Supersymmetry Theory of Disordered Heteropolymers

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March 24, 2022

Abstract

The effective motion equation that describes the different monomer alternation along the heteropolymer chain is proposed. On its basis the supersymmetry field scheme that allows to obtain the equations for the structure factor and Green function is built up. The memory and ergodicity breaking effects are investigated depending on the temperature and quenched disorder of the monomer alternation. The phase diagram that determines the existence of the non-ergodic and freezing states is provided.

PACS numbers: 61.41.+e, 05.40+j, 11.30.Pb

1 Introduction

In recent years investigation of the unusual behaviour of random heteropolymers with a random sequence of different kinds of monomers has attracted considerable attention (see [1]-[3] and references therein). With temperature decreasing such systems experience two types of phase transitions at which polymer either goes to freezing state or has a microphase separation that is inherent in protein biomolecules type.

At folding process heteropolymer chooses out of infinite set of possible states the unique frozen nonequilibrium but stationary state with fixed spatial conformation and monomer sequence (type of DNA). The problem in considering of such transitions is to build up more simple method of averaging thermodynamic values over the quenched disorder. Here, the methods of statistical physics first used in spin glass investigation are taken as basic ones [4].

Certain of polymers type of block copolymers, undergo the so-called microphase separation at which blocks of different chemical composition segregate to microdomain structures to gain a spatially inhomogeneous composition throughout the pattern. The chemical bonds between the blocks prevent the usual macroscopic phase separation observed in homopolymer blends. A variety of microphases, such as one-dimensional lamellar structures, hexagonal arrays of cylinders, body-centered-cubic arrays of spheres and so on have been observed for simple diblock copolymer melts.

At first, microphase separation had been studied within mean-field approximation [5] in the case of A-B block copolymers with arbitrary composition \( f \). It turns out that at \( f \neq 0.5 \) with temperature decrease the system undergoes a sequence of the microphase separations of the first order, where period \( 2\pi/k_0 \) of space structure is of order of block length and does not depend on temperature. In \([6]\) it was shown a principal role of the fluctuations in phase transition. By virtue of condition \( k_0 \neq 0 \) the order parameter fluctuations give divergent contribution to thermodynamic values, so that continuous phase transition transforms to the first order weak transition \([7]\).

At passage to random heteropolymers both the microphase separation and the freezing remain, but here the space period acquires strong dependence on temperature \([1,8]\). According to field considerations \([1,10]\) the fluctuations suppress both mentioned transitions in random copolymers, but copolymer melts in disordered media can suffer these transformations.

Similar to spin glass \([1]\), the main approach of statistical mechanics of random heteropolymers is the replica method \([1]\) that is not only pragmatic, but very non-descriptive and artificial. Apart from the replica trick, the transfer matrix method \([1]\), kinetic approach \([12]\) and others (see \([13]\)) are used in random heteropolymers theory as well. However, it is a well known in theory of spin glass that within the framework of Sherrington-Kirkpatrick model \([14]\) both replica method and supersymmetry (SUSY) field approach give identical results \([15]\). On the other hand, the advantage of the SUSY field usage is that its components have explicit physical meaning \([16]\).
By recent moment, SUSY method in polymer theory had been proposed by Vilgis [17], but did not obtain further development. In this work we intend to complete this problem. Our article is organized as follows. In Section 2 we build up an effective motion equation of disorder heteropolymer to describe the different monomer alternation along the heteropolymer chain [18]. The form of effective Hamiltonian of the problem under consideration is obtained in Section 3 to avoid discrepancies of different methods. Section 4 is devoted to consideration of a SUSY scheme [19] that is optimal for study of the disorder heteropolymer in weak segregation limit [20]. In Section 5 a SUSY correlator is considered to examine memory and non-ergodicity effects (Section 6). Finally, Section 7 is devoted to discussion of obtained results.

2 Effective motion equation

Usually, the SUSY method is based on the dynamic Langevin-type motion equation [19]. But covalent bonds in the polymer chain make such way inefficient because dynamic theory in polymers is much more complicated, than statistical mechanics of usual many-body systems [21]. Therefore, it is essential to obtain the effective motion equation instead of dynamic one.

Let us initiate with directed polymer that is represented by the Gaussian chain with probability $\Psi(R, N)$ to find the end-point $N$ at coordinate $R$. As is known the function $\Psi(R, N)$ obeys the Schrodinger-type equation

$$\partial \Psi / \partial N = (D \partial^2 / \partial R^2 - U(R, N)) \Psi,$$

where number $N \gg 1$, $D \equiv b^2 / 6$ is effective diffusion coefficient determined by the Kuhn segment length $b$, $U(R, N)$ is external field. In the limit $N \to \infty$ a solution of Eq.(1) can be represented in the form of functional integral over dependence $r(n)$ of chain coordinate on number of internal monomers:

$$\Psi(R, N) = \int \exp(-S R N \{r(n)\}/2D) \delta r(n).$$

Here conventional action $S(R, N) \equiv S_{RN}\{r(n)\} = \int_0^N L_0(r(n)) dn$ corresponds to the fixed end-points $r(0) = 0$, and $r(N) = R$ is determined by Lagrangian of the Euclidian field theory [19, 21]

$$L_0 = \frac{1}{2} \left( \frac{dr(n)}{dn} \right)^2 + 2D U(r, n),$$

where the effective kinetic energy, for which the continuum limit $r(n+1) - r(n) \to dr(n)/dn$ is taken into account, presents the covalent bonds between monomers of polymer chain [21]. Inserting of ansatz (2) into Eq.(1) gives the Jacobi-type equation

$$\partial S / \partial N = D \partial^2 S / \partial R^2 - \frac{1}{2} \left( \partial S / \partial R \right)^2 + 2DU.$$

After introducing generalized momentum $p \equiv \partial S / \partial R$ and total derivative $dp/dN \equiv \partial p / \partial N + (p \partial / \partial R)p$, Eq.(4) takes the linear form of Burgers equation:

$$dp/dN = D (\partial^2 p / \partial R^2 + 2\partial U / \partial R).$$

The above pointed relation of Eqs.(1)–(5) is a well-known fact in the theory of directed polymers, stochastic growth and kinetic roughening phenomena (see [22]).

