Eur. Phys. J. B **1**, 359–369 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

From molecular flexibility to shape, curvature and thermotropic transitions in pure surfaces

B. Bassetti[1,a], C.A. Mantica[1], and P. Jona[2]

[1] Università degli Studi di Milano, Dipartimento di Fisica, Via Celoria 16, 20123 Milano, Italia
[2] Politecnico di Milano, Dipartimento di Fisica, Piazza Leonardo da Vinci 32, 20123 Milano, Italia

Received: 13 November 1996 / Revised: 9 May 1997 / Received in final form: 4 November 1997 /
Accepted: 10 November 1997

Abstract. A material surface of pure constituents with a flexible molecular chain (amphiphilics) is considered; thermodynamic behaviour is studied in the chain length–temperature plane. The Hamiltonian of the system is modelled as the sum of a formation term which refers to the polymer nature of the chain, and of a fluctuation term with a specific elastic form. For closed systems the model exhibits phases with uniform curvature and conformational order/disorder or, alternatively, modulated phases; a critical chain length is found for the existence of modulated phases; the dependence of transition temperature on energy parameters is determined. A critical region is found for open systems, where conformational disorder drives spontaneous generation of curvature; this lies above a characteristic chain length and around the shape transition temperature.

PACS. 64.60.-i General studies of phase transitions – 68.35.Rh Phase transitions and critical phenomena – 87.22.-q Physics of cellular and physiological processes

1 Introduction

In order to study the role of chain flexibility in phase transitions of material surfaces (amphiphilic monolayers–membrane bilayers) [1–7], a model for a surface formed by molecules with a flexible part is presented. The main innovation in the model is that phenomenological parameters, which describe the self assembling of constituents and fluctuations of the surface shape, obtain a proper source in the conformational behaviour of the flexible chain in the molecule.

Particular attention is paid to the study of shape fluctuations in material surfaces [8–16]. In general, perturbations of surface behaviour are represented by a field phenomenologically coupled with elastic variables. For example, in Leibler's work [9], the concentration of host molecules in the layer (proteins, drugs) is represented as a scalar field, coupled to local curvature. For lipid membranes, MacKintosh *et al.* [14,15] define a coupling between tangent plane order (vectorial field) and spontaneous curvature in membranes. In the model by Honda and Kimura [13], chain configurations are considered when explaining the mechanical origin of the ripple phase. The influence of the degree of chain unsaturation on the packing behaviour of constituents is also pointed out in a different context [16]. In all these papers there is a strong dependence of the surface geometry on the given order of the surface or its constituents. In the present work, the thermodynamic behaviour of a pure surface (without structural or chemical defects) is studied by parametrizing the equilibrium geometry and couplings in the elastic energy through functions of local conformations.

In Section 2, the Hamiltonian of the model is written. A partition of the set of Flory states for the free molecular chain [17] is obtained by defining conformational *classes*, corresponding to assigned steric properties of the chain. The origin of a significant interaction between conformational and surface degrees of freedom is recognized in the multiplicity of conformations which belong to each class. The peculiarity of the model is that all the parameters which appear in the description of the surface as an elastic continuum, are functions of conformational classes instead of Flory states. After class partition, the summation over elastic degrees of freedom, or, alternatively, the summation over the conformational ones, generates either spin-like or Helfrich-like [18] effective Hamiltonians. Coupling constants show non–trivial dependence on the $T = 0$ chain length and, on the other hand, depend on temperature; as a consequence, by varying chain length the model explores regions with different criticalities of known phase diagrams.

As a special case, a partition in two classes is considered in the paper; this is referred to as a two–level model. The classes are, in general, defined when giving geometrical parameters and interaction couplings. An extension from two

---

[a] e-mail: `bassetti@mi.infn.it`

to more levels is technically feasible [19,20] and does not require further theoretical efforts. From a physical point of view, the choice between a two – three – (or more) level description is suggested by the number of phases coexisting in the system.

In Section 3, closed systems are considered (the number of constituents is fixed). After integration over the elastic degrees of freedom, the effective Hamiltonian of the model defines either an Ising model with an external field or a Brazovskii model [21], depending on the $T = 0$ chain length. In these models, conformational classes are spins. Each chain length generates a physical line in the standard phase diagram. In the first case, the Ising transition (first order or main transition) appears if the chain length is greater than a minimal value [22]. In the second case, which applies to a different range of chain lengths, modulated phases exist only for chains that are long enough (in agreement with Honda and Kimura [13]), otherwise the system exhibits a first order phase transition between phases with uniform curvature.

In Section 4, open systems are considered. The summation over conformational degrees of freedom results in an elastic Hamiltonian which exhibits curvature instability [23]; rippling phenomena are clearly associated with the switching of conformational degrees of freedom. Two cases are considered; firstly, systems are described (with a large head–to–tail section ratio) in which surface rippling is in competition with conformational disorder. A source of tension is described which, at high temperatures, generates a positive tension against rippling formation. Such a source is switched on by conformational disorder and it is independent of chain length. In the second case (small ratio) it is demonstrated that shape transition occurs with chain lengths greater than a critical value; furthermore, it is shown that the surface is unstable in a well–defined region of the chain length–temperature plane.

2 The model

In this section, the dependence of surface parameters on conformational variables is explicitly considered and the structure of the surface Hamiltonian is described.

The amphiphile molecule is represented as a rigid core (head), connected to a flexible part (tail) with the conformational behaviour of a linear – not branched – chain. In conformity with the Rotational Isomeric Model (RISM) by Volkenstein and Flory [17,24] conformational states $\{\mathbf{s}\}$ (sequences of Flory spins representing dihedral angles in the chain) and associated energies $\{h(\mathbf{s})\}$ are considered. A chain conformational variable Δ, meaning chain transversal width, is defined. It is a non–local function of Flory spins with intrinsic discrete character, due to the discretized description of conformational defects in RISM. One has $\Delta = 0$ for *all–trans* planar conformations. The unitary width $\Delta = 1$ is assigned to *one–kink* conformations (straight chains formed by two trans–planar segments joined by one kink) and, then conformations with $\Delta = 2, 3, \cdots$ are considered. The essential feature of such a variable is that each Δ value identifies a class, often large, of different Flory states; conformations with the same width, but with distinct sequences of Flory spins and energies, belong to the same Δ–class. For example, one has $\Delta = 1$ for all the conformations represented by sequences of Flory spins containing subsequences $\{1, 0, -1\}$ (the single kink), separated by an even number of 0's [25]. The chain length selects *a priori* the set of available Δ–classes for a given system.

The discrete character of Δ allows us to write the partition function for the conformational statistics of a free chain as the hierarchical sum over Δ–classes:

$$Z_{\mathrm{C}} = Z_{[0]} + Z_{[1]} + \cdots + Z_{[\Delta]} + \cdots \tag{1}$$

For small Δ values the longitudinal axis of the chain is maintained overall; in this case, the system belongs to the weak disorder universality class. The following asymptotic behaviour for large L ($T = 0$ chain length) is obtained [25,26]:

$$Z_{[\Delta]} \sim \exp(-Lu(\beta)) \tag{2}$$

where the function $u(\beta)$ is independent of L. In particular, $Z_{[1]}$ can be easily computed either by the direct combinatory or by the transfer matrix method. The energy scale for such calculations is fixed by the Flory values for the $\{0, 1\}$ sequence (0.4 kcal/mol), and for the $\{-1, 1\}$ one (2.2 kcal/mol).

In general works about amphiphilic layers, the geometric features of the molecule are represented by the transversal section of the molecule head (head size); such a quantity plays a relevant role in determining packing geometry [5, 16,27–31]. Such a role is maintained here; moreover, in this model the comparison between head size and tail transversal width becomes a criterion for selection between different kinds of couplings and constraints.

