

Symmetries of Electrostatic Interaction between DNA Molecules

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We study a model for pair interaction U of DNA molecules generated by the discrete dipole moments of base-pairs and the charges of phosphate groups, and find noncommutative group of eighth order \mathcal{S} of symmetries that leave U invariant. We classify the minima using group \mathcal{S} and employ numerical methods for finding them. The minima may correspond to several cholesteric phases, as well as phases formed by cross-like conformations of molecules at an angle close to 90° , “snowflake phase”. The results depend on the effective charge Q of the phosphate group which can be modified by the polycations or the ions of metals. The snowflake phase could exist for Q above the threshold Q_C . Below Q_C there could be several cholesteric phases. Close to Q_C the snowflake phase could change into the cholesteric one at constant distance between adjacent molecules.

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1. The DNA cholesterics have drawn considerable attention as unusual states of condensed matter [1–7]. These liquid-crystalline phases are of interest from various points of view [2]. For one thing there is a certain affinity, as packaging is concerned, between them and viruses and chromosomes, for another they could be useful for constructing nano-devices, for example sensors [8].

Cholesteric assemblies of the DNA have been observed in vivo and extensively studied in vitro [7–13]. The experimental methods for obtaining molecules of the DNA in condensed state employ either solutions of polycations, or of polymers separating phases containing molecules of the DNA. Livolant et al. [9, 10], used polycations and found the spatial characteristics of the location of DNA molecules [11]. Yevdokimov et al. [2], have used the PEG pellets for the formation of liquid crystalline phases of the DNA, and found the polymorphism by observing a change in the sign of cholesteric spiral.

By now it is generally accepted that the liquid crystalline phases of the DNA are essentially of the electrostatic nature due to the helical distribution of charge [12], the conformational properties of the DNA playing the crucial role [13, 14]. The concept of the charged duplex has made for understanding the physics of the phases, and enabled to explain the emergence of the cholesteric structure and its relation to the ion strength of solutions [15].

But the existence of different cholesteric phases of the DNA is still a challenge to the current theory. The theoretical study of pair-interaction U caused by charges of phosphate groups, dipoles of base-pairs, and ions of ambient solution, can make for understanding the phenomenon. Electric charges of molecules of the DNA are of two kinds: those due to the phosphate groups and those of the base-pairs, which are generally described by dipole moments, [16]. Kim, [17], used the helix symmetry of the set of dipole moments, for describing a torque that may deform the parallel conformation of two adjacent molecules and result in a cholesteric phase of the system (see also [18]). The idea turned out to be quite useful for the physics of the DNA. The main point about its implementation is that the discrete structure of charges presents serious difficulties for analytical treatment.

2. In this paper we study the multistability of cholesteric phases, [8], within the framework of the approach indicated above, taking into account only the electrostatic forces between molecules of the DNA in solution. We use the discrete approximation for the electrostatic interaction between pairs of molecules of the DNA [17], use extensively computer simulation, and employ symmetry arguments. Our model is essentially that of one dimensional lattice of charges and dipoles with an elementary cell of size 3.4 \AA that mimics the spatial conformation of the charges of phosphate groups and the dipoles of base-pairs. We consider short segments of the DNA, approximately 500 \AA , that is of the size of persistence length, so that to a good approximation one may consider them as segments of straight lines. We shall as-

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sume that both molecules have the same number of base-pairs that can be visualized as points on a straight line parallel to the axis of the molecule, one base-pair being located at the center of a corresponding molecule. The centers of the straight lines describing the molecules belong to the straight line perpendicular to the plane $x-y$ parallel to either of them. We shall denote by ξ the angle between the straight lines describing the molecules. We assume that both molecules are of the same helicity. The latter is determined by the rotation of the frame of the dipole moments. Thus, we model a molecule of the DNA on a one-dimensional lattice having at its sites either vectors of dipoles of the base pairs or scalars of the phosphate charges. The case of total neutralization of phosphate charges was considered in paper [19].

