Self-generated disorder and structural glass formation in homopolymer globules

V. G. Rostiashvili, G. Migliorini and T. A. Vilgis

1 Max Planck Institute for Polymer Research
10 Ackermannweg, 55128 Mainz, Germany.
2 Laboratoire Européen Associé, Institute Charles Sadron
6 rue Boussingault, 67083 Strasbourg Cedex, France.

January 8, 2022

We have investigated the interrelation between the spin glasses and the structural glasses. Spin glasses in this case are random magnets without reflection symmetry (e.g. \( p \)-spin interaction spin glasses and Potts glasses) which contain quenched disorder, whereas the structural glasses are here exemplified by the homopolymeric globule, which can be viewed as a liquid of connected molecules on nano scales. It is argued that the homopolymeric globule problem can be mapped onto a disorder field theoretical model whose effective Hamiltonian resembles the corresponding one for the spin glass model. In this sense the disorder in the globule is self-generated (in contrast to spin glasses) and can be related with competitive interactions (virial coefficients of different signs) and the chain connectivity. The work is aimed at giving a quantitative description of this analogy. We have investigated the phase diagram of the homopolymeric globule where the transition line from the liquid to glassy globule is treated in terms of the replica symmetry breaking paradigm. The configurational entropy temperature dependence is also discussed.

I. INTRODUCTION

The existing dynamical theory of the glassforming overcooled liquids and polymers are mainly applicable to the relatively high temperature area. The well-known mode-coupling theory (MCT) predicts a dynamical phase transition at the critical temperature \( T_c \) where the overcooled liquid becomes nonergodic and stays in this state upon the further cooling. It is significant that according to MCT, the characteristic times of the \( \alpha \)-relaxation or the viscosity exhibit a power law divergence: \( \tau_\alpha(T) \propto \eta(T) \propto |T - T_c|^{-\gamma} \) at a critical temperature \( T = T_c \). It has been realized now that such types of singularities are generic for a broad class of mean-field (MF) models and its appearance is an indication for the role of the activation processes which are neglected in MF-models. This means physically that the topology of the free energy landscape in the space of the coarse grained variables should be taken into consideration. At low temperatures the free energy landscape determines more or less the dynamics of the system. The size of the free energy barriers between the metastable states, however, determines the rate of any activation processes at the low temperature regime \( T < T_c \).

At the so-called Kauzmann temperature \( T_K \), which is usually \( T_K < T_c \) a genuine thermodynamic glass transition or so called Gibbs - DiMarzio transition is expected to take place. At the Gibbs - DiMarzio (or Kauzmann) temperature \( T_K \), the system is preferably in a thermodynamic unique configuration since the height of the free energy barriers grow with the system size.

The earliest analytical approach to the problem which captured these two aforementioned aspects has been worked out in several papers by Kirkpatrick, Thirumalai and Wolynes in the late 80’s. In these papers which study the phenomena by making use of the \( p \)-spin interaction spin glasses (at \( p > 2 \)) and Potts glasses with more then four components, the following conclusions have been drawn:

- The predicted phase transition temperature \( T_A \) obtained by the dynamical theory (actually equivalent to \( T_c \) of the MCT based on the Langevin dynamics in the mean field limit) is higher than the Kauzmann \( T_K \) obtained by the static theory (or by the ordinary replica theory).
- As the temperature decreases (starting from the paramagnetic phase) the metastable minima appear first exactly at \( T_A \).
- In the intermediate temperature regime \( T_K < T < T_A \) many metastable states are separated by high barriers. Therefore these states may have a long lifetime. The activated transport is the typical process in this temperature range.
The overlap order parameter within the one-step replica symmetry breaking (1-RSB) scenario undergoes a discontinuous jump at $T_K$. This reminds to a first order phase transition even so thermodynamically (e.g., in the specific heat) the transition seems to be of second order. The authors called this class of phase transitions random first order phase transition. Crisanti and Sommers confirmed essentially the same type of behavior for the $p$ - spin spherical model [5], which is different from the Sherrington - Kirkpatrick model, and is shared by the other spin - glass models without reflection symmetry [6].

Indeed it has been argued often, that many connections exist between the behavior of the structural glasses and spin glasses without reflection symmetry [2,4,6]. Most of these properties mentioned above for the spin glasses can be found in the context of structural glasses too. However, the important difference between the spin and structural glasses is that the spin glasses models contain a quenched disorder already in the Hamiltonian. In structural glasses the Hamiltonian is a regular function of the particles coordinates and does not contain disorder. Nevertheless the free energy in both systems resemble each other and posses similar properties. Thus, and disorder is in a sense self - generated and develops itself during the cooling (or glass transition) process.

The properties and possibilities of self - generated (or self - induced) disorder have been already discussed in the framework of rather special spin - models [4]. These models explicitly involve pseudo - random numbers, i.e., the spin - spin couplings, although deterministic, oscillate very rapid and can be considered as a (pseudo) - random variables. These models, however, provide some spin analogies of structural glasses but still are quite different from structural glasses [3].

Furthermore, the ideas and the methods of the mean - field spin - glasses [8,10] have been successfully used to study the freezing states in a heteropolymer globule [4]. The corresponding model considers the conformational behavior of a polymer chain with randomly quenched interactions between monomers. These random copolymers posses always a collapsed (or globular state) depending on temperature and strength of the randomness. It was successfully shown, that the disorder results in a globular and eventually in a glassy globular state. The corresponding freezing is characterized by a transition between two phases: one phase is characterized by many accessible configurations, while the other is dominated by only a few of them, i.e., an eventually frozen state. In this context the heteropolymer freezing usually serves as a simple “toy model” for the protein folding phenomenon [4]. This relationship between the freezing and folding phenomena is caused mainly by the fact that in both cases only a single conformation (which is in the context of protein folding called the native state) dominates.

In the following we are going to investigate a similar problem in homopolymer globules in poor solvent. It is well known that homopolymers in poor solvent form globules due to an attractive second virial coefficient which are then stabilized by the repulsive third virial [15]. The relevant parameter for the globule formation is the second virial coefficient which is measured by the relative distance from the so-called $\Theta$ - temperature, where the homopolymer takes Gaussian conformations. Close below $\Theta$ the polymer collapses and the deeper the temperature the more dense becomes the globule. The intuitive limit is then a dense liquid globule. We will show nevertheless, that even at lower temperatures and beyond a certain density the globule freezes and forms a glass. Homopolymer globules show a structural glass transition. Thus they will form a “nano glass”.

It is most interesting to note that in recent Monte - Carlo simulations of homopolymer globules, Milchev and Binder [15] have found a dramatic decrease of the acceptance rate of the moves which in its turn suggests to the growth of the characteristic times. They have seen also a pronounced density fluctuations which appear in the center of the globule and spread over the entire globule as a temperature is lowered. These results have been interpreted in terms of a glassy type of transition. These investigations have been restudied in papers by Kreitmeier et. al [17,18] where a similar dynamical behavior of the homopolymer globule has been verified once more and was generalized for the cyclic deformation regime. Moreover, a glass transition in a homopolymer globule (for the chain length $N < 27$ on the $3 \times 3 \times 3$ cubic lattice) has been discussed by computer simulations [20]. These authors found that the conformation space of the model consist from one huge valley and a big number of small “chambers”. These disjoint domains of the conformational space are responsible for the ergodicity breaking and freezing transition. This might be important for the final processes of folding dynamics in the protein molecules because the speed and reliability of the folding depends on whether the native state belongs to the same conformational space domain or not [13].

The thermodynamic behavior of the homopolymer globules have been studied also by discontinuous molecular dynamics simulation [21,22]. By making use a simple off-lattice model for chain length $N = 64$ the authors showed the existence of the first - order liquid - solid - like transition. The transition occurs at temperatures below the coil - globule transition temperature and has been detected by the heat capacity...
peak as well as by the Lindemann parameter jump. It is interesting that there is a qualitative similarity between homopolymers and proteins where the transition from the molten globule to the native state is also of the first order \[ 18,22 \]. In ref. \[ 22 \] a new “expanded ensemble” Monte Carlo algorithm has been introduced which helps to overcome the density slowing down in the globule state. For the chain length up to \( N = 512 \) the authors have seen the bimodal distribution in the number of contacts per monomer. This is again a clear indication of the first - order liquid - to - solid transition of the collapsed globule.