The general structure of the surface Hamiltonian will now be defined.

The material surface is modelled as the result of a three–step process.

The first step produces a *frozen chain surface* by packing together site–constituents with given conformations. It is assumed that for each choice $\{\Delta(\mathbf{x})\}$ regarding chain classes (at $\mathbf{x}$–site there is a molecule with a given, frozen conformation of width Δ, represented by the class $\Delta(\mathbf{x})$), the packing process produces a unique frozen chain surface.

Such surfaces are backgrounds for the second step of the process; elastic fluctuations are considered when frozen chain conformations are maintained.

The last step regards the onset of internal degrees of freedom; conformational disorder in flexible chains is switched on.

For each configuration $\{\Delta(\mathbf{x})\}$, the *formation energy* is the energy of the frozen chain surface. In a quite general way, this energy is written as the sum of:

i) site contributions, namely the Flory energy $h_{\mathrm{F}}(\mathbf{s}(\mathbf{x}))$ required to realize the free–chain conformational state $\mathbf{s} \in \Delta(\mathbf{x})$ for any surface site;

ii) nearest neighbours' contributions from interactions. This term represents the packing energy of constituents.

Chain-chain forces of the Lennard–Jones kind between nearest neighbouring molecules are considered, and packing energy is assumed to depend on conformational classes of involved chains (and not on conformational states). The physical meaning of such an approximation is that constituents of similar "shape" are favoured by packing energy. Roughly speaking, the number of interactions between monomers of two adjacent chains with similar shapes is higher than in the case in which different shapes allow portions of chains to be uncoupled.

Note that, in this paper an even more drastic approximation will be adopted. Interaction energies will be grouped into few levels; correspondingly, conformational classes are partitioned into groups of classes. With respect to chain–chain interactions, each element of such a partition represents a distinct chain "shape".

Given these assumptions, after summing up Flory contributions in terms of classes, the formation energy is written as a spin Hamiltonian where conformational classes (or groups of them) are the values of a spin S.

Fluctuations around frozen chain surfaces are considered as elastic deformations. For each background, the normal gauge description of the fluctuating surface is adopted [32]; configurations obtained by small, orthogonal displacements $f(\mathbf{x})$ from the background are considered. The function $f(\mathbf{x})$ gives the height of the centre of mass of the site–constituent with reference to the background. The limit of validity of this approximation is that only fluctuating surfaces close to the background are described, thus arbitrarily excluding large deformations.

Furthermore, the energy of the fluctuating surface depends only on local displacements. Deformations at distant points are independent. Long–range correlations on the surface are excluded. As discussed by David [32], locality is conserved in the normal gauge description.

The energy of elastic fluctuations is written in the form generally used for fluid membranes (Helfrich Hamiltonian)

$$\Delta H_{\text{fluct}} = \int \mathrm{d}A(f)\Big\{\frac{1}{2}\kappa(S(\mathbf{x}),L) \times \Big[c^2(f) - 2c(f)c_{\text{o}}(S(\mathbf{x}),L)\Big] + \sigma(S(\mathbf{x}),L)\Big\} \tag{3}$$

where $\kappa, \sigma, c_{\text{o}}$ are elastic energy parameters which are functions of the background.

In writing this expression, the peculiar features of the model are explicitly inserted: bending rigidity κ, spontaneous curvature c_{o} and surface tension σ depend on the background *via* site–classes and chain length L. Locality is crucial in the model, since elastic energy density at site $\mathbf{x}$ depends on the class $S(\mathbf{x})$, but it is independent of classes at different sites. No correlation between conformations of molecules at different sites is considered in the fluctuation energy; the formation term completely accounts for all chain–chain correlations.

The total Hamiltonian is a function of both the fields $f(\mathbf{x})$ and $S(\mathbf{x})$:

$$H_{\text{tot}}(f(\mathbf{x}), S(\mathbf{x})) = H_{\text{form}}(S(\mathbf{x})) + \Delta H_{\text{fluct}}(f(\mathbf{x}), S(\mathbf{x})). \tag{4}$$

In equation (3), it is required that surface vibrations are coupled to chain conformations by means of elastic parameters (in particular c_0). When flexibility of components is switched on, different backgrounds, with distinct patterns of frozen chain conformations, give rise to different descriptions of surface elasticity. The competition between these descriptions is governed by the comparison between the energetic cost of both forming and packing distorted chains and the energy spent for elastic fluctuations. The exchange of energy between conformational and elastic modes becomes effective in determining the configurational statistics of the surface.

The dependence of elastic parameters on site classes and on chain length will now be discussed in detail.

- σ is the surface tension which, in a closed system (see Sect. 3), controls the mean intermolecular distance. In open systems (Sect. 4), such a term is the chemical potential, associated with the number of constituents. In both cases, it is assumed to be proportional to the energy required to separate two rod–like molecules. With L–J interactions, a linear dependence on L with $1/L$ corrections is obtained; this is independent of conformations [33–38]. The relation $\sigma(S(\mathbf{x}), L) = \sigma_0 L$ is written.
- κ is the bending rigidity of the surface, which is related to the relative orientation of neighbouring molecules. Considering again intermolecular forces, the energy required to increase the angle between two rod–like molecules at distance l is expected to be proportional to $(L/l)^\alpha$, where $\alpha = 3$. This behaviour (which has been reported by several authors within different contexts [3,27–30,33–38]) is assumed to be independent of conformations or, at most, if large values of $\varDelta$ are considered, we expect $2 < \alpha < 3$ (see also [8]). The relation $\kappa(S(\mathbf{x}), L) = \kappa_0 L^\alpha$ is written.
- c_{o} is the spontaneous curvature of the layer, which is required to depend explicitly both on the site–class $S(\mathbf{x})$ and on the chain length; the following relation is written:

$$c_{\text{o}}(S(\mathbf{x}), L) = \gamma_0(S(\mathbf{x}))L^{-\chi} \tag{5}$$

where γ_0 is a function of *local* spin and $0 \leq \chi \leq 1$. We expect a weak dependence ($\chi \simeq 0$) for small chain length in comparison with head size.

Site dependence of curvature on spin is suggested by previous studies about packing of molecules with given shape. For instance, Israelachvili [30] shows that surface curvature of amphiphile aggregates is determined by the "critical packing shape" (cylinder, direct or inverse cone, wedge, ...) of components. In particular, geometric or packing properties depend on a critical parameter which is a function of the single component geometry (in our case, the conformational class); the inverse proportionality $c_{\text{o}} \propto 1/L$ is justified by scaling arguments.

Further reasons for chain length dependence of elastic parameters are derived from known results about layer width and curvature in various chain–molecule systems. In the present model the "width" of the surface is the mean (effective) length of distorted chains, which is proportional to L. In particular, Leibler in reference [8] suggests inverse proportionality between spontaneous curvature and layer width for fluid membranes and vesicles. For molecules fixed to a surface (polymer brushes), the dependence $1/L$ is again reported [38].

A simple realization of the present model will now be presented.

In the following, reference will be made to a two–level system, described by two Δ–classes with relevant physical interest. The reason for this choice may be recognized in classical spin models. Physical systems undergoing transitions in which only two phases are in competition will be considered; for each transition, only one order parameter is involved, corresponding to one relevant spin combination.

In the present case, a two–level choice is realized by a bi–partition of conformational classes, *e.g.* $\Delta \leq \overline{\Delta}$ and $\Delta > \overline{\Delta}$, with $\overline{\Delta}$ fixed by the comparison between tail transversal width and head size. Correspondingly, the summation of the partition function gives $Z(+) = \sum_{\Delta \leq \overline{\Delta}} Z_\Delta$ and $Z(-) = \sum_{\Delta > \overline{\Delta}} Z_\Delta$. The model is then mapped into an Ising model; S is the spin, with values $S = -1$ for $\Delta \leq \overline{\Delta}$ and $S = 1$ for $\Delta > \overline{\Delta}$.

