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Criticality of Lamellar Surfaces by Conformational Degrees of Freedom

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Abstract. — A new model for lamellar surfaces formed by anisotropic molecules is proposed. The molecules have internal degrees of freedom, associated with their flexible section of length \(N\) at zero temperature. We obtain a 2D non-standard six-vertex model, which is exactly soluble and exhibits a finite order transition. The order and the character of the transition are determined by the dominant term in the \(1/N\)-expansion of the interaction energy. The dependence of the critical temperatures on \(N\) is, instead, determined by the non-leading terms in the same expansion.

1. Introduction

In this work we shall study the statistical properties of a Hamiltonian model for a two-dimensional object formed by flexible molecules arranged in the ordinary 3D space. We think that this ideal model can not only mimic real physical surfaces such as layers of molecules forming films and interfaces or (semi)bilayers in biological membranes, but also be useful for the interpretation of the layered structures, and related transitions, observed in smectic phases of liquid crystals.

In view of our purposed description, two properties of the elementary components are of main interest. The first one is the presence in the molecule of a (long) flexible section, or tail, typically an alkyllic sequence; the conformational flexibility is associated with internal degrees of freedom which represent the rotations around skeleton bonds in the tail. In agreement with the formalism of Volkenstein and Flory [1,2] who developed the conformational theory of chain molecules, we shall refer in this paper to trans planar chains and to chain defects such as kinks, antikinks and their combinations; we shall also make use of Flory’s definition of conformational (intramolecular) energies [2]. The second structural property of interest is the presence in the molecule of a rigid core, or head, carrying an asymmetric charge distribution, equivalent to a dipole. The relative orientation of such a dipole with respect to the molecular longitudinal axis is also meaningful in our analysis. It is well known from experiments that systems
formed by molecules with these properties exhibit a rich variety of mesophases (first classified by Friedel [3]) which, beyond the perfect crystal, go toward the isotropic liquid through a progressive loss of intermolecular order [4-10]. Both thermotropic and lyotropic behavior has been observed. In thermotropic systems, one has a pure substance formed by mesogenic molecules; the transitions between mesophases occur by varying the temperature of the sample. The order parameters describe the orientational and the positional arrangement of molecules; they change with temperature and are discontinuous at critical temperatures. In lyotropic systems, one has a solution where the solute is a mesogenic molecule; the phase transitions are achieved by changing the concentration of the solute or by changing the character (ionic strength) of the solvent.

In this paper, we shall refer to thermotropic compounds. In this field, a wide collection of experiments (see, for instance, Ref. [10]), investigated the relations between structural properties of molecules and liquid crystalline basic properties; the main interest has been focused on the spatial organization of molecules in the various mesophases, the behavior of critical temperatures in series of homologues and the sequences of occurring mesophases. In particular, the layered, head-to-tail, arrangement of molecules was observed, since 1975, by Leadbetter et al. [11,12] in the smectic A phase. By X-ray diffraction on cyanobiphenyl compounds, they confirmed that the layer spacing is greater than the molecular length, consistently with the proposed setting of pairs of molecules, forming dimers, with heads facing one another in the center of the layer and tails pointing outward in opposite directions. Analogous layered arrangements were observed in smectic phases for many other thermotropic compounds; as examples we may quote the nitroderivatives [13] and cyanatophenylbenzoates [14] with alkyl tails. In these substances many different $S_A$ phases are recognized by X-ray diffraction, calorimetric [13] and dielectric [14] measurements; in each phase the head-to-tail setting occurs with a different extent of molecular overlapping and layer thickness. A great variety of smectic-smectic transitions may occur; in particular, the transition $S_{A1} \rightarrow S_{A2}$, from the phase with layer thickness equal to the molecular length, to the phase with layer thickness twice the molecular length [13] is observed for increasing temperature. The transition $S_{A1}$ to nematic is also observed [13,14].

Two notes are in order about these facts. First, the persistence of layered structures in the different smectic phases suggests the interaction between adjacent layers to be weak, compared with the intralayer forces. For this reason we think that it is meaningful to study the single, smectic-like layer as a two-dimensional, independent, neutral and thermotropic object in the 3D space. Second, the head-to-tail setting of adjacent molecules suggests the antiferroelectric arrangement of molecular dipoles, parallel to the longitudinal molecular axis, to be compatible with the alignment of molecular axis.

From a theoretical point of view, the formation of mesophases is equivalent to a sequence of symmetry breakings. Starting from the completely symmetric 3D phase (isotropic liquid), one expects the strongly asymmetric interactions between elementary constituents to promote, step by step, the orientational order, the formation of stable and weakly interacting objects with lower dimension than that of the environment (such as 2D smectic layers, or 1D columnar structures), up to the perfect crystal [15]. However, this program is rather difficult to carry out.

The first step has been overcome by Onsager, since 1949 [16,17], with an exactly soluble model for a system of rigid rods with first order isotropic to nematic (I-N) transition. There is a wide and rich literature about this transition: one has the phenomenological description by Mayer and Sauer [18], the Landau theory of orientational order parameter by de Gennes [19], and the order parameters from McMillan's model [20,21]. The presence of a flexible section in the molecule, and its effects in the I-N transition, was considered in Marčelja's self-consistent analysis of chain ordering in liquid crystals [23] and in Pink's model of odd-even effect [24].
The problem was also investigated by Martire [25] and Luckhurst [26] with molecular field methods. The orientational transition was also studied by Monte Carlo simulations (we recall the first calculation by Lebwohl and Lasher [27] and, more recently, the planar versions of the $RP^n$ model [28–30]).

