

PHASE TRANSITION IN A DOUBLE POLYMER CHAIN IN AN EXTERNAL FIELD

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The simplest model of a double polymer chain (similar to the Ising model) is used to consider the effect of an external action on a phase transition of the type of denaturation of DNA. It is shown that the presence of a phase transition is essentially determined by the parameters of the system and by the magnitude of the external field. Depending on the values of these parameters, one, two, or three phase transition points (with respect to the temperature) may occur.

IN recent times the attention of investigators has been attracted to the investigation of the unusual phase transitions which may occur in double, triple, and higher-multiple polymer chains. The essence of these transitions consists in the fact that long molecules which are twisted into "ropes" at a certain temperature unwind and separate into individual strands. The process of denaturation of DNA may serve as an example of such a phase transition; in this process the two strands which form the helical molecule are separated from each other. The problem of the melting of DNA was first theoretically considered by Zimm,^[1] and also by Lifson and Zimm.^[2] Processes analogous to denaturation, or to the melting of DNA, also occur in long protein chains.

The course of a phase transition is essentially determined by the chemical conditions in the surrounding medium, and also by the nature of the external influences acting on the system. The goal of the present article is a theoretical analysis of the simplest model of a double chain, permitting a phase transition of the type indicated above and allowing us to take a certain external influence into account.

1. FORMULATION OF THE MODEL

Let us consider a long molecule consisting of two complementary strands. By complementarity of the strands we shall understand the following property. During the formation of a single chain ("rope") out of the two strands, only the coupling of quite definite mutually-corresponding elements of the chain occurs. If we number the elements of each strand (counting from one end of the molecule), then only elements having identical numbers can be joined together. Sometimes this property is called the "memory" of the chain, emphasizing by such a name the fact that the order of connection of the elements is not determined by energy considerations but is prescribed by certain "hidden" structural properties of the molecule, which are not discussed in the problem.

We shall assume that each element of an individual chain may exist in one of two possible states (we shall denote them as the states +1 and -1) and each element interacts with the nearest neighbors of its own chain according to the law assumed in the one-dimensional Ising model. If the state of the element with number n (n = 1, 2, 3, ..., N) belonging to the strand with label s

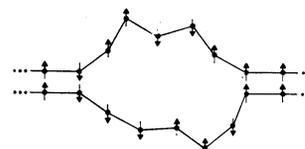


FIG. 1

(s = 1, 2) is denoted by σ_n^s , then the interaction energy of the elements of a single strand will have the form

$$E^s = -J \sum_n \sigma_n^s \sigma_{n+1}^s, \quad s = 1, 2, \quad (1)$$

where s denotes the label of the strand and n denotes the number of an element in the strand.

The interaction of complementary elements of different strands will also be regarded as an Ising-type interaction, and the corresponding energy for the complete chain can be written in a form similar to Eq. (1):

$$E^{12} = -J_0 \sum_n \sigma_n^1 \sigma_n^2. \quad (2)$$

However, we shall assume that the nature of the behavior of the system which is generated by this interaction differs in principle from that which is caused by the usual Ising interaction. Let us suppose that the linking of the strands and their disconnection are uniquely determined by the states of the complementary elements. Let us assume, for example, that for $\sigma_n^1 = \sigma_n^2$ the corresponding elements are found in a bound state, forming a segment of a "rigid" double chain (for example, a segment of the helix in the DNA molecule). The rigidity of the chain involves the small relative mobility of the neighboring paired elements. Let us denote the statistical weight of such a paired state by ω_1 . However, if $\sigma_n^1 = -\sigma_n^2$, then these elements separate, forming a segment of a split part of the molecule (see Fig. 1). In the split state the individual elements of each strand may easily turn relative to their neighbors, and their mutual orientation is limited only by the number of possible isomer compounds or by the corresponding rotation angles. We denote the statistical weight of such a state of an element on a free individual strand by $\sqrt{\omega_2}$.

Since a bound state always possesses a smaller energy than a "free" state, the described situation can be realized for $J_0 > 0$.

