compared to the internal (CH_2) monomers [7]. Although at present there are insufficient data on these surface affinities, the assumed values of the affinity differences appear to be too high. Furthermore, although according to the above explanation the surface phenomenon should be very sensitive to the chemical nature of the head group, no such dependence was observed in recent experiments on brominated alkanes [3].

In this Letter we present a different, entropic mechanism for surface freezing and show that it is a generic feature of chain molecules of intermediate length, which form bulk rotator phases. According to our model, the effect is driven by the free energy gain due to the fluctuations of the solid surface monolayer, parallel to the molecular axis, which are suppressed by neighboring layers in the bulk solid phase. The model allows one to understand the basic features of surface freezing: (a) The effect occurs only in a finite range of molecular weights (i.e., for degrees of polymerization from 14 to approximately 50); and (b) 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 or-

dered phase as the temperature of the bulk transition is approached. The quantitative results of this theory are in good agreement with available experimental data, and new predictions are made regarding the magnitude and the anomalous temperature dependence of the fluctuations of the monolayer-covered surface.

Consider a dense system of *n*-alkanes at a temperature exceeding that of the liquid-solid bulk transition T^b . In the case of a free liquid surface, the interfacial free energy γ is essentially the bare liquid surface tension γ_l . A stable ordered surface phase of *N* layers on the top of the liquid can form at a temperature $T > T^b$ if the consequent excess surface free energy per unit area,

$$\delta\gamma \equiv \gamma - \gamma_l = \delta\gamma^{(0)} + N(T - T^b) \frac{\delta S_{sl}}{A_0} - \Delta_s, \quad (1)$$

is negative. Here $\delta\gamma^{(0)} \equiv \gamma_s + \gamma_{sl} - \gamma_l$ accounts for the creation of solid-liquid and free solid interfaces instead of a single liquid surface. γ_s and γ_{sl} are the free energies per unit area associated with the solid-air and solid-liquid interfaces. The second term in (1) is the free energy penalty for the creation of a stack of *N* ordered layers, where both the molecular conformation and the ordering of molecules are taken to be the same as in the bulk solid phase. δS_{sl} is the entropy gain per molecule, associated with the solid-to-liquid bulk transition, and A_0 is the area per molecule in the ordered layer. The Δ_s term is the excess free energy of the stack per unit area, which is the difference between the free energies of a stack of *N* ordered layers in the surface and in the bulk solid phases, respectively. *Our central thesis is that the leading contribution to Δ_s is due to the plane-normal fluctuations of the molecules in the solid monolayer, which are suppressed in the bulk by the presence of the neighboring solid layers.* This effect stabilizes the monolayer-covered liquid phase against the formation of a bulk solid phase and results in only the surface being frozen. In deriving Eq. (1), we neglected the small van der Waals corrections due to the finite thickness of the surface monolayer [8].

Inspection of Eq. (1) shows that since the second term is positive, surface freezing becomes energetically

favorable at a certain temperature $T > T^b$ if, and only if

$$\Delta_s - \delta\gamma^{(0)} > 0. \quad (2)$$

Note that since $\delta\gamma^{(0)}$ is independent of the number of layers N , and since Δ_s is expected to be a decreasing function of N , the global minimum of the surface free energy, Eq. (1), is attained for $N = 1$, and we conclude that a single ordered surface monolayer is formed when condition (2) is satisfied. We now proceed to estimate the magnitudes of the two terms in inequality (2) in order to determine the conditions for surface freezing. Henceforth, we assume that a *single* solid monolayer is formed at the liquid-air interface.

To estimate $\delta\gamma^{(0)}$, we note that since nearly complete wetting is observed for an alkane liquid spread on top of an alkane solid [3], Young's equation gives $\gamma_{sl} \approx \gamma_s - \gamma_l$, and hence $\delta\gamma^{(0)} = 2\gamma_l(\gamma_s/\gamma_l - 1)$. The ratio γ_s/γ_l can be approximated by that of the corresponding Hamaker constants [9], and since the latter are proportional to the squared polarizabilities, it is proportional to the density ratio squared, $\gamma_s/\gamma_l \approx (\rho_s/\rho_l)^2$. This gives $\delta\gamma^{(0)} \approx 2\gamma_l[(\rho_s/\rho_l)^2 - 1]$ and, taking typical values for alkanes, $\gamma_l = 27$ ergs/cm² and $\rho_s/\rho_l = 1.15$, the condition for surface freezing, inequality (2), becomes $\Delta_s \geq \delta\gamma^{(0)} \approx 18$ ergs/cm². Since the area per molecule in the ordered monolayer is $A_0 = 20$ Å², this means that surface freezing will be observed if the excess fluctuation free energy is of order kT per molecule, at room temperature.