For other transitions, between different smectic phases (S-S) or for smectic to nematic transition (S-N), the research is not so widely developed; in particular, there are no exactly solved models and one turns to phenomenological theories of order parameters or to numerical simulations. For liquid crystals, the translational order parameter for S-N transition was defined by McMillan [20,21] and compared with the phenomenology of smectic phases [22]. The problem about the role played by conformational flexibility in these phases and related transitions is avoided: the molecules are ever considered as rigid rods.

On the other hand, in the field of biological membranes, Nagle [31] and, independently, Marčelja [32] developed two models for the transitional behaviour of molecular chains in smectic-like phases of lipid mono and bilayers. In these models, attention is pointed to the conformational collapse of the constituents rather than to the effect of such a collapse on the surface of the biomembrane.

Before introducing the model, which is addressed to the study of S-S and S-N transitions, we note that the criticality of layered structures is of main interest in a rather different context, namely in studying the interface formation between, e.g., two solids or film deposition; in this case the geometry of the surface is characterized by the formation of ledges and terraces, with the typical roughening transition. Surface structures and related phase transitions have been studied with exactly soluble models [33]. We recall the models of Van Beijeren (BC-Solid-On-Solid [34,35]) and of Burton (Terrace-Ledge-Kink [36]), firstly introduced for the crystal-vacuum interface. The common feature of these models is that they can implement a conservation law by a six-vertex lattice system, with exactly known [37–39] solution. Monte Carlo calculations on specific realizations of BCSOS or TLK models simulate, e.g., adatoms forming thin films [40,41] or interfacial molecules [42].

In this work, we present an exactly soluble model for a single molecular surface, namely for a 2D object like a free smectic layer of a thermotropic liquid crystal. Together with the general structural properties previously required for the constituent molecules (the presence of one head and one tail), we consider the following distinctive features:

a) we are interested in a system whose intramolecular energies, associated with conformational chain defects, are of the same order of magnitude as the intermolecular energies;

b) we represent the charge distribution associated with the molecular head by a dipole parallel to the longitudinal axis of the molecule;

c) we assume an antiferromagnetic structure of the fundamental state (the constituents are aligned with a head-to-tail setting).

There are at least two physical reasons for assuming property a). First, in many molecular systems with smectic transitions, the transition heat is of the same order as the melting heat of the crystal formed by the tails only (typically $n$-alkane lamellae) [4]. Second, in the same systems, IR and Raman spectra directly show that the alkyl part of the molecular layer is liquid like at the critical temperature; in fact, the spectroscopic markers of the conformational defects characterizing the liquid phase of $n$-alkanes are clearly observed [43].

As for the requests in b) and c), we stress that they are not independent of one another. In fact, constituents with head dipoles orthogonal to the longitudinal axis, should be compatible with a layered structure in which molecules have a head-to-head setting (as in a semi-bilayer, in which the alkyl chains point to the same direction). In this case we expect to be addressed to the phenomenology of lyotropic systems, in which the transitional properties are determined by the dominant interaction between polar heads and solvent. Alternatively, for thermotropic com-
pounds, we expect the system to have a transitional behaviour dominated by vortex formation in the plane of molecular heads [44].

Assuming longitudinal head dipoles instead, the arrangement of molecules, in a temperature regime with high orientational order, is compatible with the head-to-tail setting. We think that, in this case, there is an effective competition between the dipole-dipole and the pure chain-chain contributions to interaction energy; pairs of opposite dipoles will have a tendency to reach an antiparallel setting with aligned centers. On the other hand tails will prefer to attain the full extended trans planar conformation with aligned centers of mass. In the presence of a rigid core, this competition leads to an interaction potential with (at least) two different minima which, roughly speaking, correspond to the maximum coupling of dipoles and chains, respectively. Let us consider, in the 3D space, the packing of pairs of molecules in one of the equilibrium relative positions. We shall obtain the layered smectic-like structure, namely the single surface of interest. Furthermore, different geometries select different classes of conformational defects, which are compatible with alternative packings. We can study the stability, the thickness and the degree of conformational disorder of such a surface as a function of both the conformational energy and the energy difference between the minima of the two-body potential.

In Section 2, we construct the bare model of the surface, obtained by neglecting the conformational degrees of freedom. We show that it belongs to the class of vertex models [38]. The specific character of the interaction leads to a definition of vertex states and related energies, which are different from those in the vertex models studied in the literature. The symmetries and the conservations typical of the solved classical model do not apply in our case, except for a special choice of the interaction constants. We show that, in the general case, the bare model cannot have thermotropic phase transitions.

In Section 3 we take into account the conformational degrees of freedom and we show that the vertex states have an internal degeneracy. Therefore the model may exhibit a thermotropic transition of finite order. The thickness of the surface at the critical point is also studied.