Regarding packing energy, in such a description, only three chain–chain interaction parameters are required: $V_{+,+}$ for chains with $S = +1$; $V_{+,-}$ and $V_{-,-}$ with analogous meanings. Since energy is lowered by similar shapes, the condition $V_{-,-} \leq V_{+,+} < V_{+,-}$ is assumed.

With n.n. L–J interactions, a chain length dependence of energy parameters is expected. From previous studies about packing of rod–like molecules, it is easy to show that for straight chains $V_{.,.} \propto L \arctan L$. Such a dependence (linear on L with $1/L$ corrections) is actually independent of chain conformation.

In the two–level case, expression (5) has the following simple interpretation. Without loss of generality $c_0(S(\mathbf{x}), L) = \gamma S(\mathbf{x}) = (\gamma_0 L^{-\chi}) S(\mathbf{x})$ is written; then the sign of the spontaneous curvature is reversed if molecular chains undergo "large" conformational deformations — that is, $S(-) \to S(+)$. A similar behaviour has been reported in the literature [13].

3 Closed systems

3.1 Hamiltonian model

In this section critical behaviour will be studied for a system with fixed number of constituents — closed system [39]. In these conditions, the total area of the surface changes by fluctuations, but the projected area is fixed and proportional to the number of constituents.

The formation Hamiltonian is written as the sum of a Hamiltonian density, extended to the projected area. As stated previously, according to the hypothesis of the model, H_{form} can be modelled as a spin Hamiltonian; for two levels it is Ising-like, while, for three levels, it is given by a spin one model (Blume-Emery-Griffit model [19,20,40]).

With two levels, the packing contribution has the form:

$$H_{\text{pack}} = -J \sum_{<I,J>} S_I S_J + H \sum_I S_I \tag{6}$$

where explicit expressions for J and H are easily written:

$$J = \frac{2V_{(+,-)} - V_{(+,+)} - V_{(-,-)}}{8}$$
$$H = \frac{V_{(-,-)} - V_{(+,+)}}{4}\,. \tag{7}$$

From the basic assumption about chain-chain interactions it follows that coupling constant and field have fixed linear dependence on L with $1/L$ corrections (also quoted in Doniach's work [6]). Moreover, they have fixed positive signs. Finally, the ordering field H may contain contributions from external pressure.

The Flory contribution to formation energy has been defined as a function of conformational states; the peculiarity of the choice made about class variables is crucial here, since such a term can be summed over classes so that it can be included in the external field. In order to do this the restricted partition function $Z(S_I)$ is defined over the set of conformational states in the class S_I:

$$\sum_{\mathbf{s}_I \in S_I} \mathrm{e}^{-\beta h(\mathbf{s}_I)} = \mathrm{e}^{\ln Z(S_I)} \tag{8}$$

and the Flory contribution is written as a polynomial in S_I, with coefficients determined by $\ln Z(S_I)$.

In the two–level model the Flory contribution to the Hamiltonian density is:

$$h_{\mathrm{F}} = -\frac{1}{2}\beta \ln \frac{Z(+)}{Z(-)} S(\mathbf{x}). \tag{9}$$

For three levels, h_{F} has a similar expression. Since $S = -1, 0, 1$, the following relation is obtained:

$$h_{\mathrm{F}} = -\frac{1}{2\beta} \ln \frac{Z(+)}{Z(-)} S(\mathbf{x}) - \frac{1}{2\beta} \ln \frac{Z(+)Z(-)}{Z(0)^2} S^2(\mathbf{x}). \tag{10}$$

The dependence of these contributions on the chain length is fixed by the one-dimensional Flory description of the single chain; more precisely, a linear dependence on L with exponentially small corrections is predicted.

The whole formation Hamiltonian is thus characterized by a dominantly linear dependence on L of the coupling constant and of the external field.

The fluctuation Hamiltonian will now be considered. As stated above, the normal gauge description of elastic fluctuations around the background is adopted. By taking $\mathrm{d}A \simeq [1 + \frac{1}{2}(\nabla f)^2 + \ldots]\mathrm{d}^2x$ and $c(f) \simeq \nabla^2 f + \ldots$ truncated at the second order in f [41], the following expression is obtained from equation (3):

$$\Delta H_{\text{fluct}} = \int \mathrm{d}^2x \Big\{ \frac{1}{2}\kappa (\nabla^2 f(\mathbf{x}))^2 + \frac{1}{2}\sigma (\nabla f(\mathbf{x}))^2 - \kappa c_0(S(\mathbf{x})) \nabla^2 f(\mathbf{x}) \Big\}. \tag{11}$$

Since σ and κ are independent of classes and since the functional $\Delta H_{\mathrm{fluct}}$ depends almost only quadratically on the variations of height profile $f(x)$, Gaussian integration over elastic degrees of freedom can be performed. The effective contribution is obtained

$$\Delta H^{\mathrm{eff}}_{\mathrm{fluct}} = (-\frac{\kappa}{2}) \int \mathrm{d}^2x \mathrm{d}^2y \; c_0(S(\mathbf{x})) \Gamma(|\mathbf{x}-\mathbf{y}|) c_0(S(\mathbf{y}))$$

$$\begin{aligned} \Gamma(|\mathbf{x}-\mathbf{y}|) &= \int \mathrm{d}^2q \frac{q^2}{q^2+\xi^2} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{x}-\mathbf{y})} \\ &= \pi\delta(\mathbf{x}-\mathbf{y}) - \xi^2\pi K_0(\xi|\mathbf{x}-\mathbf{y}|) \end{aligned} \qquad (12)$$

where K_0 is a Bessel function of the third kind and $\xi = \sqrt{\sigma/\kappa}$.

The sum of all the contributions to the Hamiltonian density gives the effective Hamiltonian of the system. In particular, for the two–level model

$$\begin{aligned} H_{\mathrm{eff}} &= -\frac{\kappa\gamma^2}{2} \sum_{I,J} S_I \Gamma(|I-J|) S_J - \frac{J}{2} \\ &\times \sum_{<I,I'>} S_I S_{I'} - \Big(-H + \frac{1}{2\beta} \ln \frac{Z(+)}{Z(-)} \Big) \sum_I S_I. \end{aligned} \qquad (13)$$

A similar expression can be obtained for the three–level model. The function $c_{\mathrm{o}}(S)$ has to be generalized in order to consider three-value spin; this means including a quadratic term in S, as happens for Flory contribution.

3.2 Results

In this section the predicted results of the present model within the specific two–level choice are discussed. The following analysis, however, has a wider meaning, since it applies to a two–level case as well as to more–level systems. The extension to the three-level case should be carried out by using the phase diagram of the spin one model. With more levels, of course, calculation becomes technically more complex.

The model Hamiltonian H_{eff} is characterized by a coupling between spins which is short–range attractive and long–range repulsive. Such competition makes the quadratic form of equation (13) not positive defined, and causes the generation of instability at a mechanical level, associated with the existence of modulated phases (this is typical of a large class of models exhibiting patterns [9,21,42–44]).

The occurrence of modulated phases is better understood if the quadratic part of the effective Hamiltonian is written in the moments space:

$$H_{\mathrm{eff}} = \sum_q \frac{1}{2} \Big\{ -\kappa\gamma^2 \frac{q^2}{q^2+\xi^2} + Jq^2 \Big\} \tilde{S}_q \tilde{S}_{-q} + \cdots \qquad (14)$$

A modulated phase appears if the coefficient of $\tilde{S}_q \tilde{S}_{-q} < 0$ for some $q \neq 0$ [9–12]. In the present model this condition gives a constraint on chain length; in fact, by inserting the dominant dependences of the constants on L ($J = j_0 L, \kappa(L) = \kappa_0 L^\alpha, \gamma(L) = \gamma_0$), the previous condition gives:

$$L^{2\alpha-2} > \frac{\xi_0^2 j_0}{\kappa_0 \gamma_0} \equiv L_{\mathrm{B}}^{2\alpha-2}. \qquad (15)$$

This means that, in order to observe modulated phases, the length of the molecular chain must be greater than the critical value L_{B}.

