

One-Dimensional Hamiltonian for Columnar Liquid Crystals

R. D'hulst¹ and A. Caillé¹

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A one-dimensional Hamiltonian is derived upon microscopic considerations to model the columnar phases of a liquid crystal made of molecules of discrete rotational symmetry. The study deals with the ground state of this Hamiltonian, only the orientational degrees of freedom being taken into account. The intracolumnar interaction is described by the natural cantedness of an isolated column, while interaction parameters H and G characterize the amplitude of the local crystal field at a site originating from the other surrounding columns. The phase diagrams of the orientational ordering along the column are numerically investigated and a previous analytical approach is briefly recalled. A new perturbation development is proposed. This allows us to analyse a multiphase point and to explain the appearance of an infinity of phases in the vicinity of this point. The anisotropy of the columnar lattice is then investigated with the use of the same perturbation development, and some of the properties of a complex phase diagram are examined numerically as well as analytically.

KEY WORDS: Commensurate incommensurate transition; discontinuity.

I. INTRODUCTION

The liquid crystal state is an intermediate state of aggregation between the perfect crystalline solid and the amorphous liquid states.⁽¹⁾ From a macroscopic point of view, it implies a hydrodynamic theory based upon 6 to 8 hydrodynamic variables.⁽²⁾ However, our approach is rather based upon microscopic considerations. The perfect crystalline solid state is characterized by long-range order, which means that the knowledge of one

¹ Centre de Recherche en Physique du Solide et Département de Physique, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1; Thermodynamique des Phénomènes Irréversibles, Université de Liège, 4000 Liège, Belgium; e-mail: alain.caille@umontreal.ca, rdhulst@ulg.ac.be.

elementary cell allows for the entire determination of the static state of the whole crystal. The dynamic enters afterwards as fluctuations around these static locations. Experimentally, the X-ray investigations give sharp Bragg reflections, calling for a density-density correlation function described by a periodic function of the basis vectors. In contrast, for the amorphous liquid state, there is simply no way to express the density pair correlation function except through the mean density. Liquid crystal states appear as intermediate states of matter as, cooling from the amorphous high-temperature liquid phase, the various degrees of freedom arrange themselves progressively, or, heating from the ordered low-temperature crystalline solid phase, the long-range order of various degrees of freedom is progressively washed out by the thermal fluctuations. Progressively means here that not all degrees of freedom order or fall into disorder simultaneously, but the transition from long-range to quasi-long or short-range order is sharp enough to define beyond doubt a transition temperature.⁽³⁾

The columnar liquid crystal state corresponds to a state of long-range positional order in two dimensions and liquid-like order over the positions in the third dimension. A two-dimensional crystalline lattice of liquid columns is a convenient device to picture this state of aggregation.⁽³⁾ More precisely, the constitutive molecules stack one upon the other like plates to form liquid-like columns, no long-range positional order being expected along the columns. These columns are displayed on a regular two-dimensional lattice. As a consequence, the density-density correlation function corresponds to an anisotropic function of the relative positions, periodic in only two dimensions. The so-described phase is usually referred to as a disordered columnar phase. On the other hand, cooling from this high temperature disordered columnar phase, a sharpening in the Bragg reflections may happen, revealing the appearance of some positional order along the columns.⁽⁴⁾ As if this corresponds to a true long-range order or only to quasi-long range order is not yet fully elucidated.⁽⁵⁾ We do not try to answer this question in this work, but concentrate our investigations over these so-called ordered columnar phases. More particularly, the orientational ordering along one column of an ordered columnar mesomorphic phase built up with molecules of discrete rotational symmetry is investigated. This study is motivated by the special case of the rufigallol-n-hexaoctanoate (RHO) which exhibits two different columnar mesophases in an interval of temperature ranging from 95 °C to 127 °C.^(6, 7) The molecules of RHO are characterized by a discrete rotational symmetry, having an axis of rotational symmetry of order two.

No true long-range order being thermodynamically stable at finite temperature in one-dimensional systems for short-range interactions,⁽⁸⁾ it

becomes clear that the interplay between the intracolumnar interactions and the intercolumnar interactions is of fundamental interest. A microscopic hamiltonian is derived to model the influence of the columnar lattice symmetry over the orientational order along one column. Only the first-neighboring interactions both for the intra and the intercolumnar interactions are taken into account. This work is an analysis of the ground state of this hamiltonian. It can be interpreted as a step in the understanding of systems generalizing notions traditionally restricted to magnetic systems.

The outline of this paper is as follow. Section II is devoted to the presentation of the mathematical model and the associated hamiltonians. In Section III, a perfect triangular array of columns is investigated: previous results with dominant intracolumnar interactions are shortly recalled to be compared with the new results presented in the second part of Section III. This second part considers the opposite case where the intercolumnar interactions are dominant. In Section IV, the effect of the lattice anisotropy is introduced and agreement between an analytical and a numerical solution is discussed.

II. THE MODEL

The model is restricted to the consideration of one column assimilated to a one-dimensional lattice, each site being occupied by one molecule. This assumption limits us to the investigation of only the orientational degrees of freedom of the molecules, having in mind that the positional degrees of freedom have ordered at least partially at a higher temperature. As a consequence, the treatment is done at zero temperature. Each molecule is assumed to be represented by a two-dimensional rigid body with an axis of rotational symmetry of order 2, labelled C_2 . This axis is directed perpendicularly to the core of the modelled entity and coincide with the columnar axis. Finally, the so-defined column is supposed to be part of a two-dimensional lattice of identical columns.

The molecules in the investigated column can rotate around their C_2 axis and their angular positions are located by the angular deviation θ_n from a reference direction fixed in the lattice of columns. The influence of this lattice is restricted to the first neighboring columns. With all these assumptions, a method initiated by Heinonen and Taylor⁽⁹⁾ is used to derive a microscopic one-dimensional hamiltonian. The remaining hypotheses are that the array of columns is triangular and that the column under study is under the influence of the averaged field of their six first neighbors. The resulting hamiltonian is

$$H'_N = - \sum_{n=1}^N \cos(2(\theta_n - \theta_{n-1} - A)) + H \sum_{n=1}^N \cos(6\theta_n) \quad (1)$$

with Δ , the natural cantedness of the column, defined as the relative orientation of two succeeding molecules in a column without any interaction with the two-dimensional lattice. H is an interaction parameter, expressing the magnitude of the intercolumnar interaction in unit of the intracolumnar interaction. The sums in Eq. (1) extend over the whole column and periodic boundary conditions are chosen. The r.h.s. of Eq. (1) can be divided into two sums, the value 2 of the argument of the cosine of the first sum being related to the symmetry of the building blocks while the value 6 of the argument of the cosine of the second sum is related to the columnar lattice symmetry. However, to avoid differentiating physically identical configurations, the change of variables $\varphi_n = 2\theta_n$ is suitable, leading to the reduced hamiltonian

$$H'_N = - \sum_{n=1}^N \cos(2(\varphi_n - \varphi_{n-1} - \alpha)) + H \sum_{n=1}^N \cos(r\varphi_n) \quad (2)$$

with the redefinition of the natural cantedness $\alpha = 2\Delta$ and the introduction of a new parameter r , with the particular value $r = 3$ for the purpose of the study of RHO. To extend this study to a more general class of hamiltonians, the value of this argument is most of the time supposed to be any positive integer. Readily, r corresponds to the ratio of the order of the columnar lattice symmetry to the order of the constitutive molecules symmetry.