As already mentioned, most important is that the globule formed from ordinary homopolymers does not contain any quenched disorder. If this system forms glassy states the disorder has to be self - generated. Nevertheless, to form glassy states certain frustrations are necessary. These may have its origin in the interplay between attractive interaction (negative 2\textsuperscript{nd} virial coefficient \( v \)), repulsion (positive 3\textsuperscript{rd} virial coefficient \( w \)) and the constraints imposed by the chain connectivity. These frustrations might be already sufficient to provide the structural glass transition from a liquid globule to a glassy globule.

The main purpose of the present paper is to investigate these problems in more detail by analytic means. We will indeed show that the linear homopolymer in the condensed globular phase undergoes a genuine structural glass transition of the similar type as in the \( p - \) spin - interaction spin - glass with \( p > 2 \) or Potts glasses models. We stress once more, that the homopolymer is a pure system and does not contain quenched disorder. Nevertheless the \( n - \) component field theory formulation for linear polymers \[ 28,29 \] provides already a natural and solid basis \[ 27 \]. As we will show below, the homopolymer globule is a generic system where frustrations rather than quenched disorder trigger the glass formation. As a starting point we employ the field - theoretical description of the self - interacted polymeric chain in a poor solvent \[ 28,29 \]. So far, in ref. \[ 28,29 \] it has been shown that the Laplace transformation (with respect to the chain length \( N \)) of the polymeric correlation function can be associated with the corresponding correlator within the \( n \rightarrow 0 \) limit of the \( n - \) component \( \psi_a^2, \psi_b^2 \) - field theory (where \( a = 1, \ldots n \)). We argue instead that the same \( n - \) component field theory can be mapped onto some kind of disordered one - component model where the imposed random field is a non - Gaussian (a color noise) and its statistical moments are determined only by virial coefficients \( v, w, \ldots \). In this case the index \( a \) acts as a replica index for spin glasses \[ 8,9 \] or random magnetics \[ 10 \]. This mapping has been suggested for spin glasses already three decades ago \[ 30,31 \] but was never actually used. At this point we should add a general remark: Throughout the paper we use the large globule approximation, i.e., we consider the chain length \( N \) to be very large. This is necessary to avoid additional complications close to the surface of the globule. Intuitively it is obvious, that monomers close to the globule surface experience a different dynamic environment, such that different mechanisms of freezing processes take place. We will come back to this point in a later publication.

II. THE HOMOPOLYMER GLOBULE AS A DISORDERED SYSTEM

A. The field theory representation

In this section we will provide the basic formulations and the field theory for polymers in poor solvent, i.e., with attractive interactions. To do so, we start from usual continuous description of a homopolymer chain of the length \( N \) in the poor solvent. Its Hamiltonian has the following form

\[
H[\mathbf{r}(s)] = \frac{d}{2a^2} \int_0^N ds \left( \frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 - \frac{|v|}{2} \int_0^N dsds' \delta (\mathbf{r}(s) - \mathbf{r}(s'))
\]

\[
+ \frac{w}{3} \int_0^N dsds'ds'' \delta (\mathbf{r}(s) - \mathbf{r}(s')) \delta (\mathbf{r}(s') - \mathbf{r}(s'')) ,
\]

(2.1)

where we allowed already that the 2\textsuperscript{nd} virial coefficient is negative, \( v < 0 \) and the 3\textsuperscript{rd} virial coefficient \( w > 0 \). Usually the second virial coefficient is measured by its distance from the \( \Theta \) temperature, i.e., \( |v| \simeq a^3|T - \Theta|/\Theta = a^3 \tau \). The third virial coefficient is always of order of \( w \sim \mathcal{O}(a^6) \). The density of the globule is easily estimated by \( \rho \simeq |v|/w \), which provides a naive limit of the temperature at \( \rho a^3 = 1 \). Indeed at sufficient low temperatures the globule is dense, and the entropy term (first term) becomes less and less important. The remaining entropic fluctuations are only important on length scales \( \xi \simeq a/\tau \). This observation will allow us later the safe use of corresponding mean field theories.

The next step is \[ 28,29,32 \] (see also Appendix A) to employ the the Laplace transformation of the polymeric correlation function \( \Xi(\mathbf{r}_1, \mathbf{r}_2; N) \)
where the replicated Hamiltonian is
\[ H_n[\tilde{\psi}; \mu] = \frac{1}{2} \int d^d r \sum_{a=1}^n \psi_a(r) \left[ \mu - \frac{a^2}{2d} \right] \bar{\psi}_a(r) - \frac{|\psi|}{8} \int d^d r \left[ \sum_{a=1}^n \psi_a^2(r) \right]^2 
+ \frac{w}{384} \int d^d r \left[ \sum_{a=1}^n \bar{\psi}_a^2(r) \right]^3 + \ldots, \] (2.4)

As usual the vector field \( \psi \) corresponds to the polymer density in the usual manner, i.e., \( \rho \propto \langle \psi_1^2 \rangle \). The relationship between \( \mu \) and \( N \) has the form
\[ N = - \frac{\partial}{\partial \mu} \int d^d r_1 d^d r_2 \Xi(r_1, r_2; \mu) \] (2.5)

The attractive interaction term of the order \( \psi^4 \) changes the behavior of the field theory. Correlations of the self avoidance are no longer important and we must take care on the balance between the attractive and repulsive forces. Although we mentioned above the relative unimportance of the connectivity term, we have to take track on it as well. The careful analysis below shows that it provides at sufficient low second virial coefficients significant contributions on small scales \( (\xi \sim O(a)) \) contributions only by connectivity. These are in part responsible for frustration.

**B. Mapping onto a random model**

Now we are going to map this field theory onto a random system. It can be shown (see Appendix B) that the free energy of the globule state \( F_{G1} \) can be interpreted as the free energy of a one-component random model with Hamiltonian
\[ \mathcal{H}\{\psi\} = \frac{1}{2} \int d^d r \left[ \mu \psi^2(r) + \frac{a^2}{2d} (\nabla \psi)^2 + t(r)\psi^2(r) \right], \] (2.6)

where the random field \( t(r) \) is non-Gaussian with its generating functional of the form
\[ \Phi\{\rho(r)\} \equiv \exp \left\{ - \int d^d r t(r) \rho(r) \right\} \]
\[ = \exp \left\{ \frac{|\psi|}{8} \int d^d r \rho^2(r) - \frac{w}{384} \int d^d r \rho^3(r) \right\}, \] (2.7)

and where the bar means the averaging over \( t(r) \). It is interesting to underline that only for this combination of signs of the virial coefficients \( (v < 0, w > 0) \) the even central moments \( \langle t(r_1) t(r_2) \ldots t(r_{2m}) \rangle \) (see eqs. (2.8) - (2.11)) are positive, as it should be for the real field \( t(r) \). The aforementioned mapping takes the form
\[ F_{G1} = - \lim_{n \to 0} \frac{1}{n} \log Z_n, \] (2.8)

where the replicated partition function is
\[ Z_n = \int D\tilde{\psi} \exp\{-H_n\}. \] (2.9)

In the present paper we are going to use this analogy between the homopolymer model (which is a “pure” model, i.e. does not include a quenched disorder in its Hamiltonian) and a random model (2.6).
C. Legendre transformation

As a next step we should go to the two-replica variables, $Q_{ab}(r)$, or Parisi overlaps [8] for polymers [27]. One can merely implement it using the Legendre transformation of the interaction part of the Hamiltonian (2.4) which can be represented in the form

$$K[u_{ab}] = \frac{|v|}{8} \int d^4r \sum_{a,b=1}^{n} u_{ab} u_{ba} - \frac{w}{3} \int d^4r \sum_{a,b=1}^{n} u_{ab} u_{bc} u_{ca}$$

$$- \frac{z}{4!16} \int d^4r \sum_{a,b=1}^{n} u_{ab} u_{bc} u_{cd} u_{da} + O(u_{ab}^5),$$

(2.10)

where the pair field $u_{ab}(r) \equiv \psi_a(r) \psi_b(r)$ and where we have also kept the 4th virial coefficient $z$. Let us introduce the integral transformation

$$\exp \{ K[u_{ab}] \} = \left( \prod_{c,d} DQ_{cd} \right) \exp \left\{ W[Q_{ab}] + \int d^4r \sum_{a,b} Q_{ab}(r) u_{ab}(r) \right\},$$

