

# Phase transition between A and B forms of DNA: A free-energy perspective

Devashish Sanyal\*

*Theoretical Condensed Matter, Institute of Physics, Bhubaneswar 751005, India*

(Received 9 December 2009; revised manuscript received 4 February 2010; published 29 March 2010; corrected 2 April 2010)

We study the structural transition from B form of DNA to A form of DNA using group theoretic methods. The transition is not of the order-disorder type and hence to construct a Landau kind of theory for the transition we define a higher symmetry and relevant order parameters. We also discuss the issue of all the conformations, observed experimentally during the course of transition, being fundamentally different or not.

DOI: [10.1103/PhysRevE.81.032901](https://doi.org/10.1103/PhysRevE.81.032901)

PACS number(s): 87.15.Zg, 87.14.gk

## I. INTRODUCTION

DNA can exist in many conformations, the most stable among them being A, B, and Z forms. A and B forms of DNA form right-handed double helix while Z DNA forms left-handed double helix with varying number of turns per rotation. In this Brief Report we examine the transition between B and A forms theoretically. B DNA is the most commonly occurring DNA existing in highly humid conditions. It may be transformed to the A form by methylation. The transition from B form to A form was observed during the first x-ray studies by Franklin and Goslin [1] who characterized the change in the helix structure as “a substantial rearrangement of the molecule.” Experiments [2,3] have been performed to observe the transition from B form to A form in a more detailed manner and this Brief Report is an attempt to explain the fundamental features of the experiments. Recent experiments [4] to study the dynamics of the transition from B to A observe that the helical states are clearly separated from one another in terms of activation energy with the time scale of the dynamics of transition being of the order of ms. In the following paragraphs we will try to address the question of whether the transition from B form to A form is a phase transition as defined in statistical physics. The study of the B to A transition from the first principles by including the interaction between the various bases and their interaction with the environment can be very challenging. The Landau analysis may provide a sophisticated method to study the phase transition.

## II. SYMMETRY OF A AND B FORMS

The Landau theory for the study of phase transition is considered as one of the important achievements of Landau. In Landau theory the free energy is written in terms of the order parameter which in turn depends on the symmetry of the phase having the higher symmetry through one of its irreducible representations. The free energy remains invariant under the symmetry operations of the higher symmetry. Phase transitions involving multiferroics [5], complicated structures such as intercalation compounds [6] and antiferromagnets [7] have been studied using the Landau theory. In this Brief Report the Landau theory will be used to study the

phase transition between A and B forms of DNA. Experimental studies, among other techniques, use crystallography to study the structure of DNA. The various conformations take on different crystallographic structures [2,3] corresponding to different space groups. The space groups depend on the detailed symmetry of the molecule, length of the sequence, etc. The use of space groups may not be the most reliable method to study the transition theoretically. After all, the DNA exists as a single macro molecule and we would prefer to treat it like that.

In the present approach the DNA is considered to be double helix with Watson-Crick bonding between the two strands. We would not go into the detailed coordinates of the atoms in the two forms but would like to explain the transition from the point of view of change in symmetry resulting in the difference between A and B forms. With this objective in mind, we consider the DNA macromolecule to be infinitely long along the axis. Hence, it can be looked upon as a transition where the line group changes [8]. The view along the axis of A and B DNA is shown in Fig. 1 [9].

Apart from a pure translational symmetry  $a$  along the axis, B form has the screw symmetry  $10_1$ . The rotation part of the group is cyclic with order  $10(C_{10})$  [9]. A form of DNA has screw symmetry  $11_1$ . The rotation part of the group is cyclic with order  $11(C_{11})$ . In the subsequent analysis we employ group theoretic arguments to construct the order parameter in order to write down the free energy. The irreducible representation for the rotation part, say of order  $\alpha$ , may be deduced from the relation  $z^\alpha=1$  as the group is cyclic. So  $z = e^{i2\pi n/\alpha}$  where  $n=0, 1, \dots, \alpha-1$ . Since the groups  $(C_{10}, C_{11})$  are Abelian, all the representations are one dimensional.  $D^n$  represents the  $n$ th irreducible representation.