In the second part of this work, the discrepancy between the real lattices and a perfect triangular lattice of columns is investigated. In fact, the experimental results for RHO rather suggest columns displayed on rectangular lattices distorted for about 10% from perfect triangular arrays.⁽⁶⁾ As a consequence, a uniaxial deformation is locally added to deform continuously the triangular array into a rectangular one. This method reveals the first corrections to Eq. (2) and the hamiltonian

$$H''_N = - \sum_{n=1}^N \cos(2(\varphi_n - \varphi_{n-1} - \alpha)) + H \sum_{n=1}^N \cos(3\varphi_n) - G \sum_{n=1}^N \cos(\varphi_n) \quad (3)$$

seems convenient, with the same change of variables. G corresponds to an intercolumnar interaction parameter in unit of the intracolumnar interaction and the relative signs of H and G are chosen to have both H and G of the same sign for the physical configurations of interest. It is worth mentioning that even if the rectangular array does not depart very much from a triangular one, the contribution of the last term in Eq. (3) can nevertheless be important. As an example, a rather crude estimation of the relative importance of G and H , taking into account the measured

intercolumnar spacings and a van der Waals-like interaction potential gives $G = 4.5H$. This estimation is rather crude because it makes use of three-dimensional and finite temperature results for a one-dimensional model at zero temperature, but the relative scale is certainly meaningful.

To be complete, a short explanation of a commonly-used notation for the different states of the column is required.⁽¹⁰⁾ Suppose we progress along the column following the succeeding molecular orientations, the sign of α defining the direction of rotation. Starting with a given molecular orientation at an arbitrary site n , it may happen that after Q sites, we have made P full rotations around the column and that we are back to the same orientation at site $n + Q$. Taken the minimal integer values of P and Q that respect this property, such as the entire column can be built by joining end to end similar sequences of Q molecules, the corresponding state of the column is called P/Q . In particular, in a P/Q phase, for any value of n ,

$$\varphi_{n+Q} = \varphi_n + 2\pi P \quad (4)$$

The averaged twist of the column $\omega = P/Q$ is called the winding number. This obviously can only be used to describe commensurate phases while for the incommensurate phases, the winding number is an irrational quantity.

III. ONE COLUMN IN A TRIANGULAR ARRAY

As explained in the previous section, the energy of a column in a fictitious field modelling the influence of six equivalent neighboring columns is suitably described by Eq. (2). The phase diagram is numerically investigated with the use of the effective potential method of Griffith and Chou⁽¹¹⁾ and the limits of the phases covering most of the diagram are presented at Fig. 1, with the particular choice $r = 3$. The boundaries of various commensurate phases are determined by the search for minimum energy configurations imposed by intracolumnar constraints and by the intercolumnar interactions with the surrounding columnar lattice. As a result, the interaction parameter H is plotted as a function of the natural angle $\alpha/2\pi$. Note that the axes are limited to H in $[0, 1]$ and $\alpha/2\pi$ in $[0, 1/6]$. From one side, the symmetries of the hamiltonian allow the determination of the entire phase diagram from the knowledge of the diagram for $\alpha/2\pi$ in $[0, 1/2r]$. On the other side, the ordinate scale is sufficient to appreciate the diagram topology as it will be shown afterwards.

Such a phase diagram was already the subject of a lot of researches^(10, 12) and well-known results are recalled. Subsection A is mainly concerned with the $H \ll 1$ limit, and we therefore refer to this limit as the

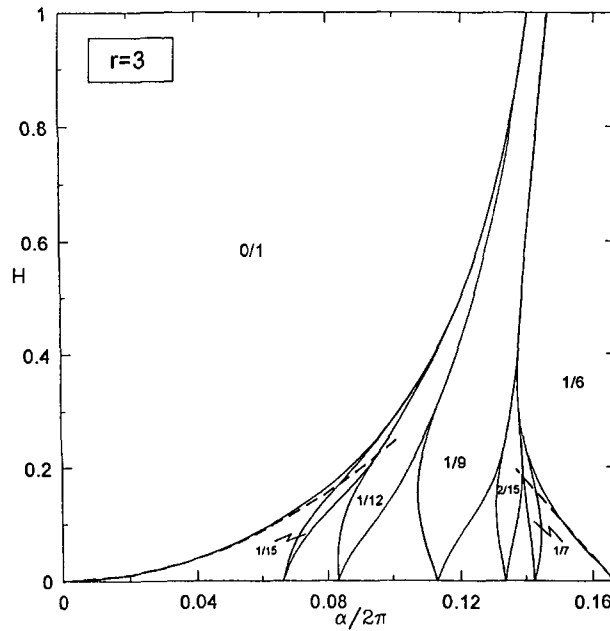


Fig. 1. Phase diagram of a column in a triangular array of columns. The continuous lines are the numerical stability of the phases covering most of the phase diagram. More phases exist in the unnamed spaces between the represented phases, and they can be determined by increasing the numerical accuracy. The two dashed lines correspond to the stability limits of the $0/1$ and the $1/6$ phases, from left to right, as determined by a soliton theory.

weak coupling limit, having in mind that the intracolumnar interactions are dominant. In contrast, the strong coupling limit refers to $H > 1$, implying strong interactions with the columnar lattice.

For all positive integer values of r other than $r = 1$, the numerical phase diagrams corresponding to Eq. (2) are very alike. A first common feature is the existence of an infinity of phases on the straight line $H = 0$, any value of $\alpha/2\pi$ giving the winding number of the ground state corresponding to this point. A second common feature is that at any given value of $H < 1$, all the investigated commensurate phases seems to extend over a space of finite measure in the limit of numerical accuracy. A third common feature is the progressive expansion of r particular phases throughout the phase diagram as H is further increased. Remark that these similarities between phase diagrams corresponding to different values of r are also roughly quantitative. This can be easily pictured by the superposition of many $(\alpha r, r^2 H)$ diagrams for various values of r .⁽¹³⁾ The value $r = 1$ is discussed below.

