

Self-Consistent-Field Lattice Gas Model for the Surface Ordering Transition of *n*-Hexadecane

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It is known from experiments that the solid-liquid phase transition of *n*-alkanes involves surface freezing. On cooling, a monomolecular surface layer crystallizes first. Upon further cooling, the bulk solidifies. The orientational ordering aspect of *n*-hexadecane freezing is modeled with a self-consistent-field lattice gas theory, showing that both events are first-order transitions. It is assumed that the CH₃ segments are more surface active than the CH₂ ones. This initiates at high *T* a slight orientational bias, but at low *T* a cooperative alignment of the C₁₆ perpendicular to the interface.

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The behavior of surfaces in the vicinity of a solid-liquid phase transition has lately attracted interest from the scientific community. Since molecules situated in a gas-liquid or gas-solid interface usually experience less attraction than molecules in the bulk of the dense phase, one anticipates that the interface is a region with increased entropy density. One therefore expects the surface tension to decrease with temperature, and this is commonly found. In addition, careful studies of the solid surface have shown that the surface often melts a few degrees below the bulk. For example, water, a common but not one of the most simple liquids, has a freezing point at 273.15 K (at *p* = 1 atm). A surface layer of ice remains liquidlike below this temperature [1,2], which is (partly) why it is possible to skate on it.

Recently there has been accumulated experimental evidence that the opposite occurs for *n*-alkanes of high enough molecular weight (range C₁₄ to C₅₀) [3,4]. Here, a surface freezing was found which shows that a liquidlike bulk, at well-controlled temperatures near the freezing point, was capable to support a monomolecular solid surface layer in contact with its vapor. In this Letter we focus on the question why this phenomenon occurs and show that a simple lattice gas model can well account for several of the experimental findings.

The theory that is used is based on the inhomogeneous self-consistent-field (SCF) approach initiated by Scheutjens and Fleer for the problem of polymer adsorption at solid-liquid interfaces. This theory has recently been reviewed in detail [5]. It makes use of a lattice that serves as a system of coordinates onto which segments are positioned. In its simplest form, the theory employs mean-field approximations in each lattice layer and first-order Markov chain statistics. The theory has been extended to study the self-assembly of phospholipids into flat bilayer membranes by Leermakers and Scheutjens [6]. The new element introduced here was the use of bond orientation weighting factors, which could lead to cooperative alignment. The extended theory correctly predicts that a first-order so-called gel to liquid phase transition exists

in membranes, where the alkyl chains of the bilayer go from a high temperature liquidlike disordered state into a low temperature ordered one. Since surface freezing goes along with orientational ordering, we decided to use this version of the SCF theory for the present problem. Below the term "surface freezing" is used, but it is understood that our model only generates the orientational ordering aspects of this phenomenon [7].

It is useful to mention a few characteristics and give the basic equations of this theory. As told above, to reproduce the correct main phase behavior in lipid bilayers, it was shown that it is essential, for finding the probability for unoccupied sites, to go beyond the traditional mean-field approximation. The probability *P*(*z*) of placing a segment of a molecule in a layer *z* is commonly taken to be $P(z) = 1 - \varphi(z)$ where $\varphi(z)$ is the fraction of already occupied sites. The next level of approximation is based on the idea that, at high densities, bonds tend to align parallel, because in this configuration they do not intersect. It is thus necessary to consider pairs of segments; in other words, relative bond directions are also taken into account in calculating *P*. For lattice models this level of approximation was pioneered by DiMarzio who studied rigid rods on a lattice [8,9]. As soon as intermolecular and intramolecular bond orientation correlations (excluded volume) are inserted into the weighting factors, one obtains a kind of chain statistics that features cooperative alignment transitions.

Chain conformations are sampled in a rotational isomeric state (RIS) scheme. This is a third-order Markov approximation where short-range correlations along the chain with *gauche* (*g*⁺, *g*⁻) and *trans* (*t*) configurations are taken into account over a distance of four segments (three bonds). So-called *g*⁺*g*⁻ sequences are not excluded, nor do we prevent double occupancies of lattice sites by segments that are more than three bonds apart. Two (indirect) corrections for the excluded volume problem are included as discussed below. The energy difference between a *gauche* and a *trans* configuration *U*_{GT} controls the chain stiffness.

We consider a condensed phase of linear alkanes $\text{CH}_3-(\text{CH}_2)_{N-2}-\text{CH}_3$ (chain length N , denoted by C_N) in equilibrium with a phase rich in free volume (vapor). Free volume is modeled as a monomeric component V_1 . There are thus three types of units and consequently three short-range Flory-Huggins interaction parameters $\chi(x, y)$ that characterize the system: $x, y = \text{CH}_3, \text{CH}_2, V_1$. It is relevant to mention that these interaction parameters can be measured experimentally.