In Section 4, we analyze the critical dependence of the energy parameters of the model on the length of the molecule flexible section. We obtain the dependence of the order of the transition and of the critical temperature on such length. We then compare our results with some experimental data.

In the last section we point out two lines of development of our model: the first in view of a description of bilayers and the second toward an interpretation of the multiplicity of mesophases in liquid crystals.

2. The Bare Model

We are interested in modelling a surface exhibiting orientationally ordered phases, so that we will assume the existence of a fixed director along which the molecules are aligned.

At first, we do not consider the flexibility of molecular tails: in the bare model the conformational degrees of freedom are frozen, the molecules are rigid objects.

Representing the surface through the centers of mass of the molecules, we consider their projections in the orthogonal plane to the director and we assume that such projections define a square $L \times L$ lattice, formed by intertwined sublattices A and B. Each lattice site in A (B) is occupied by a molecule with head dipole oriented up (down) with respect to the lattice plane; in this way we achieve the head-to-tail setting of molecules, which, as described in the introduction, has been observed in smectic layers [11–14].

The translational degrees of freedom of the molecules are constrained along the director. Moreover, we do not consider vibrations (relative oscillations along the director, around the configurations which minimize the two-body energy).
Fig. 1. — a) The link state (0) (left) is a local minimum for the attractive interaction between molecular tails. The link state (1) (right) is a local minimum for the dipole-dipole interaction between molecular heads; b) The exchange from link state (0) to (1) is obtained by shifting an A site molecule downward or by shifting a B site molecule upward.

The surface can now be characterized by the scalar field \( \{ h_{i,j} \} \) of the altimetric heights of the molecular centers of mass, relative to a given reference.

For a pair of molecules corresponding to adjacent sites in the lattice, the competition between dipole-dipole and chain-chain interactions determines two stable link states (with minimal energy). If the attractive chain-chain interaction prevails, we have two neighbouring molecules with tails facing one another and head dipoles forced in a non-equilibrium (relative) position (see Fig. 1a): this configuration defines the link state (0). If, instead, the antiferromagnetic interaction between head dipoles prevails, we have the link state (1), representing facing heads and tails forced to point toward opposite directions (see Fig. 1a). Note that the direction of the line containing the centers of mass (local surface orientation) with respect to the director is different in the two configurations.

Both link states (0) and (1) are minima for the pair interaction. In fact, a displacement around the configuration 1 increases the dipole-dipole contribution to interaction energy, whereas the tails are too far to compensate. Analogously, a displacement around 0 decreases the attraction between the tails, but the opposite dipoles are again too far. The change from link-state (0) to (1) is obtained by shifting an A site molecule downward, or by shifting a B site molecule upward (Fig. 1b). Since vibrations are excluded, the single molecule may only shift up or down of one unit length, relatively to its neighbours.

In the bare model, given a distribution of links on the lattice, the height of a molecule in the site \((I, J)\), relative to the height of the molecule in the site \((0, 0)\) (of type A), is a function of the values (0 and 1) of link states. We have:
\[ h_{I,J} = \sum_{j=0}^{J-1} (-)^j x_{0,j} + (-)^j \sum_{i=0}^{I-1} (-)^i y_{i,J} \]

where \( x_{i,j}, y_{i,j} \) are the values of the links \((i, j), (i, j + 1)\) and \((i, j), (i + 1, j)\), respectively.

Note that the sign of the height variation between a site and its nearest neighbour depends on the parity of the site. Furthermore, the sum of the height variations, over any loop on lattice sites, must be zero. This is a constraint for the distributions of links on the lattice.

Let us define a plaquette as a loop of four links and a plaquette state as the set of values of such links, the constraint selects 6 of the 16 possible plaquette states, namely those where:

\[ x_{I,J} - y_{I,J+1} - x_{I+1,J} + y_{I,J} = 0 \]

The previous description can be given in the formalism of vertex models [38]. The plaquettes are identified with the sites of the dual lattice and the plaquette states with the vertices on such sites. A vertex is defined by four arrows entering or exiting the site (arrows-in/out) and connecting it with the nearest neighbours. It is easy to set a one-to-one correspondence between plaquette states and vertices.

The so-called 8-vertex (8V) model is built on vertices with an even number of arrows-in (8 allowed states per site). The 6-vertex (6V) models have 6 allowed states per site. In particular the vertices of the classical 6V model must satisfy the so-called ice rule: two arrows-in and two arrows-out.

The configurations of the model are sets of compatible nearest neighbouring vertices. The energy of a configuration is the sum of the energies assigned to the vertices. In the classical, exactly soluble models, the energy is invariant with arrows reversing. If such symmetry is broken, one has a model with external field.

The allowed plaquette states of our model are mapped in 6 of the 8 vertices of the 8V model, as represented in Figure 2. This procedure formally leads to a 6V model, but, in comparison to the classical 6V, we have a different choice among the 8V vertices (vertices 7 and 8 instead of 3 and 4).

The configuration energy in the bare model is the sum of plaquette energies. For symmetry reasons the plaquette states 5,6,7,8 must have the same energy \( e \), whereas the energy of states 1 and 2 can be set to the values \(-\omega/2\) and \(+\omega/2\), respectively, by an appropriate choice of the zero for the energy scale.