A. Weak Coupling

The value of r is kept as a positive parameter taking any value in the set of the integer numbers, including the value $r = 1$. In this limit, it seems reasonable to suppose that the configurations of the different phases do not depart much from the ones adopted at $H = 0$. Therefore, one postulates a structure characterized by

$$\varphi_n = 2\pi\omega n + \xi_n + \phi \quad (5)$$

for the P/Q phase with $\omega = P/Q$. The first term on the r.h.s. of Eq. (5) is the free-to-rotate structure solution for $H = 0$; the second term is the deformation introduced by the local crystalline field H , a term vanishing for $H = 0$; and the last term is a constant phase term describing the pinning of the structure to the array of columns. This last term can take any value for $H = 0$, reflecting the rotational symmetry of an isolated column. For $H \ll 1$, it is assumed that the deformation ξ_n stays small. So, the hamiltonian of Eq. (2) reduces to the hamiltonian of Frenkel and Kontorova.⁽¹⁴⁾ Using the continuous limit method initiated by Frank and Van der Merwe⁽¹⁵⁾ and generalized by Theodorou and Rice,⁽¹⁶⁾ the column is now treated as a continuous media. The previously integer variable n is allowed to vary continuously and the sums in Eq. (2) transform into integrals. Allowing the phase angle ϕ defined at Eq. (5) to depend on n , the stability limits of the P/Q phase can be determined. The first instability corresponds to the zero creation energy of an isolated deformation localized over a few sites. Such an entity is called a soliton. The transition from the P/Q configuration to another one is the result of the zero creation energy of a lattice of solitons, which induces the change of commensurability. The scaling behavior of the spread δ of any P/Q phase can be characterized by⁽¹⁷⁾

$$\delta \equiv \left| \frac{\alpha}{2\pi} - \frac{P}{Q} \right| \sim H^e \quad (6)$$

where e is an integer constant related to the P/Q phase in the following way: if Q and r are relative prime integers, $e = Q/2$, otherwise, $e = Q/2r$. Extending to incommensurate phases this result obtained for commensurate phases, it becomes evident that the incommensurate phases extend over a space of zero measure for all values of $H \neq 0$.

The dashed lines starting at $(0, 0)$ and $(1/6, 0)$ in the $(\alpha/2\pi, H)$ phase diagram correspond to the stability limits of the 0/1 and 1/6 phases, respectively. For a more explicit presentation of this treatment and further results, we refer the reader to the original paper of Frank and Van der

Merwe,⁽¹⁵⁾ or, more recently, to the review proposed by P. Bak⁽¹⁷⁾ and other instructive papers on the subject.⁽¹⁸⁾

B. Strong coupling

The effect of the local field H is to pin around r orientations an otherwise free to rotate structure, promoting r commensurate phases. Consequently, the value $r=1$ has to be distinguished. As a matter of fact, the numerical phase diagram obtained for $r=1$ ⁽¹⁰⁾ has a different topology from those obtained for $r \neq 1$, especially for $H > 1$. The difference clearly arises from the lack of competition for $r=1$. Effectively, in this case, above a given value of H , the 0/1 phase is the only remaining ground state for all the α values. In other words, over a critical value of H , the parameter α becomes inefficient. For the sake of clearness, we will restrict temporarily our attention to the particular value $r=3$. As H is increased, all the molecules tend to align with one of the three favoured angular positions and the three commensurate 0/1, 1/3 and 2/3 phases expand progressively throughout most of the phase diagram. At infinite value of H , the ground state solutions have to be built from the three favoured angular positions and this allows the existence of the 0/1 phase in $] -1/6, 1/6[$, the 1/3 phase in $] 1/6, 1/2[$ and the 2/3 phase in $] 1/2, 5/6[$. These are open intervals over $\alpha/2\pi$ values because at the particular points 1/6, 1/2 and 5/6, the 0/1, 1/3 and 2/3 phases are degenerated in pairs. And so is any combination of these degenerated phases. These particular points, where the degeneracy of the ground state is infinite, are called multiphase points.

The first step of our approach is to consider the coexistence of the 1/2 phase with the 1/3 phase, as if these phases were the only ones to exist. From the analytical expressions of the energy of these phases, it can be inferred that the 1/2 phase is never totally hidden by the 1/3 phase: up to infinite value of H , the 1/2 phase is always of lower energy than the 1/3 phase over a finite domain of the phase diagram. This is the proof that up to infinite value of H there remains a space of finite measure in the phase diagram where the ground state is not any of the three favoured phases.

The second step of our approach is based upon general considerations over the configuration of the 1/2 phase: it appears that, as H is increased, the configuration approximately corresponds to the alternation of angular deviations of $2\pi/3$ and $4\pi/3$. Apparently, the 1/2 structure can be correctly described by a racemic mixture of the 1/3 and the 2/3 phases, with an added deformation. More, the 1/2 domain of the phase diagram develops around the vertical line $\alpha/2\pi = 1/2$, which is the line where the 1/3 and the 2/3 phases are degenerated in pair. Therefore, it seems reasonable to suppose that a mixture of the 1/3 and 1/2 phases with an added deformation

should develop around the line where the $1/3$ and the $1/2$ phases are degenerated in pair. Now, going back to any positive integer value of r but $r=1$, the study is restricted to the region $\alpha/2\pi$ in $[0, 1/2r]$. Suppose we start from the multiphase point $(1/2r, \infty)$ in the $(\alpha/2\pi, H)$ phase diagram. The corresponding degenerate ground states can be interpreted as combinations of various sequences of the $0/1$ and the $1/r$ phases. Consider only one type of these configurations: sequences of N sites having parallel alignment, separated by a $2\pi/r$ rotation at their intersite junction. In each sequence, all the molecules are pointing in one of the preferred orientations $\varphi_n = (2k+1)\pi/r$, where k is an integer. To this value of N corresponds a $1/rN$ phase, in the previously explained notation. Notice that this type of configurations was present in the multisoliton solution existing for small values of H : the instability of the ferromagnetic $0/1$ phase, f.i., was the result of the appearance of repeating sequences of $0/1$ phase connected by a continuous and localized variation of the angular orientation.⁽¹⁵⁾ Obviously, when increasing H , the continuous character was no longer valid, calling for the above discontinuous character.

Relaxing from the infinite value of H to a finite value $H \gg 1$, a deformation at each site in is also added to the above identified configurations. Because of the translational invariance of our chosen configurations, the mean energy for a site H_m can be estimated by averaging over N molecules, its expression being:

$$H_m = -\frac{1}{N} \left(\cos \left(\xi_1 - \xi_N + \frac{2\pi}{r} - \alpha \right) + \sum_{n=2}^N \cos(\xi_n - \xi_{n-1} - \alpha) \right) - \frac{H}{N} \sum_{n=1}^N \cos(r\xi_n) \quad (7)$$

The minimization for each ξ_n gives for $n=1$,

$$\sin \left(\xi_1 - \xi_n + \frac{2\pi}{r} - \alpha \right) - \sin(\xi_2 - \xi_1 - \alpha) + rH \sin(r\xi_1) = 0 \quad (8)$$

for $n=2, \dots, N-1$,

$$\sin(\xi_n - \xi_{n-1} - \alpha) - \sin(\xi_{n+1} - \xi_n - \alpha) + rH \sin(r\xi_n) = 0 \quad (9)$$

and for $n=N$,

$$\sin(\xi_N - \xi_{N-1} - \alpha) - \sin \left(\xi_1 - \xi_N + \frac{2\pi}{r} - \alpha \right) + rH \sin(r\xi_N) = 0 \quad (10)$$