The basic observation for our purpose is that the Schrodinger-type equation (1) takes the form of the Fokker-Planck equation

$$\frac{\partial P}{\partial N} = \left( D \frac{\partial^2}{\partial R^2} - \frac{\partial}{\partial R} \right) P$$

for distribution probability

$$P(R, N) = \Psi(R, N) \exp\{-V(R)/2D\},$$

which dependence on $R$ is determined by effective potential
\[ V \equiv -\int F dR. \]  

Corresponding force \( F \) relates with the initial potential \( U \) in Eq. (1) as follows:

\[ U = \frac{1}{4D} F^2 + \frac{1}{2} \frac{\partial F}{\partial R}. \]  

As is well known [24], Eq. (1) determines the probability to realize solution of corresponding Langevin-type equation

\[ \frac{\partial R}{\partial N} = F(R, N) + \zeta(N) \]  

for stochastic variable \( R = R(N) \). Here the separated stochastic force \( \zeta \) is fixed by the white-noise conditions

\[ \langle \zeta(N) \rangle = 0, \quad \langle \zeta(N) \zeta(N') \rangle = 2D\delta(N - N'), \]  

where the angular brackets denote average with respect to the distribution (7).

In going from the above considered case of directed polymer to the main object of our interest, the random heteropolymer AB, the coordinate \( R \) of end-point \( N \) turns into a stochastic Ising variable \( \theta(n) \), where \( \theta(n) = 1 \) if \( n \)-th segment is of type A and \( \theta(n) = -1 \) otherwise. Corresponding to the quenched disorder in fixed sequence of different type segments, the law \( \theta(n) \) of monomer alternation along the chain is described by master equation of that determines the Glauber dynamics [25]. Corresponding sequence correlator \( \sigma(n)\sigma(n') \) for effective spin \( \sigma(n) \equiv \theta(n) - \overline{\theta(n)} \), being deviation of microscopic value \( \theta(n) \) from average \( \overline{\theta(n)} \), takes the form [11]

\[
\overline{\sigma(n)\sigma(n')} = C_2 \exp(-|n-n'|/l), \\
C_2 \equiv 4f(1-f), \quad f \equiv (1/2)(1+\overline{\theta(n)}),
\]

where overbar denotes the averaging over composition (quenched disorder). Here two sequence characteristics appear being correlation length \( l \) and fraction \( f \) of type-A monomers.

Stochastic variable \( \sigma(n) \) that possesses of the correlator (12) with exponential form, is governed by the effective motion equation

\[
d\sigma/dn = -\sigma/l + s(n),
\]

where the stochastic source \( s(n) \) is the white noise:

\[
\overline{s(n)} = 0, \quad s(n)s(n') = 2C_2 t^{-1}\delta(n-n').
\]

Relation between the microscopic value \( \sigma(n) \) and stochastic \( \delta \)-correlated variable \( s(n) \) is given by equation

\[
\sigma(n) = \int_0^n e^{-(n-m)/l}s(m)dm,
\]

that is the solution of Eq. (13). On the contrary to the colored noise \( \sigma(n) \), the white noise \( s(n) \) possesses of the Gauss distribution function

\[
P\{s(n)\} = (4C_2\pi/l)^{-1/2}\exp\left\{-\frac{l}{4C_2} \int_0^n s^2(n)dn\right\},
\]

that determines quenched disorder with intensity \( 4C_2 l^{-1} \). Respectively, the local averaged field

\[
\eta(r, n) \equiv (4C_2)^{-1/2}\overline{\sigma(n)\delta(r-r(n))}
\]

represents the order parameter (here and below the monomer volume takes to be equal unity).

Apart from usual terms type of that in Eq. (14), effective motion equation for the field (17) must contain the inhomogeneity contribution \( D\partial^2\eta/\partial r^2 \) (as the first term in r.h.s. of Eq. (14)) that takes Fourier transform \(-Dk^2\eta_k\). As a result, the motion equation for the Fourier transformation

\[
\eta_k(n) = N^{-1/2}\int \eta(r, n)e^{-ikr}dr
\]
of the field \( \langle \chi \rangle \) takes the Langevin form:

\[
\frac{\partial \eta_{nk}}{\partial n} = -(ak)^2 \eta_{nk} - \partial \mathcal{H}/\partial \eta^*_k + \zeta_k.
\]  

(19)

Here, as above, the continuum approximation for effective time \( n \gg 1 \) is used, the characteristic distance \( a \equiv D^{1/2} = b^{-1/2} \) is determined by the Kuhn segment length \( b \), and determination of effective force \( f_k = -\partial \mathcal{H}/\partial \eta^*_k \) (cf. Eq. (8)) are taken into account. The white noise \( \zeta_k = \zeta_k(n) \) is defined by conditions type of Eqs. (11):

\[
\langle \zeta_k \rangle = 0, \quad \langle \zeta_k(n)\zeta_k(n') \rangle = \delta_{kk}\delta(n-n'),
\]  

(20)

where angular brackets denote average over thermal disorder.