A segment x is conjectured to probe a dimensionless segment potential $u_x(z)$ of the type

$$u_x(z) = u'(z) + \sum_y \chi(x, y) [\langle \varphi_y(z) \rangle - \varphi_y^b], \quad (1)$$

where $u'(z)$ is the so-called excluded-volume potential. It is related to the Lagrange parameter coupled to the density constraint $\sum_x \varphi_x(z) = 1$, introduced in optimizing the partition function. The site-average density is given by $\langle \varphi(z) \rangle = \sum_{a=-1,0,1} \lambda_a \varphi(z+a) \approx \varphi(z) + \lambda_1 \partial^2 \varphi(z) / \partial z^2$. We have used $\lambda_{-1} = \lambda_0 = \lambda_1 = 1/3$, a choice that minimizes so-called lattice artifacts as it allows more easily the placing of a sharp interface onto the lattice than in, e.g., a cubic lattice. In Eq. (1), φ_x^b is the bulk concentration of segment type x . We take the bulk as the phase with low alkane density (vapor phase) far away from the interface. In the bulk no inhomogeneities on a larger length scale than the lattice sites are present. Free segment distribution functions $G_x(z) = \exp[-u_x(z)]$ are defined and generalized such that $G(z, s) = G_x(z)$ when segment s is of type x .

The density profiles are computed by an efficient propagator formalism. This formalism is equivalent with generating all allowed conformations c of a test chain in the field of all other chains and solvent molecules. The statistical weight of each conformation is computed and a summation over configuration space is carried through. A conformation c is fully specified when the coordinates of all segments are known. The number n_c of chains in a conformation c normalized by the number of lattice sites in each layer L is given by

$$\frac{n_c}{L} = C \prod_{s=1}^N G^c(z, s) \prod_{\sigma=1}^{N-1} G^c(z, \sigma) \prod_{\sigma=2}^{N-2} \lambda^{c\sigma} \left[\frac{1}{4} \times \frac{1}{3} \right], \quad (2)$$

where C is a normalization constant. For a conformation c not only the coordinate z of any segment s is known, but also the direction of each bond σ . The multiple product over s gives the overall Boltzmann weights of the segments in conformation c . The second product runs over all bonds. Below an expression for the orientation dependent weighting factors for placing bonds σ , $G^c(z, \sigma)$, is given. Finally, $\lambda^{c\sigma}$ accounts for the *gauche* and *trans* probabilities relevant for conformation c ; $\lambda^{c\sigma} = \lambda^{gauche} = 1/[2 + \exp(U_{GT}/k_B T)]$ if bonds $\sigma - 1$ and $\sigma + 1$ point in different directions and $\lambda^{c\sigma} = 1 - 2\lambda^{gauche} = \lambda^{trans}$ otherwise. The energy dif-

ference, U_{GT} , between a local *gauche* and a *trans* configuration is experimentally accessible. The two quotients within brackets account for placing the first $\sigma = 1$ and last $\sigma = N - 1$ bonds, respectively. Generating all conformations c and applying Eq. (2) gives access to both the density distribution $\varphi_x(z)$ and the density distributions of bonds. These last quantities are collected into two profiles: $\varphi^-(z)$ for bonds within a layer and $\varphi^1(z)$ for bonds between layers z and $z + 1$. From these the orientation dependent weighting factors are found. If bond σ in conformation c is between layers z and $z + 1$, we write $G^c(z, \sigma) = G^1(z)$ and in other cases $G^c(z, \sigma) = G^-(z)$ where

$$G^1(z) = \frac{1 - \varphi^{1b}}{1 - \varphi^1(z)}, \quad (3a)$$

$$G^-(z) = \frac{1 - \varphi^{-b}/2}{1 - \varphi^-(z)/2}. \quad (3b)$$

In Eq. (3b) it is assumed that bonds in a layer distribute isotropically between two directions, so that the probability that a bond in a given direction is $\varphi^-(z)/2$. From Eq. (3a) it can be seen that when $\varphi^1(z) \rightarrow 1$ the weighting factor $\varphi^1(z)$ rises steeply, which provides the cooperativity needed for the freezing transition. A real divergence does not occur due to finite chain length effects (the number of bonds is one less than the number of segments in a chain). The density distribution of the vacancies is found also by Eq. (2), which reduces for monomers to $\varphi_V(z) = \varphi_V^b G_V(z)$. From the set of conformations $\{n_c\}$ it is possible to generate intramolecular density-density correlation functions, which can be used as a characteristic of the average conformation of the molecules. This is not done in this Letter.