To a considerable extent such a description is

analogous to the formal assignment of an "Ising" spin to each element of the chains. Therefore we shall characterize an external influence on the molecule by a certain interaction of its elements with an external "field," choosing this interaction in the standard form used for the interaction of spins with a magnetic field. Then the total energy of the molecule consisting of N pairs of elements in an external field will be given by

$$E_N = -J_0 \sum_{n=0}^N \sigma_n^1 \sigma_n^2 - J \sum_{s=1}^2 \sum_{n=0}^{N-1} \sigma_n^s \sigma_{n+1}^s - B \sum_{s=1}^2 \sum_{n=0}^N \sigma_n^s$$

$$= -1/2 J_0 \sigma_0^1 \sigma_0^2 - 1/2 B \sum_{s=1}^2 \sigma_0^s + \sum_{n=0}^{N-1} E_{n, n+1} - 1/2 J_0 \sigma_N^1 \sigma_N^2 - 1/2 B \sum_{s=1}^2 \sigma_N^s \quad (3)$$

where B denotes the intensity of the effective external field, and

$$E_{n, n+1} = -1/2 J_0 (\sigma_n^1 \sigma_n^2 + \sigma_{n+1}^1 \sigma_{n+1}^2) - \sum_{s=1}^2 [J \sigma_n^s \sigma_{n+1}^s + 1/2 B (\sigma_n^s + \sigma_{n+1}^s)] \quad (4)$$

2. EVALUATION OF THE PARTITION FUNCTION

In order to construct the thermodynamics of a double molecule we shall use the grand canonical ensemble method and we calculate the corresponding partition function

$$Z(\mu) = \sum_{N=1}^{\infty} [e^{\beta \mu N} Z_0(N)], \quad (5)$$

where $\beta = 1/T$, μ denotes the chemical potential, N denotes the number of pairs of elements in the chain, and $Z_0(N)$ is the partition function for a chain consisting of N pairs of elements. By definition

$$Z_0(N) = \sum_{\{\sigma_n^s\}} g \{ \sigma_n^s \} \exp [-\beta E_N \{ \sigma_n^s \}]. \quad (6)$$

where $E_N \{ \sigma_n^s \}$ denotes the total energy of the chain for a given configuration of the spins $\{ \sigma_n^s \}$, $g \{ \sigma_n^s \}$ denotes the statistical weight of the corresponding spin configuration, and the summation goes over all possible configurations.

It is convenient to carry out the evaluation of the partition function (5) by using the standard matrix method (see, for example, [3]). Since in either the paired or in the split states of the chain each pair σ_n^1, σ_n^2 takes only two values, then it is convenient to distinguish the spin states of a pair of elements, which in what follows we shall regard as a single link of the chain, with the aid of an index α which takes the values 1 or 2. Then, in the one-dimensional Ising model which describes the spin states in our problem, it is sufficient to introduce the corresponding matrices of the second rank. In particular, one can represent expression (6) in the form

$$Z_0(N) = \text{SAE} \hat{Z}(N) \equiv \sum_{\alpha, \alpha'=1}^2 Z_{\alpha\alpha'}(N), \quad (7)$$

where we have introduced the symbolic notation $\hat{Z}(N)$ for the matrix $Z_{\alpha\alpha'}(N)$ ($\alpha, \alpha' = 1, 2$) where the first subscript refers to the first link of the chain and the second refers to the last link in the chain. In order to be definite, we shall assume that for the appropriate link in the paired state $\alpha = 1$ if $\sigma^1 = \sigma^2 = 1$, and $\alpha = 2$ if $\sigma^1 = \sigma^2 = -1$. In the split state $\alpha = 1$ if $\sigma^1 = -\sigma^2 = 1$, and $\alpha = 2$ if $\sigma^1 = -\sigma^2 = -1$.