(2.11)

and find $W[Q_{ab}]$ in the form of a functional expansion. For this purpose one should use the saddle point method in eq.(2.11) which can be carried out in the same spirit as in references [33,34]. This results in the Legendre transformation with respect to the extremum field $Q_{ab}$

$$K[u_{ab}(r)] = W[Q_{ab}(r)] + \int d^4r \sum_{a,b=1}^{n} Q_{ab}(r) u_{ab}(r).$$

(2.12)

As a result [35] we get:

$$\frac{\delta K}{\delta u_{ab}} = Q_{ab}(r),$$

(2.13)

$$\frac{\delta W}{\delta Q_{cd}(r)} = -u_{cd}.$$  

(2.14)

By making use of the expansion (2.11) in eqs.(2.13) and (2.14) one obtain for $W[Q_{ab}]$ the following expression:

$$W[Q_{ab}(r)] = -\frac{2}{|v|} \int d^4r \ Tr(Q^2) - \frac{4w}{3|v|^3} \int d^4r \ Tr(Q^3)$$

$$- \frac{2}{|v|^4} \left( \frac{w^2}{|v|} + \frac{z}{3} \right) \int d^4r \ Tr(Q^4) + O(Q^5).$$

(2.15)

After the transformation (2.11) the replicated partition function (2.9) takes the following form

$$Z_n = \int \prod_{c,d} DQ_{cd}(r) \exp \left\{ -\frac{1}{2} \text{Tr} \log \left\{ [\mu - a^2 \nabla^2] \delta_{ab} - 2Q_{ab}(r) \right\} + W[Q_{ab}(r)] \right\},$$

(2.16)

So far only mathematical identities have been used. Nevertheless the use of the overlap variables $Q_{ab}$ allow to detect completely different correlations as the classical $O(n)$ field theory in the limit $n \to 0$ for self avoiding walks. They will allow to probe for a more complicated phase space and provide information on the presence of glassy type correlations in the globules. With this in mind it appears instructive to express the generalization of the polymeric correlation function (2.3)

$$\Xi_{ab}(r_1, r_2; \mu) = \langle \psi_a(r_1) \psi_b(r_2) \rangle$$

(2.17)

in terms of overlaps $Q_{ab}(r)$. For this end we add the source-term $\psi_a(r) h_a(r)$ in eq.(2.11). After substitution in (2.3) and integration over $\psi$ one gets
describes the replica symmetrical (RS) solution \([8–10]\). The matrix \(\Delta_{ab}\) during the calculation of the traces in eq. (3.1) it is convenient to use Parisi’s representation of \(\Delta\), responsible for the replica symmetry breaking (RSB) \([8–10]\). The use of the decomposition (3.3) in eq. (3.3) the symmetric part \(R_{ab}\) in the MF-theory of the spin glass models \([8–10]\), we decompose the Parisi matrix \(Q\)

\[
\Xi_{ab}(r, r'; \mu) = \left\langle \left\{ \hat{1} \cdot G_0^{-1} - 2Q \right\}^{-1} \right\rangle_{ab}(r, r'),
\]

(2.18)

where \(G_0^{-1} = \mu - (a^2/2d)\nabla^2\). The corresponding polymer correlator (2.3) is nothing but the \(\Xi_{11}(r, r'; \mu)\) element of the matrix (2.18).

The correlator \(\Xi_{ab}(r, r'; \mu)\) measures the probability to find chain configurations started at \(r\) in the replica \(a\) provided that it ends at \(r'\) in the replica \(b\). From eq. (2.18) this correlator also can be seen as a scattering amplitude of a free “particle” with the Green function \(G_0\) on the “scatterers” whose density is described by \(Q_{cd}\).

The present representation \((2.16)\) is very promising and reminds on the corresponding expressions for the spin glass models \([8–10]\). The striking difference between these two cases is that in eq. (2.16) only the pure model parameters (Kuhn’s segment length and virial coefficients) are involved. As a result the representation can provide a good starting point for the phenomenon of self-generated disorder which, as we believe, is behind the structural glass formation.

III. MEAN FIELD TREATMENT

A. Landau-type expansion

In order to simplify the mean field treatment of the integral (2.16) let us expand the effective Hamiltonian in eq. (2.16) to the 4\textsuperscript{th} order. We then obtain by this procedure

\[
\Xi = \int \prod_{a,b=1}^{n} DQ_{ab}(r) \exp\left\{ - \sum_{a,b=1}^{n} \int d^4r_1 d^4r_2 \Gamma^{(2)}(r_1, r_2) Q_{ab}(r_1) Q_{ba}(r_2) \right. \\
- \sum_{a,b,c=1}^{n} \int d^4r_1 d^4r_2 d^4r_3 \Gamma^{(3)}(r_1, r_2, r_3) Q_{ab}(r_1) Q_{bc}(r_2) Q_{ca}(r_3) \\
- \sum_{a,b,c,d=1}^{n} \int d^4r_1 d^4r_2 d^4r_3 d^4r_4 \Gamma^{(4)}(r_1, r_2, r_3, r_4) Q_{ab}(r_1) Q_{bc}(r_2) Q_{ca}(r_3) Q_{de}(r_4) \right\},
\]

(3.1)

where the coefficients

\[
\Gamma^{(2)}(r_1, r_2) = \frac{2}{|v|} \delta(r_1 - r_2) - G_0(r_1 - r_2) G_0(r_2 - r_1) \\
\Gamma^{(3)}(r_1, r_2, r_3) = \frac{4}{3} \left[ \frac{|w|}{|v|^3} \delta(r_1 - r_2) \delta(r_2 - r_3) - G_0(r_1 - r_2) G_0(r_2 - r_3) G_0(r_3 - r_1) \right] \\
\Gamma^{(4)}(r_1, r_2, r_3, r_4) = \frac{2}{|v|^4} \left( \frac{|w|^2}{|v|^3} \frac{w}{3} \delta(r_1 - r_2) \delta(r_2 - r_3) \delta(r_3 - r_4) \right. \\
- G_0(r_1 - r_2) G_0(r_2 - r_3) G_0(r_3 - r_4) G_0(r_4 - r_1). \]

(3.2)

As often in the MF-theories the order parameter \(Q_{ab}\) does not depend on the spatial coordinate \(r\). As it is custom in the MF-theory of the spin glass models \([8–10]\), we decompose the Parisi matrix \(Q_{ab}\) in the following form

\[
Q_{ab} = (q - f)\delta_{ab} + f + \Delta_{ab}.
\]

(3.3)

In eq. (3.3) the symmetric part \(R_{ab} = (q - f)\delta_{ab} + f\), with the diagonal \(q\) and off-diagonal \(f\) elements, describes the replica symmetrical (RS) solution \([8–10]\). The matrix \(\Delta_{ab}\) equal zero for \(a = b\) and is responsible for the replica symmetry breaking (RSB) \([8–10]\). The use of the decomposition (3.3) in eq. (3.3) allows in the MF-approximation to separate the total free energy into RS- and RSB-parts. During the calculation of the traces in eq. (3.3) it is convenient to use Parisi’s representation of \(\Delta_{ab}\) by a function \(\Delta(x)\), where \(0 \leq x \leq 1\). Then for the free energy is found to be

\[
\lim_{n \to 0} \frac{1}{n V} F(Q_{ab}) = f_{RS}(q, f) + f_{RSB}(q, f; \Delta(x)),
\]

(3.4)

where RS-free energy
and the RSB-free energy

\[
\begin{align*}
 f_{\text{RSB}}\{q,f;\Delta(x)\} &= -w_1 \int_0^1 dx \Delta^2(x) - w_2 \left[ \int_0^1 dx \Delta(x) \right]^2 \\
 &- w_3 \int_0^1 dx \left[ x \Delta^3(x) + 3 \Delta(x) \int_0^x dy \Delta^2(y) \right] + w_4 \left[ \int_0^1 dx \Delta(x) \right]^3 \\
 &+ w_5 \left\{ 4 \int_0^1 dx \Delta(x) \int_0^x dy y \Delta^3(y) + \int_0^1 dx x^2 \Delta^4(x) \right\} \\
 &+ 2 \int_0^1 dx \Delta^2(x) \left\{ \left[ \int_0^1 dy \Delta(y) \right]^2 + 2 \left[ \int_x^1 dy \Delta(y) \right]^2 - 2 \int_0^x dy \Delta(y) \int_y^1 dz \Delta(z) \right\} \\
 \end{align*}
\]

(3.6)