The deformations in power of $1/H$ are expressed as

$$\xi_n = \xi_n^{(0)} + \frac{\xi_n^{(1)}}{H} + \frac{\xi_n^{(2)}}{H^2} + \dots \quad (11)$$

The coefficients $\xi_n^{(i)}$ are determined by equating terms of equal order in $1/H$ in the minimization equations [19]. The solutions are functions of N and are obtained for $r=3$ and $N=2, 3$ and 4. Restricting the diagram to the corresponding $1/6$, $1/9$ and $1/12$ phases and the $0/1$ phase, their boundary lines are reported as dashed-dotted lines on Fig. 2. The full lines corresponds to the numerical stability limits of these phases obtained with the effective potential method of Chou and Griffith.⁽¹¹⁾ As examples, the mean energy for a site for the $1/6$ phase up to the first order in $1/H$ is

$$\varepsilon_{1/6} = -H = \frac{1}{2} \cos(\alpha - \pi/3) - \frac{1}{6H} \cos^2(\alpha - \pi/3) \quad (12)$$

while the mean energy for a site for the $1/9$ phase up to the second order in $1/H$ is

$$\begin{aligned} \varepsilon_{1/9} = & -H - \frac{1}{3} (2 \cos \alpha + \cos(2\pi/3 - \alpha)) - \frac{1}{9H} \cos^2(\alpha - \pi/3) \\ & + \frac{\sqrt{3}}{81H^2} \sin \alpha \cos^2(\alpha - \pi/3) \end{aligned} \quad (13)$$

The limit of this analysis is clearly associated to the truncated expansion in powers of $1/H$ of the energy. To observe a given phase, it is necessary to push the development to a minimal power of integer value e .

The third step of our work is to generalize the previous development to any value of N keeping r as a free integer parameter, but again excluding the value $r=1$. Similar configurations as above defined are considered: sequences of N aligned molecules, the sequences being separated by an angular deviation of $2\pi/r$ at their intersite junction. All the molecules of one sequence are pointing in one of the favored directions. That is to say

$$\varphi_n = \frac{2\pi i}{r} + \frac{\pi}{r} + \xi_n \quad (14)$$

where i is an integer parameter numbering the successive sequences, and ξ_n corresponds to an added deformation expected to be present as H is

relaxed from infinite value to a finite value, $H \gg 1$. With these structures, succeeding sequences of N molecules define a $1/rN$ phase. Equation (14) is substituted in the hamiltonian of Eq. (2) and the energy is minimized as a function of the deformations ξ_n . The result is Eqs. (8), (9) and (10), a system of N coupled equations of N unknowns. Again, the deformation at each site ξ_n is developed in powers of $1/H$, as in Eq. (11). Expanding the minimization equations to the lowest order in $1/H$, we find that

$$\xi_n^{(0)} = 0 \quad \forall n = 1, I, N \quad (15)$$

that

$$\xi_n^{(k)} = \frac{(\xi_{n+1}^{(k-1)} + \xi_{n-1}^{(k-1)}) \cos \alpha}{r^2} \quad (16)$$

is the first non-vanishing term for the n th site and that

$$\xi_1^{(1)} = -\xi_N^{(1)} = -\frac{\sin \alpha + \sin(2\pi/r - \alpha)}{r^2} \quad (17)$$

As consequences of these relations, it becomes obvious firstly that $\xi_n^{(n)}$ is the first nonvanishing term of the power expansion of ξ_n for $n \leq N/2$ for even values of N and for $n \leq (N+1)/2$ for odd values of N . Secondly, the analytical expression for this term is

$$\xi_n^{(n)} = -\frac{(\sin \alpha + \sin(2\pi/r - \alpha)) \cos^{n-1} \alpha}{r^{2n}} \quad (18)$$

Thirdly, if the configuration characterized by $N+1$ is built from the configuration characterized by N by inserting one site in the center of the latter, the deformation associated to the common sites of the two configurations are equivalent up to the order $1/H^{N/2}$ or $1/H^{(N-1)/2}$, if N is even or odd, respectively. It has to be added that the deformation is antisymmetric, that is to say that $\xi_n = -\xi_{N-n+1}$.

We are now ready to express the energy of a $1/r(N+1)$ phase as a function of the energy of the $0/1$ and $1/rN$ phases. In fact, the hypotheses are that the $1/r(N+1)$ phase develops around the degeneracy line of the $0/1$ and the $1/rN$ phases and that the new phase can be interpreted as a mixture of the two latter phases, with an added deformation. Schematically,

$$\text{phase } 1/r(N+1) = \text{phase } 0/1 + \text{phase } 1/rN + \text{deformation} \quad (19)$$

This means that

$$\begin{aligned}
 \varphi_1 &= \frac{\pi}{r} + \varphi_1^{(N)} + \chi_1 \\
 \varphi_2 &= \frac{\pi}{r} + \varphi_1^{(N)} + \chi_2 \\
 &\vdots \\
 \varphi_{N/2} &= \frac{\pi}{r} + \varphi_{N/2}^{(N)} + \chi_{N/2} \\
 \varphi_{N/2+1} &= \frac{\pi}{r} \\
 \varphi_{N/2+2} &= \frac{\pi}{r} + \varphi_{N/2+1}^{(N)} + \chi_{N/2+2} \\
 &\vdots \\
 \varphi_{N+1} &= \frac{\pi}{r} + \varphi_N^{(N)} + \chi_{N+1}
 \end{aligned} \tag{20}$$

are the successive angles of one sequence characterizing the $1/r(N+1)$ phase for the even values of N , while

$$\begin{aligned}
 \varphi_1 &= \frac{\pi}{r} + \varphi_1^{(N)} + \chi_1 \\
 \varphi_2 &= \frac{\pi}{r} + \varphi_2^{(N)} + \chi_2 \\
 &\vdots \\
 \varphi_{(N-1)/2} &= \frac{\pi}{r} + \varphi_{(N-1)/2}^{(N)} + \chi_{(N-1)/2} \\
 \varphi_{(N+1)/2} &= \frac{\pi}{r} - \varphi_{(N-1)/2}^{(N)} + \chi_{(N+1)/2} \\
 \varphi_{(N+3)/2} &= \frac{\pi}{r} + \varphi_{(N+1)/2}^{(N)} + \chi_{(N+3)/2} \\
 &\vdots \\
 \varphi_{N+1} &= \frac{\pi}{r} + \varphi_N^{(N)} + \chi_{N+1}
 \end{aligned} \tag{21}$$