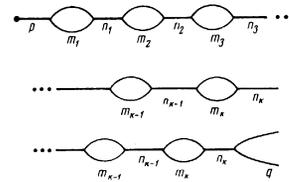


FIG. 2

In order to represent the partition function (5) in the form of a matrix product, let us consider a certain subdivision of the total double chain into paired and split segments (see Fig. 2). Let there be 2k points in the chain corresponding to the separation of the paired and split segments (in what follows we shall call such points junctions). It is obvious that k coincides with the number of "rings" along the chain shown in Fig. 2. Let us denote by m_i and n_i ($i = 0, 1, \dots, k$) the number of links on the split and paired segments, respectively. Then, assuming that at least one link of the chain is always found in the paired state, one can postulate the following representation for the partition-function matrix:

$$\hat{Z}(N) = \hat{z}_0 \sum_k \sum_{p, m_i, n_i, q} \hat{Z}^I(p) R \left\{ \prod_{i=1}^k \hat{Z}^{II}(m_i) \hat{Z}^I(n_i) \right\} (\hat{z}_0 + \hat{Z}^F(q)), \quad (8)$$

where p denotes the number of links in the paired segment at the extreme left in Fig. 2 ($p \geq 0$), and q denotes the number of links occurring in the free split state at the extreme right edge of the chain in Fig. 2 ($q \geq 1$). The summation in Eq. (8) is carried out under the obvious condition that

$$p + \sum_{i=1}^k (m_i + n_i) + q = N. \quad (9)$$

The letter R in Eq. (8) in front of the product sign indicates that the noncommuting factors corresponding to different values of i are arranged in order of increasing value of i from the left to the right. The matrices appearing in formula (8) have the following meanings:

$\hat{Z}^I(n)$ is the standard form of the symmetrized statistical matrix for a chain of n links which are in the paired state. It is obvious that one can write this matrix in the form

$$\hat{Z}^I(n) = (\hat{z}_1)^n, \quad (10)$$

$$\hat{z}_1 = \omega_1 e^{\epsilon_0} \begin{pmatrix} e^{\epsilon+2H} & e^{-\epsilon} \\ e^{-\epsilon} & e^{\epsilon-2H} \end{pmatrix}, \quad (11)$$

where the notation $\epsilon_0 = \beta J_0$, $\epsilon = 2\beta J$, $H = \beta B$ has been introduced.

The appearance of the matrix factor \hat{z}_0 in formula (8) is related to the symmetrization of the energy (4) and to the fact that the matrix (11) only includes the symmetrized part of the total energy (3). It is obvious that

$$\hat{z}_0 = e^{\epsilon_0/\alpha} \begin{pmatrix} e^H & 0 \\ 0 & e^{-H} \end{pmatrix}. \quad (12)$$

The characteristics of the junctions do not appear in the expression for the matrix $\hat{Z}^I(n)$; from this it follows that they must be taken into consideration in the definitions of the remaining matrices. The basic property of a junction is that it connects links that exist in different states. Therefore the matrix corresponding to it must

transform the definitions of the various matrices from the classification corresponding to paired states to the classification corresponding to split states, and vice versa. In order to demonstrate the form of the matrix which carries out the transition from a paired state to a split state, let us write down the expression for the matrix $\hat{Z}^F(q)$:

$$\hat{Z}^F(q) = \hat{\Gamma}_1 (\hat{z}_2)^q \hat{z}_f, \quad (13)$$

$$\hat{z}_2 = \omega_2 e^{-\epsilon_0} \begin{pmatrix} e^\epsilon & e^{-\epsilon} \\ e^{-\epsilon} & e^\epsilon \end{pmatrix}, \quad (14)$$

$$\hat{\Gamma}_1 = \gamma \frac{e^{\epsilon_0}}{2 \operatorname{ch} \epsilon} \begin{pmatrix} e^H & e^H \\ e^{-H} & e^{-H} \end{pmatrix}, \quad (15)$$

$$\hat{z}_f = e^{-\epsilon_0/2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad (16)$$

where the factor γ is introduced in order to take account of the restrictions on the mobility of the link at the junction point, and the matrix \hat{z}_f , associated with the last pair of elements in the split state, has the same origin as the matrix \hat{z}_0 .