The above set of equations is solved numerically (up to 7 significant digits) with reflecting boundaries on both sides of the system. The amount of C_{16} is fixed [this specifies the constant C in Eq. (2)], so that the interface between the condensed alkane and its vapor is displaced from the boundaries.

Results are reported for the orientational ordering of C_{16} mixed with a monomeric component V_1 (vacancies). The Flory-Huggins (FH) interaction parameters are fixed rather *ad hoc* to $\chi(\text{CH}_3, \text{CH}_2) = 0.5$, $\chi(\text{CH}_3, V) = 1.0$, and $\chi(\text{CH}_2, V) = 1.6$. For simplicity it is assumed that these parameters are not a function of the temperature [10]. The $\chi(\text{CH}_2, V)$, and to a lesser extend $\chi(\text{CH}_3, V)$, parameter is such that the concentration of V_1 in the hexadecane phase is near 6% in the liquid state. This low value is needed to obtain a high density of bonds so that the system is easily triggered to go through the solid-liquid transition. A much higher vacancy concentration puts the system too far from this transition point. The repulsive $\chi(\text{CH}_3, \text{CH}_2)$ interaction gives some internal driving force for orientation of the molecules, significant for the bulk freezing, but more important is the difference

in repulsion for the V phase between the CH_2 and CH_3 units. The latter repels the V phase slightly less than the former. The remaining parameter U_{GT} is used to drive the system through its transition. For convenience $U_{GT} = 1$ at $T = 300$ K for any sequence of four segments in the chain. We note that the temperature scale $T = 300/U_{GT}$ is only qualitatively correct. The system is 60 lattice layers in size and numbered arbitrarily ($z = 0$ is near the interface, $z < 0$ is the vapor, and $z > 0$ is the alkane phase). It has reflecting boundary conditions and contains in all cases 40 equivalent monolayers of hexadecane and thus 20 equivalent monolayers of free volume. The dimension of a lattice cell is equivalent to the size of a C-C bond.

Some typical density profiles are shown for the hexadecane- V interface for three different temperatures, characteristic for the liquid, liquid plus surface layer, and solid in Fig. 1. The interfacial width (the intrinsic width) is only a few lattice layers wide (capillary wave excitations are not included) and does not change much as a function of T (FH parameters are fixed). For high temperature only a modest orientation of the C_{16} at the interface is noticed. The V fraction in the fluid is almost homogeneous throughout this phase. This changes dramatically for the intermediate temperature range. Here a monomolecular surface layer has fully oriented. This can be seen from the drop in the V fraction by a factor of 10. The CH_3 profile shows peaks on both sides of

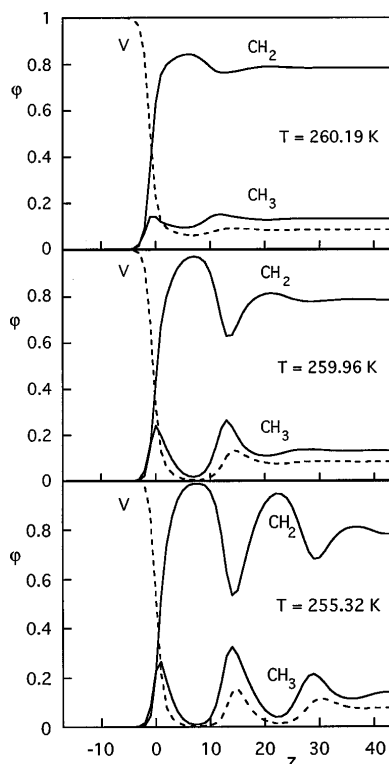


FIG. 1. Segment density profile across a V - C_{16} interface. Parameters are given in the text. Profiles of the V , CH_2 , and CH_3 units are given for three temperatures as indicated.

this highly ordered region at the expected distance away from the interface, and inspection of the orientation of the molecules shows that indeed the molecules in the first layer are nearly all in an all-*trans* configuration (not shown). The alignment is not perfect; the probability of finding *gauche* defects is highest near the ends of the molecule. The CH_3 groups that accumulate on the C_{16} side of the frozen layer cause a local maximum of the free volume in the condensed phase. This is the nucleation site for further ordering of the rest of the hexadecane. At the lowest temperature we see that indeed a second layer has solidified. Because of the finite size effects of our box the third layer could not reach a high level of ordering. At this stage we have no information whether a third or subsequent layer order at the same temperature as the second one, or whether these layers “freeze” at slightly lower temperatures. Important for a potential cascade of surface ordering phase transitions is the amount of surface-induced orientational bias that is transferred from one (ordered) alkane layer to the next (fluid) one. The decay length ξ of this alignment transfer is not expected to be long for alkanes.