In the special case \( \omega = 0 \) (vertices 1 and 2 with the same energy), we can use the symmetry properties of the partition function of the 8V model with zero field (Ref. [38], Chapter 10) to prove that the partition function of the bare model is equal to the partition function of the classical 6V model with ice rule [45].

Therefore, in this special case, our bare model is equivalent to the 6V model and it can be exactly solved.

However, there is no physical reason to assume that tail-tail interactions have the same energy as dipole-dipole interactions, so that, in general, vertices 1 and 2 have unequal energies. In this case, the symmetry property, which is crucial in proving the above statement, cannot be generalized. It follows that, in a physically meaningful regime, our bare model is not equivalent to the classical 6V. Indeed, we have a specific version of the 8V model with external field \( \omega \).

Even if, to our knowledge [33,38], the 8V model has not been solved exactly with non-vanishing field, the specific features of the present model make it easy to study.

From the convexity properties of the free energy and of the order parameter as functions of the field \( \omega \), we can prove that in the bare model the free energy is differentiable with respect to \( \omega \) except, at most, in \( \omega = 0 \) [45].
It follows that we have no chance for thermotropic transitions in the fully oriented physical regime, as far as rigid molecules are considered.

In the next section we shall show that the special case $\omega = 0$ has a physical meaning if the internal degrees of freedom of the flexible molecules are considered.

For this reason, we recall here the results of the classical 6V model that are relevant to our description.

- According to the exact solution [38], one has two possibilities. First, if the energy $\epsilon$ is strictly negative, the system is disordered; at any temperature the free energy is analytic and the path of the point representing the system in phase space lies in the disordered phase region. Second, if $\epsilon > 0$, for low temperatures the system is in the antiferroelectric
phase and has a phase transition, of infinite order, at the critical temperature \( \beta_C = \frac{\ln(2)}{\epsilon} \), to the disordered phase.

- The classical definition of order parameter, becomes, in our case:
  \[
m = -\frac{\partial}{\partial \omega} \ln Z|_{\omega=0} = \left( \frac{1}{L^2} [n_1 - n_2] \right)
\]
  namely the expectation of the difference between the numbers of plaquettes of type 1 \((n_1)\) and 2 \((n_2)\).

- The correlation length \( \xi \), which is obtained from the behaviour of \( \frac{\partial^2 \ln Z}{\partial \omega_I \partial \omega_{I',J'}} \) for large distance of the sites \((I, J)\) and \((I', J')\), is finite for \( \beta > \beta_C \) and diverges for \( \beta < \beta_C \) (Ref. [38], Chapter 8).

- The susceptibility \( \chi \) associated with \( m \), defined as \( \chi = \frac{\partial^2}{\partial \omega^2} \ln Z \), turns out to be finite for \( \beta > \beta_C \) and diverges for \( \beta < \beta_C \) [35,39].

In order to refer our bare model to known results, the altimetric description suggests the comparison with the BCSOS model [33,34]. Therefore, we represent each plaquette by the mean height of the four constituent molecules and we identify the order parameter \( m \) in equation (3) with the roughness of the surface.

We carried on a numerical calculation, by transfer matrix method, for the bare model with \( \omega = 0 \). In fact, in terms of our link variables the transfer matrix has an iterative structure which is very simple and easily computable [45]. In particular, we checked the critical behaviour of the order parameter \( m \) and of the associated susceptibility \( \chi \).

Our results about the order parameter (reported in Fig. 3) approach, at the critical temperature \( T_C \), the infinite system asymptotic form, predicted by the exact solution \( m \sim (T_C - T)^{-1/2} \exp \{-A(T_C - T)^{-1/2}\} \). The associated susceptibility (Fig. 4a) and its critical divergence with lattice size \( (\chi L(T_C) \sim L) \), see Fig. 4b) show a good agreement with Monte Carlo calculations on BCSOS [40].

With reference to Figure 3, we note that the order parameter, as a function of temperature, is antisymmetric with \( \omega \rightarrow \omega_\pm \) (we shall indicate these functions with \( m^\pm(\beta) = -m^- (\beta) \)). This fact, which comes from the invariance of the partition function of the bare model with respect to the exchange \( \omega \leftrightarrow -\omega \), will be crucial in the following.

We are also interested in evaluating the dispersion \( \delta^2(h) \) of the height, related to the thickness of the surface [40,41]. According to the BCSOS model, \( \delta^2(h) \) is expected to behave as \( \ln \xi \) for \( \beta > \beta_C \) and to diverge as \( \ln L \) with lattice size \( L \) for \( \beta < \beta_C \) [35,41]. From a phenomenological point of view, we shall associate such a divergence with the surface breakdown (see Section 3).

3. Switching on the Internal Degrees of Freedom

In this section, we shall consider the conformational degrees of freedom and prove that their switching on gives rise to a thermotropic transition of finite order.

According to Flory's model of free chains, the single molecular tail is described in terms of conformational states. As we did for the case of alkane lamellae [46], we use a collective conformational variable \( \Delta \) and write the chain partition function as a hierarchical sum:

\[
Z_{Tot} = 1 + Z_{\Delta=1} + Z_{\Delta=2} + \cdots
\]
Fig. 3. — Numerical calculation by transfer matrix of the order parameter as a function of temperature for different lattice sizes. The dotted line represents the exact behaviour (see text); in our calculation $A = \pi^2 T_0 / 16\sqrt{2}$.