### 3 Effective Hamiltonian

To obtain the effective Hamiltonian \( \mathcal{H}\{\eta\} \equiv \Omega'\{m\} \) in Eq. (13) the thermodynamic potential \( \Omega'\{m\} \), being the average with respect to both the conformation and the sequence scattering, should be determined as a function of the averaged order parameter

\[
m(r) = \sum_n \langle \eta(r,n) \rangle = (4C_2)^{-1/2} \sum_n \langle \sigma(n) \delta(r-r(n)) \rangle.
\]  

(21)

With this aim, let us write the partition function in the form of the functional integral (19)

\[
Z = \int \delta m(r) \exp \left\{ C_2 \chi \int m^2(r) dr \right\} \times
\]

\[
\times \left\{ \delta \left\{ \sum_n \delta(r-r(n)) - 1 \right\} \delta \left\{ \sum_n (4C_2)^{-1/2} \sigma(n) \delta(r-r(n)) - m(r) \right\} \right\}.
\]  

(22)

Here \( \chi > 0 \) is the composition Flory parameter, the first \( \delta \)-function takes into account incompressibility condition, the second one reduces to determination (21) of order parameter \( m(r) \). Further, one follows to represent the \( \delta \)-functions as functional Laplace expansions over auxiliary fields \( J_p \), \( J_m \). Then the average expression in Eq. (22) takes the exponential form with the exponent \( \int (J_p + J_m m) dr - \Omega\{J_p, J_m\} \), where the last term, being averaged over sequence and configuration sets, gets conventional free energy at given fields \( J_p \), \( J_m \). The steady-state magnitudes \( J_p \), \( J_m \) of these fields are determined by conditions \( \delta \Omega/\delta J_p = 0 \), \( \delta \Omega/\delta J_m = -m \). Inserting expression for \( J_p \), \( J_m \) to functional \( \Omega\{J_p, J_m\} \) gets the thermodynamic potential defined by equation

\[
Z = \int \delta \Omega_m \exp(-\Omega'\{m_k\}),
\]  

(23)

Here the inhomogeneity contribution is taken into account in the quadratic term, averaging procedure with respect to the quenched disorder (13) results in appearance of \( l^{-1} \)-terms, double \( k \)-dependence of the kernel \( w_{kk'} = 4N^{-1}(l a^{-2})(k^2 + k'^2)^{-1} \) is stipulated by averaging over the distribution (8). It is worth mentioning that expression (23) agrees with Refs. [1, 11], whereas in Refs. [9, 28], where replica approach was used, the second summand of Hamiltonian (23) with the opposite sign was obtained. To correspond the self-action effects the integrand in last term has the usual expansion form [1, 11]

\[
v = -(\mu/3!)m^3 + (\lambda/4!)m^4;
\]

\[
\mu \equiv 12C_3 C_2^{-1/2} l^{-1}, \quad \lambda \equiv 24(1 + 5C_3^2/C_2) l^{-1},
\]

\[
C_2 \equiv 4 f(1-f), \quad C_3 \equiv |1 - 2 f|.
\]  

(24)


As mentioned above, this method is based on the Eqs. (22) that allows to express quenched disorder correlator within the transfer matrix approach. If one uses the more popular replica method, then the field $J_m$ and the order parameter $m$ must take a replica index $\alpha$ under which in the Hamiltonian (23) the summation from 1 to $n \to 0$ should be made [3]. Then the quadratic contribution takes the form
\[
\frac{1}{2} \sum_{k_\alpha} A_{\alpha\alpha}(k) |m_\alpha(k)|^2 + \frac{1}{2} \sum_{k_{\alpha\beta}} A_{\alpha\beta}(k)m_\alpha(k)m_\beta(-k),
\]
(25)
where in the limit $n \to 0$ for coincided replica indices is $A_{\alpha\alpha}(k) \to 2\gamma_k$. As it was found out in spin glasses, the peculiarity of the systems with quenched disorder is governed by the hierarchy of the phase space that is characterized by random overlapping of the different replicas [3]. Therefore overlapping parameter $A_{\alpha\beta}(k)$ in the second term (25) is the stochastic variable under which the average should be made. Let us take the corresponding distribution in the simplest Gauss form
\[
\mathcal{P}\{A_{\alpha\beta}(k)\} \propto \exp\left\{-\frac{1}{8} \sum_{k_1,k_2} \frac{1}{u_{k_1,k_2}} A_{\alpha\beta}(k_1)A_{\alpha\beta}(-k_2)\right\}
\]
(26)
where dispersion $u_{k_1,k_2} \equiv \sigma^2(la)^{-2}N^{-1}(k_1^2 + k_2^2)^{-1}$ is given by parameter $\sigma$ (see [3]). Then after averaging of the partition function $Z = \int Dm_k \exp(-\Omega'(m_k))$ the second term in Eq. (25) takes the form
\[
-\frac{1}{2} \sum_{k_1,k_2} u_{k_1,k_2} m_\alpha(k_1)m_\beta(-k_1)m_\alpha(-k_2)m_\beta(k_2).
\]
(27)
As a result the thermodynamic potential (27) in the replica form is
\[
\Omega' = \sum_{k_\alpha} \gamma_k |m_\alpha(k)|^2 + \frac{1}{2} \sum_{k_1,k_2} \frac{w_{k_1,k_2}}{u_{k_1,k_2}} |m_\alpha(k_1)|^2 |m_\alpha(k_2)|^2 + \\
+ \sum_{\alpha} \int v(m_\alpha) dr - \frac{1}{2} \sum_{k_1,k_2} u_{k_1,k_2} m_\alpha(k_1)m_\beta(-k_1)m_\alpha(-k_2)m_\beta(k_2).
\]
(28)
The Eq. (28) removes the above mentioned contradiction in the choice of the effective Hamiltonian form: the positive contribution of the second term is governed by the intra-replica interaction (see [11, 1]), whereas negative contribution in [28, 3] is determined by replica overlapping. The distinction of mentioned terms makes itself evident in the fact that the former leads to renormalization of the value $\gamma_k$, whereas the latter corresponds to the memory and non-ergodic effects.