The matrix $\hat{Z}^{\text{II}}(m)$ in formula (8) denotes the contribution to the partition function from the states of a "ring" containing m pairs of elements. In order to calculate this quantity, it is necessary to correctly take account of the number of different configurations in which split segments of the molecule can occur. Let us recall that the split segments of the chain may freely travel in space, and their position is limited only by the nature of the connections between the elements and by the length of these segments. Therefore the number of configurations of interest to us is determined by the probability that the two strands, each of which has the same number of moving links going out of a common point, will encounter their own ends. If the chains consist of freely coupled elements then the mentioned probability is equal to the probability that two diffusing particles, going away from the same point, meet after a certain identical number of elementary steps. For a ring consisting of m pairs of elements, we shall denote the number of indicated configurations by the letter A_m . For a chain of free coupled elements and for large values of m ($m \gg 1$) one can assume $A_m = \text{const} \cdot m^{-3/2}$. Precisely such a dependence of the coefficients on m was assumed in the work of Zimm.^[11] However it is necessary to keep in mind that this is the weakest of the possible dependences of A_m on m . It is easy to indicate examples in which the exponent r in the formula $A_m = \text{const} \cdot m^{-r}$ is larger than the value adopted in^[11] ($r > 3/2$). In addition, this dependence may not be a power-law dependence at all, but we shall assume that the series $\sum_m A_m$ always converges.

Returning to the notion $\hat{Z}^{\text{II}}(m)$, let us represent it in the form

$$\hat{Z}^{\text{II}}(m) = \hat{\Gamma}_1 A_m (\hat{z}_2)^m \hat{\Gamma}_2, \quad (17)$$

where \hat{z}_2 is defined by formula (14), and the correcting matrix is given by the expression

$$\hat{\Gamma}_2 = \gamma \frac{e^{\epsilon_0}}{2 \operatorname{ch} \epsilon} \begin{pmatrix} e^H & e^{-H} \\ e^H & e^{-H} \end{pmatrix}. \quad (18)$$

After discussing all of the factors inside the summation sign in (8) one can go on to perform the summation,

which is contained in the initial definition (5) for the partition function $Z(\mu)$. However it is convenient to perform this summation up to the operation (7) by introducing the matrix

$$\hat{Z}(\mu) = \sum_{N=1}^{\infty} e^{\beta \mu N} \hat{Z}(N). \quad (19)$$

The evaluation of the sum (19) is carried out in exactly the same way as in the articles by Lifson and Zimm.^[2,4] The result of this calculation is the following:

$$\hat{Z}(\mu) = \hat{z}_0 \hat{Z}^{\text{I}}(\mu) \{ \hat{I} - \hat{Z}^{\text{II}}(\mu) \hat{Z}^{\text{I}}(\mu) \}^{-1} (\hat{z}_0 + \hat{Z}^F(\mu)) \\ = \hat{z}_0 \{ \hat{I} - t \hat{z}_1 - \hat{Z}^{\text{II}}(\mu) \}^{-1} (\hat{z}_0 + \hat{Z}^F(\mu)), \quad (20)$$

where $t = e^{\beta \mu}$. The individual factors in (20) are defined in an obvious manner:

$$\hat{Z}^{\text{I}}(\mu) = \sum_{n=0}^{\infty} t^n \hat{Z}^{\text{I}}(n) = \sum_{n=0}^{\infty} (t \hat{z}_1)^n = (\hat{I} - t \hat{z}_1)^{-1}, \quad (21)$$

$$\hat{Z}^F(\mu) = \sum_{q=1}^{\infty} t^q \hat{Z}^F(q) = \hat{\Gamma}_1 \sum_{q=1}^{\infty} (t \hat{z}_2)^q \hat{z}_f = \hat{\Gamma}_1 t \hat{z}_2 (\hat{I} - t \hat{z}_2)^{-1} \hat{z}_f, \quad (22)$$

$$\hat{Z}^{\text{II}}(\mu) = \sum_{m=2}^{\infty} t^m \hat{Z}^{\text{II}}(m) = \hat{\Gamma}_1 \psi(t \hat{z}_2) \hat{\Gamma}_2, \quad (23)$$

and the function $\psi(x)$ is equal to the sum of the series:

$$\psi(x) = \sum_{m=2}^{\infty} A_m x^m. \quad (24)$$

It is clear that formulas (21), (22), and (24) are valid provided all of the corresponding series converge.