The coefficients in eqs. (3.5) and (3.6) have the following form (see Appendix C for the details)

\[
\begin{align*}
 A &= \frac{2}{|v|} - \left( \frac{d}{2 \pi a^2} \right)^{d/2} \Gamma \left( \frac{4-d}{2} \right) \mu \left( \frac{\mu}{2 \pi a^2} \right)^{d/2} \\
 B &= \frac{4}{3} \left[ \frac{w}{|v|^3} - \left( \frac{d}{2 \pi a^2} \right)^{d/2} \Gamma \left( \frac{6-d}{2} \right) \frac{\mu}{2 \pi a^2} \right] \\
 C &= \frac{2}{|v|^4} \left( \frac{w^2}{|v|} + \frac{z}{3} \right) - \left( \frac{d}{2 \pi a^2} \right)^{d/2} \Gamma \left( \frac{8-d}{2} \right) \frac{\mu}{3 \pi a^2} \\
 w_1 &= A + 3B(q - f) + 6C(q - f)^2 \\
 w_2 &= -3Bf - 4 Cf^4 \\
 w_3 &= -B - 4 C(q - f) \\
 w_4 &= -4 Cf \\
 w_5 &= -C. \\
\end{align*}
\]

(3.7) (3.8) (3.9) (3.10) (3.11) (3.12) (3.13) (3.14)

The minimization of \( f_{\text{RS}} \) leads to the RS-solution, \( q_m \) and \( f_m \), whereas the maximization (as it is the case for the spin glasses \( \mathbb{S} \) \( \mathbb{S}^\text{B} \)) of \( f_{\text{RSB}} \) results in the RSB-solution in terms of the overlap matrix \( \Delta(x) \). The coefficients in the Landau-expansion of \( f_{\text{RSB}} \) depend also from the RS-solution.

In order to take into account the spatial correlation in RS-sector (see Sec.VB), it is convenient to assume that the variable \( q \) and the coefficients \( A, B \) and \( C \) are weakly \( k \)-dependent. In this case the Landau-expansion is more involved and is given in Appendix C.

### B. Density in terms of \( Q_{ab} \)

The essential issue is to express the globule density \( \rho \) in terms of the order parameter \( Q_{ab} \). This allows to detect any glassy features inside the globule and to distinguish between the liquid and glassy phase. Moreover it will show any unusual properties of the phase space. As mentioned already in the introductory remarks the density is determined by the \( \psi \)-fields. Especially in the MF-approximation the local monomer density is given in terms of the grand canonical partition function as

\[
\rho(\mathbf{r}) = \int_0^N ds \frac{\int d^4r \Xi(\mathbf{r}; s) \Xi(\mathbf{r} - \mathbf{r}'; N - s)}{\int d^4r \Xi(\mathbf{r}; N)},
\]

(3.15)

which should be supplemented by the normalization condition (mass conservation), i.e.,

\[
\int d^4r \rho(\mathbf{r}) = N.
\]

(3.16)

By making use of eqs. (3.14), (3.16) and after Laplace transformation we find
\[
\int d^d r \int d^d r' \Xi(r'; \mu) \Xi(r - r'; \mu) = -\frac{\partial}{\partial \mu} \int d^d r \Xi(r; \mu), \tag{3.17}
\]

where \( \Xi(r; \mu) \) is the Laplace transformation of \( \Xi(r; N) \) (see eq. (2.4)). Then the equation which determines the chain length becomes

\[
N = -\frac{\partial}{\partial \mu} \log \left\{ \int d^d r \Xi(r; \mu) \right\} \tag{3.18}
\]

and takes the form

\[
N = \frac{\int d^d r \int d^d r' \Xi(r'; \mu) \Xi(r - r'; \mu)}{\int d^d r \Xi(r; N)}. \tag{3.19}
\]

In the MF-approximation eq. (2.3) reads

\[
\Xi(r) = \psi_1^{mf}(r)\psi_1^{mf}(0), \tag{3.20}
\]

where \( \psi_1^{mf}(r) \) is the MF-solution for \( \psi_1(r) \). Combining eqs. (3.20) with (3.19) and (3.16) leads to the expected result

\[
\rho(r) = [\psi_1^{mf}(r)]^2. \tag{3.21}
\]

In order to express finally the density in terms of \( Q_{ab} \) we recall that the pair field \( u_{ab}^{mf} = [\psi_1^{mf}(r)]^2 \) (see Sec.IIC). Combining this with eqs. (2.14), (2.13) and taking into account the decomposition (3.3) one obtain for the density the following expansion

\[
\rho = \frac{4}{|v|} q + \frac{4w}{|v|^3} q^2 + \frac{8}{|v|^4} \left( \frac{w^2}{|v|^2} + \frac{z}{3} \right) q^3 + \frac{4w}{|v|^3} \left[ \int_0^1 dx \Delta^2(x) \right] + \frac{8}{|v|^4} \left( \frac{w^2}{|v|^2} + \frac{z}{3} \right)
\]

\[
\times \left[ -3q \int_0^1 dx \Delta^2(x) + \int_1^2 dx \left( x \Delta^3(x) + 3 \Delta(x) \int_0^x dy \Delta^2(y) \right) \right]. \tag{3.22}
\]

In eq. (3.22) we have used Parisi’s representation of \( \Delta_{ab} \) and taken into account that the off-diagonal element vanishes, \( f = 0 \) (see below). The “singularity” \( |v| \to 0 \) in eq. (3.22) is spurious, as we will see in the next subsection in the MF-approximation the value of \( q \) becomes \( |v| \) dependent itself, i.e., \( q \propto |v|^2 \) and \( \Delta(x) \propto |v|^2 \), so that \( \rho \to 0 \) at \( v \to 0 \) as it should be close to the \( \Theta \) - temperature.

**IV. THETA POINT REGIME: COIL-GLOBULE TRANSITION**

The question which must be resolved first is the ordinary coil globule transition. In any case the present general approach should reproduce the physical properties of the standard coil globule transition [20, 36]. To do so we investigate the system close below to the \( \Theta \) - temperature \( T < \Theta \). In ref. 28 the standard \( O(n) \) - field theoretic formulation (see Sec.IIA) has been used in order to treat this problem beyond scaling. The method of pair fields, which is a simpler version of the present formulation [37] has been developed and applied for the coil-globule transition. At that earlier paper of one of the present authors the third virial coefficient has not been taken into account, which corresponds to an expansion around the \( \Theta \) point regime. Here, the Legendre transformation method from Sec.IIC allows easily to take into account an arbitrary number of virial coefficients.

In the theta point region (i.e. at \( T \leq \Theta \)) the globule conformations are very close to Gaussian form so that for the chemical potential one can expect the following scaling: \( \mu = \mu_0/N \). In this case it is convenient to rescale the virial coefficients \( |v|, w \) and \( z \) in the following way

\[
x = \frac{|v|}{a^d} N^{\frac{d}{2-d}}, \tag{4.1}
\]

\[
y = \frac{w}{a^2} N^{3-d}, \tag{4.2}
\]

\[
t = \frac{z}{a^3} N^{\frac{3}{2-d}}, \tag{4.3}
\]
which shows the upper critical dimensions of the different terms in the virial expansion. After that the scaling form of the coefficients (3.7), (3.8) and (3.9) is given by

\[
A = \frac{N^{4-d}}{a^d} \left[ \frac{2}{x} - \left( \frac{d}{2\pi} \right)^{d/2} \frac{\Gamma \left( \frac{d-4}{2} \right)}{\mu_0} \right],
\]

(4.4)

\[
B = \frac{4N^{2-d}}{3a^{2d}} \left[ \frac{y}{x^3} - \left( \frac{d}{2\pi} \right)^{d/2} \frac{\Gamma \left( \frac{6-d}{2} \right)}{2\mu_0} \right],
\]

(4.5)

\[
C = \frac{N^{8-d}}{a^{3d}} \left[ 2 \frac{y^2}{x^5} + \frac{2}{3} \frac{t}{x^4} - \left( \frac{d}{2\pi} \right)^{d/2} \frac{\Gamma \left( \frac{8-d}{2} \right)}{3\mu_0} \right].
\]

(4.6)

In the theta point regime \(|v| = a^d(1-T/\Theta) \to 0\) and \(N >> 1\), so that at \(d = 3\) \(x \approx 1\), \(y \approx 1\) and \(t << 1\), i.e. the forth virial coefficient becomes irrelevant.