The dipoles are suggested to have the helix symmetry with $\pi/5$ rotation $/bp$, corresponding to the structure of the ideal double helix of the DNA. The distance between the centers κ , which is fixed, is an important parameter of the model. In what follows we use the distance between adjacent base-pairs, that is 3.4\AA , as the unit of length, and take a unit of charge for which the dipole moment of 1 Debye is equal to 1. We perform all calculations in the dimensionless units generated by these quantities.

The energy of electrostatic interaction of two molecules can be cast in the sum

$$\epsilon U = U_0 + u_{dd} + u_{dc} + u_{cd} + u_{cc} \quad (1)$$

in which ϵ is the dielectric permeability of solvent and U_0 is the self energy of the pair, which does not influence its conformation, the first term describes the interaction between dipoles of the first molecule and those of the second; the second term – dipoles of the first and phosphate charges of the second; the third – charges of the first and dipoles of the second; the fourth – charges of the first and the second. The interactions are given by the equations

$$u_{dd}(\mathbf{r}, \mathbf{r}') = e^{-\nu\rho} \left[g(\rho) \frac{1}{\rho^3} (\mathbf{p} \cdot \mathbf{p}') - 3h(\rho) \frac{[\mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')][\mathbf{p}' \cdot (\mathbf{r} - \mathbf{r}')] }{\rho^5} \right], \quad (2)$$

$$u_{dc}(\mathbf{r}, \mathbf{r}') = e^{-\nu\rho} k(\rho) Q \frac{\mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')}{\rho}, \quad (3)$$

$$u_{cd}(\mathbf{r}', \mathbf{r}) = e^{-\nu\rho} k(\rho) Q \frac{\mathbf{p}' \cdot (\mathbf{r}' - \mathbf{r})}{\rho}, \quad (4)$$

$$u_{cc}(\mathbf{r}, \mathbf{r}') = e^{-\nu\rho} \frac{Q^2}{\rho}, \quad (5)$$

in which ν is the inverse Debye length $\nu = \lambda^{-1}$, and

$$\rho = |\mathbf{r} - \mathbf{r}'|.$$

We shall take the screening functions $k(\rho), g(\rho), h(\rho)$ in Schwinger's form

$$k = g = 1 + \nu\rho, \quad h = 1 + \nu\rho + \frac{1}{3}\nu^2\rho^2.$$

The important point about the electrostatic interaction between molecules of the DNA is a wise choice of the screening factor. The common practice is to employ the Debye-Hückel theory, or its modifications that might accommodate the dipole charges, the so-called Schwinger screening. The full treatment of this problem requires a separate investigation. In this paper we confine ourselves to the Debye-Hückel and the Schwinger theories [20].

3. In what follows we shall use the standard technique of group theory, which enables us to formulate the properties of minima for potential U in a concise and clear form (see Fig.1 which gives the illustration of our results).

It is worth noting that the pair potential U is invariant as regards the change of helicity: if we change the sign of angle ξ between the axes of the two molecules, at the same time as the sign of helicity, the potential U remains the same. Thus, there is the invariance rule as regards the transformation

$$(\text{right helicity}, \xi) \Leftrightarrow (\text{left helicity}, -\xi). \quad (6)$$

There are symmetry rules for the helices of the same kind. One may convince oneself, for example by writing explicit expressions for the interactions given by Eqs. (2)–(5) with the help of angles ϕ_1, ϕ_2 between the dipole moments at the centers of the two molecules and axis z , and the angle ξ introduced above, that the following transformations

$$t_1 : (\phi_1, \phi_2, \xi) \rightarrow (\phi_1, \pi - \phi_2, \xi + \pi), \quad (7)$$

$$t_2 : (\phi_1, \phi_2, \xi) \rightarrow (\pi - \phi_1, \phi_2, \xi + \pi), \quad (8)$$

$$t_3 : (\phi_1, \phi_2, \xi) \rightarrow (\phi_2 + \pi, \phi_1 + \pi, \xi) \quad (9)$$

leave the potential U invariant. The angles are defined within limits

$$-\pi \leq \phi_1 \leq \pi, \quad -\pi \leq \phi_2 \leq \pi, \quad -\pi \leq \xi \leq \pi$$

values $\pm\pi$ corresponding to the same configurations of the molecules.