In order to carry out such renormalization (see [26]) using of the mean-field approximation it needs to replace one of the multiplier $|m_\alpha(k)|^2$ in the second term of Eq. (28) by the bare Green function $G_{k_0}$ that corresponds to $v = 0$, $u_{k_1,k_2} = 0$ and is determined by equation
\[
G_{k_0}^{-1} = r + 2a^2(k - k_0)^2,
\]
(29)
independent on replica number $\alpha$. To determine the parameters $r$, $k_0$ one needs to substitute the Eq. (29) into the corresponding Dyson equation
\[
G_{k_0}^{-1} = \gamma_k + \sum_{k'} w_{kk'} G_{k'0}.
\]
(30)
Then after integration over wave vector $k'$ one obtains
\[
\gamma_k = \tau + (3/4\pi)l^{-2}(2r)^{-1/2}, \quad \gamma_0^{-1} = 2\pi^{1/2}l(2r)^{1/4}a.
\]
(31)
According to the first equation the positive determined parameter \( r \) increases smoothly with growth of bare parameter \( \tau (r \sim \tau^{-2}) \) at \( \tau < 0 \), \( |\tau| \gg 1 \) and \( r \sim \tau \) at \( \tau \gg 1 \) (see Fig.1a)). It means that without self-action effect, random heteropolymer is stable with respect to the microphase separation \( [8] \). The second equation \( (31) \) means that space period \( \lambda \equiv 2\pi/k_0 \) depends on renormalized thermodynamic parameter \( r \), as it is inherent in random copolymers \( [1] \). According to Fig.1b with increasing of \( \tau \) the value \( \lambda \) grows monotonously from 0 to \( \infty \). In so doing the greater the correlation length \( l \), the faster change of the period \( \lambda \) near the point \( \tau = 0 \).

The final form of the effective Hamiltonian of random heteropolymer follows from the thermodynamic potential \( (28) \) renormalized under acting of the fluctuations

\[
\mathcal{H} = \sum_{k\alpha} \eta_k |\eta_k(k)|^2 + \sum_{\alpha} \int v(\eta_{\alpha})\text{d}r - \frac{1}{2} \sum_{k_1,k_2} u_{k_1,k_2} \eta_{\alpha}(k_1) \eta_{\beta}(-k_1) \eta_{\alpha}(-k_2) \eta_{\beta}(k_2),
\]

\( (32) \)

\[
r_k \equiv r + 2\alpha^2(k - k_0)^2, \quad u_{k_1,k_2} \equiv \sigma^2(\alpha) - 2^(-1)(k_1^2 + k_2^2)^{-1}.
\]

Here the kernel \( v(\eta_{\alpha}) \) is determined by Eqs.\( (24) \), where \( m \) is replaced by \( \eta_{\alpha} \).

4 Supersymmetric scheme

To build a SUSY scheme on a basis of effective motion equation \( (19) \) let us introduce the generation functional \( [19] \)

\[
Z\{\eta_k\} = \left\langle \delta \left( \frac{\partial \eta_k}{\partial n} + \frac{\delta \mathcal{H}}{\delta \eta_k} - \zeta_k \right) \right\rangle \det \left| \frac{\delta \zeta_k}{\delta \eta_k} \right|, \quad \frac{\delta \mathcal{H}}{\delta \eta_k} \equiv \frac{\partial \mathcal{H}}{\partial \eta_k} + 2\alpha^2(k - k_0)^2 \eta_k,
\]

\( (33) \)

averaged over noise \( \zeta_k(n) \), where \( \delta \)-function considers the motion equation \( (19) \), the determinant is Jacobian of transfer from \( \zeta_k \) to \( \eta_k \). Then, the functional Laplace representation is used for \( \delta \)-function that introduces a ghost field \( \varphi_k(n) \). To attach exponential form for the determinant in Eq.\( (33) \) Grassmann conjugate fields \( \psi_k(n) \), \( \bar{\psi}_k(n) \) should be used, that obey the conditions \( [19] \)

\[
\{\psi, \bar{\psi}\} = \{\bar{\psi}, \psi\} = \{\bar{\psi}, \bar{\psi}\} = 0,
\]

\[
\int \delta \psi = \int \delta \bar{\psi} = 0, \quad \int \bar{\psi} \psi \delta^2 \psi = 1, \quad \delta^2 \psi = \delta \psi \delta \bar{\psi},
\]

\( (34) \)

where figure brackets denote anticommutator. Then, assuming that the averaging over \( \zeta_k(n) \) in Eq.\( (33) \) is determined by Gauss distribution with variance 1 (see Eqs.\( (20) \)), the standard form of the partition function is obtained:

\[
Z\{\eta\} = \int P\{\eta, \varphi; \psi, \bar{\psi}\} \delta \varphi \delta^2 \psi,
\]

\[
P\{\eta, \varphi; \psi, \bar{\psi}\} = \exp(-S\{\eta, \varphi; \psi, \bar{\psi}\}), \quad S = \int_0^N L\text{d}n,
\]

\[
L = \int [(-\varphi \bar{\psi} - \bar{\psi} \varphi^2/2) + (\mathcal{H}'\{\eta\} \varphi - \bar{\psi} \mathcal{H}''\{\eta\} \psi)]\text{d}r.
\]

\( (35) \)

Here point denotes derivative over \"time\" \( n \), the prime denotes the functional derivation with respect to the field \( (17) \), the last expression is taken in \( r \)-representation.