In the present regime only RS-solution makes physical sense, since no other solution than the onset of the liquid globule can be expected. Thus we minimize RS-free energy (3.5) with respect to \(q\) and \(f\). The resulting solution reads

\[
f_m = 0 \quad (4.7)
\]

\[
q_m = -3B + \sqrt{(3B)^2 + 32A|C|} \quad (4.8)
\]

so that the RS-free energy becomes

\[
f_{RS}\{q\} = A q^2 + B q^3 + C q^4. \quad (4.9)
\]

Let us consider the possible second order phase transition and impose the following conditions: \(A \leq 0\), \(B > 0\) and \(C > 0\). In the vicinity of the transition point the coefficient \(A\) becomes small \(|A| << 1\), and the order parameter takes the value

\[
q_m \approx \frac{2 |A|}{3B}. \quad (4.10)
\]

As is seen from eqs. (4.4) and (4.5), in \(d = 3\) the order parameter scales as \(q_m \propto 1/N\). Thus, as it follows from eq. (3.22) the density scales as \(\rho = 4q_m/|v|\), which means physically \(\rho = 1/N^{1/2}\) (note also \(x \approx 1\) and \(|v| \propto N^{-1/2}\)). Therefore we reproduce the correct scaling for the density, which is found also from naive scaling.

We can also obtain the transition line in the \(|v| - w\) plane, which will be the first step towards a more general phase diagram spanned by the virial coefficients. This line is defined by the conditions \(A = 0\), \(B > 0\) and \(C > 0\), which again for three dimensions \(d = 3\) yields

\[
\mu_0 = \left( \frac{x}{2} \right)^2 \left( \frac{3}{2\pi} \right)^3 \left[ \Gamma \left( \frac{1}{2} \right) \right]^2, \quad (4.11)
\]

\[
\frac{y}{x^3} > \left( \frac{3}{2\pi} \right)^{3/2} \frac{\Gamma \left( \frac{5}{2} \right)}{2\mu_0^{3/2}}, \quad (4.12)
\]

\[
\frac{y^2}{x^5} > \left( \frac{3}{2\pi} \right)^{3/2} \frac{\Gamma \left( \frac{5}{2} \right)}{6\mu_0^{3/2}}. \quad (4.13)
\]

It is interesting that if eq.(4.11) valid then conditions (4.12) and (4.13) merge and convert into the globule stability condition: \(y > 16\pi^{3/2}/27\). We can eliminate \(\mu_0\) in eq.(4.11) by combining eq.(3.18) with the polymer correlation function

\[
\Xi(k; \mu) = \frac{1}{k^2 + \mu - 2q_m}. \quad (4.14)
\]

We recall that in eq. (4.14) \(\mu = \mu_0/N\) and \(q_m = q_m^0/N\). The result of the combining reads
\[ \mu_0 = 1 + 2q^0_m - 2 \frac{\partial}{\partial \mu_0} \phi^0_m. \]  

(4.15)

By making use of eqs. (4.11) and (4.12) in eq. (4.15) for the transition line, one gets

\[ \left( \frac{x}{2} \right)^2 \left( \frac{3}{2\pi} \right)^3 = 1 + \left( \frac{4}{3} \right) \frac{16 \pi^2}{y - 16 \pi^2}, \]  

(4.16)

where the globule stability condition \( y > 16\pi^2/27 \) is implied.

For completeness we check for the possibility of a first order phase transition. The necessary conditions for this are: \( A > 0, B < 0 \) and \( C > 0 \) (see eq. (4.9)). It is simple to see by eqs. (4.4-4.6) that these conditions are contradictory. This means that within our MF-approach only the second order coil - globule phase transition is possible which is in accordance with the well known result [36]. Therefore the present field theoretic formulation is able to reproduce the standard coil globule transition as the replica symmetric solution at conditions close to the \( \Theta \) - temperature.

V. DEEPER IN THE GLOBULE STATE: LIQUID VERSUS GLASSY REGIME

A. RSB solution in the globule

In the following section we investigate the possibility of replica broken solutions deeper in the globular state. The globule density from naive scaling is given by \( \rho_\text{a} = a^3 |v|/w = \tau \) and has natural limit at \( \tau = 1 \). Physically this limit corresponds to a dense globular state without any solvent inside. At temperatures below the coil - globule phase transition, but still far above \( \tau = 1 \) the system is usually characterized by a monomer - monomer correlation length \( \xi << R_{\text{Gl}} \propto N^{1/3} \). In this case the chemical potential and the density are no longer \( N \)- dependent. It can be seen from dimensional analysis and simple scaling arguments [22] that the chemical potential scales as \( \mu \propto |v|^2/w \propto \tau^2 \), the density \( \rho_{\text{Gl}} \propto |v|^2/w \propto \tau \) and \( \xi \propto 1/|v| \propto \tau^{-1} \).

In this regime fluctuations can be still important unless \( a \leq \xi << R_{\text{Gl}} \), where the MF solution, which we have discussed in Sec.III, becomes valid. Here one can expect that because of competitive interactions (negative second virial coefficient versus positive third virial one) and the constraints imposed by the chain connectivity only a few conformations are dominated. This could manifest itself as the glass transition (negative second virial coefficient versus positive third virial one) and the constraints imposed by the chain connectivity only a few conformations are dominated. This means that within our MF-approach only the second order coil - globule phase transition is possible which is in accordance with the well known result [36]. Therefore the present field theoretic formulation is able to reproduce the standard coil globule transition as the replica symmetric solution at conditions close to the \( \Theta \) - temperature.

Before doing this extremization let us find first the corresponding equation for the chemical potential. In the RSB case we should calculate the \( \Xi_{11} \) element from equation (2.18) and substitute it into (3.18). We use here the so called one step replica symmetry breaking (1-RSB) scenario, which is generic for the glass transition in \( p \)- spin model [37], random - energy model [38] and random heteropolymers [39]. Formally speaking, this transition shows itself as a nontrivial solution which maximizes the RSB - free energy functional (3.4).

Then Parisi’s function \( \Delta(x) \) is defined by only two parameters

\[ \Delta(x) = \begin{cases} 0 & , \ x < x_0 \\ \sigma & , \ x > x_0 \end{cases} \]  

(5.1)

The interpretation of \( \sigma \) and the break point \( x_0 \) is the following [3]. Within the 1-RSB scenario all replicas are grouped into two clusters so that \( 1 - x_0 \) is the fraction of the replicas which belongs to the overlap cluster with the overlap strength \( \sigma \). The rest of the replicas does not overlap. After this simplification the inversion in eq. (2.18) can be done analytically (see eq. (AII7) of ref. [39]). After a straightforward calculation one gets

\[ \Xi_{11}(k; \mu) = \frac{1}{x_0 \left[ \frac{4}{3\pi^2} k^2 + \mu - 2q - 2(1 - x_0)\sigma \right]} - \frac{1 - x_0}{x_0 \left[ \frac{4}{3\pi^2} k^2 + \mu - 2q - 2\sigma \right]} \]  

(5.2)

Insertion of eq. (5.2) in eq. (3.18) simply yields

\[ \mu - 2q_m - 2(1 - x_0)\sigma_m = \mathcal{O} \left( \frac{1}{N} \right), \]  

(5.3)

where \( q_m \) and \( \sigma_m \) are the solutions which extremize the free energies (3.5) and (3.6) correspondingly. With 1-RSB assumption (see eq. (5.1)) the free energy (3.8) becomes
It is convenient to represent the chemical potential in the form
\[
\mu = \frac{|v|^2}{s(|v|, w)},
\] (5.5)
where \(s(|v|, w)\) is a function of \(|v|\) and \(w\). For convenience we switch to dimensionless variables (by keeping for simplicity the same notations):
\[
\frac{v}{a^3} \rightarrow v, \quad \frac{w}{a^6} \rightarrow w, \quad \frac{z}{a^9} \rightarrow z, \quad \frac{s}{a^9} \rightarrow s,
\]
\[Aa^3 \rightarrow A, \quad Ba^3 \rightarrow B, \quad Ca^3 \rightarrow C. \] (5.6)

We also introduce the reduced (with a bar) values:
\[
\bar{A} = A|v|, \quad \bar{B} = B|v|^3, \quad \bar{C} = C|v|^5, \quad \bar{q}_m = \frac{q_m}{|v|^2}, \quad \bar{\sigma}_m = \frac{\sigma_m}{|v|^2},
\]
\[
\bar{w}_1 = w_1|v|, \quad \bar{w}_3 = w_3|v|^3, \quad \bar{w}_5 = w_5|v|^5.
\] (5.7)