The transformations given by Eqs. (7)–(9) verify the equations

$$t_1^2 = t_2^2 = t_3^2 = id, \quad t_2 t_3 = t_3 t_1, \quad t_1 t_2 = t_2 t_1,$$

where id is a transformation that leaves all ϕ_1, ϕ_2, ξ invariant. Using the above equations one can easily convince oneself that t_1, t_2, t_3 generate a *non-commutative*

group of 8-th order, \mathcal{S} . Its maximal subgroup \mathcal{H} is a normal subgroup of 4-th order, commutative, and generated by the transformations

$$f_1 = t_3, \quad f_2 = t_1 t_2 t_3. \quad (10)$$

Elements f_1, f_2 in its turn generate subgroups \mathcal{H}_1 and \mathcal{H}_2 of \mathcal{H} , respectively. It is worth noting that $\mathcal{H}_1, \mathcal{H}_2$ are of second order, both. They are conjugate subgroups of \mathcal{S} , that is for an element g of \mathcal{S} we have $f_1 = g^{-1} f_2 g$, or we may state $\mathcal{H}_1 = g^{-1} \mathcal{H}_2 g$, in the notations of group theory, which can be cast in the form of the diagram

$$\mathcal{H}_1 \longleftrightarrow \mathcal{H}_2. \quad (11)$$

The element

$$f_3 = t_1 t_2 \quad (12)$$

generates subgroup \mathcal{H}_3 of \mathcal{H} . It is important that \mathcal{H}_3 is a normal subgroup of \mathcal{S} , that is $g^{-1} \mathcal{H}_3 g = \mathcal{H}_3$ for any element g of \mathcal{S} . Thus, we have the diagram of subgroups inside the symmetry group \mathcal{S} :

$$\begin{array}{ccccc} \mathcal{H}_1 & & & & \\ & \searrow & & & \\ \mathcal{H}_3 & \longrightarrow & \mathcal{H} & \longrightarrow & \mathcal{S} \\ & \nearrow & & & \\ \mathcal{H}_2 & & & & \end{array} \quad (13)$$

in which the arrows signify the imbedding of subgroups.

The group of symmetries, \mathcal{S} , plays the key role in finding minima of the potential U . The following general arguments, based on the theory of groups, are quite useful in this respect. Consider a point μ of space \mathcal{X} of the angles ϕ_1, ϕ_2, ξ . Suppose that μ is a minimum of U . Then points

$$\mu' = g \cdot \mu,$$

called the orbit of the point μ under the action of the group \mathcal{S} , are also minima of U . The number of points μ' of the orbit can vary. In fact, let us consider all transformations g of \mathcal{S} that leave μ invariant, that is $\mu' = g \cdot \mu = \mu$. It is alleged to be known that the transformations form a subgroup of \mathcal{S} , called stationary subgroup \mathcal{H}_μ . The stationary subgroups, \mathcal{H}_μ and \mathcal{H}_ν , for points μ and ν of an orbit, are conjugate, that is $\mathcal{H}_\mu = g^{-1} \mathcal{H}_\nu g$ for an element g of \mathcal{S} . The number of different points μ' equals to the ratio of the orders of \mathcal{S} and \mathcal{H}_μ , that is to 2 or 4, depending on the choice of point μ . To be specific, consider a point μ having a stationary subgroup \mathcal{H}_μ that coincides with the subgroup \mathcal{H} . The latter is a normal subgroup of \mathcal{S} of index 2, that is the factor set \mathcal{S}/\mathcal{H} consists of two elements. Thus,

the orbit of μ under the action of \mathcal{S} consists of only two points that correspond to the same value of U and have the same stationary subgroup \mathcal{H} , because the latter is a normal subgroup of \mathcal{S} . The situation is quite different if we take a point ν having stationary subgroup \mathcal{H}_1 , which is different from \mathcal{H}_2 . The subgroups do not coincide in \mathcal{S} , even though they are conjugate. The orbit of μ under the action of \mathcal{S} indicated above consists of four points that we may sort out as follows: two points having the stationary subgroup \mathcal{H}_1 and two points having \mathcal{H}_2 . This is due to the fact that for one thing the subgroup \mathcal{H} is commutative and therefore its elements generate points of the orbit but with the same stationary subgroup, that is \mathcal{H}_1 , and for another there is an element g that gives points of the orbit having the stationary subgroup \mathcal{H}_2 . In contrast, a point μ having the stationary subgroup \mathcal{H}_3 has the orbit consisting of four points which have the same stationary subgroup \mathcal{H}_3 , because the latter is a normal subgroup of \mathcal{S} .