The last expression in Eqs.\( (35) \) takes the simplest form \( [21] \)

\[
L = \int \Lambda(\Phi)\text{d}^2 \vartheta, \quad \Lambda \equiv \sum_k \langle \mathcal{D} \Phi_k \rangle(\mathcal{D} \Phi_k) + \mathcal{H}\{\Phi_k\}, \quad \text{d}^2 \vartheta \equiv \text{d} \vartheta \text{d} \bar{\vartheta}
\]

\( (36) \)

if one introduces SUSY generators

\[
\mathcal{D} \equiv \frac{\partial}{\partial \vartheta} - 2\vartheta \frac{\partial}{\partial n}, \quad \bar{\mathcal{D}} \equiv \frac{\partial}{\partial \bar{\vartheta}}
\]

\( (37) \)

and SUSY field
\[ \Phi = \eta + \bar{\psi} \theta + \bar{\theta} \psi + \bar{\theta} \partial \varphi, \]  

(38)

where Grassmann coordinates \( \theta, \bar{\theta} \) obey the same relations (34) as for the fields \( \psi, \bar{\psi} \). Here functional \( \mathcal{H}\{\Phi\} \) has the same form as the effective Hamiltonian (32), where order parameter \( m_{\kappa, \alpha} \) is replaced by superfield \( \Phi_{\kappa}(\theta) \), Eq. (38). In this case replica index \( \alpha \) is removed by Grassmann variable \( \theta \) that is the formal reason of the replica and supersymmetry methods identity. The advantage of the latter method is in the Grassmann conditions (34) that correspond to the limit \( n \to 0 \) in the replica method.

According to consideration \( [16, 20] \), the physical meaning of the components of the SUSY field (38) is as follow: \( \varphi \) is the most probable value of fluctuations of the field conjugated to the order parameter \( \eta \), and combination \( \bar{\psi} \psi \) determines density of sharp interphases. So, using the 4-component SUSY field (38) corresponds to the strong segregation limit \( [2, 3] \). Further we shall consider more simple case of the weak segregation limit where \( \bar{\psi} \psi \equiv 0 \). Then, the SUSY field (38) is reduced to the 2-component form

\[ \phi = \eta + \theta \varphi, \]

(39)

where self-conjugate nilpotent variable \( \theta \equiv \bar{\theta} \theta \) is introduced. Respectively, Lagrangian (36) takes the form

\[ L = \int \Lambda(\phi)d\theta, \quad \Lambda \equiv \sum_k \phi_k^* D\phi_k + \mathcal{H}\{\phi_k\}; \]

\[ D = -\frac{\partial}{\partial \theta} + \left( 1 - 2\theta \frac{\partial}{\partial \theta} \right) \frac{\partial}{\partial n}. \]

(40)

The motion equation for the nilpotent field (39) that corresponds to Lagrangian (40) reads

\[ D\phi_k = -\delta \mathcal{H}/\delta \phi_k^*. \]

(41)

In the component form it leads to the equations for the order parameter \( \eta(n) \) and the amplitude of the more probable fluctuation \( \varphi(n) \) of the conjugate field (see [20]).

## 5 Correlators

Now let us consider SUSY correlator

\[ C_k(n, \theta; n', \theta') \equiv \langle \phi_k^*(n, \theta) \phi_k(n', \theta') \rangle. \]

(42)

Multiplying Eq. (41) by value \( \phi_k^* \) and averaging within zeroth approximation \( (v = u = 0 \) in Eqs. (32)) one gets

\[ C_{\nu k}^{(0)}(\theta, \theta') = \frac{1 + (r_k - iv)\theta + (r_k + iv)\theta'}{r_k^2 + \nu^2}. \]

(43)

Here conventional frequency \( \nu \) denotes Fourier transformation over "time" being the monomer number \( n \), for example

\[ C_{\nu} = \int_0^N C(n)e^{i\nu n}dn. \]

(44)

The expression (43) has characteristic structure with respect to combination of the nilpotent variables \( \theta, \theta' \), that is inherent in, obviously, not only zeroth approximation but arbitrary supercorrelator. In this connection it is convenient to introduce basis supervectors

\[ A(\theta, \theta') = \theta, \quad B(\theta, \theta') = \theta', \quad T(\theta, \theta') = 1, \]

(45)

that have functional production

\[ X(\theta, \theta') = \int Y(\theta, \theta'') Z(\theta'', \theta)d\theta''. \]

(46)
for any vectors $X, Y, Z$. It is easy to see, that the basis SUSY vectors \([15]\) obey the following multiplication rules: $A^2 = A, B^2 = B, BT = T, TA = T$, other products are zero. Because the set of vectors $A, B, T$ is complete, it is convenient to expand any SUSY correlator over this basis:

$$C = G_- A + G_+ B + ST.$$  \hfill (47)

Here and below subscripts $k, \nu$ are suppressed for brevity. Using Eqs.(39), (42), one obtains for coefficients of the expansion (47)

$$G_\pm = \langle \eta \varphi^* \rangle, \quad G_\pm + = \langle \eta^* \varphi \rangle, \quad S = \langle |\eta|^2 \rangle.$$  \hfill (48)

So, $G_\pm$ represent advanced and retarded Green functions and $S$ is the structure factor. In accordance with Eqs.(43), (45), (47), these functions within zeroth approximation take the form

$$G_\pm^{(0)} = (r \pm i \nu)^{-1}, \quad S^{(0)} = G_+^{(0)} G_-^{(0)} = (r^2 + \nu^2)^{-1}. \hfill (49)$$

The Dyson equation for SUSY correlator \([12]\) is as follows \([29, 20]\)

$$C^{-1} = (C^{(0)})^{-1} - u C - \Sigma.$$  \hfill (50)