are the successive angles of one sequence characterizing the $1/r(N+1)$ phase, for the odd values of N . The relation for $\varphi_{N/2+1}$ and $\varphi_{(N+1)/2}$ corresponds to the added part of 0/1 phase for the even and the odd values of N , respectively. $\varphi_i^{(N)}$ takes into account all the deformations already present in the $1/rN$ phase. In the $1/r(N+1)$ phase, these deformations will also be present, but a new deformation χ_n characteristic of the new length of the succeeding sequences has to be added. For the even values of N , the antisymmetry of the deformation implies the absence of any deformation at the added site $N/2+1$, while for the odd values of N , this antisymmetry implies the presence of the deformation $-\varphi_{(N+1)/2}^{(N)}$ at the added site $(N+1)/2$. If it is supposed that

$$\chi_n = A \sin\left(\frac{2\pi n}{N+1} + \phi\right) \quad (22)$$

the antisymmetry of the deformations implies a phase angle $\phi = -\pi/(N+1)$. The results of the previous paragraph, namely Eqs. (15), (16), (17) and (18), imply that

$$\varphi_{N/2}^{(N)} = -\varphi_{N/2+1}^{(N)} \sim H^{-N/2} \quad (23)$$

and

$$\chi_n \sim H^{-H/2-1} \quad (24)$$

for the even values of N , while

$$\varphi_{(N-1)/2}^{(N)} = -\varphi_{(N+1)/2}^{(N)} \sim H^{-(N-1)/2} \quad (25)$$

and

$$\chi_n \sim H^{-(N+1)/2} \quad (26)$$

for the odd values of N .

Inserting all these relations in Eq. (2), the averaged energy at a site can be estimated up to order N in $1/H$. For the even values of N and up to this order,

$$(N+1) \varepsilon_{1/r(N+1)} = N\varepsilon_{1/rN} + \varepsilon_{0/1} - \frac{(\sin \alpha + \sin(2\pi/r - \alpha))^2 \cos^{N-1} \alpha}{(r^2 H)^N} \quad (27)$$

We deduce that the introduction of a new site results in the lowering of the energy for a given domain of the phase diagram even without adding any

deformation. The influence of an "adequate" deformation results in the modification of the energy at the order $N + 1$ in $1/H$. On the other hand, for the odd values of N , it is found in a similar way that the energy of a sequence is

$$(N + 1) \varepsilon_{1/r(N+1)} = N\varepsilon_{1/rN} + \varepsilon_{0/1} - \frac{4(\sin \alpha + \sin(2\pi/r - \alpha))^2 \cos^{N-1} \alpha \sin^2(\pi/(N + 1))}{(r^2 H)^N} \quad (28)$$

up to order N in $1/H$. But for the odd values of N , it is necessary to determine the variational parameter A to obtain Eq. (28). As a result, the introduction of a new site in a sequence of N sites need to be conjugated with an added deformation if N is odd. The change in the energy does appear at the order N in $1/H$. It is worth mentioning that the introduction of the value $r = 3$ for $N = 2$ and 4 gives back the particular results previously explained, while the results for $N = 3$ seems quite different: in fact, the last term on the r.h.s. of Eq. (27) corresponds to the lowering in energy obtained by deforming the mixture of the phases $1/rN$ and $0/1$. But the first term on the r.h.s. of Eq. (27) also gives a contribution to the same order. In contrast, in Eq. (13), the two contributions are taken into account.

The fourth step of our work is the generalization to any P/Q phase for $\alpha/2\pi$ in $[0, 1/2r]$, which is quite straightforward: in fact, any P/Q phase with Q and r relative prime integers is created from the $1/(Q - 1)$ phase by adding Pr molecules belonging to the $1/r$ phase to the sequence of $Q - 1$ molecules composing the elementary pattern. In contrast, if r divides Q , the P/Q phase is created from the $1/(Q/r - 1)$ phase by adding P molecules belonging to the $1/r$ phase to the sequence of $Q/r - 1$ molecules composing the elementary pattern of the $1/(Q/r - 1)$ phase. Of course, to compensate the increasing in $1/r$ phase concentration, an added deformation is required. As example, a $1/r$ phase can be added to a $1/rN$ phase to create a $2/r(N + 1)$ phase. The result is essentially the same as above, namely

$$(N + 1) \varepsilon_{2/r(N+1)} = N\varepsilon_{1/rN} + \varepsilon_{1/r} - \mathcal{O}\left(\frac{1}{H^N}\right) \quad (29)$$

with the detailed expression of the last term depending upon the parity of N . This procedure can be used recurrently. So, the energy has to be expanded up to the $(Q - 1)$ th order in $1/H$ to verify that a P/Q phase is a ground state of the system for a certain domain of the phase diagram. This result concerns the P/Q phases with Q and r relative prime integers and $0 < \omega = P/Q < 1/2r$. If r divides Q , it can be deduced that the P/Q phase is

a ground state of the system if the energy is expanded up to the $(Q/r - 1)$ th order in $1/H$, again with $0 < \omega = P/Q < 1/2r$.

In the fifth step of our work, we deduce that the $0/1$ and the $1/rN$ phases are bordering the $1/r(N+1)$ phase if the system energy is expanded up to order N in $1/H$. Consequently, the spread of the $1/r(N+1)$ phase is measured by the distance between the lines determined by

$$\varepsilon_0 = \varepsilon_{N+1} \quad (30)$$

and

$$\varepsilon_N = \varepsilon_{N+1} \quad (31)$$

For a given value of $H > 1$, Eq. (30) implies that

$$|\alpha_g - \alpha_c| \sim \frac{1}{(r^2 H)^N} \quad (32)$$

with α_g denoting the value of α on the degeneracy line of the $0/1$ and the $1/r(N+1)$ phases, while α_c denotes the value of α on the degeneracy line of the $0/1$ and the $1/rN$ phase. Eq. (32) is obtained with the further hypothesis of $\alpha - \pi/r \ll 1$ in the domain of interest. Of course, it is always possible to make this quantity as small as wanted, simply by increasing the value of H . A similar relation holds for the degeneracy line of the $1/r(N+1)$ and the $1/rN$ line. Those two relations express the measure of the spread of the $1/r(N+1)$ phase. Generalizing this result to any P/Q phase, one obtains

$$\delta \sim \frac{1}{(r^2 H)^{q-1}} \quad (33)$$

with δ defining as above the spread of the P/Q phase. $q = Q$ for a P/Q phase with Q and r relative prime integers, while $q = Q/r$ otherwise. Equation (33) is to be compared with Eq. (6).