Each term in the sum corresponds to a class of states characterized by conformations with a fixed transversal width $\Delta$ (with respect to the director). The first term (1) is the contribution of the all trans chains. The second term (with $\Delta = 1$) comes from 1-kink or 1-antikink conformations and from all conformations with sequences of alternating kink and antikink. The $\Delta = 2$ term collects all the contributions from conformations with twice the unitary width, and so on.

To construct the partition function of the system, we have to define the structure of the interaction between molecules which have different tail conformations and belong to different plaquette configurations.

We assume that the multiplicity of available conformational states depends, for each molecule, on the type of plaquette the molecule belongs to; the intermolecular interaction energies, instead, are assumed to be independent of the particular conformational state (provided it is available). This is argumented as follows. Let us consider a dressed plaquette of type 1 (see Fig. 2; the molecules have facing tails and may form conformational defects). Since the tails are strictly packed, they can only contain defects with small width $\Delta$ and the interaction is independent of the defect site in the chains. Considering now a dressed plaquette of type 2 (facing heads), the molecular tails are rather free and then may contain conformational defects with large $\Delta$.

From a general point of view, these assumptions represent a packing-flexibility constraint whose specific realization (see Section 4) will not affect the general results discussed in this section.
Fig. 4. — a) Numerical calculation of susceptibility as a function of temperature from transfer matrix results for different lattice sizes; b) Size dependence of susceptibility at $T_C$ in agreement with $\chi_L(T_C) \sim L$ (dotted line).
We write the partition function of the system in the form:

$$Z = \sum_{\{P_j\}} e^{-\beta \sum_i h(P_i)} \sum_{\{S_{ij}\}} e^{-\beta \sum V h(S_v)} , \quad (5)$$

where the first sum is over the plaquette states \(\{P_j\}\) of allowed configurations and the second sum is over the conformational states of the molecule in the lattice sites \(V\), constrained by the packing-flexibility condition with respect to the four adjacent plaquettes. The quantity \(h(S_v)\) is the Flory energy of the state \(S_v\) and \(h(P)\) is the plaquette energy.

We can factorize the packing-flexibility constraint in such a way that we can sum over the conformational states and, using the geometry of the lattice, share the result among the plaquettes. The total contribution to the \(Z\) function from a single dressed plaquette takes the form:

$$e^{-\beta h(P)} [Z_1 \delta_{1,P} + Z_2 \delta_{2,P} + Z_0 \sum_{x=5}^{8} \delta_{x,P}] \quad (6)$$

where \(Z_1, Z_2\) are the partition functions of a single chain with states compatible with the plaquette of type 1 and 2, respectively and \(Z_0\) refers to the other configurations.

In terms of the plaquette energies \(\pm \frac{\omega}{2}\) (states 1 and 2) and \(\epsilon\) (states 5,6,7,8) we have:

$$Z(\beta, \epsilon, \omega) = \sum_{\{P_j\}} e^{-\beta \sum_i \left[ \frac{\omega}{2} - \frac{1}{\beta} \ln Z_1(\beta) \right] \delta_{1,P_i}} \times e^{-\beta \sum_i \left[ \frac{\epsilon}{2} - \frac{1}{\beta} \ln Z_2(\beta) \right] \delta_{2,P_i}} \times e^{-\beta \sum_i \left[ \epsilon - \frac{1}{\beta} \ln Z_0(\beta) \right] \sum_{x=5}^{8} \delta_{x,P_i}} \quad (7)$$

One easily sees that this partition function has the same form as in the bare model: due to the conformational degrees of freedom, the bare interaction constants become the effective, temperature dependent, energy parameters:

$$\bar{\omega} = \omega + \frac{1}{\beta} \ln \frac{Z_1}{Z_2} \quad (8a)$$

$$\bar{\epsilon} = \epsilon - \frac{1}{\beta} \ln \left[ \frac{Z_0}{Z_1} \left( \frac{Z_1}{Z_2} \right)^{1/2} \right] \quad (8b)$$

The quantity \(\frac{Z_1}{Z_2}\) is a function of both the chain length \(N\) and \(\beta\); with fixed \(N\), it can be written as a ratio of polynomials [46]; for \(\beta \to \infty\) such ratio tends to 1 and for \(\beta \to 0\) it tends to the ratio between the number of constrained states (small \(\Delta\)) and the number of free states (large \(\Delta\)).

The physical meaning of the additional terms in expressions (8a,b) – for brief \(f_{11}^{(N)}\) and \(f_{00}^{(N)}\) – is the difference between the free energy of a chain without and with steric constraints.

The function \(f_{11}^{(N)}(\beta)\) is negative, monotonic, continuously differentiable with respect to \(\beta\); \(f_{00}^{(N)}(\beta)\) has analogous properties.

From what precedes it follows that, with fixed \(N\) and provided \(Z_{11} \neq Z_{22}\), one inverse temperature \(\beta^*\) may exist, such that:

$$f_{11}^{(N)}(\beta^*) = -\omega \quad (9)$$
For any $\beta \neq \beta^*$, since the energy $\bar{\omega}$ is not equal to zero, with the analysis in Section 2, we exclude the occurrence of any phase transition.