4. It is to be noted that numerical evaluation of the minima runs across a poor convergence of standard algorithms for minimization, because of rather flat surfaces of constant value for the function of three variables, $U(\phi_1, \phi_2, \xi)$. To some extent, one may get round the difficulty by observing that for points that remain fixed with respect to a subgroup \mathcal{G} of \mathcal{S} , the minimization problem is reduced to that for a smaller number of variables. This is due to the fact that for degrees of freedom perpendicular to the set of invariant points the necessary conditions for extremum are verified automatically and one needs only to study the conditions for longitudinal variables, that is to solve a smaller system of equations.

To see the point let us consider a function $f(x, y, z)$ of variables x, y, z even in x , so that $f(x, y, z) = f(-x, y, z)$. The set of invariant points is $y - z$ plane, and we may look for minima of the function $f(x = 0, y, z)$, thus we need to solve only the two equations

$$\frac{\partial}{\partial y} f(x = 0, y, z) = 0, \quad \frac{\partial}{\partial z} f(x = 0, y, z) = 0$$

For larger groups of symmetries the number of variables necessary for calculations can be reduced even further, as happens for the minimization of $U(\phi_1, \phi_2, \xi)$ we are studying. It is easy to convince oneself that the sets of fixed points (ϕ_1, ϕ_2, ξ) , that is invariant under the action of a subgroup of \mathcal{S} , read as follows

$$\mathcal{F}_1 : (\phi_1 = \phi, \phi_2 = \phi + \pi, \xi), \quad (14)$$

$$\mathcal{F}_2 : (\phi_1 = \phi, \phi_2 = -\phi, \xi), \quad (15)$$

$$\mathcal{F}_3 : (\phi_1 = \pm \frac{\pi}{2}, \phi_2 = \pm \frac{\pi}{2}, \xi) \quad (16)$$

in which the \mathcal{F}_i are invariant under the action of subgroups \mathcal{H}_1 , \mathcal{H}_2 , \mathcal{H}_3 , respectively.

The analysis of symmetries of U given above enables us to sort out the minima according to the effective value of the phosphate charge Q , determined by the Debye-Hückel screening (see Figs.2,3).

It should be noted that minima of the pair-interaction U depend on the distance between molecules κ , and the effective phosphate charge Q . The latter is the control parameter we employ in numerical simulation. It is also useful for the description of possible experimental results. In this paper we are considering κ to within 10.2–34 Å. Effective charge Q of phosphate groups determines the neutralization; it varies to within 0 – .6, in dimensionless units, $Q = 0$ corresponding to the total neutralization. Charges Q that correspond to the charge inversion, have not been considered. The Debye length, λ , has been varied to within 7–35 Å, depending on the ion strength of solution.

The numerical data and the symmetry analysis given above suggest that there should be the following three types of the minima.

1. Type I characterized by the molecules having a cross-like conformation, “snowflakes”, that is ξ being close to $\pi/2$. It exists for Q large enough. Its symmetry subgroup depends on the value of Q and may take values \mathcal{H}_1 , \mathcal{H}_2 , \mathcal{H}_3 , \mathcal{H} . Therefore, we may claim that there exist four sub-types of minima I: $I_{\mathcal{H}_1}$, $I_{\mathcal{H}_2}$, $I_{\mathcal{H}_3}$, $I_{\mathcal{H}}$, each of them consisting of two subtypes which are given by specific conformations of the angle variables.
2. Type II for which ξ taking values to within 0.1° . Their symmetry subgroups are \mathcal{H}_1 and \mathcal{H}_2 , each type consisting of two sub-types.
3. Type III for which ξ is to within 1° , that is larger than for II. The symmetry subgroup is \mathcal{H}_3 , and there are four constituent types of the same symmetry.