Here $\Sigma$ is self-energy function, $u = \sigma^2 (2N)^{-1} (\text{lat}_{\text{a}})^{-2}$ is the typical value of the interreplica overlapping $u_{kk'}$ at $k = k' = k_0$. By analogy with the expansion (47) the self-energy superfunction $\Sigma$ that describes the self-action effects is

$$\Sigma = \Sigma_- A + \Sigma_+ B + \Sigma T.$$  \hfill (51)

Then using Eqs.(49), the Dyson equations for component $G_\pm, S$ take the form

$$G_\pm^{-1} + uG_\pm = (r \pm i \nu) - \Sigma_\pm, \hfill (52a)$$

$$S = (1 + 2 \pi C_2 l^{-1} \delta(\nu) + \Sigma)G_+ G_- (1 - u G_+ G_-)^{-1}. \hfill (52b)$$

Here $\delta$-term is caused by quenched disorder.

To complete the system (52) it needs to express the components of the self-energy superfunction by super-correlators. Using the SUSY perturbation theory with accounting of the cubic and quartic anharmonicities \([24]\) for matrix element of the self-energy function one obtains \([19]\)

$$\Sigma(z, z') = \frac{\mu^2}{27} (C(z, z'))^2 + \frac{\lambda^2}{3!} (C(z, z'))^3.$$  \hfill (53)

Here $z \equiv \{r, n, \theta\}$ denotes the set of coordinate $r$, ”time” $n$, and nilpotent coordinate $\theta$. It is important that the multiplication rule in Eq.(53) is not the same as for the functional product \([46]\). Here the ordinary product should be used according to the following multiplication rules \([15, 20]\): $AT = TA = A, BT = TB = B, T^2 = T$, other products are zero. Then coefficients of the SUSY expansion \([15]\) take the form

$$\Sigma_\pm (n) = \left( \mu^2 + \frac{\lambda^2}{2} S(n) \right) S(n) G_\pm (n), \hfill (54a)$$

$$\Sigma(n) = \frac{1}{2} \left( \mu^2 + \frac{\lambda^2}{3} S(n) \right) S^2(n), \hfill (54b)$$

where $r$-representation for macroscopically homogeneous system is used.
6 Memory and non-ergodicity effects

Following to Edwards and Anderson [30] let us introduce the composition memory parameter \( q \equiv \langle \eta(n = N)\eta(n = 0) \rangle \), which value determines the long-range correlation in the different monomer alternation along the whole heteropolymer chain. Moreover, the non-ergodic parameter \( \Delta \equiv g_0 - g \) that is difference between the isothermal susceptibility \( g_0 \equiv G_-(\nu = 0) \) and thermodynamic value \( g \equiv G_-(\nu \to 0) \) is used. Then, the main correlators acquire the elongated form:

\[
G_\pm(\nu) = \Delta + G_{\pm 0}(\nu), \quad S(n) = q + S_0(n),
\]

where index 0 denotes the components corresponding to ergodic system without memory. Substitution of Eqs. (55) into Eqs. (54) gives

\[
\Sigma_\pm(n) = \left( \mu^2 + \frac{\lambda^2}{2} q \right) q (\Delta + G_{\pm 0}(n)) + \Sigma_{\pm 0}(n),
\]

\[
\Sigma_{\pm 0}(n) \equiv (\mu^2 + \lambda^2 q) S_0(n) G_{\pm 0}(n) + \frac{\lambda^2}{2} S_0^2(n) G_{\pm 0}(n);
\]

\[
\Sigma(n) = \frac{1}{2} \left( \mu^2 + \frac{\lambda^2}{3} q \right) q^2 + \left( \mu^2 + \frac{\lambda^2}{2} q \right) q S_0(n) + \Sigma_0(n),
\]

\[
\Sigma_0(n) \equiv \frac{1}{2} (\mu^2 + \lambda^2 q) S_0^2(n) + \frac{\lambda^2}{6} S_0^3(n).
\]  

Here the terms, being non-linear with respect to correlators \( G_{\pm 0}, S_0 \), are included into summands \( \Sigma_{\pm 0}, \Sigma_0 \), the terms that contain production \( S_0 \Delta \approx 0 \) have been dropped and, finally, one separates out the first summands that disappear when parameter \( q \) goes to zero. It is characteristic that to determine the self-energy functions (56) the "time"-representation was used, whereas the Dyson equations (52) require "frequency" Fourier transformations of non-linear expressions (56). To avoid this difficulty the fluctuation-dissipation theorem is used [30]

\[
S_0(n \to 0) = G_{\pm 0}(\nu \to 0) \equiv g,
\]

\[
\Sigma_{\pm 0}(\nu \to 0) = \Sigma_0(n \to 0) \equiv \frac{1}{2} (\mu^2 + \lambda^2 q) g^2 + \frac{\lambda^2}{6} g^3,
\]

where Eq. (56b) is taken into account in the last equation.