The free energy of the model will now be considered. The quadratic kernel of H_{eff} is expanded for small magnetization. Near the critical point, that is, for small moments, the following expression is obtained:

$$\begin{aligned} \mathcal{F} = \sum_{q<\frac{1}{a}} & \frac{1}{2} \Big\{ (J - \frac{\kappa^2\gamma^2}{\sigma}) q^2 + \frac{\kappa^3\gamma^2}{\sigma^2} q^4 \\ & + \frac{1}{a^2}(T-4J) \Big\} m_q m_{-q} \\ & + \frac{T}{12a^2} \sum_{q_1 q_2 q_3} m_{q_1} m_{q_2} m_{q_3} m_{-(q_1+q_2+q_3)} \\ & - \frac{1}{a^2} \Big(-H + \frac{1}{2\beta} \ln \frac{Z(+)}{Z(-)} \Big) m_0 \end{aligned} \qquad (16)$$

where m is magnetization and a is the microscopic cutoff. Equation (16) describes a Landau–Ginzburg model. When chain length is allowed to vary, it explores sections in two different regions of the phase diagram; reference will be made to the *Ising domain* for $L < L_{\mathrm{B}}$ and to the *Brazovskii domain* for longer chains ($L > L_{\mathrm{B}}$). This result stresses the relevant role of chain length in determining the real phase behaviour of the system [13,22,31,45].

3.2.1 Ising domain

When $L < L_{\mathrm{B}}$, the coefficient of the term $m_q m_{-q} q^2$ is positive and the free energy is reduced to an Ising model. When defining the quantities $a_2(L,T) \equiv T - 4J$ and $B(T,L) \equiv -H + \frac{1}{2\beta} \ln \frac{Z(+)}{Z(-)}$, a first order transition line is obtained for

$$a_2 < 0; \quad B = 0 \qquad (17)$$

and a critical point exists at $a_2 = B = 0$.

In the present case, a physical line, which corresponds to a specific system, is generated in the phase diagram by fixing chain length. In Figure 1 each line is a path of increasing temperature for a fixed value of L.

The first order (Ising) transition occurs from a conformationally ordered phase to a disordered one (*main transition* [4,6]) at the critical temperature given by the solution of $B = 0$:

$$T^* = \frac{2H}{\ln \frac{Z(+)}{Z(-)}} \cdot \qquad (18)$$

Furthermore, phase transition occurs only when L is greater than a *critical length* L^*. In fact, since at T^* the condition $a_2 < 0$ must be satisfied, the following relation is immediately written:

$$L^* = \frac{T^*}{4j_0} \cdot \qquad (19)$$

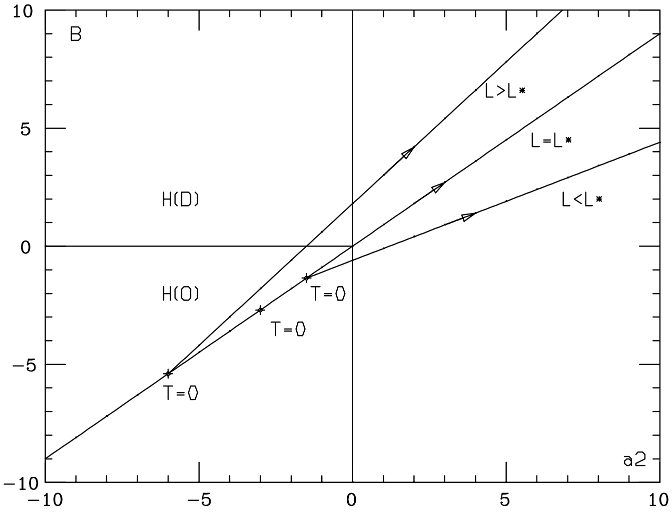

Fig. 1. Closed systems - Ising domain; each line represents a system of components with fixed chain length L. Arrows indicate increasing temperatures. The critical length L^* ($a_2 = 0$, $B = 0$) selects between 1) $L > L^*$: systems with first order transition between phases with uniform curvature and conformational order/disorder, and 2) $L < L^*$: systems with no phase transitions.

Furthermore, from equation (18) the behaviour of transition temperature with chain length is obtained: $T^* = T_\infty + \frac{a}{L} + \frac{b}{L^2} + \cdots$. This result is consistent with chain length behaviour of $\log\frac{Z(+)}{Z(-)}$ (linear in L with exponentially small corrections) and $H = h_0 L \arctan L$; the latter leading to negative corrections. The coupling $J = j_0 L$ gives, instead, equation (19). It must be stressed that subdominant terms in T^* expansion derive essentially from the chain length dependence of chain-chain interaction parameters.

These results are in accordance with experiments. Latent heat at main transition has been observed to vanish for L below a critical value [22]; the predicted behaviour of T^* with chain length can fit experimental data. For example, observed inverse transition temperatures of PC [6,7,46], are represented by: $\beta^* = \beta_\infty + \frac{a}{L} + \frac{b}{L^2}$ where $T_\infty = 400$ K [7], $a = 0.0015$, $b = 0.15$.

Transitional heat and the entropy jump are also evaluated. In the Ising domain, the entropoy jump is essentially due to internal degrees of freedom (for uniform magnetization, differential operators containing elastic constants are removed). The evaluation of ΔS involves the entropy of the classes $S = +1$ and $S = -1$. The following relation is obtained: $\Delta S = k_{\mathrm{B}} m \beta^2 \frac{\partial}{\partial\beta}[\frac{1}{\beta}\ln\frac{Z(+)}{Z(-)}]$. This means a dominantly linear dependence of ΔS on chain length, independent of the values of the exponents α and χ. This result agrees with experimental data by several authors [7,46]; for instance, the entropy jumps reported by Kimura *et al.* result from the expression $\Delta S = -0.01675 + \frac{L}{400} + \frac{0.13905}{L} - \frac{1.095}{L^2}$ (kcal/mol K).

3.2.2 Brazovskii domain

When $L > L_{\mathrm{B}}$ the coefficient of the term $q^2 m_q m_{-q}$ in (16) becomes negative; the free energy defines a Brazovskii model, in which modulated phases are predicted [9,21,42,43]. The most favoured wave vector for the modulation can easily be calculated:

$$q^* = \left|\frac{D}{2C}\right|^{1/2} \tag{20}$$

where $D = J - \frac{\kappa\gamma^2}{\xi^2}$ and $C = \frac{\kappa\gamma^2}{\xi^4}$.

In order to discuss the phase diagram, the following rescaled quantities are defined (by analogy with Leibler's procedure [9]): $h = (\frac{3D^2}{2TC})^{1/2} B$ and $\epsilon = (\frac{2C}{D^2}) a_2$. Notice that ϵ is an absolute quantity. On writing explicitly the dependence of rescaled quantities on phenomenological parameters and chain length (in particular, $\kappa = \kappa_0 L^3$ and $\gamma = \gamma_0$ independent of L), the following equations are obtained:

$$\epsilon(T,L) = A\Big[\frac{L^5}{(L_{\mathrm{B}}^4 - L^4)^2}\Big](T - T^*\frac{L}{L^*})$$

$$h(T,L) = \frac{1}{2L}\ln\frac{Z(+)}{Z(-)}\sqrt{\frac{3}{AT}}\frac{|L_{\mathrm{B}}^4 - L^4|}{L^{\frac{3}{2}}}(T - T^*) \tag{21}$$

where:

$$A = \frac{2}{\kappa_0\gamma_0^2 a^2}\cdot \tag{22}$$

Note that T^* and L^* — respectively the main transition temperature equation (18) and the associated critical length equation (19) — are determined by phenomenological parameters appearing in formation energy and are independent of system elasticity.