After that, the equation (5.3) for \(s(|v|, w)\) (or for the chemical potential) takes the compact form
\[
\frac{1}{s} = 2\bar{q}_m + 2(1 - x_0)\bar{\sigma}_m,
\] (5.8)
where
\[
\bar{q}_m = \frac{-3\bar{B} + \sqrt{(3\bar{B})^2 + 32A|\bar{C}|}}{8\bar{C}},
\] (5.9)
\[
\bar{\sigma}_m = \frac{3|\bar{w}_3|(2 - x_0) + \sqrt{(3|\bar{w}_3|(2 - x_0))^2 - 32\bar{w}_1|\bar{w}_5|(3 - 3x_0 + x_0^2)}}{8|\bar{w}_5|(3 - 3x_0 + x_0^2)},
\] (5.10)
\[
\bar{w}_1 = \bar{A} + 2\bar{C}\bar{q}_m^2, \quad \bar{w}_3 = -\bar{B} - 4\bar{C}\bar{q}_m, \quad \bar{w}_5 = -\bar{C}.
\] (5.11-5.13)

and the reduced coefficients reads
\[
\bar{A} = 2 - \left(\frac{3}{2\pi}\right)^{3/2} \Gamma\left(\frac{1}{2}\right) s^{1/2},
\] (5.14)
\[
\bar{B} = \frac{4}{3} \left[ w - \frac{1}{2} \left(\frac{3}{2\pi}\right)^{3/2} \Gamma\left(\frac{3}{2}\right) s^{3/2} \right],
\] (5.15)
\[
\bar{C} = 2w^2 + \frac{2}{3} z|v| - \frac{1}{3} \left(\frac{3}{2\pi}\right)^{3/2} \Gamma\left(\frac{5}{2}\right) s^{5/2}.
\] (5.16)

Eqs. (5.9) and (5.10) are the result of extremization of eqs. (4.9) and (5.4) correspondingly. Throughout the remainder of the paper we will retain the conditions: \(\bar{A} < 0, \bar{B} < 0, \bar{C} > 0, w_1 > 0, w_3 < 0, w_5 < 0\). This assures that the nontrivial solution \(\sigma_m\) shows up via a first order phase transition, in a similar manner as in \(p\) - spin spin glasses (39) or the random - energy model (38). On the coexistence line between liquid and glassy phases additionally \(f_{\text{HSB}}(\sigma_m, x_0) = 0\) and this leads to the corresponding equation
\[
\frac{\bar{w}_1|\bar{w}_5|}{|\bar{w}_3|^2} = \frac{(2 - x_0)^2}{4(3 - 3x_0 + x_0^2)}.
\] (5.17)
The equation for the reduced globule density, \( c = \rho |v| \), can be easily obtained from eq.(3.22) under the 1-RSB assumption. The calculation yields

\[
c = 4q_m + \frac{4w^2 q_m^2}{|v|^2} + \frac{8}{|v|^3} \left( \frac{w^2}{|v|^2} + \frac{z}{3} \right) q_m^3 - \frac{4w}{|v|^2} \sigma_m^2 (1 - x_0) + \frac{8}{|v|^3} \left( \frac{w^2}{|v|^2} + \frac{z}{3} \right) q_m^3 \times \left[ -3q_m^2 \sigma_m^2 (1 - x_0) + \frac{\sigma_m^3}{2} (1 - x_0^2) + \frac{3}{2} \sigma_m^3 (1 - x_0)^2 \right]
\]

Eqs.(5.8) - (5.16) for the function \( s(|v|, w) \) can be solved numerically at given values of the forth virial coefficient \( z \) and break point \( x_0 \). After substitution of this solution \( s(|v|, w) \) in eq.(5.17) we arrive at the equation for the coexistence line in the plane of \( |v| \) and \( w \). By changing \( x_0 \) one can obtain a whole set of \( x_0 \)- isolines. We will give the corresponding numerical solution in Sec.V C but before we analyze the validity of the MF - approximation which has been given above.

### B. Role of fluctuations in RS - sector

As have been mentioned above, the MF-solution is valid when the fluctuations are negligible. Generally speaking, this should be required for RS - and RSB - sectors of the replica space. In the present paper it is not our intention to consider fluctuations in the RSB-sector, which is rather involved, and we leave it for a future publication.

In the RS - sector spatial fluctuations are described by the correlation function (C13) (see Appendix C). It is easy to calculate from eq.(C13) the radial distribution function \( g(r) = \frac{4\pi r^2}{X} \langle \Delta q(r) \Delta q(0) \rangle \) at \( d = 3 \). Again we turn to the reduced variables (5.5) - (5.7). After the inverse Fourier transformation of eq.(C13), the radial distribution function reads

\[
g(r) = \frac{r^2}{2X} \exp \left\{ -3|v| \sqrt{\frac{X}{Y}} r \right\} , \tag{5.19}
\]

where

\[
X = \widetilde{A} + 3q_m \widetilde{B} + 6q_m^2 \widetilde{C}
\]

and

\[
Y = \frac{1}{24\pi} \left( \frac{3}{2} \right)^{3/2} \left[ s^{3/2} + 5q_m s^{5/2} + \frac{63}{4} q_m^2 s^{7/2} \right] \tag{5.21}
\]

It is important to note here once more, that the quantities \( \widetilde{X} \) and \( \widetilde{Y} \) do not have any additional \( |v| \) - dependence.

We estimate now the Ginzburg parameter, \( \varepsilon_G \), (see e.g. [40]) as the ratio of \( g(r) \) at its maximum to \( g_m^2 = q_m^2 |v|^4 \). Then for the Ginzburg criterion we have the following equation

\[
|v|^2 = \frac{1}{6e \varepsilon_G q_m^2 \sqrt{X(|v|, w)Y(|v|, w)}} \tag{5.22}
\]

where \( e \) is the Napier number. Eq.(5.22) for a reasonably small \( \varepsilon_G \) represents a line in the \((|v|, w)\) plane which separate fluctuating and MF regimes. From now on we will call these two regimes as the liquid globule and the glassy globule correspondingly.

From eq.(5.19) the correlation length is given by

\[
\xi = \frac{1}{3|v|} \sqrt{\frac{X}{Y}} \propto r^{-1} , \tag{5.23}
\]

which is qualitatively in line with the standard result [26,29,36] and the correct scaling.

From the Gaussian approximation for the effective Hamiltonian in the RS case (C11) it is easy to calculate the corresponding RS - free energy, which takes the following form
\[ f_{RS}\{q_m\} = |v|^3 \left[ Aq_m^2 + Bq_m^3 + Cq_m^4 \right] + \frac{T}{2} \int \frac{d^3\kappa}{(2\pi)^3} \log \left[ |v|^2X + \kappa^2Y \right] . \] (5.24)

The last integral in eq.(5.24) diverges at large \( \kappa \). This ultraviolet divergence is of no significance as soon as the \(|v|\) - dependence is the only one we are interested in. For the second derivative of the integral in eq. (5.24) with respect to \(|v|^2\) one has

\[ I_{|v|^2}'' = -\frac{TX^2}{4\pi^2} \int_0^\infty \frac{\kappa^2 d\kappa}{[|v|^2X + \kappa^2Y]^2} = -\frac{T}{16\pi} \left( \frac{X}{Y} \right)^{3/2} \frac{1}{|v|} . \] (5.25)

After that the expression for the RS - free energy takes the form

\[ f_{RS} = |v|^3 \left[ Aq_m^2 + Bq_m^3 + Cq_m^4 \right] - \frac{T}{12\pi} \left( \frac{X}{Y} \right)^{3/2} |v|^3 . \] (5.26)

We ascribe this branch of the free energy to the liquid globule state and will consider it in more details in the next subsection.

C. Numerical calculations: chemical potential, phase diagram and configurational entropy

Finally we are going to compute the phase diagram for the polymer globule. We recall here that the first step carried out earlier in this paper, i.e., the RS - solution corresponds to the classical coil globule transition. Here we are now in the position to calculate from the 1-RSB free energy the transition to the glassy state. The numerical solution of eqs.(5.8) - (5.16) at \( z = 9 \) and \( x_0 = 0.88 \) is shown in Fig.1. As can be seen the function \( s(|v|, w) \) depends linearly from \( w \) and almost does not depend from \(|v|\). This is in agreement with well known result \[ 29,36 \]: \( \mu \propto |v|^2/w \) (see eq.(5.5)). We have also calculated \( s(|v|, w) \) at \( x_0 = 0.90, x_0 = 0.92, x_0 = 0.95 \) and have used these results as an input in eq.(5.17). This eventually leads to \( x_0 \) - isolines in the glassy globule phase which are plotted in Fig.2.