Now, it seems crucial to explain the physical points of interest for such a calculation, which is apparently only on value for $H > 1$. Firstly, we think that it points strongly to the non-existence of any discontinuity in such phase diagrams. And this kind of phase diagrams is quite common in the study of ordering with competitive interactions. Even if in the present case the strong coupling limit seems rather an academic preoccupation, we hope our work will find applications for some physical systems, or particular physical situations. Secondly, it clearly shows why a soliton-like theory is not able to sustain the high coupling limit: the description of the

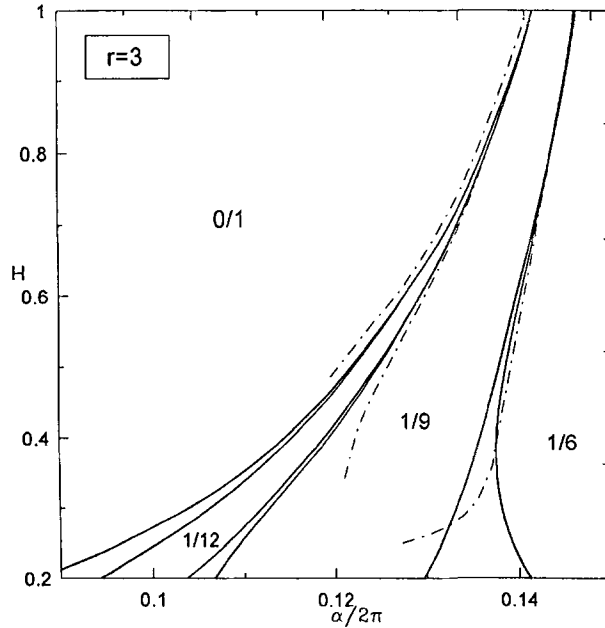


Fig. 2. Details of Fig. 1. The continuous lines are the numerical stability limits of the corresponding phases. The dashed-dotted lines correspond to the degeneracy lines of the adjacent represented phases.

structure needs discontinuous entities that apparently correspond to the discontinuous equivalent of the solitons. Thirdly, and it is the most important fact for our interest, some results are reported on Fig. 2 and the consideration of the ordinate is very instructive: while we propose a systematic development for $H > 1$, the results seem to agree on a much larger scale. In fact, the well-known quotient criteria for series convergence implies that

$$\frac{\varphi_n^{(i+1)}}{H\varphi_n^{(i)}} < 1 \quad (34)$$

for the series expansion of φ_n to converge. The quantity on the l.h.s of Eq. (34) scales as $1/r^2H$ rather than $1/H$.

IV. ONE COLUMN IN A RECTANGULAR ARRAY

After the detailed study of a column in an averaged field originating from six surrounding equivalent columns, the purpose of this section is to analyze the influence of an anisotropy of the field. More precisely, the minimal energy configurations corresponding to the hamiltonian of Eq. (3) are

investigated. This section is in the continuity of the preceding one, making use of the strong coupling limit results, and again showing that results in the strong coupling limit are often very helpful to understand a phase diagram, even in the opposite limit. The discussion is divided in two parts, the first one dealing with the ratio $G/H = d$ kept as a constant, while in the second part, the parameter G is kept constant. Remember that H is the same interaction constant as defined above with $r=3$ and that G is a measure of the anisotropy and is associated with a magnetic-like term in Eq. (3).

A. Constant Anisotropy

The influence of the parameter $d = G/H$ is investigated. As was previously remarked, the topology of the phase diagram corresponding to Eq. (2) is very different in the high coupling limit for $r = 1$ or $r \neq 1$. In fact, for $r = 1$ there is a critical value of the coupling parameter above which the ferromagnetic phase is the only ground state of the system, no matter the value of the natural cantedness. Up to now, a magnetic-like behaviour will refer to such a property of the phase diagram. In contrast, for all integer value of $r \neq 1$, there remains an infinity of phases up to infinite value of H where all these phases except r of them, are restricted to isolated points called multiphase points. A multiphase-like behavior will refer to this situation.

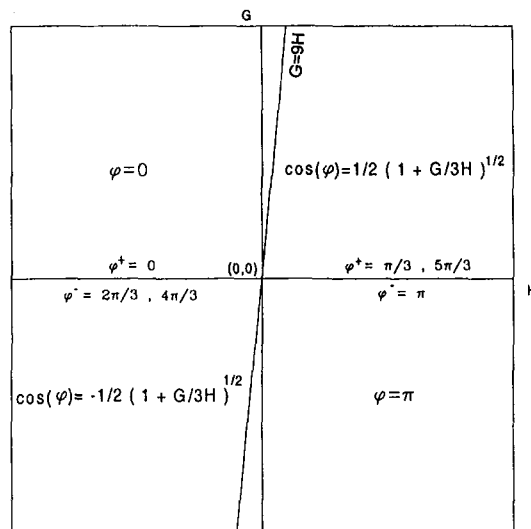


Fig. 3. Analytical phase diagram representing the 0/1 phases corresponding to a ground state of a column in a rectangular array of columns.

As it has been discussed above, in a multiphase-like diagram, any phase expands around the degeneracy lines of two other phases. Obviously, this is the competition between those two phases that gives birth to a third one. Of course, a magnetic-like diagram clearly illustrates the lack of competition. So, to determine the high coupling limit topology of the phase diagram associated to Eq. (3), the ferromagnetic ground states with d constant are determined. The solutions are presented at Fig. 3. The high coupling limit means here that both G and H are higher than unity, but with the ratio d kept as a constant.

For $0 < d < 9$, we found two degenerate ferromagnetic ground states, suggesting a multiphase-like topology for the corresponding phase diagrams, while for $d > 9$, the ferromagnetic ground state is sole, calling for magnetic-like topologies. These results do agree with the numerical solutions presented at Fig. 4a and 4c, obtained with the use of the effective potential method

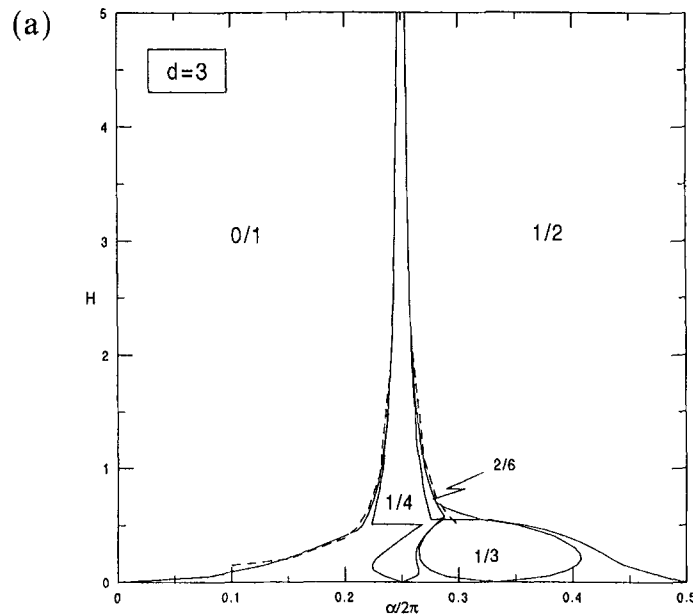


Fig. 4. The continuous lines correspond to the numerical phase diagrams of a column in a rectangular array of columns, for various values of the parameter d . d is the ratio G/H . The phases covering most of the phase diagrams are represented: (a) $d=3$. The dashed lines correspond to the degeneracy lines of the 0/1 and the 1/4 phases on the left and the 1/4 and the 1/2 phases on the right, as determined by an $1/H$ expansion of the energy; (b) $d=9$. The dashed line corresponds to the degeneracy lines of two 1/4 phases of different structure; (c) $d=10$. The dashed line corresponds to the degeneracy lines of two 1/4 phases of different structures. The 0/1 and 1/2 degeneracy line is also represented but is undistinguishable from the numerical solution.