For operations with the matrices $\hat{Z}^{\text{II}}(\mu)$ and $\hat{Z}^F(\mu)$ it is convenient to use the representation in which \hat{z}_2 is diagonal. Let us write the transformation $\hat{\Lambda}^{(2)}$ which reduces \hat{z}_2 to diagonal form in the standard form:

$$\hat{\Lambda}^{(2)} = \hat{S}_2^{-1} \hat{z}_2 \hat{S}_2, \quad (25)$$

where the matrices

$$\hat{S}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}, \quad \hat{S}_2^{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}. \quad (26)$$

The diagonal elements of the matrix $\hat{\Lambda}^{(2)}$ are determined by the following simple formulas:

$$\lambda_1 = \Lambda_{11}^{(2)} = 2\omega_2 e^{-\epsilon_0} \operatorname{ch} \epsilon, \quad \lambda_2 = \Lambda_{22}^{(2)} = 2\omega_2 e^{-\epsilon_0} \operatorname{sh} \epsilon. \quad (27)$$

Finally, by performing simple but cumbersome matrix operations, we may evaluate the desired partition function:

$$Z(\mu) = \text{SAE} \hat{Z}(\mu) = 2e^{\epsilon_0} \Delta^{-1}(t) (\operatorname{ch} 2H - 2t\omega_1 e^{\epsilon_0} \operatorname{sh} \epsilon) \left(1 + \frac{\gamma}{\operatorname{ch} \epsilon} \frac{t\lambda_1}{1 - t\lambda_1} \right), \quad (28)$$

where

$$\Delta(t) = 1 + 2(t\omega_1 e^{\epsilon_0})^2 \operatorname{sh} 2\epsilon - 2t\omega_1 e^{\epsilon_0 + \epsilon} \operatorname{ch} 2H \\ + (2t\omega_1 e^{\epsilon_0} \operatorname{sh} \epsilon - \operatorname{ch} 2H) \frac{\gamma^2 e^{2\epsilon_0}}{\operatorname{ch}^2 \epsilon} \psi(t\lambda_1). \quad (29)$$

Formulas (28) and (29) determine the partition function of the grand canonical ensemble as a function of μ , T , and B .

3. ANALYSIS OF THE PHASE TRANSITION

In order to clarify the question of the possible existence of a phase transition of the type of denaturation in the system under consideration, it is convenient to consider the behavior of the chemical potential μ as a function of T and B . As is well known,^[5] in the method

of the grand canonical ensemble the function $\mu = \mu(T, B)$ is found from the condition

$$\partial\Omega / \partial\mu = -N, \tag{30}$$

where N denotes the number of pairs of elements in the chain being studied, and

$$\Omega = -T \ln Z(\mu). \tag{31}$$

If a phase transition is possible in the system, then as $N \rightarrow \infty$ a singularity appears in the function $\mu = \mu(T, B)$ obtained from Eq. (30), this singularity corresponding to a point of intersection of the two branches of the solution of the equation

$$\partial\Omega / \partial\mu = -\infty. \tag{32}$$

In the present case such a situation is possible in principle since from the explicit form of the partition function (28) it follows that the solution of Eq. (32) may be found either from the condition

$$t\lambda_1 = 1, \tag{33}$$

or as the solution of the transcendental equation

$$\Delta(t) = 0. \tag{34}$$

We recall that $t = e^{\beta\mu} \equiv e^{\mu/T}$. It is easy to figure out that the function $\mu = \mu(T, B)$, which is obtained from Eq. (33), pertains to the states of the completely separated chain and is the chemical potential of the denatured phase. The solution (34) gives the chemical potential of the phase in which paired and separated segments of the chain simultaneously exist. A phase transition occurs at that temperature for which the chemical potentials of these two phases coincide. Since the corresponding temperature depends on the value of B , a phase transition curve $T = T(B)$ exists. It is clear that this curve can be found from condition (34) in which $t = 1/\lambda_1$. If one introduces the notation

$$x = e^{2\epsilon_0} \left(\frac{\omega_1}{\omega_2} + \frac{\gamma^2 \psi(1)}{\text{ch}^2 \epsilon} \right) \tag{35}$$

$$y = e^{2\epsilon_0} \frac{\omega_1}{\omega_2} \text{th } \epsilon, \tag{36}$$

then the phase transition curve is determined by the solution of the transcendental equation

$$1 + xy - (x + y) \text{ch } 2H = 0 \tag{37}$$

under the compulsory condition

$$xy \leq 1. \tag{38}$$

Condition (38) is the requirement in order that the largest root of the matrix $t\hat{z}_1 + \hat{\Gamma}_1 \psi(t\hat{z}_2)\hat{\Gamma}_2$ does not exceed unity. This natural requirement is the condition for the analytical form of the partition function (28).