As in the Ising case, the phases available to a specific system are determined by a line, generated by fixing the value of L in the above expressions. The task here is to represent the path of increasing temperature for fixed values of L in the (ϵ, h) plane, where transition lines of the Brazovskii model are drawn (see Fig. 2).

For low temperatures, both ϵ and h are negative and the physical point lies in the ordered phase. Near T^* (weak field), the sign of ϵ depends on the ratio L/L^*; we are interested in the case $L^* < L_{\mathrm{B}}$. With such a choice, physical systems with $L \simeq L_{\mathrm{B}}$ exhibit a first order transition between phases with uniform curvature, described either in the Ising domain $L^* \le L \le L_{\mathrm{B}}$, or in the Brazovskii one. In the latter case, the parameter ϵ takes a very negative value at the transition temperature T^* and the physical line crosses the $h = 0$ line. By increasing L, this behaviour is maintained for all the systems with $L < \bar{L}$, where $\bar{L}$ is such that $\epsilon(T^*, \bar{L}) = -4.45$ (the critical value for the existence of modulated phases in the Brazovskii model, as discussed by Leibler and Andelmann [9]). All the physical lines with $L > \bar{L}$ cross the region of modulated phases; then all these systems exhibit a modulated phase between the homogeneous ones (which have uniform curvature). This result agrees with the observation of ripple phases disappearing for short chain lengths [13].

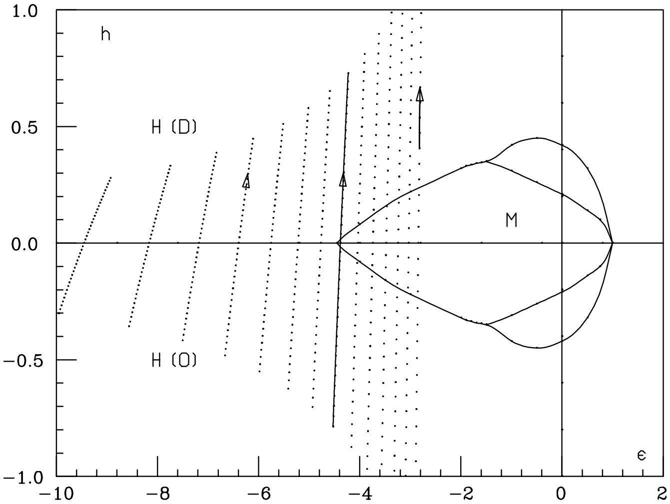

Fig. 2. Closed systems - Brazovskii domain; dotted lines represent systems with $L > L_{\mathrm{B}} > L^*$ (see text). Calculation with $L^* = 5$, $T^* = 300(\mathrm{K})$, $L_{\mathrm{B}} = 10$, $A = 50$; lines are reported for $17 \leq L \leq 30$; temperature increases as arrows show. The adimensional quantity ϵ, calculated at $h = 0$, takes the critical value $\bar{\epsilon} = -4.45$ at $\bar{L} = 24$ (full line). Lines with $L < \bar{L}$ cross the $h = 0$ axes (order/disorder transition between phases with uniform curvature); lines with $L > \bar{L}$ cross modulated phase region.

The value of $\bar{L}$ and the width (in temperature) δ of the existence range for the modulated phase as a function of chain length, can be estimated from equations (21) and, by inspection, from Figure 2; the function $\delta(L)$ is reported in Figure 3. Both $\bar{L}$ and δ depend on the values of elastic constants in the calculation. Such quantities have been evaluated by using available experimental data for bending rigidity and spontaneous curvature. Quoted values of κ [47] range from $25k_{\mathrm{B}}T$ (bilayers in water) to $0.5k_{\mathrm{B}}T$ (microemulsions); in the present case, lower values are significant because the model is applied to monolayers. In the calculation $\kappa \simeq 1k_{\mathrm{B}}T$ was used; moreover it was assumed that $\gamma_0 a \simeq 1$.

Consistently, $\bar{L} \simeq 24$ is obtained. The width δ of the modulated phase range of existence decreases with chain length as $L^{-5/2}$ for large L (Fig. 3).

It is worth commenting on the choices made $\gamma_0 a \simeq 1$ and $\chi = 0$.

In this case the physical curvature γ_{phys} of the surface is inversely proportional to head size a. In particular, $\gamma_{\mathrm{phys}} = \gamma_0 m$, where m is the mean value of the spin. Since $m \sim 10^{-1} \div 10^{-2}$ for temperatures of interest (see for example the calculation by Dawson [48,49]), the physical radius of curvature $R_{\mathrm{phys}} = \frac{1}{\gamma_0 m} \simeq 10a \div 10^2 a$ is obtained. This value is equal to the value of the persistence length calculated for a surface with bending rigidity $\kappa \simeq k_{\mathrm{B}}T$. In fact, the relation between persistence length ξ and the microscopic cutoff a (as defined by de Gennes and Taupin *e.g.* in Ref. [50]) implies $\xi_k \simeq 10a \div 10^2 a$. (This value is very sensitive to the value of the rigidity constant; see for instance the discussion by Taupin [51] or Sornette and Ostrowsky in Ref. [3], Ch. 5.) Even if there is no direct relation between radius of curvature and persistence length, their comparison is suggested by the condition usually written for persistence length, that is: $\langle \mathbf{n}(0) \cdot \mathbf{n}(\xi) \rangle \leq e^{-1}$ ($\mathbf{n}$ is the normal to the surface). The same condition is, in fact, verified if we consider the normals to a surface with mean radius of curvature R at two sites which are a distance of order R apart.

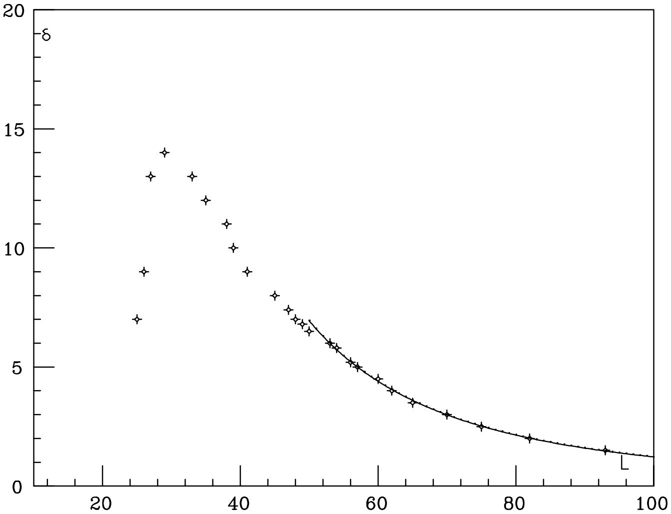

Fig. 3. Width in temperature δ of the existence range for modulated phases as a function of chain length; cross points from calculation of Figure 2; the behaviour with large L (full line) is $\delta \sim L^{-5/2}$.

4 Results for open systems

In the previous section the thermodynamic behaviour of a system in the approximation of fixed number of constituents was analysed; when the exchange rate of material between surface and reservoir is low, such a constraint has to be removed.

In order to account for a variable number of constituents, the formation energy is written as an integral over a varying area [39]. Even in the simplest case in which $J = 0$ (non–interacting tails, essentially conformational formation energy), the coupling between conformational and elastic degrees has to be included. Such a coupling comes from the varying area, namely from the term $\{h(\mathbf{s}(x)) + HS(x)\}\sqrt{1 + (\nabla f)^2}$.