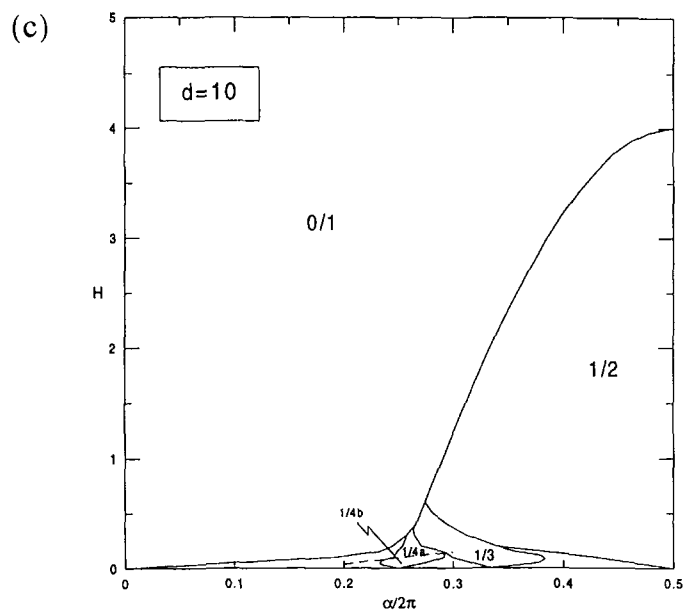
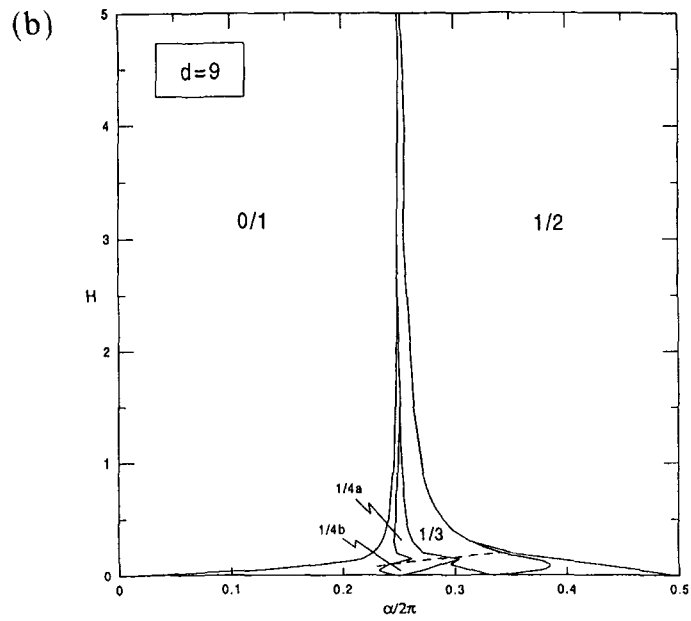


Fig. 4. (Continued)

of Griffith and Chou. The value $d=9$ appears like a hinge point between the two above identified behaviors. The corresponding phase diagram is presented at Fig. 4b. As can be expected, when the interaction parameters H and G are increased, all the molecules tends to align with the ferromagnetic direction. For values of $d > 9$, the perfect alignment is realised at a finite value of $H = G/d$. For instance, the $1/2$ phase can be assimilated to an alternate structure around the magnetic direction. With this assumption, the energy of this phase is easily determined as well as the degeneracy line between the $0/1$ and the $1/2$ phases. This line is reported at Fig. 4c but is undistinguishable from the numerical solution. For values of d in $]0, 9[$, there are two degenerate ferromagnetic directions: as the coupling parameters H and G are increased, all the molecules of any structure tend to align with one of these two directions, resulting in an infinity of conceivable configurations. Of course, the two extremal solutions take the best part of the situation and extend over the largest domain of the phase diagram. Namely, configurations where all the molecules have chosen the same direction, resulting in a $0/1$ phase and the opposite case, where one over every two molecules have chosen one direction and the other one the other direction, resulting in a $1/2$ phase. As a consequence, there remain multiphase points at infinite value of H and G . The case $d=0$ simply gives back the previously investigated hamiltonian. For such multiphase diagrams, the systematic development previously introduced is of major interest: the energy expressions of the $1/4$ and $1/3$ phases are expanded up to first order in $1/H$ and the degeneracy limits of these phases and the $0/1$ and $1/2$ phases are reported at Fig. 4a. Anew, the numerical accord is perfect, with the $1/3$ phase never being a ground state for the system, up to this order in $1/H$.

For $d=9$, an intermediate solution is found: all the molecules of any given configuration tend to align with the two degenerate ferromagnetic directions. But these two directions also moves towards one another, coinciding in the limit of infinite value of H . Also, though an infinity of phases seems to extend up to infinite value of H , the $0/1$ phase is the only phase existing as the limit is reached: the transition from a multiphase-like diagram to a magnetic-like proceeds by the asymptotic transformation of all the phases degenerated at the multiphase point into the same configuration. Or equivalently, from the magnetic-like point of view, the $0/1$ phase is effectively the only remaining phase for all values of α above a critical value of H , but at $d=9$, this critical value of H diverges. It seems interesting to express the way the previously finite degeneracy limit between the $1/2$ phase and the $0/1$ phase goes on to infinite value of H as d decreases to 9. Defining a critical exponent ν as usual as

$$H \sim (9 - d)^{-\nu} \quad (35)$$

the value $\nu = 1$ is found. More, if any P/Q phase corresponds to a modulation around the ferromagnetic direction, the energy can be rewritten as

$$\begin{aligned} \varepsilon_{P/Q} = & -\cos \alpha + H - G + \frac{\cos \alpha}{2Q} \sum_{n=1}^Q (\varphi_n - \varphi_{n-1})^2 \\ & + \frac{1}{2Q} \sum_{n=1}^Q \varphi_n^2 (G - 9H) \end{aligned} \quad (36)$$

Defining

$$F_1(P, \{\varphi_k\}) = \sum_{n=1}^Q (\varphi_n - \varphi_{n-1})^2 \sim P \quad (37)$$

and

$$F_2(Q, \{\varphi_k\}) = \sum_{n=1}^Q \varphi_n \sim Q \quad (38)$$

the degeneracy line between two given phases P_1/Q_1 and P_2/Q_2 is given by

$$H \sim \frac{\cos \alpha (F_1(P_1) - F_1(P_2))}{(G - 9H)(F_2(Q_1) - F_2(Q_2))} \quad (39)$$

which clearly indicates that $\nu = 1$ for all phases and that the $1/2$ phase is the last phase standing with the $0/1$ phase as H is increased.