The basis for the representations is given by  $e^{-in\phi}$  where  $n=0, 1, \dots, 9$  for  $C_{10}$  and  $n=0, 1, 2, \dots, 10$  for  $C_{11}$ .  $R(\Delta\phi)$

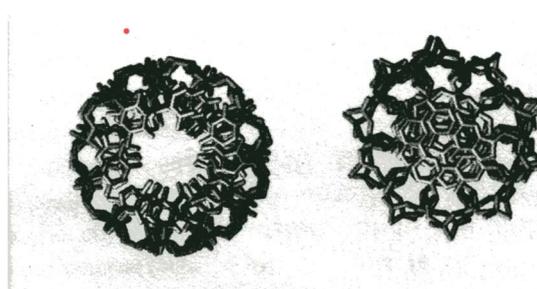


FIG. 1. (Color online) Axial view of A and B forms.

\*deva@iopb.res.in

be an operator that rotates the coordinate system by  $\Delta\phi$ . If  $\Delta\phi = \frac{2\pi}{10}$  (say), then  $R(\Delta\phi)e^{-in\phi} = e^{i2n\pi/10}e^{-in\phi}$ ,  $n$  being the index of representation. Thus  $e^{i2n\pi/10}$  is a representation of rotation by  $2\pi/10$  with index  $n$ . We can thus calculate the representations of  $C_{10}$  and  $C_{11}$  corresponding to the various irreducible representations. The irreducible representation of the line group is given by  $e^{-in\phi}e^{ikz}$ ,  $e^{ikz}$  being the basis for the representation of translation along the DNA axis. The representation is labeled by the pair  $(n, k)$ .

### III. CONSTRUCTION OF THE ORDER PARAMETER

The order parameter, which is used to describe order-disorder transition, is the expectation value of an operator which does not remain invariant under the full symmetry group, taking the value 0 in the disordered phase and a finite value in the ordered phase. It, though, remains invariant under a subgroup of transformations. In order to introduce the order parameters in the problem we need to define disordered phase (high symmetry phase). We consider  $10_1$  (B DNA) and  $11_1$  (A DNA) as the ordered phases in comparison to the disordered phase (high symmetry phase) given by the symmetry  $(10 \times 11 \times m)_1$ ,  $m$  being some integer. This is so as they are subgroups of the high symmetry phase. We take  $m = 1$  in this case for the sake of convenience. Let  $R(\frac{2\pi q}{10})T(\frac{qa}{10})$  ( $q=0, \dots, 9$ ) be a symmetry operation of B DNA with  $R$  standing for the rotation and  $T$  standing for the translation;

$$R\left(\frac{2\pi q}{10}\right)T\left(\frac{qa}{10}\right)e^{-in\phi}e^{ikz} = e^{i2\pi nq/10}e^{ikqa/10}e^{-in\phi}e^{ikz}. \quad (1)$$

We want  $e^{i2\pi nq/10}e^{ikqa/10}$  to be unity since the order parameter transforms as some irreducible representation and remains invariant under a subgroup of transformation in the ordered phase. Hence  $\frac{2\pi n}{10} + \frac{ka}{10} = 2\pi A$ ,  $A$  being an integer. It leads to