If $\beta = \beta^*$, the plaquettes of type 1 and 2 have zero effective energy, whereas the others have positive effective energy $\bar{\epsilon}(\beta^*)$. It follows that, at $\beta = \beta^*$, the equivalence condition with the classical 6V model is verified.

In order to study the behaviour of the free energy of the system $f(\beta, \bar{\epsilon}, \bar{\omega})$ as $\beta \to \beta^*_\pm$, we consider the derivative of $f(\beta, \bar{\epsilon}, \bar{\omega})$ with respect to $\beta$. We have:

$$\left(\frac{df}{d\beta}\right) = \left(\frac{\partial f}{\partial \beta}\right) + (\frac{\partial f}{\partial \omega})(\frac{\partial \omega}{\partial \beta}) + (\frac{\partial f}{\partial \bar{\epsilon}})(\frac{\partial \bar{\epsilon}}{\partial \beta})$$

(10)

As $\beta \to \beta^*_\pm$, the partial derivatives $\frac{\partial f}{\partial \omega}$ and $\frac{\partial f}{\partial \bar{\epsilon}}$ approach the values of the order parameters, calculated at $\beta^*$, of the bare model with vanishing external field ($\omega \to 0_\pm$). In particular, due to the antisymmetry of $m$, we can write:

$$\left(\frac{\partial f}{\partial \omega}\right)_{\beta^*_\pm} = m^\pm(\beta^*)$$

(11)

We now compare the solution $\beta^*$ of equation (9) with the critical inverse temperature $\beta_C$ of the classical 6V model.

If $\beta^* > \beta_C$, we have:

$$m^+(\beta^*) = -m^-(\beta^*) \neq 0$$

(12)

namely, the first derivative of the free energy is discontinuous.

In this case $\beta^*$ is the critical inverse temperature of a first-order thermotropic transition.

The latent heat at the transition $\Delta H$ is the difference between the right and the left derivatives calculated at $\beta^*$ in equation (10) and we easily:

$$\Delta H = 2m(\beta^*)[\beta^* \frac{\partial f(N)}{\partial \beta}|_{\beta=\beta^*}]$$

(13)

In the above expression, the quantity $\beta^* \frac{\partial f(N)}{\partial \beta}$ represents the melting heat of the tail. In fact, $f(N)$ is the difference between the free energy of tails with straight conformations and with completely disordered conformations. Since the order of magnitude of $m$ is 1, the transitional latent heat and the melting heat of the tails are really comparable.

It is interesting to consider the critical behaviour of the following variance, which, within the limit of infinite size, represents the thickness of the surface:

$$\delta^2(s) = \delta^2(h) + \delta^2(D)$$

(14)

In this expression, the quantity $\delta^2(h)$ is the dispersion of the height of the molecular centers of mass, as defined in the bare model and the quantity $\delta^2(D)$ is the dispersion of the end-to-end distance of the molecular tails. At $\beta^*$, the dispersion $\delta^2(h)$ is finite and continuous (in fact, from the classical results, since $\beta^* > \beta_C$, one has $\delta^2(h) \sim \ln \xi$ with $\xi$ finite). On the other hand, since the molecular tails undergo conformational transition at $\beta^*$ (associated with the change from plaquette of type 1 to plaquette of type 2), the quantity $\delta^2(D)$ abruptly changes from the characteristic value of straight conformations to that of disordered chains: both values are finite. This proves that, at the first-order transition, the thickness of the surface is discontinuous, but finite.
Last, we recall that the orientation of the longitudinal axis of the molecules with respect to the surface plane changes in going from link (0) to link (1) and as a consequence, the mean orientation of the layered molecules is discontinuous at the transition. In conclusion, from a phenomenological point of view, the first-order thermotropic transition changes the (mean) geometry and the mutual positions of the molecules, but preserves the surface. This behaviour has been observed in smectic-smectic transitions; as said in the introduction, experiments show that molecules maintain the layered arrangement in the smectic phases, even if with different layer thickness and molecular overlapping (see for instance the \( S_{A1} - S_{A2} \) transition described in Ref. [13]). It is also shown that the orientation of molecular axis with respect to the layer is different in the various smectic phases [9, 10].

We now consider the case \( \beta^* < \beta_C \). One has:

\[
m^4(\beta^*) = m^-(\beta^*) = 0,
\]

which implies that the first derivative of the free energy is continuous at \( \beta^* \). In this case no first-order transition occurs.

Clearly, the bare model critical behaviour is again maintained around \( \beta^* \); in particular, the susceptibility \( \chi \) diverges. If we consider the specific heat \( c_v \), at \( \beta^* \) we expect the same divergence as \( \chi \) (in fact, \( c_v \sim \frac{\delta^2 f}{\delta^2 \beta^2} \)). This behaviour suggests the existence of a second-order transition. From what is said in Section 2, the fact that the zero field condition \( \bar{\omega} = 0 \) is reached at \( \beta^* < \beta_C \) implies that the correlation length diverges at the critical point. In this situation, also the variance \( \delta^2(s) \) diverges, due to the size divergence of \( \delta^2(h) \).