The resulting model is studied by summing over conformational variables (spin classes), and an elastic Hamiltonian is obtained where coefficients are changed with regard to the "bare" ones. In this way, the connection between internal degrees and curvature instability can be explicitly shown.

The total Hamiltonian (with $\gamma(S(x)) = \gamma S(x)$ and $J = 0$) is written as:

$$H_{\mathrm{tot}} = \sum_x \left\{ \frac{1}{2}\kappa c^2(f) - \kappa\gamma c(f) S(x) + \sigma + h(\mathbf{s}(x)) + HS(x) \right\} \times \sqrt{1 + (\nabla f)^2} \qquad (23)$$

where $c(f) = \left\{\boldsymbol{\nabla} \cdot \frac{\boldsymbol{\nabla} f}{\sqrt{1+(\nabla f)^2}}\right\}$.
By varying coefficients H and γ, two main cases, corresponding to different physical systems, may be considered.

4.1 Buckling instability

The condition $\gamma = 0$ and $H = 0$ is assumed in equation (23). In this case, spontaneous curvature does not depend on conformational degrees, due to very large head size in comparison with tail section; in such a situation lateral pressure cannot arise.
The direct sum over conformational states is available. Noting that:

$$\sum_{\mathbf{s}(1)} \cdots \sum_{\mathbf{s}(N)} \mathrm{e}^{-\beta'(1)h(\mathbf{s}(1))} \ldots \mathrm{e}^{-\beta'(N)h(\mathbf{s}(N))} = \prod_x \mathrm{e}^{\ln Z(\beta'(x))} \tag{24}$$

where $\beta'(x) \equiv \beta\sqrt{1+(\nabla f)^2}$ and expanding the quantity $\ln Z(\beta')$ up to the fourth order in f, the effective Hamiltonian becomes:

$$\begin{aligned} H_{\text{eff}} = {} & \frac{1}{2}\kappa(\nabla^2 f)^2 + \frac{1}{2}[\sigma - \frac{\partial \ln Z(\beta)}{\partial \beta}](\nabla f)^2 \\ & + \frac{1}{8}[-\sigma + \frac{\partial \ln Z(\beta)}{\partial \beta} - \beta\frac{\partial^2 \ln Z(\beta)}{\partial \beta^2}](\nabla f)^4 \\ & + \frac{\kappa}{4}(\nabla^2 f)^2(\nabla f)^2 - \frac{1}{\beta}\ln Z(\beta). \end{aligned} \tag{25}$$

A Helfrich-like Hamiltonian whose coefficients depend on the conformational partition function is obtained. In particular, after summation, a surface tension term is found, even if no term of such a kind was included in the bare Hamiltonian. This result recalls the relevance of tension in a Renormalization Group analysis [39,41,52,53].

At high temperatures, the surface is stable against ripples production because surface tension is positive, independently of the sign of σ. This is due to the dominant contribution of *internal* conformational energy $(\frac{-\partial \ln Z}{\partial \beta})$. At low temperatures, instead, buckling instability and ripples production are a consequence of choosing $\sigma < 0$.
A negative value for σ is physically meaningful for those systems which have vanishing surface tension; this fact has been observed in certain systems of surfactants and amphiphilic membranes. According to Sornette and Ostrowski [47], the origin of such a null value for the macroscopic observable is pointed out when a negative bare surface tension is considered, which is increased by logarithmic corrections coming from renormalization. The same corrections have been obtained by David and Leibler [39] for fluctuating membranes in different regimes. Milner [37] has shown that Langmuir monolayers with a very small – or even negative – surface tension exhibit surface instability when subjected to external pressure.
Regarding Hamiltonian (25), the $(\nabla f)^4$–term is positive at low temperatures for $\sigma < 0$; this guarantees the physical meaning of the truncation of the Hamiltonian at the four-th order (independently of the sign of the $(\nabla f)^2$–term). On the contrary, with $\sigma > 0$, the $(\nabla f)^4$–term is systematically negative, thus a truncation at the four-th order is not significant and higher–order terms must be considered.
The chain length dependence of this kind of instability is analogous to the one found for closed systems in the Ising domain (Sect. 3). A critical temperature T^* will exist, which distinguishes between two regimes (ripples production and tension generation); such a temperature will be independent of L in the zero order approximation $\sigma = \sigma_0 L$; the subdominant terms in σ will generate $1/L$ corrections to T^*.

It is interesting that an open physical system, which at low temperatures tends to increase its own surface and at high temperatures generates a positive tension against surface increase, is realized with a cellular membrane.

4.2 Curvature instability

The case with $\gamma \neq 0$ and $H \neq 0$ will now be considered. Molecules whose head size is comparable with the tail section are being dealt with; curvature is a function of conformational classes and, possibly, there is lateral pressure. A more complicated scenario arises because one has to reconsider the restricted partition functions Z_{S_I} over the set of states belonging to the conformational classes S_I. If the relation $\sum_{\mathbf{s}(x)\in S(x)} \mathrm{e}^{-\beta h(\mathbf{s}(x))\sqrt{1+(\nabla f)^2}} = Z_{S(x)}(\beta')$ is used and the sum over spin variables is performed, the following expression is obtained for the total Hamiltonian of the two–level model:

$$\begin{aligned} H_{\text{tot}} = \sum_x \Big\{ & (\frac{1}{2}\kappa c^2(f) + \sigma)\sqrt{1+(\nabla f)^2} \\ & + \Big[(-\kappa\gamma c(f) + H)\sqrt{1+(\nabla f)^2} - \frac{1}{2\beta}\ln\frac{Z_+(\beta'(x))}{Z_-(\beta'(x))}\Big] \\ & \times S(x) - \frac{1}{2\beta}\ln[Z_+(\beta'(x))Z_-(\beta'(x))]\Big\}. \end{aligned} \tag{26}$$

By summing over classes and expanding $\ln Z_\pm(\beta')$ up to Gaussian order in f, a Helfrich-like effective Hamiltonian is obtained, in which the quadratic term reads:

$$\begin{aligned} \mathcal{H}_{\text{eff}} = \frac{1}{4}\Big\{ & -\tanh(y)\Big[\dot{u}_+(\beta) - \dot{u}_-(\beta) - 2H\Big] \\ & - \Big[\dot{u}_+(\beta) + \dot{u}_-(\beta)\Big] + 2\sigma\Big\}(\nabla f)^2 \\ & + \frac{1}{2}\Big[\kappa - \kappa^2\gamma^2\beta\cosh^{-2}(y)\Big](\nabla^2 f)^2 + \cdots \end{aligned} \tag{27}$$

where

$$y \equiv \frac{1}{2}[u_+(\beta) - u_-(\beta)] - \beta H \quad ; \quad \dot{u}_\pm(\beta) \equiv \frac{\partial \ln Z_\pm}{\partial \beta} \cdot \tag{28}$$

Furthermore a linear term in the form $-(\gamma\kappa\nabla^2 f)\tanh(y)$ is obtained.
The peculiar dependence of linear and quadratic terms on temperature allows the interpretation of two phenomena

of great interest: shape transition and curvature instability.

Shape transition is due to the switching of conformational degrees of freedom in the linear term of $\mathcal{H}_{\rm eff}$. This acts as a source of spontaneous curvature with a temperature–dependent coefficient. In particular, the function y changes sign if chains are thermally excited to states with large transversal width. More precisely, by considering the probabilities P_+ and P_- to have a free chain in the classes $(+)$ and $(-)$ respectively (in presence of the external field H), one can see that $\tanh(y) = P_+ - P_-$, and the coefficient of the linear term changes sign ($y = 0$; $P_+ = P_-$) at a temperature T^* which is again given formally by equation (18).