Inserting Fourier transformations of Eqs. (55), (56) to Dyson equation (52b), within the \( \nu \)-representation one obtains

\[
q_0 \left[ 1 - u g_0^2 - \frac{1}{2} \left( \mu^2 + \frac{\lambda^2}{3} q_0 \right) q_0 g_0^2 \right] = C_2 l^{-1} g_0^2,
\]

\[
S_0 = \frac{(1 + \Sigma_0) G_+ G_-}{1 - [u + (\mu^2 + \lambda^2 q/2) q] G_+ G_-}.
\]

The first of these equations corresponds to \( \delta \)-term being caused by memory effects, the second one - to "frequency" \( \nu \neq 0 \). At \( \nu \to 0 \) the characteristic production is \( G_+ G_- \to g^2 \), so that the pole of structure factor \( S_0 \)

\[
u + \left( \mu^2 + \frac{\lambda^2}{2} q \right) q = g^{-2}
\]

determines the point of ergodicity breaking. By analogy, substituting of Eqs. (56a), (57b) into the Dyson equation (52a) and taking into account \( g \equiv G_-(\nu \to 0) \) for microscopic susceptibility and memory parameter we have

\[
1 - r g + u g^2 + \frac{\mu^2}{2} g \left[ (g + q)^2 - q^2 \right] + \frac{\lambda^2}{6} g \left[ (g + q)^3 - q^3 \right] = 0.
\]
The thermodynamic behaviour of random heteropolymer in the vicinity of the ergodicity breaking point is described by the system of equations (58)-(60). By analogy with spin glass [4], Eqs. (58), (61) play role of Sherrington-Kirkpatrick equations, and Eq. (59) determines the point of de Almeida-Thouless instability. On further analyzing of these equations one should distinguish macro- and microscopic values $q_0$, $q$ of the memory parameter and corresponding susceptibilities $g_{\nu}$, $g$. The peculiarity of such a hierarchy is that microscopic values, which conform to the limit $\nu \to 0$, are the usual thermodynamic parameters and depend on temperature (Flory parameter $\chi$). The macroscopic values $q_0$, $g_{\nu}$ conform to the point $\nu = 0$ and only depend on quenched disorder parameter $l$. In the non-ergodic area macroscopic quantities take the values at the point of ergodicity breaking.

Because the system of three equations (58), (60) is insufficient for determination of four quantities $q_0$, $q$, $g$, $g_{\nu}$, it must be completed by equation

$$q \left[ 1 - qg^2 - \frac{1}{2} \left( \mu^2 + \frac{\chi^2}{3} q \right) qg^2 \right] = C_2 l^{-1} g^2,$$

(61) that is microscopic analogue of the equation (58) obtained as a result of separating out of the singular $\delta$-terms for the structure factor in the Dyson equation. As is known from the spin glass theory [4], the hierarchy of such singularities, which correspond to a set of infinitely decreasing "frequencies" $\nu \to 0$, is a key point of the non-ergodic systems. In our case, the equations (58), (61) correspond to the point $\nu = 0$ and a minimal of these "frequencies" respectively. In turn, at $\nu = 0$ the equation (59) reads:

$$u + \left( \mu^2 + \frac{\chi^2}{2} q_0 \right) q_0 = g_{\nu}^{-2}.$$

(62) Eqs. (58), (60)-(62) are the complete system for determination of the quantities $q_0$, $q$, $g$, $g_{\nu}$.

### 7 Discussion

According to Eqs. (58), (62) the macroscopic memory parameter is given by cubic equation

$$(\mu^2 / 2 + \lambda^2 q_0 / 3) q_0^2 = C_2 l^{-1}.$$

(63) The characteristic form of the dependence of the value $q_0$ on intensity of quenched disorder $l$ is depicted in Fig.2. For copolymers close to symmetric composition $f = 0.5$ ($C_3 \ll C_2$) the first term in brackets of Eq. (63) is negligible, and the dependence $q_0 \propto l^{1/3}$ takes place. In the opposite case of dilute copolymer, where $f \ll 1$ ($C_2 \ll C_3$), one obtains the dependence $q_0 \propto f^{1/2}$.

Simultaneous solution of Eqs. (58), (60) and (62) gives the point of ergodicity breaking $\chi_0$, which dependence on correlation length $l$ is depicted in Fig.3 (solid curve). A characteristic of this phenomenon is that non-zeroth value of $\chi_0$ appears above a critical value of correlation length $l$, and with further growth of $l$ dependence reaches its maximum and then monotonously falls down. In so doing, ergodic region is located under curve $\chi_0(l)$ and contracts with correlation length growth. Condition $dg/d\chi = -\infty$ added by Eqs. (58), (62) gives the equation

$$u + \mu^2 (g f + q) + \frac{\lambda^2}{2} (g f + q)^2 = g_f^{-2},$$

(64) that defines $\chi_f$ value of Flory parameter in the freezing point, under which the microscopic susceptibility $g$ takes zeroth value (see Fig.4). Corresponding dependence $\chi_f(l)$ on the correlation length $l$ is depicted in Fig.3 (thin curves). A characteristic is that the dependence $\chi_f(l)$ is under ergodicity breaking curve $\chi_0(l)$ and has the same form. The influence of the composition on the values of $\chi_0$ and $\chi_f$ is shown in Fig.3a. As we recede from the composition $f = 0.5$, the growth of the above mentioned parameters is observed. The more complicated behaviour is realized at the growth of the interreplica overlapping $\sigma$ (see Fig.3b). At small magnitudes of the correlation length $l$, the growth of both $\chi_0$ and $\chi_f$ values is observed with $\sigma$ increasing, whereas at large magnitudes $l$, parameters $\chi_0$ and $\chi_f$ decrease.

Dependencies of the macroscopic $g_0$ and microscopic $g$ susceptibilities on the parameter $\chi$ are depicted in Fig.4. Under point of ergodicity breaking $\chi_0$, these susceptibilities and corresponding memory parameters $q$, $q_0$ coincide. The dependence $g(\chi)$ has a cut-off at the point $\chi = \chi_f$ (below it, susceptibility $g$ takes zeroth value that corresponds to the freezing state). Above the ergodicity breaking point $\chi_0$, the macroscopic susceptibility $g_0$ is constant and the microscopic one has smooth decrease (latter can be obtained by simultaneous solution of Eqs. (60), (62)). According to Fig.4a, with moving away from the composition $f = 0.5$, the values of the
susceptibilities $g_0$, $g$ in the freezing point and in the point of ergodicity breaking decrease but corresponding values of parameters $\chi_0$ and $\chi_f$ increase. The dependence on the correlation length $l$ is shown in Fig.4b: with increasing of $l$ ergodic area contracts as it should be. The influence of the interreplica overlapping is shown in Fig.4c. With increasing of the corresponding parameter $\sigma$, the values of the susceptibilities $g(\chi)$ and $g_0(\chi)$ decrease and hence the interreplica overlapping prevents the heteropolymer freezing.