According to our assumption, Δ_s is dominated by fluctuations along the molecular axis, so that the entropy excess per unit area is $\Delta_s \sim (kT/A_0)\ln(\delta_s/\delta_b)$, where δ_s and δ_b are the typical relative shifts of neighboring molecules in the monolayer in the surface and the bulk solid phases, respectively. The condition $\Delta_s \geq kT/A_0$ can therefore be satisfied only when δ_s considerably exceeds δ_b . Note that this cannot occur in low molecular weight solids near the solid-liquid transition, in which the amplitude of fluctuations is limited by the Lindemann criterion of melting (about 10% of the lattice spacing) and therefore cannot differ substantially in the bulk and surface phases. In the case of chain molecules which crystallize into layered structures, the out-of-plane periodicity is determined by the stretched length of the molecules. *Fluctuations along the molecular axis can, in principle, exceed the typical monomer size without violating the Lindemann criterion of melting, and we conclude that an ordered surface monolayer can possess an entropy of order kT per surface molecule due to such fluctuations.* The resulting reduction of the free energy, $\Delta_s \sim kT/A_0$, may lead to the formation of a stable solid surface monolayer under thermodynamic conditions when the bulk is still in the liquid phase.

In order to obtain a more accurate estimate of Δ_s we have to consider the energy penalty associated with fluctuations along the molecular axis in the solid surface monolayer. The resulting free energy should then be

compared with that of a solid monolayer in the bulk to determine the excess Δ_s . Details of the calculation will be reported elsewhere [10], and here we only summarize the main ideas and results.

The basic physics of molecular fluctuations normal to the ordered surface layer is described by the following model Hamiltonian:

$$H = \sum_{\text{neighbors}} \left\{ \frac{J}{2} |h_{\mathbf{r}} - h_{\mathbf{r}'}| + \frac{wn}{2} \left[1 - \cos \frac{\pi(h_{\mathbf{r}} - h_{\mathbf{r}'})}{l} \right] \right\}. \quad (3)$$

Here, $h_{\mathbf{r}}$ is the out-of-plane displacement of an end of a stretched molecule whose position in the hexagonally packed layer is given by the two-dimensional vector \mathbf{r} . The two parts of the Hamiltonian account for two types of "mismatch" effects due to relative shift of neighboring chains, illustrated in Fig. 1. The first is an *end mismatch* due to the decreased overlap between the ends of neighboring molecules. This contribution is present even when the molecules are modeled as structureless cylinders. The corresponding energy penalty is proportional to the absolute value of the relative shift. The parameter J can be related to the literature value for the van der Waals binding energy per monomer in the bulk rotator phase, assuming that the shift of a single molecule along its axis by h is energetically equivalent to the transfer of an internal molecular fragment of length h onto the surface. This yields $J \approx 0.8 \times 10^{-6}$ dyn for normal alkanes.

The second part of the Hamiltonian is due to a mismatch between the *internal* monomers of neighboring chains, produced by the relative shift of parallel, *all-trans*, neighboring molecules. This effect expresses the deviation from uniform cylindrical geometry along the chain contour, in real alkane (and other) chains. Because of the symmetry of the *all-trans* chains, this contribution is periodic in the translation, with a period of $2l$, where l is the length of a chemical bond. Since the *internal mismatch* energy penalty is additive along the chain, the magnitude of the periodic term in the Hamiltonian is proportional to the degree of polymerization n . This

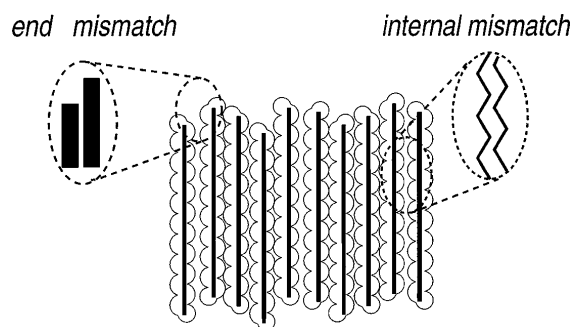


FIG. 1. End and internal mismatch effects in a fluctuating solid layer.

contribution 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 and the internal mismatch effect allows only discrete shifts of the molecules. A rough estimate, which takes into account the deviation of the symmetry of the all-*trans* molecule from that of a cylinder, gives $w \sim 10^{-16}$ erg for rotator phase.