5. The minima of the pair-interaction could provide a useful clue to the problem of finding possible conformations of large ensembles of molecules, even though the pair-interaction we have employed is a rough approximation for studying closely packed suspensions. It is as much as to say that the molecules in dispersions be packed in such a way that the pair-interaction should take on the lowest possible values. Following these guidelines we feel that the study of its minima could allow certain conjectures concerning liquid crystalline phases of the DNA. In particular, we may suggest that

there is a number of different phases, some of them being the cholesteric ones. In this respect our results are in agreement:

1. with papers [6] and [8] in which it has been verified that the cholesteric phases are related to small or almost zero effective charges of the DNA,
2. with the theoretical conclusions of papers [12–15] concerning the electrostatic mechanism of generating cholesteric phases of the DNA,
3. with paper [8] as regards the existence of polymorphism or multistability.

We suggest that the description of cholesteric phases of the DNA should take into account the symmetries described by group \mathcal{S} for the electrostatic interaction for pairs of molecules of the DNA. Our results are described by a sequence of the embedded subgroups given by diagram (13).

The symmetry classification of the minima, and possible phases, enables us to see differences between liquid crystalline phases which at first sight appear to be physically identical. Thus the snowflake phase, which seems unique, if superficially estimated with the value of angle ξ , may have several different types. The same is true for “cholesteric” phase II. In contrast, cholesteric phase III is unique, in the sense that its symmetry subgroup is only \mathcal{H}_3 . The subgroups provide a concise means for describing conformations of pairs of DNA molecules that determine the liquid crystalline phases.

The physical parameter we use in our numerical work, is the effective charge Q , due to the phosphate charge of the DNA and the Debye-Hückel screening. It enables us, at least qualitatively, to take into account the experimental setting. In fact, the charge distribution, mimicked by Q , can be effected by changing the constituency of solvent. The numerical results illustrated in Fig.1 are very suggestive.

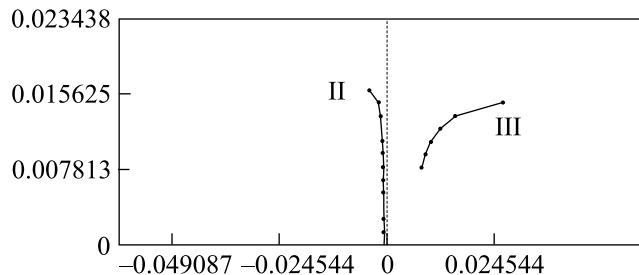


Fig.1. Charge Q against energy E for minima of U . Curves II, III correspond to minima of the types II, III, respectively

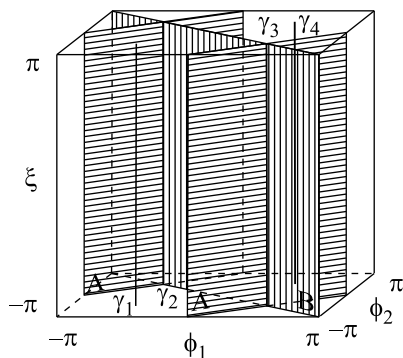


Fig.2. Cube of the symmetries indicating sets in space ϕ_1, ϕ_2, ξ invariant with respect to subgroups of \mathcal{S} . Main diagonal plane, B , corresponding to subgroup \mathcal{H}_2 ; two rectangles A perpendicular to B to \mathcal{H}_1 ; solid lines γ_1, γ_4 , and γ_2, γ_3 corresponding, to \mathcal{H}_3 and \mathcal{H} , respectively