We associate this transition with the surface breakdown, in fact the divergence of \( \delta^2(s) \) means that the long-range correlation between heights at different sites is lost. With reference to the phenomenology of nematics [9, 10], we note that our model behaves like a smectic layer of a system undergoing S-N transition. In fact, we are in a fully oriented regime and we go from a phase with strong long-range correlation of heights (the layered structure of smectics) to a phase with completely uncorrelated heights (the nematic disorder in the orthogonal direction to the layer).

We conclude this section by noting that, if \( Z_{[1]} = Z_{[2]} \), namely if the small \( \Delta \) class extinguishes all the available chain conformations, we have no transitions at all (of course, since the orientational order is preserved in our analysis).

4. Chain Length Dependence

In this section we study the solution of equation (9) as a function of chain length \( N \). The results obtained depend on the qualitative properties of \( f, \omega, \epsilon \) as functions of \( N \); more precisely, they are determined by the fact that such functions must have the same asymptotic behaviour for large \( N \) but have different scaling law for finite size effects.

In order to study equation (9) we first give the explicit choice for the packing-flexibility constraint and the associated representation of \( f_{[1]} \) and \( f_{[0]} \). We assume that molecules in plaquette state 1 can sustain only trans chain conformations; furthermore, we assume that molecules in plaquette state 2 may have any conformation. Consistently, we take: \( Z_{[1]} = 1 \) and \( Z_{[2]} = Z_{[0]}^{(N)} \). As for \( Z_{[0]} \), the structure of plaquettes, with two link states (1), i.e., conformationally "free" chains, and two link states (0), i.e., packed chains, suggests \( Z_{[0]} = (Z_{[1]}Z_{[2]})^{\frac{1}{2}} \).

(Alternatively, one may describe a system where at most \( \Delta = 1 \) conformations are compatible with plaquette of type 1; in this case: \( Z_{[1]} = 1 + Z_{\Delta=1}^{(N)} \).)
The dependence on $N$ of $f_{[1]}$ and $f_{[0]}$ is completely determined by Flory’s theory. We consider the extremal cases: with $N < 4$, we have no conformational defects and then $f_{[1]} = f_{[0]} = 0$; with large $N$, the function $f_{[1]}$ takes the asymptotic form:

$$f_{[1]}^{(N)}(\beta) = N f(\beta) + \eta(N, \beta)$$  \hspace{1cm} (16)

where $f$ is independent of $N$ and the function $\eta$ represents the finite size correction. It is rather easy to verify that such a correction decreases exponentially with $N$ as a consequence of the (mono)dimensionality of the chain. For example, one may estimate $f_{[1]}^{(N)}(\beta)$ with the transfer matrix method. Analogous considerations apply to $f_{[0]}$.

The problem is to model the dependence on $N$ of the energy parameters. Contrary to the previous functions, such quantities are strongly affected by finite size effects and we are just interested in a range of lengths ($N \sim 10/40$), where such effects have to be considered. In order to justify our choices in modelling, we stress here some points.

Let us consider the Lennard-Jones interaction between two molecular chains. With faced and straight chains, as in the link state (0), the interaction energy behaves asymptotically like $N \times \arctan(N)$; this implies linearity in $N$, with power law corrections ($-\frac{1}{N} + \cdots$) for large $N$. With shifted and disordered chains, as in the link state (1), the interaction has, instead, a dominant term which is independent of $N$, again with power law corrections.

Consider now the dipole-dipole interaction between molecular heads: the interaction energy is independent of $N$ in the link state (1) (faced dipoles) and is high order in $1/N$ in the link state (0) ($N$ measures the dipole-dipole distance).

Given a plaquette configuration, the contribution of next nearest molecules in the plaquette is essential in determining the sign of the total first correction in $1/N$ to the plaquette energy. For example, in the plaquette configuration 2, the next nearest neighbour chains are faced and statistically closer than in the plaquette configuration 1. This fact may change the sign of the $1/N$ term in the sum which determines $\omega$.

Carrying on such an analysis, we obtain the following general form:

$$\omega = N \omega_0 (1 + \Omega(N))$$  \hspace{1cm} (17)

and the analogue for $\epsilon$. In this expression, $\Omega(N)$ is the finite size correction, with power law dependence on $1/N$. In particular, for what is said above, the sign of the first correction is characteristic within a given system.

We now search the solution of equation (9) in the form $\beta^*(N) = \beta_\infty + \delta \beta(N)$ and we obtain two equations. The first one is independent of $N$:

$$-\omega_0 = f(\beta_\infty)$$  \hspace{1cm} (18)

the solution $\beta_\infty$ fixes the order of critical temperatures within a given class of homologues; in fact, the quantity $T_\infty = \frac{1}{k_B \beta_\infty}$ is the observed value of transition temperature for large $N$.

The second equation, regarding finite size corrections, is:

$$\delta \beta(N) = \frac{\omega_0}{\frac{\partial f}{\partial \beta}} |_{\beta_\infty} \Omega(N)$$  \hspace{1cm} (19)

Since the prefactor is negative, critical temperatures may increase or decrease with $N$, depending on the sign of $\Omega(N)$.