The influence of the thermodynamic parameter $\chi$ on the microscopic memory parameter $q$ is depicted in Fig.5. The absence of memory below $\chi_f$ is the characteristic feature of the freezing region. Non-zeroth value of $q$ appears in the freezing point $\chi_f$ and with further growth of the parameter $\chi$, the memory parameter monotonously increases. The step-like behaviour of the parameter $q$ is inherent in the first order transition. Evidently, the physical reason of the mentioned behaviour is the fluctuation contribution into the thermodynamic potential of the heteropolymer. According to Fig.5a, with moving away from the composition $f = 0.5$, the dependence $q(\chi)$ becomes more slight. On the contrary, the growing of the correlation length $l$ results in more abrupt growth of the memory parameter (see Fig.5b). At last, one can see from Fig.5c that influence of the interreplica overlapping $\sigma$ above and below of the ergodicity breaking point occurs to be opposite.

According to the Fig.6, the non-ergodicity parameter $\Delta(\chi)$ grows monotonously with increasing $\chi$ from the ergodicity breaking point $\chi_0$. The deflection from the composition $f = 0.5$, the decrease of the correlation length $l$ and the growth of the interreplica overlapping $\sigma$ result in weakening of the non-ergodicity effects (see Fig.6).

In the search for a new polymers with predetermined features, the phase diagram plays the basic role that defines possible thermodynamic states at different values of the Flory parameter $\chi$ and composition $f$. According to Fig.7, such diagram has a concave form for both the freezing point $\chi_f(f)$ and the point of ergodicity breaking $\chi_0(f)$. A region of the large $\chi$ adjacent to the composition $f = 0.5$ corresponds to the non-ergodic unfreezing state. With decreasing of the values $\chi$ and $|f - 1/2|$, at first the system goes to the ergodic state and then it freezes. The comparison of the Fig.7a and Fig.7b shows that the increasing of the correlation length $l$ results in expansion of the unfreezing and non-ergodic phases. On the contrary, from Fig.7a and Fig.7c one can see that interreplica overlapping leads to its contraction.
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Captions

Fig.1 Dependence of the parameter $r$ (a) and the period $\lambda$ (b) on $\tau$ at different values of the correlation length $l$ (curves 1, 2, 3 correspond to $l = 0.5; 1; 10$).

Fig.2 Dependence of the macroscopic memory parameter $q_0$ on the value of the correlation length $l$ (curves 1, 2, 3 correspond to $f = 0.5; 0.3; 0.1$).

Fig.3 Dependence of the characteristic values of the Flory parameter in the point of ergodicity breaking $\chi_0$ (thick curve) and in the freezing point $\chi_f$ (thin curve) on the correlation length $l$: a) at $\sigma = 0$ and different values of the composition $f$ (curves 1, 2 correspond to $f = 0.5; 0.3$); b) at $f = 0.5$ and different values of the interreplica overlapping $\sigma$ (curves 1, 2 correspond to $\sigma = 0; 2$).

Fig.4 Dependence of the microscopic $g$ and macroscopic $g_0$ susceptibilities on the parameter $\chi$: a) at $\sigma = 0, l = 0.1$ and different values of the composition $f$ (curves 1, 2 correspond to $f = 0.5; 0.3$); b) at $f = 0.5, \sigma = 0$ and different values of the correlation length $l$ (curves 1, 2, 3 correspond to $l = 0.05; 0.1; 0.2$); c) at $f = 0.5, l = 0.1$ and different values of the interreplica overlapping parameter $\sigma$ (curves 1, 2 correspond to $\sigma = 0; 2$).

Fig.5 Dependence of the microscopic memory parameter $q$ on the Flory parameter $\chi$: a) at $\sigma = 0, l = 0.1$ and different values of the composition $f$ (curves 1, 2 correspond to $f = 0.5; 0.3$); b) at $f = 0.5, \sigma = 0$ and different values of the correlation length $l$ (curves 1, 2, 3 correspond to $l = 0.05; 0.1; 0.2$); c) at $f = 0.5, \sigma = 0$ and different values of the interreplica overlapping parameter $\sigma$ (curves 1, 2 correspond to $\sigma = 0; 2$).

Fig.6 Dependence of the non-ergodicity parameter $\Delta$ on the parameter $\chi$: a) at $\sigma = 0, l = 0.1$ and different values of the composition $f$ (curves 1, 2 correspond to $f = 0.5; 0.3$); b) at $f = 0.5, \sigma = 0$ and different values of the correlation length $l$ (curves 1, 2, 3 correspond to $l = 0.05; 0.1; 0.2$); c) at $f = 0.5, l = 0.1$ and different values of the parameter $\sigma$ (curves 1, 2 correspond to $\sigma = 0; 2$).

Fig.7 Phase diagram of the disordered heteropolymer: a) at $\sigma = 0, \alpha = 1; l = 0.1$; b) at $\sigma = 0, \alpha = 1; l = 5$; c) at $\sigma = 2, \alpha = 1; l = 0.1$. Thick curve corresponds to the ergodicity breaking point and thin curve corresponds to freezing point; $FE$, $NE$, $NN$ correspond to freezing ergodic, non-freezing ergodic, non-freezing non-ergodic phases.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7