$$k = \frac{2\pi(10A - n)}{a}. \quad (2)$$

One may repeat the same arguments for A DNA to obtain

$$k = \frac{2\pi(11A - n)}{a}. \quad (3)$$

We note that  $n=0, \dots, 109$  since the higher symmetry is denoted by  $(10 \times 11)_1$ . We take  $n=1, A=1$  for convenience. For B DNA  $k = \frac{18\pi}{a}$  and for A form  $k = \frac{20\pi}{a}$  though there could be different values of  $k$  corresponding to different values of  $n$  and  $A$ . We would work in the space of basis  $(k_1, n_1)$  and  $(k_2, n_2)$  where  $k_1 = \frac{20\pi}{a}$ ,  $n_1 = 1$  and  $k_2 = \frac{18\pi}{a}$ ,  $n_2 = 1$ . There is no mixing between  $(k_1, n_1)$  and  $(k_2, n_2)$ , so the system is defined by two order parameters  $\alpha_a$  and  $\alpha_b$  transforming, respectively, as the representations determined by the above basis.  $(\alpha_a, 0)$  is invariant under the symmetry operations of  $11_1 - \alpha_a$  remains invariant due to (3) and 0 remains so under the operation—thereby representing the A DNA phase. For similar reasons  $(0, \alpha_b)$  being invariant under the operations of  $10_1$  represents the B DNA phase.  $(0, 0)$  being invariant under the larger symmetry group represents the melt or the higher symmetry. The picture of the phase transition is

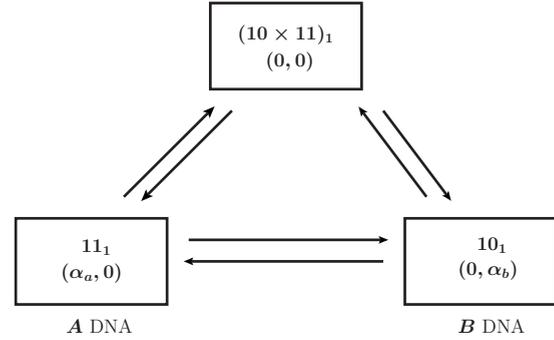


FIG. 2. Schematic diagram representing the Landau theory for transition between A and B forms of DNA.

presented in Fig. 2. We try to establish the transition between B DNA and A DNA by looking at the transitions, possibly fictitious, between the disordered phase and the ordered phases. We consider  $\alpha_a$  and  $\alpha_b$  to be complex quantities. Having constructed the two order parameters we may now attempt to write down the free energy of the system. It may be seen that under a general operation of  $(10 \times 11)_1$   $\alpha_a$  and  $\alpha_b$  pick up a phase. Hence a very general form of the free energy in the form of a polynomial in  $\alpha$  and  $\alpha^*$  until the quartic order, invariant under the symmetry of the higher symmetry group, may be written down;

$$f = \frac{1}{2}r(|\alpha_a|^2 + |\alpha_b|^2) - \frac{1}{2}g(|\alpha_a|^2 - |\alpha_b|^2) + u_1|\alpha_a|^4 + u_2|\alpha_b|^4 + 2u_{22}|\alpha_a|^2|\alpha_b|^2, \quad (4)$$

where  $u_1, u_2 > 0$ . It may be seen here that the coefficients of  $|\alpha_a|^2$ ,  $|\alpha_b|^2$  have been split among  $r$  and  $g$  as they separately carry different information. The transition from B DNA to A DNA is carried out through the addition of a chemical agent ( $c$ ). In the above equation we put  $r \propto (T - T^*)$  and  $g \propto (c - c^*)$ ,  $T^*$  and  $c^*$  (chemical conc) are some constants and  $T$ , not necessarily the temperature, may not be a realizable parameter.  $u_{22}$  is the term that is responsible for the coexistence of phases. The reason for this would be clear when we discuss the solutions to Eq. (4).

The minimization of the free energy gives the following combinations for the possible values of  $\alpha_a$  and  $\alpha_b$ ;

$$|\alpha_a| = 0, \quad |\alpha_b| = 0, \quad (5a)$$

$$|\alpha_a| = 0, \quad |\alpha_b| \neq 0, \quad (5b)$$

$$|\alpha_a| \neq 0, \quad |\alpha_b| = 0, \quad (5c)$$

$$|\alpha_a| \neq 0, \quad |\alpha_b| \neq 0. \quad (5d)$$

We first consider the case where  $u_{22} > 0$ . A complete analysis involving the stability of the solutions in the  $r-g$  plane is shown below [10]. Figure 3 corresponds to the case  $u_1u_2 - u_{22}^2 < 0$  and Fig. 4 corresponds to the case  $u_1u_2 - u_{22}^2 > 0$ .