The comparison between $\beta_C = \frac{\ln 2}{N(\epsilon_0 + \omega_0)}$, and $\beta^*(N)$ leads to determine one critical length $N^*$: we have $\beta_C(N^*) = \beta^*(N^*)$. 

Fig. 5. — Fitting of critical temperatures as a function of the number of carbon atoms in the alkyl chain. The fitting has been obtained with: \( \beta^* = 1.47993 - \frac{1.34839}{N} + \frac{4.50493}{N^2} - \frac{5.90955}{N^3} \) for observed \([49] \) S-S transition temperatures of alkyl esters (●); \( \beta^* = 1.14883 - \frac{0.08927}{N} \) and \( \beta^* = 1.12009 - \frac{0.11465}{N} \) for observed \([50] \) S-S transition of halogeno-terminated aminoketone compounds ((○) Br and (□) I).

According to our results, for homologues with \( N > N^* \) the first order thermotropic transition occurs, whose main property is to preserve the layered structure as it happens in S-S transitions. For \( N < N^* \) homologues, instead, the second-order transition occurs, associated with surface breakdown as it happens for a smectic layer at the S-N transition.

These general results agree with observations of phase transitions in liquid crystals. As said in the introduction, many data are available about homologous series of one-chain molecules, with typical regularities (see, for instance, Ref. [10]). In particular, a phenomenological expression, similar to that used for phospholipids and bilayers [47,48], describes the observed S-S transition temperatures as a function of the number of carbons per chain. We stress that both the characteristic polynomial dependence on chain length and the infinite chain transition temperature, which appear in such expressions, in our case come directly from equations (18) and (19) which give the solution \( \beta^* \) of the model.

As an example, we report, in Figure 5, the fitting of critical temperatures of S-S transition in alkyl esters [49] and halogeno-terminated compounds with alkyl chain [50]; in the figure caption, we report the parameters of the fitting for each series of homologues.

5. Conclusions

The model presented in this work is a simple, exactly soluble, model of surface which takes into account the flexibility of the constituent molecules.

It proves the existence of transitions with different character and order, controlled by the length \( N \) of the flexible section of the molecule (a single linear chain).
The character of the transition is determined by the dominant term in the $1/N$ expansion of the interaction energy and the dependence of critical temperatures on $N$ is instead determined by the non-leading terms in the same expansion.

The predicted transition leads, with increasing temperature, from a layered phase (smectic) to a different smectic or to a nematic phase, through conservation or, respectively, breaking down of the surface.

In particular, if the surface is maintained, the transition is first order and is associated with the conformational collapse of molecular tails and a change in the mean orientation of molecules with respect to the surface plane.

While at low temperatures the surface is characterized by exposed molecular heads, which are polar and hydrophilic, in the high temperature phase the surface is formed by molecules with aligned heads and exposed, liquid-like chains, which are hydrophobic and weakly reactive. Regarding 3D interactions, the surface has a "soft" character, e.g., we expect a temperature dependent solubility: in the high temperature regime the solubility process has a higher energetic cost, associated with the loss of surface polarity.

As a conclusion we point out two lines of development of the present work.

The first regards the reciprocal orientation of nearest neighbouring head dipoles. In the present model we explicitly require that adjacent head dipoles are opposite; this defines sites of type A and B in the lattice. If this requirement is removed, nearest molecules may get configurations with equally oriented head dipoles. Netz and Berker [51] points out the relevant role played by reversing molecular heads in liquid crystal transitions. For our molecules, with polar heads, the phases in which such reversed configurations are favoured must exhibit macroscopic polarity. We think that, at low temperatures, the energetic cost of dipole reversing is not compensated by the entropic gain, whereas with increasing temperature, reversed configurations may be favoured.

From a technical point of view, to achieve this improvement, the model should be changed by introducing a new link state and a new energy parameter. In such a situation the analytical treatment of the model will get much more involved.

The second line regards a more accurate description of tail interaction. We think that it would be interesting to consider the multiplicity of minima (decreasing in depth) which corresponds to relative shifts of adjacent chains of multiples of the intrachain periodicity (monomer-monomer distance). Clearly, the link state associated with each one of these minima represents two partially facing chains, having the active section of length $l < N$. If we consider only one of such further minima, we can repeat the present analysis noting that, in this case, we have $f_{[1]} \propto l$ and $\omega \propto l(1 + \omega(N))$. In so doing we find that the latent heat is proportional to $l$ and independent of $N$, while the behaviour of critical temperatures is again determined by $1/N$ expansion. These results agree with latent heats measured in S-S transitions of liquid crystals [52] which are rather constant, regardless of the chain length. We could think that the interaction among distinct surfaces determines a mean separation and, as a consequence, favours a specific value for the active length $l$.

We find technically difficult to achieve the solution of a model with all simultaneously active minima; on the other hand, the experimental evidence of a variety of re-entrant phases and the analysis of such phenomena carried on by Netz and Berker [51], suggest the complexity of the problem. In this regard, we note that if, in our model, we considered the oscillations around the minima, we would not obtain a real modification of the present description: with harmonic oscillations, e.g., we could exactly sum over the associated degrees of freedom and obtain simply a redefinition of the energy parameters.
References

[49] Gray G.W., see reference [9], Chapter 12, Figure 2.