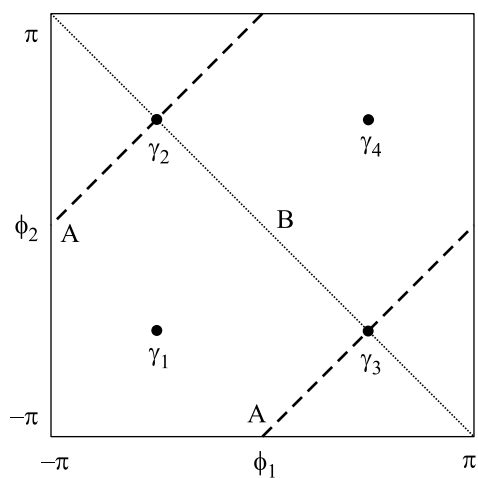


Fig.3. Cube of the symmetries view from the top. Dotted line describes invariant points \mathcal{F}_2 , corresponding to subgroup \mathcal{H}_2 ; dashed line points \mathcal{F}_1 and subgroup \mathcal{H}_1 ; solid circles γ_1 and γ_4 to subgroup \mathcal{H}_3 ; γ_2 and γ_3 to subgroup \mathcal{H}

We see that for Q larger than a certain threshold value Q_C the energy of the minima corresponding to phase I, called the snowflake phase, is smaller than that corresponding to phases II and III. Therefore we may suggest that for solvents that provide sufficiently high value of the effective charge Q there are no cholesteric phases *proper* and the snowflake phase could be present.

It is surprising that liquid crystals with the symmetry properties described in this paper have so far remained unobserved. At least in part it might be due to the fact that the snowflake phase could be misinterpreted in the X-ray experiments. It is worth noting that the formation of the snowflake phase is similar to that of the Wigner crystal [21], in that it is due to the long-ranged Coulomb

interaction of particles at low density, the inter-particle repulsion leading to the conformational organization.

The phase diagram illustrated in Fig.1 describes the behavior of the effective charge at *constant inter-helical distance*. Therefore, special precautions are to be taken so as not to change the latter while modifying the effective charge, with a view to see the transition of the snowflake phase into the cholesteric one.

It is also worthwhile to look for different cholesteric phases at small values of Q , that is less than Q_C . The guideline being given by the fact that the size of ξ differs by orders of magnitude for the phases II and III, at the same time values of the effective charge Q being equal. According to Fig.4 one may expect phase transitions in which the cholesteric angle ξ changes both its order of magnitude and sign.

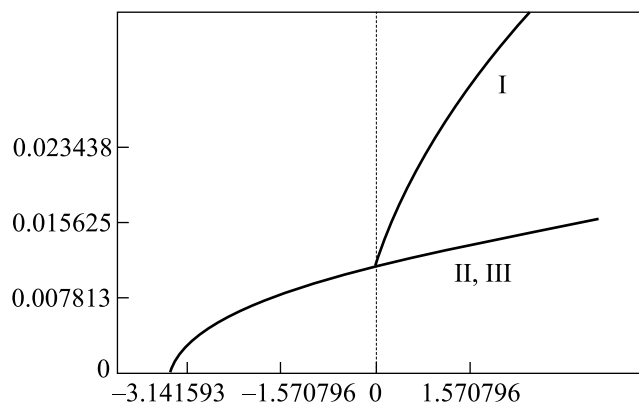


Fig.4. Charge Q against ξ for minima of U . Curves I, II, III correspond to minima I, II, III. Curves II and III are given by the same line due to the chosen precision

The formation of liquid crystalline phases of the DNA involves the degeneracy of \mathcal{S} -symmetry, in accord with the general prescription of condensed matter theory, larger subgroups corresponding to more isotropic phases. For the phases under consideration in the present paper it could be effected owing to the increment of frustration of the molecules trying to satisfy both the packing and electrostatic constraints. The symmetry considerations playing the key part, one may expect there could be phase transitions accompanied by changes in symmetry described by subgroups of group \mathcal{S} .

One may attempt to employ the conformation of charges of the molecule of the DNA that relies on the pyrophosphate groups rather than on the phosphate ones as usual. By now there has been a considerable progress in studying molecules of the DNA with substituted pyrophosphate internucleotide groups [22]. The samples studied in paper [22] had the double charges, -2 electron charge, due to the pyrophosphate groups inserted

periodically, usually one group for every ten base-pairs of the DNA. One can expect that the study of dispersions of the DNA based on molecules carrying pyrophosphate internucleotide groups, could make for understanding the part played by electrostatic forces in generating liquid crystalline phases of the DNA. The design of novel DNA probes [23], provides new opportunities in this respect.

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