Let us carry out a graphical analysis of the solutions (37). Let us start with the case $B = 0$. Then from Eq. (37) it follows that either $x = 1$ or $y = 1$. However from the definitions (35) and (36) it follows that $x \geq y$; therefore, taking the restriction (38) into account, we notice that the temperature of the phase transition for $B = 0$ is determined by the condition $x = 1$, which is equivalent to

$$f(\beta) = e^{-2\beta J_0}, \quad f(\beta) \equiv \frac{\omega_1}{\omega_2} + \frac{\gamma^2 \psi(1)}{\text{ch}^2 2\beta J}. \tag{39}$$

Let us assume that $f(0) < 1$. Then, as follows from a

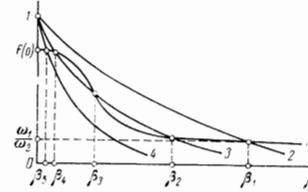


FIG. 3

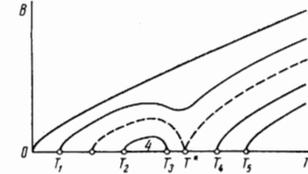


FIG. 4

consideration of Fig. 3, the existence of a solution to Eq. (39) depends on the value of J_0 . If J_0 is very small ($J_0 \rightarrow 0$), the curves for the functions $f(\beta)$ (curve 1) and $\exp(-2\beta J_0)$ (curve 2) intersect at a single point ($\beta = \beta_1$). With increasing values of J_0 the point $\beta = \beta_1$ moves to the left along the axis and curve 2 descends. At a certain value $J_0 = J_0^{(1)}$ a point of contact of the curves 1 and 2 arises, lying to the left of β_1 . If J_0 somewhat exceeds the value $J_0^{(1)}$, then there are three points of intersection of the corresponding curves (the points β_2, β_3 , and β_4 corresponding to the points of intersection of curves 1 and 3). With a further increase of J_0 the points β_2 and β_3 converge, but the point β_4 moves to the left. Finally, there exists a value $J_0 = J_0^{(2)}$ at which $\beta_2 = \beta_3$. It is clear that for $J_0 > J_0^{(2)}$ (curve 4) once again a single point of intersection, $\beta = \beta_5$, is left.

Going on to clarify the temperature regions in which the various phases exist, we note that the denatured phase corresponds to values of B lying below the curve $B = B(T)$, satisfying Eq. (37). From this it follows that for $B = 0$ and $J_0 < J_0^{(1)}$ the denatured phase exists for $T > T_1 = 1/\beta_1$ (see Fig. 3). However, if $J_0^{(1)} < J_0 < J_0^{(2)}$, then for $B = 0$ the denatured phase exists in the interval $T_2 < T < T_3$ where $T_2 = 1/\beta_2$, $T_3 = 1/\beta_3$, and also for temperatures $T > T_4 = 1/\beta_4$. Finally, if $J_0 > J_0^{(2)}$ then the denatured phase is realized for $T > T_5 = 1/\beta_5$.