Carrying out a variational calculation (see, e.g., Ref. [6]) of the free energy excess with respect to the bulk phase in which fluctuations are strongly suppressed, we obtain

$$\Delta_s = \frac{kT}{2A_0} \ln\left(\frac{T}{T_0}\right) - \frac{3wn}{A_0}. \quad (4)$$

The first, temperature-dependent, term is due to the entropy associated with fluctuations along the molecular axis in the solid surface layer. It has only a weak logarithmic dependence on the value of the model-dependent temperature parameter $T_0 \sim 25$ K, which is determined by J and the mean-square amplitude of fluctuations in the bulk. The second part of expression (4) is the perturbation due to internal mismatch effect.

The condition for surface freezing, inequality (2) holds only if the fluctuation free energy Δ_s is large enough to overcome the interfacial energy penalty $\delta\gamma^{(0)}$. Since Δ_s depends on the degree of polymerization n mostly through the increase of the melting temperature with n , there must be a minimal molecular weight above which surface freezing will be observed. The conditions $T^s(n_{\min}) = T^b(n_{\min})$ and $\Delta_s = \delta\gamma^{(0)}$ yield $T^s(n_{\min}) \approx 280$ K and $n_{\min} \approx 15$, in excellent agreement with the experimental data. This result is nearly independent of the value of w , since the internal mismatch contribution becomes negligible in the limit of small molecular weights. For alkanes with $n > n_{\min}$, condition (2) is satisfied and surface freezing takes place up to a certain chain length n_{\max} , at which the energy penalty associated with internal mismatch effects exceeds the free energy gain due to the formation of the surface monolayer. This upper cutoff of the chain length is determined by the magnitude of the parameter w and is of order of 100.

The temperature range over which the solid surface monolayer is stable can be easily obtained from the surface free energy, Eq. (1):

$$\Delta T(n) \equiv T^s - T^b = \frac{A_0}{\delta S_{sl}(n)} [\Delta_s(n) - \delta\gamma^{(0)}]. \quad (5)$$

Another quantity of interest is the difference between the surface tension of the liquid with the solid monolayer at the bulk phase transition point and that of the bare liquid:

$$\Delta\gamma \equiv \delta\gamma(T^b) = \Delta_s(n) - \delta\gamma^{(0)}. \quad (6)$$

Using literature data on the bulk freezing temperature and the transition entropy (the latter is smoothed with respect to rapid variations associated with the odd-even effect in

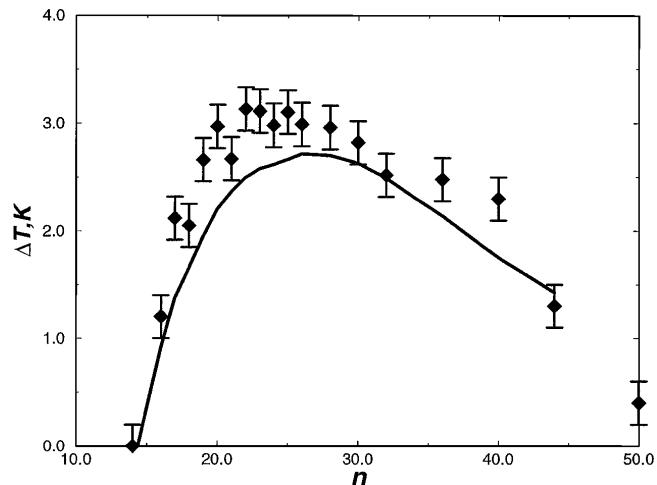


FIG. 2. Molecular weight dependence of the temperature shift of surface freezing with respect to the bulk transition point T^b (in degrees K). The experimental points are given by diamonds (error bars are shown) and the theoretical curve by the solid line.

alkanes), we obtain the molecular weight dependencies of ΔT and $\Delta\gamma$ shown in Figs. 2 and 3, respectively. The best fit to the experiment is achieved for $w = 1.2 \times 10^{-16}$ erg, which is consistent with our rough estimate.

A direct experimental test of our model can be provided by measuring the mean square fluctuation amplitude of the monolayer surface $\langle h^2 \rangle$. We predict [10]

$$\langle h^2 \rangle = \frac{(kT)^2}{24J^2} \ln(A/A_0). \quad (7)$$

Note that in the case of a Gaussian fluctuation Hamiltonian the temperature dependence would be linear rather than quadratic. The unusual quadratic dependence is re-