![FIG. 1. The dependence of the parameter \( s \) (see eq.(5.4)) on the virial coefficients at \( z = 9 \) and \( x_0 = 0.88 \)](image)

The line, which is associated with eq.(5.22) corresponds to the Ginzburg criterion for fluctuations in RS-sector and separates the glassy globule from the liquid one. Obviously, the position of this line depends from the value of \( \varepsilon_G \ll 1 \) and should be better seen as a crossover from the fluctuating regime to the mean field one. In Fig.2 this line is given at \( \varepsilon_G = 0.033 \). We have not shown more \( x_0 \) - isolines.
explicitly, but it is important to remind that by changing \( x_0 \) continuously one can span up the whole phase diagram from left to right. It is interesting that the \( x_0 \)-isolines in Fig.2 are almost vertical. This means that in a real experiment (upon changing the solvent quality \( |v| \) by temperature) always some particular value of \( x_0 \) is hit in the glassy phase and stays with it as \( |v| \) increases. We recall that \( 1 - x_0 \) is the fraction of replicas which overlap with the strength \( \sigma_m = \bar{\sigma}_{m|v|^2} \).

The fact that on the transition line the value of \( x_0 \) is less than one, \( x_0 < 1 \) shows that the transition is thermodynamically of the first order. This is contrary to \( p \)-spin spin glasses \([4-6]\) and random heteropolymer \([12]\). It is well known that in these cases transition has no latent heat (i.e. thermodynamically of the second order) since \( x_0 = 1 \) at the transition point, whilst the order parameter \( \sigma \) undergoes a jump (i.e. displays the first-order transition). In our case the transition is of the first order thermodynamically as well as with respect to the order parameter. In Fig.2 we have shown also the line which corresponds to the coil-globule second order transition (see eq.(4.16)) at the chain length \( N = 250 \). The critical value \( |v|_{cr} \) on this line is scaled as \( 1/\sqrt{N} \).

Fig.3 shows the reduced density behavior (see eq.(5.18)) at \( x_0 = 0.88 \) in the same as in Fig.2 intervals of \( |v| \) and \( w \). It can be seen that the density on the transition line is fairly small to justify the use of the virial expansion.
Let us now calculate the configurational entropy $S_{\text{conf}}$ (or the complexity) which is usually of interest for glass forming liquids. The configurational entropy in the liquid globule state can be defined as the difference

$$S_{\text{conf}} = S_{\text{liquid}} - S_{\text{valley}},$$

(5.27)

where

$$S_{\text{liquid}} = -\frac{\partial f_{\text{RSB}}}{\partial T},$$

(5.28)

and $S_{\text{valley}}$ is the entropy (per particle) which corresponds to one pure state or a valley in the free energy landscape. In order to estimate $S_{\text{valley}}$ let us recall from reference 42 that the order parameter $\sigma$ describes the structure of space of valleys through the probability, $P(\sigma)$, that two valleys picked at random, have an overlap $\sigma$. For the 1-RSB scenario this function has a rather simple form: $P(\sigma) = x_0 \delta(\sigma) + (1 - x_0) \delta(\sigma - \sigma_m)$. The dimension of the matrix $\Delta_{ab}$, which within 1-RSB is parameterized by $n(x_0 - 1)/2$ parameters $\sigma$, becomes negative at $n \to 0$ and $0 \leq x_0 \leq 1$. Therefore the free energy $f_{\text{RSB}}$ (see eq.(5.4)) becomes negative, and the factor $-(1-x_0)$ in eq.(5.1) can be treated as “fraction of valleys” with overlap $\sigma_m$. In this case the intra-valley free energy can be obtain by dividing out a common factor of $-(1-x_0)$ in eq.(5.4): $f_{\text{valley}} = -f_{\text{RSB}}/(1-x_0)$. Then we can estimate $S_{\text{valley}}$ in a following way:

$$S_{\text{valley}} = \frac{1}{1-x_0} \frac{\partial f_{\text{RSB}}}{\partial T}.$$

(5.29)

The configurational entropy in the glassy globule state is given by the same way as in the $p$-spin spin glasses:

$$S_{\text{conf}} = \frac{1}{N} [\psi(1) - \psi(1-x_0)],$$

(5.30)

where $\psi(x)$ is the digamma function.
FIG. 4. The configurational entropy \( S_{\text{conf}}(T) \) as the function of temperature whilst the globule is cooling from the liquid to the glassy state

By cooling the system along the \( x_0 \) - isoline at \( x_0 = 0.88 \), we have calculated the configurational entropy for liquid (see eqs. (5.27) - (5.29)) and glassy (eq. (5.30)) globule. Figure 4 gives the result of this calculations. As discussed above the transition is of the first order, i.e., the \( S_{\text{conf}} \) undergoes a jump which is qualitatively in line with Molecular dynamics [21,22] and Monte Carlo [23] simulations. It must bear in mind that the transition temperature in Fig.4 is also defined by the Ginzburg criterion for fluctuations (see the intersection point of the upper solid line and the \( x_0 = 0.88 \) isoline in Fig.2), so that this transition can be treated as a crossover from the fluctuating regime to mean field, where only few states are dominated. This possibility is shown in Fig.4 by dotted line. On the other hand, this behavior is quite different from low molecular systems or polymer melts where \( S_{\text{conf}} \) goes to zero continuously as soon as \( T \rightarrow T_K \).

VI. CONCLUSION AND OUTLOOK

We have shown that the homopolymer globule problem can be formulated within the \( n \rightarrow 0 \) limit of free \( n \)-component \( \psi_a, \psi_b \) - field theory and then be mapped onto the disordered one - component model with a non - Gaussian random noise. It is of interest, that the statistical moments of this noise can be expressed only through the virial coefficients of the pure model, the fact which gives grounds to discuss the self - generated disorder. On the other side, the \( n \rightarrow 0 \) limit is responsible at the same time both for the polymer conformations and for the nontrivial structure of the replica space. Physically this means that units with competitive interactions and stipulated by the connectivity posses good pre-conditions for the glass formation.

The Legendre transformation from the pair fields \( \psi_a(r) \psi_b(r) \) to the Parisi overlap parameters \( Q_{ab}(r) \) leads to the effective Hamiltonian which is akin to corresponding expressions for the spin glass models. We have investigated this resulting replicated model within mean field Landau - type treatment. First of all, the RS - solution of the corresponding equation is associated with the conventional coil - liquid globule transition whereas the RSB - solution in the deeper globule state is related with the glassy regime. This mean field glassy globule phase can be only assured if the fluctuations in RS - and RSB - sectors are small. In this paper we have only studied the fluctuations in the RS - sector and have sketched the corresponding Ginzburg criterion line on the phase diagram. We have calculated the configurational entropy for the liquid and glassy globules and shown that the transition between them is a first order one, as also is in the MD and MC computer simulations [21,22,23], whereas for the random heteropolymer [24] the freezing is thermodynamically a second order transition. On the other side, the computer simulation [24] and experiment [24] shows that the folding in proteins has a latent heat, i.e. the random heteropolymer is a
poor model of protein-folding thermodynamics. It was shown [14,43] that in the heteropolymer models where some sequences of monomers have especially low energy in their native conformation the folding is thermodynamically a first-order transition.

Nevertheless, our calculations shows that already for the homopolymer globule, because of competitive interactions (virial coefficients of different signs) and connectivity, the transition with a latent heat is possible. In this respect the revisiting of the random heteropolymer problem within our field theoretical approach (as oppose to the density functional method [12–14]) would be very interesting. This could elucidate the problem how the self-generated disorder interplay with quenched disorder and eventually modify the freezing conditions.

The dynamical aspects of the thermodynamic transition discussed above is a matter of crucial importance. The first and foremost question which should be investigated is related with the formation of the entropic droplets [4,44] in the RSB-sector of the replica space.

ACKNOWLEDGMENTS

V.G.R acknowledges greatfully the support by the Sonderforschungsbereich SFB 262 of the Deutsche Forschungsgemeinschaft.