B. Varied Anisotropy

The phase diagrams as G is kept constant are shortly investigated. In fact, the topology of the phase diagrams at constant value of d and in the limit of a strong coupling with the lattice of columns are rather well understood. In contrast, when H and G are of the order of the unity, strange discontinuities like horizontal lines are numerically determined. We will now explain the origin of these strange discontinuities, making use of the systematic development in terms of a $1/H$ expansion of the energy. Consider the infinite value of H limit, keeping G to a given finite value: the corresponding phase diagrams are reported on Fig. 5. The drawn lines are

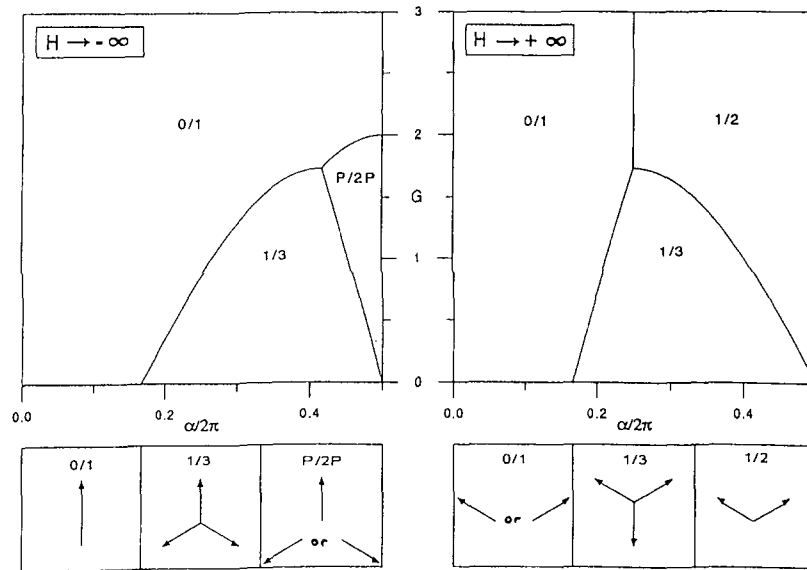


Fig. 5. Analytical phase diagram of a column with H taking infinite value and G varying. The detailed structure are depicted under the phase diagrams, with the convention of a reference direction pointing on the upper direction.

multiphase lines in the same sense that the multiphase points previously defined and we also note the existence of a multiphase region of finite extension ($P/2P$). However, our attention is concentrated over the existence of a $1/3$ phase at infinite value of H . This characteristic is a clue indicating that for small values of G , the phases deform in the same way as in the case of $G=0$. To be more specific, the special case of the $1/4$ phase is investigated. Two possible structures for this phase are pictured above Fig. 6: on the right, the expected structure if the configuration is deformed according to the symmetry associated with the parameter H , while on the left, the expected structure at high values for both H and G . Expanding the energy of Eq. (3) for both these situations up to the first order in $1/H$, the degeneracy line between the two configurations is reported on Fig. 6 as a discontinuous line. Obviously, the correspondence with the numerical solution is very interesting. The discontinuity line of the $1/4$ phase is thus to be attributed to the flop of one molecule. It seems conceivable to think that, for phases of higher commensurability, the flop of more than one molecule is necessary and that a set of discontinuities is present. This result is in agreement with previous numerical results.⁽¹¹⁾

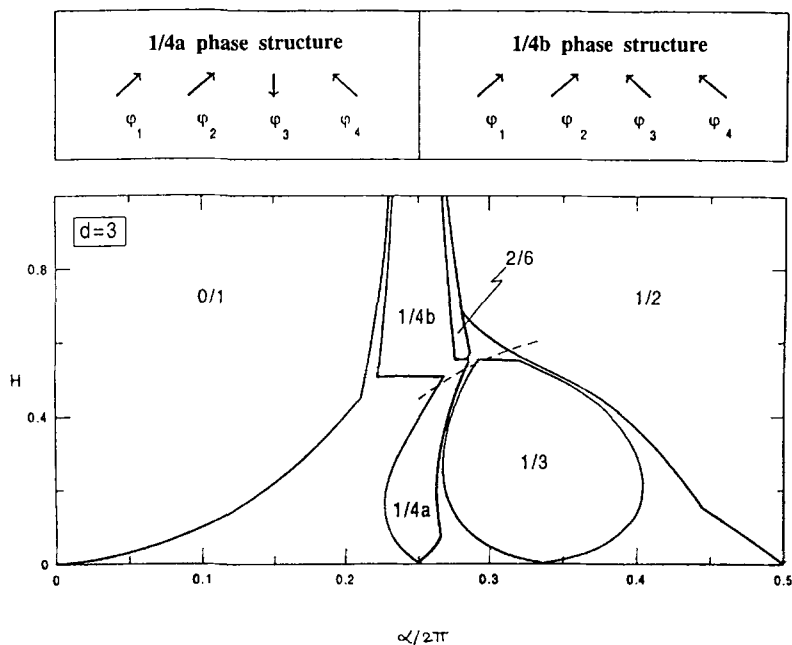


Fig. 6. Details of Fig. 4a. The continuous lines correspond to the numerical phase diagram of a column in a rectangular array of columns characterized by $d=3$. The dashed line is the degeneracy lines of the two $1/4$ structures depicted over the phase diagram. The H interaction parameter favors the left-hand-side structure ($1/4a$ phase), while the combination of the H and G parameters favors the right-hand-side structure ($1/4b$ phase).

V. CONCLUSIONS

The influence of the interplay of the constitutive molecules symmetry and the lattice symmetry over the orientational order along one column is investigated. A detailed study of the hamiltonian of Eq. (2) is proposed, particularly in the limit where $H > 1$. This brings as a result a better understanding of the topology of phase diagrams like those presented on Fig. 1. Moreover, the splitting of a multiphase point into an infinity of phases is investigated, giving the variation of a phase spread in the hypothetical case of a strong coupling with the array of columns. As these results can be partly extended to a domain where $H < 1$, they complement the well-known results obtained in this limit.

As an extension of this work, the influence of the anisotropy of the lattice of columns is studied. As it has numerically be shown, even small distortions from the perfect triangular lattice can bring rather fundamental

changes, with the possibility of the appearance of discontinuities. We do apply our systematic development to this more complex phase diagram and it allows us to explain these discontinuities, finding results that do perfectly agree with previous numerical results of Yokoi, Tang and Chou.⁽¹⁰⁾ The other important characteristics of the hamiltonian of Eq. (3) is that it allows a continuous transition from the two different behaviors that were studied at Section III. As a consequence, the appearance of a multiphase point becomes obvious. However, the structure of the phase diagram corresponding to Eq. (3) is very rich and there is yet a lot of open questions, such as the concentration of discontinuity points over the boundaries of various phases^(10, 11) and the structure of more complex phases. More generally, an analytical method working for weak values of the coupling parameters is still missing. As a consequence, the very simple development we propose seems to be the only alternative to obtain an analytical expression for the energy.

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