It is worth observing that this kind of instability cannot be corrected. In the model there is no term, with the role of a shear term, that allows us to apply the same argument as that used by Peliti and others in order to stabilize the flat phase [54–56]. This implies that a Renormalization Group procedure will not destroy the effect of the source of curvature.

For these reasons we maintain that T^* distinguishes between two phases with opposite curvature: a shape transition occurs.

The quadratic part of the Hamiltonian will now be considered.

The effective rigidity coefficient can be recognized

$$\kappa_{\rm eff} = \kappa\Big(1 - \beta\kappa\gamma^2\cosh^{-2}y\Big) \tag{29}$$

which is generally reduced, for all temperatures, with respect to the "bare" quantity κ. This means that the persistence length is generally reduced too (the surface is thus more "crumpled" [50]). Such a reduction of the bending rigidity, due to an integration over internal degrees of freedom, agrees with known results by Leibler [23] and other authors (see for instance Peliti in Ref. [57]).

The minimum value of $\kappa_{\rm eff}$ is reached at T^*, where shape transition occurs ($y = 0$).

At T^*, the sign of $\kappa_{\rm eff}$ depends on chain length; the following expression is obtained:

$$\frac{\kappa_{\rm eff}}{\kappa} = 1 - \frac{\kappa_0\gamma_0^2 L^{\alpha-2\chi}}{T^*} \tag{30}$$

which is negative if

$$L^{\alpha-2\chi} > \frac{T^*}{\kappa_0\gamma_0^2} \equiv \tilde{L}^{\alpha-2\chi}. \tag{31}$$

For $T = T^*$ and $L > \tilde{L}$, the surface is highly critical, due to contemporary occurrence of shape transition and *curvature instability.*

The value of rigidity is negative for a whole region $L > \tilde{L}$ and T around T^*. This can be seen by studying equation (29) in the (L, T) plane. In Figure 4, the region of negative rigidity is drawn for the case $\tilde{L} = 50$; in this calculation $\alpha = 2.5$ and $\chi = 1$ were used in the expressions of κ and γ. The width of such region on the temperature scale depends on chain length and decreases for large L as $\frac{\ln L}{L}$. The maximum width is $D \simeq 0.05T^*$.

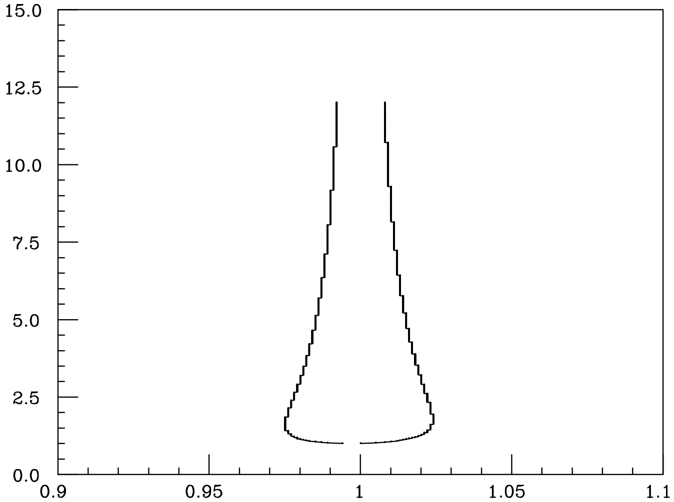

Fig. 4. Open systems: the region of curvature instability in the $(\frac{L}{\tilde{L}}, \frac{T}{T^*})$ plane (T^* is the shape transition temperature and $\tilde{L}$ is the minimum length for which such a transition occurs). With $\tilde{L} = 50$, the region reaches the maximum width $D \simeq 0.05T^*$.

The role of conformational disorder in reducing the value of $\kappa_{\rm eff}$ is clear from equation (29); in fact, roughly speaking, $\cosh^{-2}(y) = \frac{1}{4}P_+P_-$ may be read as the probability of finding different classes at adjacent sites.

When the system is near critical temperature T^*, the equality $P_+ = P_-$ holds and the formation energy does not distinguish between the classes $(-)$ and $(+)$. In these conditions, highly disordered background surfaces prevail for entropic reasons. As a consequence, the shape of the physical surface contains *ab initio* modulations at any length. In equation (27) the effect of such a background disorder is recognizable because, when $k_{\rm eff} < 0$, the Hamiltonian is not limited from below. Since in the same region, the coefficient of $(\nabla f)^2$ is positive ($\sigma_{\rm eff} > 0$), any modulation with $q^* > \sqrt{\frac{\sigma_{\rm eff}}{\kappa_{\rm eff}}}$ makes the energy decrease.

This is a different kind of instability from the one generating rippled structures (modulated phases of closed systems and buckling instability). In that case, the Hamiltonian provides a finite characteristic length $\lambda = \frac{2\pi}{q^*}$, which corresponds to a minimal energy modulation. Here, on the contrary, a minimal energy modulation does not exist and it is necessary to consider quartic terms in order to get a physically meaningful Hamiltonian. For example, the term $(\nabla f)^2(\nabla^2 f)^2$ drives the surface of minimal energy towards local curvature maximization and area minimization. This behaviour may be identified with a phenomenon of *spontaneous generation of curvature*, which describes dramatically disordered surface profiles.

Since an open system is studied, and since the quadratic term of the Hamiltonian is not positive defined, the physics of the system would be better understood with a critical–dynamics analysis. In its work about membranes with intercalated particles, Leibler has found an analogous scenario: equation (27) recalls the effective unstable Hamiltonian studied in reference [23]. In that case it is shown that the coupling between density fluctuations and curvature modes may completely destabilize the flat phase. As discussed by the author, the result is very interesting, especially with regard to shape modifications of cell membranes (echinocytosis).

5 Conclusions

The flexibility of surface constituents is represented as a process of generation of conformational defects in a polymer chain; as a consequence, it is possible to prove the existence of the main temperature T^*, around which various configurational transitions of the system may occur. The value of T^* is determined by the balance between two terms representing the external field in the formation Hamiltonian. The first term comes from the packing energy required to realize a given configuration of the surface; the second is essentially the entropic contribution from the multiplicity of chain conformations compatible with each of such configurations. This result is very general. Its formalization is simple in a two–level model and the generalization to systems of multi–value spins is realistic. In fact, for any partition into steric classes, the conformational contribution to the formation Hamiltonian will affect the external fields only.

At T^* temperature, the generation of conformational disorder may jump, due to the interaction term in the formation energy, and may compete with the existence of extended elastic deformations (which cannot be reduced to small fluctuations of the uniform curvature). The system becomes critical, as happens in the main transition or in transitions to modulated phases, or even in the presence of spontaneous generation of curvature. The length of the flexible section of constituents controls the criticalities of the system. This is essentially due to different scaling laws of the chain length dependent terms appearing in the Hamiltonian.

These results have been obtained in a minimal-coupling picture for flexibility. In fact, interactions between chains at different sites appear uniquely in the formation term, while no such coupling has been imposed in the fluctuation term. Moreover, only the spontaneous curvature has been explicitly required to depend on steric classes.

If the model were extended to membranes, we think it would be more realistic to write the spontaneous curvature as a function of nearest neighbours' conformations (for example, facing sites in the membrane bilayer must have spontaneous curvatures correlated). We expect the predictivity of the model to be quite similar to the present one.

A different situation would arise if the bending rigidity were required to depend on conformational classes. In this case, the summation over conformational (or over elastic) degrees would generate a propagator which depends on the elastic (conformational) field. This means that the effective Hamiltonian would have a strong non–local nature; the vertices with derivative character coming from the propagator inversion would be of arbitrary order both in fields and in derivatives (but with a constant canonical dimension). Therefore, in this case, the extension of the model would require a perturbative analysis in the κ parameter for an adequate description.