The dotted lines in the figures denote second-order transition while the wiggly line denotes first-order transition line. Being on the wiggly line signifies the state of coexistence as

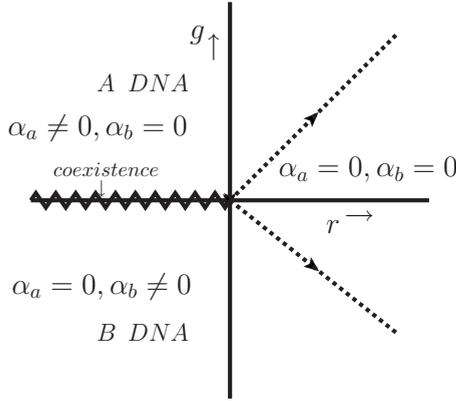


FIG. 3. Phase diagram corresponding to the free energy given by Eq. (4) in the  $r$ - $g$  plane for  $u_1u_2 - u_{22}^2 < 0$ . This diagram corresponds to the transition between A and B forms.

shown in Fig. 3. In Fig. 3 we observe that the disordered phase ( $|\alpha_a|=0, |\alpha_b|=0$ ) is separated from the ordered phase (B form and A form) by the second-order lines while the ordered phases themselves are separated by first-order line. The second order and the first-order lines meet at the bi critical point. In Fig. 4 we observe the emergence of another ordered phase ( $|\alpha_a| \neq 0, |\alpha_b| \neq 0$ ) separated from the other two ordered phases by second order lines. If  $u_{22}$  is sufficiently positive so that the condition for Fig. 3 is satisfied, we have coexistence, otherwise not. Considering  $u_{22} \rightarrow 0$ , the condition for Fig. 4 is easily satisfied and hence no phase coexistence as should be the case. For  $u_1 > 0$ ,  $u_2 > 0$ , and  $u_{22} > 0$  we get consistent solutions for Eq. (4). But if  $u_{22} < 0$ , it can be shown that the requirement of the stability of the solutions gives rise to inconsistent picture. This result is entirely an analytical outcome of Eq. (4) and is independent of DNA. We have used group theoretic arguments to construct the order parameters and write the free-energy expression. The free energy gives certain phase diagrams which can be explained in the light of experimental results. It may be noted here that any transition taking us from the group  $p_1$  to  $q_1$  may be represented by a similar theory.

#### IV. INTERPRETATION OF THE ORDER PARAMETER

Having constructed the order parameters we would now like to identify them. In condensed-matter systems, we may have multicomponent order parameter determined by the possible irreducible representation of the point group of the relevant vector  $\vec{k}$  in the reciprocal lattice as well as the star of  $\vec{k}$ . In the case of antiferromagnets [6] we may, for example, have the magnetization perpendicular to the antiferromagnetically coupled ferromagnetic planes or situated in the plane. For the intercalation compounds, the components of the order parameter are in a way related to the Fourier components of the density of the alkali atoms corresponding to the stars of  $\vec{k}$ . In the present case, however, we are dealing with two single component order parameters for a system whose structure does not fall under the category of Bravais

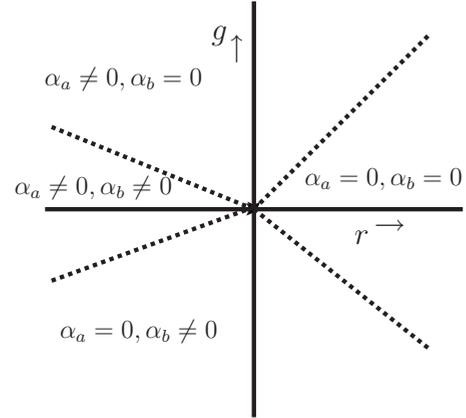


FIG. 4. Phase diagram corresponding to the free energy given by Eq. (4) in the  $r$ - $g$  plane for  $u_1u_2 - u_{22}^2 > 0$ .