After this it is easy to represent the qualitative shape of the phase transition curves for $B \neq 0$. The following curves are represented schematically on Fig. 4: 1—for $J_0 = 0$, 2—for $0 < J_0 < J_0^{(1)}$, 3—for $J_0 = J_0^{(1)}$ (this curve approaches the temperature axis at the point $T = T^*$), 4—for $J_0^{(1)} < J_0 < J_0^{(2)}$, and 5—for $J_0 \geq J_0^{(2)}$. Thus, it turns out that for $f(0) < 1$ and for arbitrary values of B a phase transition always exists in the system under consideration. In addition, for sufficiently small values of B there exists a range of values of the parameter J_0 for which this transition is repeated three times. The very low-temperature phase is a cohesive phase, and the very high-temperature phase is a denatured phase. As $T \rightarrow \infty$ the phase transition curve has the form of a straight line

$$B = T \text{ Arch } f^{-1}(0). \tag{40}$$

Naturally expression (40) has meaning for $f(0) < 1$. In that case when the phase transition occurs three times

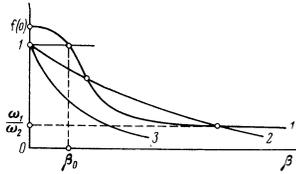


FIG. 5

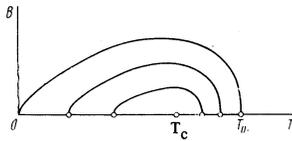


FIG. 6

on the temperature axis, a finite interval appears in which the denatured phase exists, bounded by temperature intervals in which the cohesive phase is realized.

We note that at the points where the phase transition curves approach the temperature axis on Fig. 4, the curve $B = B(T)$ has a vertical tangent, and in the vicinity of these points it corresponds to the graph of a quadratic parabola.

Now let us go on to the case $f(0) > 1$. The graphical investigation of the phase transition curves in this case is clear from Fig. 5, on which curve 1 represents the graph of the function $f(\beta)$ and curves 2 and 3 represent graphs of the function $\exp(-2\beta J_0)$ for small and large values of J_0 respectively. We at once deduce the schematic shape of the phase transition curves (see Fig. 6) corresponding to different values of J_0 . For $J_0 = 0$ the curve $B = B(T)$ starts from the origin of coordinates and ends at the point $T = T_0$, but for a certain value $J_0 = J_0^{(k)}$ the loop of this curve shrinks to a point on the temperature axis ($T = T_c$). For $J_0 > J_0^{(k)}$ the phase transition in such a system is absent. An interesting property of the system with $f(0) > 1$ is the fact that the most high-temperature phase is the cohesive phase. However, one can easily verify by a direct calculation that with an increase of the temperature the number of split segments (the "rings" shown in Fig. 2) and the length spanned by their parts of the chain increase. As $T \rightarrow \infty$ the ratio of the length of all split segments of the chain to the total length of the chain tends to unity.

The nature of the phase transition very significantly depends on the value of the derivative of the function $\psi = \psi(z)$ at the point $z = 1$, i.e., on the quantity $\psi'(1)$. In

order to illustrate this dependence, let us consider the first derivative of the thermodynamic potential Ω , which formally coincides with the average value of the spin (or magnetic moment) of a single element in the chain, namely, the quantity

$$M = \frac{1}{2} \frac{\partial \Omega}{\partial B} / \frac{\partial \Omega}{\partial \mu}. \tag{41}$$

It is quite clear that $M = 0$ in the denatured phase and $M \neq 0$ in the cohesive phase (for $B \neq 0$). Let us present the expression for M at the phase transition point, denoting it by M_c :

$$M_c = \frac{(x + y) \operatorname{sh} 2H}{1 - xy + (\operatorname{ch} 2H - y)s}, \tag{42}$$

where x and y are defined by formulas (35) and (36), and the parameter s is given by

$$s = \gamma^2 \frac{e^{2\epsilon_0}}{\operatorname{ch}^2 \epsilon} [\psi'(1) - \psi(1)], \tag{43}$$

and the quantities T and B are taken at the corresponding phase transition point.

If the value of $\psi'(1)$ is bounded, then from Eq. (42) it follows that the quantity M has a finite discontinuity (for $B \neq 0$) associated with the phase transition. This means that the corresponding transition ($B \neq 0$) is a phase transition of the first kind. However if $\psi'(1) = \infty$, then $M_c = 0$ and the quantity M is continuous at the phase transition point. It turns out that under the condition $\psi'(1) = \infty$ the other first derivatives of the thermodynamic potential are also continuous at the phase transition point; therefore we may conclude that the corresponding transition will be a transition of the second kind or of higher order.

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