References

1. E. Evans, K.R. Skala, *Mechanics and Thermodynamics of Biomembranes* (CRC., Press Boca Raton, 1980).
2. *Statistical Mechanics of Membranes and Surfaces, Jerusalem Winter School for Theoretical Physics, Jerusalem 28 Dec. 87 – 6 Jan 88*, edited by D. Nelson, T. Piran, S. Weinberg (World Scientific, 1989).
3. *Micelles, Membranes, Microemulsion and Monolayers*, edited by W.M. Gelbart, A. Ben-Shaul, D. Roux (Springer, Berlin, 1993).
4. J.F. Nagle, J. Chem. Phys. **58**, 252 (1973).
5. S. Marčelia, Biochimica et Biophysica Acta **367**, 165 (1974).
6. S. Doniach, J. Chem. Phys. **68**, 4912 (1978); ibid. **70**, 4587 (1979).
7. A. Caillè, D. Pink F. De Verteuil, M.J. Zuckermann, Can. J. Phys. **58**, 581 (1980).
8. S. Leibler, *Equilibrium Statistical Mechanics of Fluctuating Films and Membranes", Statistical Mechanics of Membranes and Surfaces, Jerusalem Winter School for Theoretical Physics, Jerusalem 28 Dec. 87 – 6 Jan 88*, edited by D. Nelson, T. Piran, S. Weinberg (World Scientific, 1989), p. 46.
9. S. Leibler, D. Andelmann, J. Phys. France **48**, 2013 (1987).
10. H. Kodama, S. Komura, J. Phys. II France **3**, 1305 (1993).
11. Z.G. Wang, J. Chem. Phys. **99**, 4191 (1993).
12. T. Kawakatsu, D. Andelmann, K. Kawasaki, T. Taniguchi, J. Phys. II France **3**, 971 (1993).
13. K. Honda, H. Kimura, J. Phys. Soc. Jpn **60**, 1212 (1991).
14. C.M. Chen, T.C. Lubensky, F.C. MacKintosh, Phys. Rev. E **51**, 504 (1995).
15. T.C. Lubensky, F.C. MacKintosh, Phys. Rev. Lett. **71**, 1565 (1993).
16. T.M. Fisher, J. Phys. II France **2**, 327 (1992).
17. P. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969).
18. W. Helfrich, J. Phys. France **46**, 1263 (1985); Z. Naturforsh **A33**, 305 (1978); ibid. **28c**, 693 (1973).
19. M. Blume, V.J. Emery, R.B. Griffiths, Phys. Rev. A **4**, 1071 (1971).
20. see also G. Gompper, M. Schick, *Self–assembling Amphiphilic Systems, Phase Transitions and Critical Phenomena*, Vol. **16**, edited by C. Domb, J.L. Lebowitz (Academic Press, London, 1994), p. 22
21. S.A. Brazovskii, Zh. Eksp. Teor. Fiz. **68**, 175 (1975); Sow. Phys. JETP **41**, 85 (1975).
22. D.C. Wack, W.W. Webb, Phys. Rev. Lett. **61**, 1210 (1988).
23. S. Leibler, J. Phys. France **47**, 507 (1987).
24. M.V. Volkenstein, *Configurational Statistics of Polymeric Chains* (Interscience, New York, 1963).
25. B. Bassetti, V. Benza, P. Jona, J. Phys. France **51**, 259 (1990).
26. B. Bassetti, G. Mazzoletti, P. Jona, J. Phys. I France **5**, 1161 (1995).

27. J.N. Israelachvili, D.J. Mitchell, B.W. Ninham, J. Chem. Soc. Faraday Trans. **72**, 1525 (1976); Biochim. Biophys. Acta **470**, 185 (1977).
28. D.J. Mitchell, B.W. Ninham, J. Chem. Soc. Faraday Trans. **77**, 601 (1981).
29. J.N. Israelachvili, S. Marcelja, R.G. Horn, Quart. Rev. Biophys. **13**, 121 (1980).
30. J.N. Israelachvili, *Thermodynamic and Geometric Aspects of Amphiphile Aggregation into Micelles, Vesicles and Bilayers, and the Interactions between them, in "Physics of Amphiphiles: Micelles, Vesicles and Microemulsions", Varenna, Italy, 19–29 July 1983*, edited by V. DeGiorgio, M. Corti (North Holland, 1985).
31. J.M. Carlson, J.P. Sethna, Phys. Rev. A **36**, 3359 (1987).
32. F. David, *Geometry and Field Theory of Random Membranes, Statistical Mechanics of Membranes and Surfaces, Jerusalem Winter School for Theoretical Physics, Jerusalem 28 Dec. 87 – 6 Jan 88*, edited by D. Nelson, T. Piran, S. Weinberg (World Scientific, 1989) 158.
33. S. Alexander, J. Phys. France **38**, 983 (1977).
34. P.G. de Gennes, J. Phys. France **37**, 1443 (1976); Macromolecules **13**, 1069 (1980); C. R. Acad. Sci. Paris **300**, 839 (1985).
35. P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).
36. A.G. Petrov, I. Bivas, Prog. Surface Sci. **16**, 389 (1984).
37. S.T. Milner, J.F. Joanny, P. Pincus, Europhys. Lett. **9**, 495 (1989).
38. S.T. Milner, T.A. Witten, J. Phys. France **49**, 1951 (1988).
39. F. David, S. Leibler, J. Phys. II France **1**, 959 (1991).
40. M. Schick, W.H. Shih, Phys. Rev. Lett. **59**, 1205.
41. L. Peliti, S. Leibler, Phys. Rev. Lett. **54**, 1690 (1985).
42. T. Garel, S. Doniach, Phys. Rev. B **26**, 325 (1982).
43. D. Andelmann, F. Brochard, J.F. Joanny, J. Chem. Phys. **86**, 3673 (1987).
44. J.V. Selinger, Z.-G. Wang, R.F. Bruinsma, C.M. Knobler, Phys. Rev. Lett. **70**, 1139 (1993).
45. R.E. Goldstein, S. Leibler, Phys. Rev. Lett. **61**, 2213 (1988); Phys. Rev. A **40**, 1025 (1989).
46. H. Kimura, H. Nakano, J. Phys. Soc. Jpn **43**, 1477 (1977).
47. D. Sornette, N. Ostrowsky, *Lamellar Phases: Effect of Fluctuations, Micelles, Membranes, Microemulsion and Monolayers*, edited by W.M. Gelbart, A. Ben-Shaul, D. Roux (Springer, Berlin, 1993) p. 251; see also: *Interactions between non–ionic vesicles. Importance of the aliphatic–chain phase transition, in "Physics of Amphiphiles: Micelles, Vesicles and Microemulsions", Varenna, Italy, 19–29 July 1983*, edited by V. De Giorgio, M. Corti (North Holland, 1985).
48. K.A. Dawson, Phys. Rev. A **36**, 3383 (1987).
49. K.A. Dawson, M.D. Lipkin, J. Chem. Phys. **88**, 5149 (1988).
50. P.G. de Gennes, C. Taupin, J. Phys. Chem. **86**, 2294 (1982).
51. C. Taupin, *New Ideas for microemulsion structure: the Talmon–Prager and De Gennes models, in "Physics of Amphiphiles: Micelles, Vesicles and Microemulsions", Varenna, Italy 19–29 July 1983*, edited by V. De Giorgio, M. Corti (North Holland, 1985).
52. D. Forster, Phys. Lett. **114A**, 115 (1986).
53. H. Kleinert, Phys. Lett. **114A**, 263 (1986).
54. D.R. Nelson, L. Peliti, J. Phys. France **48**, 1085 (1987).
55. E. Guitter, F. David, S. Leibler, L. Peliti, J. Phys. France **50**, 1787 (1989).
56. F. David, E. Guitter, L. Peliti, J. Phys. France **48**, 2059 (1987).
57. L. Peliti, Physica **140A**, 269 (1986).