lattice. Hence the above prescription would not be followed while identifying the order parameter. Being a structural phase transition, we would relate the order parameters to densities. For the double helix DNA,  $11_1$ ,  $10_1$ , or  $(10 \times 11)_1$  symmetry uniquely defines the sites on the strands.  $\rho_a$  denotes the densities of sites satisfying  $11_1$  symmetry and  $\rho_b$  the density of sites satisfying  $10_1$ . We identify the modulus of the order parameters as related to  $\rho_a - \rho_b$  and  $\rho_b - \rho_a = 0$  if  $\rho_a > \rho_b$  and vice versa. In the A phase  $\rho_b = 0$  and in the B phase  $\rho_a = 0$ . In the case of  $\rho_a = \rho_b$  (disordered phase), we have for both the order parameters  $\rho_a - \rho_b = 0$ . With the above definition of the order parameters, we are able to identify the two ordered phases and the disordered phase, as depicted in Fig. 3.

Experiments that have been carried out to study the phase transition [2,3] report conformations in which both A type and B type features are there apart from only A type or B type features. We interpret this as coexistence of phases. This may suggest that the transformation is first-order in nature as depicted in Fig. 3, coexistence being a characteristic of first order transition. The two phases coexist for the order parameters jump discontinuously at the first-order line. In first-order phase transition when one goes from one phase to another there is jump in the order parameter at the transition point. Similarly when one goes back to the same phase there is a jump. This only implies coexistence of phases at the transition point. Further, it may be noted that the DNA molecule, under experimentation in [2,3], being not a long molecule, has a finite region of coexistence in the  $r$ - $g$  plane, whereas Fig. 3 shows a line (wiggly) representing the coexistence valid for infinitely long molecule.  $|\alpha_a| \neq 0, |\alpha_b| \neq 0$  is the most ordered phase and in our problem should reflect a phase that has the lowest symmetry. But such a phase which will have a lower symmetry than both  $10_1$  and  $11_1$  is not possible. This perhaps tells us that Fig. 3 represents the likely phase picture and Fig. 4 may be ruled out.

If we refer to the experimental results of [2,3], it is mentioned that the transition from B DNA to A DNA takes place through 14 conformations. Further, the experimental data in [2,3], where they have measured certain quantities such as tilt angle, axial distance, etc. do not actually tell us whether

there has been a phase transition or not. But in the light of the above analysis, it may be concluded that the transition from B to A is a first-order phase transition with all the conformations being not fundamentally different but belong

to different phases (B and A) and the region of coexistence.

#### ACKNOWLEDGMENT

Criticism by the referees is gratefully acknowledged.

- 
- [1] R. E. Franklin and R. G. Goslin, *Nature (London)* **171**, 740 (1953).
- [2] R. E. Dickerson and H.-L. Ng, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 6986 (2001).
- [3] J. M. Vargason, K. Henderson, and P. Shing Ho, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 7265 (2001).
- [4] D. Jose and D. Porschke, *Nucleic Acids Res.* **32**, 2251 (2004); *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **59**, 620 (2003).
- [5] A. B. Harris, *Phys. Rev. B* **76**, 054447 (2007).
- [6] P. Bak and E. Domany, *Phys. Rev. B* **20**, 2818 (1979).
- [7] D. Mukamel and S. Krinsky, *Phys. Rev. B* **13**, 5065 (1976).
- [8] M. Vujcic, I. B. Bozovic, and F. Herbert, *J. Phys. A* **10**, 1271 (1977).
- [9] J. D. Watson, T. A. Baker, S. P. Bell, A. Gann, M. Levine, and R. Losick, *Molecular Biology of the Gene*, 5th ed. (Pearson Education, New Delhi, 2007).
- [10] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics*, 1st ed. (Cambridge University Press, Cambridge, 1995).