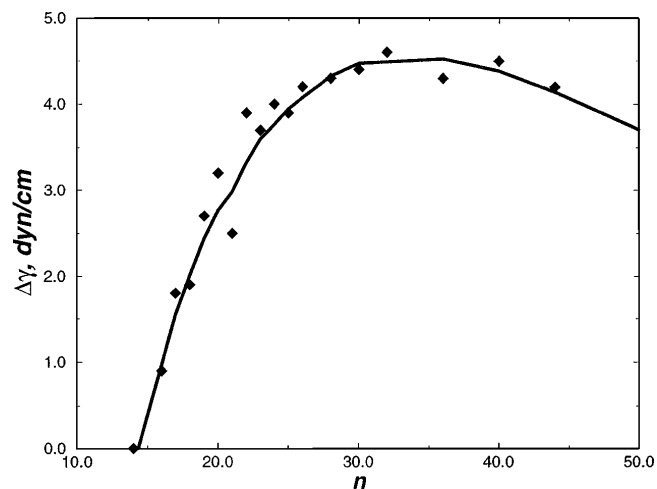


FIG. 3. Correction to liquid surface tension (in dyn/cm) due to the existence of the ordered monolayer at temperature T^b vs degree of polymerization n . The experimental points are given by diamonds and the theoretical curve by the solid line.

lated to the nonanalytic form of the end mismatch contribution to the Hamiltonian, Eq. (3), which depends *linearly* on the *absolute* value of the relative displacement of neighboring molecules. The amplitude of the plane-normal fluctuations depends logarithmically on the area A of the solid monolayer, a behavior characteristic for fluctuations of a liquid interface. The estimated value for the root mean square fluctuation amplitude is about 5 Å for a 1000 Å domain.

The proposed mechanism of surface freezing presumes that the ordered bulk phase possesses a high degree of 3D positional order, with strongly suppressed out-of-plane fluctuations. A different scenario takes place in smectic liquid crystals, in which the bulk transition is of a *weak-crystallization* type, and in which the strong fluctuations in the ordered bulk phase are suppressed rather than enhanced at the free surface. This gives rise to parallel-to-the-interface layering with liquidlike in-plane structure, observed in some liquid crystalline systems above the bulk transition point [11,12]. Because of the weak crystalline order in such systems, the thickness of the surface-ordered phase (the correlation length) increases while approaching the bulk transition point and can exceed the spacing between smectic layers.

The entropic mechanism proposed in this Letter 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 [13], thiols, 1,2-diols [3], and alcohols [14] (in the latter case, a surface bilayer is observed). Our model also accounts well for the appearance of only a single layer (or bilayer) in each case. The theoretical results for the chain-length dependence of the temperature shift and the surface tension correction are in good agreement with the experimental data on alkanes. Our model gives a simple qualitative explanation of the finite range of chain lengths for which the effect takes place. In the limit of long molecules the energy penalty due to the mismatch of the chains becomes too large and suppresses the fluctuations of the surface layer. The entropic mechanism is also suppressed in the limit of short chains because of the dramatic decrease of the freezing temperature with molecular weight. 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. Fluctuations along the molecular axis in a uniaxially ordered surface monolayer can be directly observed by scattering experiments which can provide a direct test of the proposed scenario of fluctuation-stabilized surface freezing of chain molecules.

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- [1] X.Z. Wu, E.B. Sirota, S.K. Sinha, B.M. Ocko, and M. Deutsch, *Phys. Rev. Lett.* **70**, 958 (1993).
 - [2] X.Z. Wu, B.M. Ocko, E.B. Sirota, S.K. Sinha, M. Deutsch, B.M. Cao, and M.W. Kim, *Science* **261**, 1018 (1993).
 - [3] M. Deutsch (private communication).
 - [4] D.M. Small, *The Physical Chemistry of Lipids* (Plenum, New York, 1986).
 - [5] E.B. Sirota, H.E. King, Jr., D.M. Singer, and H.H.J. Shao, *Chem. Phys.* **98**, 5809 (1993).
 - [6] S.A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, Reading, MA, 1994).
 - [7] F.A.M. Leemakers and M.A. Cohen Stuart (to be published).
 - [8] Such corrections were considered in Ref. [2] where an unphysically large value of Hamaker constant had to be assumed in order to obtain a good fit to the experimental data.
 - [9] J.N. Israelashvili, *Intermolecular and Surface Forces* (Academic, New York, 1992), 2nd ed.
 - [10] A. V. Tkachenko (to be published).
 - [11] B.M. Ocko, A. Braslau, P.S. Pershan, J. Als-Nielsen, and M. Deutsch, *Phys. Rev. Lett.* **57**, 94 (1986).
 - [12] J.V. Selinger and D.R. Nelson, *Phys. Rev. A* **37**, 1736 (1988).
 - [13] X.Z. Wu, B.M. Ocko, H. Tang, E.B. Sirota, S.K. Sinha, and M. Deutsch, *Phys. Rev. Lett.* **75**, 1332 (1995).
 - [14] M. Deutsch, X.Z. Wu, B.M. Ocko, H. Tang, E.B. Sirota, S.K. Sinha, and O.M. Magnussen, *Europhys. Lett.* **30**, 283 (1995).