In Fig. 2 the proof is presented that both the surface and the bulk freezes by first-order phase transitions. In this figure the amount of free volume on various z coordinates in the condensed part of the system is given as a function of the temperature. The layers $z = 8$ half-way the first and $z = 23$ half-way the second C_{16} layer have been selected for this. As long as the amount of free volume is as large as 6% the local environment is fluidlike, whereas a solidlike state is characterized by a dramatic reduction of vacancies (at least a factor of 10 for the first layer and slightly less than a factor of 10 for the second one). From Fig. 2 it can be seen that the surface layer freezes at $T = 260$ K and the bulk at $T = 255.5$ K. Consistent with experimental findings, it was possible to detect hysteresis regions for both transitions ranging over a few tenths of a degree [11]. It is noteworthy that as the first layer solidifies the density in the liquid bulk adjoining the surface layer is affected. Perhaps more

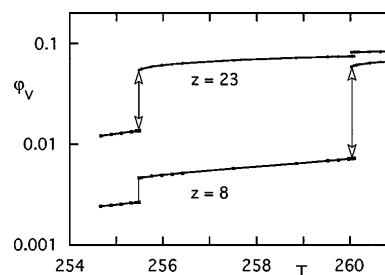


FIG. 2. The amount of free volume [$\varphi_v = 1 - \varphi(\text{alkane})$] at the midpoint of the first monomolecular layer next to the V phase, $z = 8$, and at $z = 23$ (second layer) as a function of the temperature T . The arrows indicate the main transition points. Only part of the van der Waals loops can be calculated by our numerical procedure.

surprisingly, when the second layer solidifies, the density in the first layer is affected as well; clearly the first layer compacts even more, and the orientational order of the chains increases. These density changes are important to estimate ξ and to judge how many subsequent ordering (freezing) transitions might be expected. Furthermore, there is a critical value of alkane density at which the ordering sets in. The fluid both in the first layer and in the next layer become unstable and then solidify as the fraction of V drops below $\varphi_V = 0.055$. Again, this can be controlled not only by the chain stiffness but also by the appropriate FH interaction parameter. It is also of considerable interest to mention that the density in the first frozen layer is significantly higher than in the second one. This is because the CH_3 groups cause the alkanes to orient at the interface, and this helps to reduce the number of defects. In the second layer there are many more defects, which may partly be due to the inability of the third layer to solidify.

The results shown above show good resemblance with experimental data [3,4]. In experiments the freezing point for C_{16} is at higher temperatures. In our model the point at which surface ordering is found increases by, e.g., increasing the FH parameter for CH_2 and V contacts. More important is the difference between the bulk and surface freezing temperatures, which is in practice only of the order of 1 K. The too large gap between the surface and bulk ordering is introduced in the model by a slightly overestimated difference in surface affinity between the CH_3 and CH_2 groups.

In this Letter we have concentrated on the C_{16} system. To extend our model to cover the full range of chain lengths N it is necessary to choose, in addition to the temperature dependence of the chain stiffness, an appropriate scaling for the FH parameters with temperature, e.g., $\chi \sim T^{-1}$. Then interesting issues like the chain length dependence of the difference between the bulk and surface freezing can be addressed. Moreover, it is then possible to examine why there is a lower limit $N \sim 14$ and an upper limit $N \sim 50$ for this peculiar freezing phenomenon. Work along this line is in progress.

Related to the orientation of the alkane molecules at the interface is that those alkanes have interesting autophobic wetting behavior. This has been noted before by others [3], and is convincingly reproduced by our calculations.

In summary, we developed a theory based upon the idea that two effects are important for alkane surface freezing. First, there must be a tendency for the chains to become

rigid and aligned in a dense packing. Furthermore, there must be a driving force for the enrichment in the surface of one particular kind of group, which we supposed is the CH_3 group. It is shown that a simple SCF lattice-gas model can capture these aspects, and a proof is given in *n*-hexadecane indeed can develop a highly oriented and ordered surface layer. The surface-induced 2D ordering is known to be present for other molecular weights (according to experiments for alkanes between C_{14} and C_{50}), and for molecules such as those forming liquid crystals. Our model can be used to study these systems as well.

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 - [10] Any reasonable temperature dependence for the FH parameters will keep the transitions as discussed intact. It will, however, influence details such as the difference between the surface and bulk freezing temperatures. Usually, however, the correct influence of the temperature on $\chi(x,y)$ is not known as it may contain both entropic and enthalpic contributions.
 - [11] Calculations near the transition zone are met with considerable difficulties. The freezing of the bulk was most difficult to calculate as this event causes a shift (for the numerical procedure catastrophic) of the interface and thus a shift of the first layer to slightly higher z values. It was therefore not possible to exactly “measure” the sizes of the van der Waals loops of the transitions. A detailed analysis of the transitions is not the main goal of this Letter.