APPENDIX A: FIELD-THEORETICAL REPRESENTATION FOR A GENERAL SELF-INTERACTING CHAIN

Let us represent the Hamiltonian of the self-interacting chain in the following form

\[ H[r(s)] = \frac{d}{2a^2} \int_0^N ds \left( \frac{\partial r}{\partial s} \right)^2 \]

\[ + \sum_{m=1}^{\infty} \frac{v_{m+1}}{(m+1)!} \int_0^N ds_0 ds_1 \cdots ds_m \prod_{i=1}^m \delta(r(s_0) - r(s_i)) \quad \] (A1)

where \( v_{m+1} \) denote the virial coefficients. It is convenient to introduce the density

\[ \rho(r) = \int_0^N ds \delta(r - r(s)) \] ,

(A2)

then the partition function of the polymer chain

\[ Z = \int Dr(s) \exp \{-H[r(s)]\} \]

(A3)

takes the form

\[ Z = \int Dr(s) D\rho(r) \delta \left[ \rho(r) - \int_0^N ds \delta(r - r(s)) \right] \]

\[ \times \exp \left\{ -\frac{d}{2a^2} \int_0^N ds \left( \frac{\partial r}{\partial s} \right)^2 - \sum_{m=1}^{\infty} \frac{v_{m+1}}{(m+1)!} \int d^d r \rho^{m+1}(r) \right\} \]

(A4)

By making use of the integral representation for the \( \delta \)-function eq.(A4) can be recast in a form

\[ Z = \int Dr(s) D\phi(r) D\rho(r) \exp \left\{ i \int d^d r \phi(r) \rho(r) \right. \]

\[ - \sum_{m=1}^{\infty} \frac{v_{m+1}}{(m+1)!} \int d^d r \rho^{m+1}(r) \right\} \int d^d r d^d r' G(r,r';[\phi];N) \] ,

(A5)
where

\[ G(r, r'; [\phi]; N) = \int_{r(0)=r}^{r(N)=r'} Dr(s) \exp \left\{ -\frac{d}{2a^2} \int_0^N ds \left( \frac{\partial r}{\partial s} \right)^2 - i \int_0^N ds \phi(r(s)) \right\} . \]  \hspace{1cm} (A6)

The corresponding equation for \( G \) reads

\[ \left[ \frac{\partial}{\partial N} - \frac{a^2}{2d} \nabla^2 + i\phi(r) \right] G(r, r'; [\phi]; N) = \delta(r - r')\delta(N) . \]  \hspace{1cm} (A7)

It is convenient to make the Laplace transformation

\[ G(r, r'; [\phi]; \mu) = \int_0^\infty dNG(r, r'; [\phi]; N) \exp(-\mu N), \]  \hspace{1cm} (A8)

after which the equation for \( G(r, r'; [\phi]; \mu) \) yields

\[ G(r, r'; [\phi]; \mu) = \frac{\int D\psi(r)\psi(r') \exp \left\{ -\frac{1}{2} \int d^dr \psi(r) \left[ \mu - \frac{a^2}{2d} \nabla^2 + i\phi(r) \right] \psi(r') \right\}}{\int D\psi \exp \left\{ -\frac{1}{2} \int d^dr \psi(r) \left[ \mu - \frac{a^2}{2d} \nabla^2 + i\phi(r) \right] \psi(r') \right\}} . \]  \hspace{1cm} (A9)

In order to avoid the denominator in eq.(A9) we should upgrade the field \( \psi \) by introducing \( n \)-component field \( \vec{\psi} = \{ \psi_1, \psi_2, \ldots \psi_n \} \). Then by using the replica trick, we have

\[ G(r, r'; [\phi]; \mu) = \lim_{n \to 0} \int \prod_{a=1}^n D\psi_a \psi_1(r)\psi_1(r') \exp \left\{ -\frac{1}{2} \sum_{a=1}^n \int d^dr \psi_a(r) \left[ \mu - \frac{a^2}{2d} \nabla^2 + i\phi(r) \right] \psi_a(r') \right\} \]  \hspace{1cm} (A10)

One can make now the Laplace transformation from both sides of eq.(A5) and substitute in it eq.(A10). The integration first over the field \( \phi(r) \) and then over \( \rho(r) \) results in the following expression for grand canonical partition function of a polymer chain with ends fixed at points \( r \) and \( r' \):

\[ \Xi(r, r'; \mu) = \lim_{n \to 0} \int \prod_{a=1}^n D\psi_a \psi_1(r)\psi_1(r') \exp \left\{ -\frac{1}{2} \int d^dr \psi(r) \left[ \mu - \frac{a^2}{2d} \nabla^2 \right] \psi(r') \right\} , \]  \hspace{1cm} (A11)

where

\[ H_n[\vec{\psi}; \mu] = \frac{1}{2} \int d^dr \sum_{a=1}^n \psi_a(r) \left[ \mu - \frac{a^2}{2d} \nabla^2 \right] \psi_a(r') + \sum_{m=1}^{\infty} \frac{\nu_{m+1}}{(m+1)!} \int d^dr \sum_{a=1}^n \left[ \frac{1}{2} \psi_a^2(r) \right]^{m+1} . \]  \hspace{1cm} (A12)

**APPENDIX B: THE CONNECTION TO A RANDOM MODEL**

Here we prove that in a poor solvent the polymer problem (see eqs.(2.3) and (2.4)) can be connected to a one-component random model. We shall restrict our consideration only to second and third virial coefficients. The generalization to the case with an arbitrary number of virial coefficients is straightforward.

Let us consider the one component random model with Hamiltonian

\[ \mathcal{H}\{\psi\} = \frac{1}{2} \int d^dr \left[ \mu \psi^2(r) + \frac{a^2}{2d} (\nabla \psi)^2 + t(r)\psi^2(r) \right] , \]  \hspace{1cm} (B1)

where \( t(r) \) is a non-Gaussian random field with the generating functional

\[ \Phi\{\rho(r)\} = \int Dt(r)P\{t(r)\} \exp \left\{ -\int d^4t \rho(t)\rho(t) \right\} = \exp \left\{ \frac{|v|}{8} \int d^4r \rho^2(r) - \frac{w}{38} \int d^4r \rho^3(r) \right\} . \]  \hspace{1cm} (B2)
In eq. (B3) \( P\{t(r)\} \) is the distribution functional of the field \( t(r) \). One can easily check that the replication of the Hamiltonian (B1) and the subsequent averaging over \( t(r) \), i.e.

\[
Z^n = \int \prod_{a=1}^{n} D\psi_a \exp \left\{-\sum_{a=1}^{n} \mathcal{H}(\psi_a)\right\},
\]

(B3)

leads to the effective replicated Hamiltonian (2.4).

From the probabilistic interpretation (B2) one can explicitly find the central moments of \( t(r) \). The expansion of both sides of eq. (B2) yields

\[
\sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \int dr_1 \ldots dr_m t(r_1) t(r_2) \ldots t(r_m) \rho(r_1) \rho(r_2) \ldots \rho(r_m)
\]

\[
= \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{l=0}^{k} \frac{k!}{l!(k-l)!} \left[ \frac{|v|}{8} \int d^d r \rho^2(r) \right]^{k-l} \left[ \frac{w}{38} \int d^d r \rho^3(r) \right]^{l}.
\]

(B4)

By making the \( m \)-terms of \( \rho(r) \) on both sides of eq. (B4) equal, one gets

\[
\int dr_1 \ldots dr_m t(r_1) t(r_2) \ldots t(r_m) \rho(r_1) \rho(r_2) \ldots \rho(r_m)
\]

\[
= \sum_{k=\{m/3\}}^{\lfloor m/2 \rfloor} \frac{m!}{(m-2k)! (3k-m)!} \left[ \frac{|v|}{8} \int d^d r \rho^2(r) \right]^{3k-m} \left[ \frac{w}{38} \int d^d r \rho^3(r) \right]^{m-2k},
\]

(B5)

where \( \lfloor m/2 \rfloor \) stands for the greatest integer number less than \( m/2 \) and \( \{m/3\} \) is the smallest integer number larger than \( m/3 \). By making use the representations \( \int d^d r \rho^2(r) = \int d^d r d^d r_2 \delta(r_1 - r_2) \rho(r_1) \rho(r_2) \) and \( \int d^d r \rho^3(r) = \int d^d r_3 d^d r_2 d^d r_3 \delta(r_5 - r_4) \delta(r_5 - r_3) \rho(r_3) \rho(r_4) \rho(r_5) \) one finally gets:

\[
\overline{t(r_1) t(r_2) \ldots t(r_m)} = \sum_{k=\{m/3\}}^{\lfloor m/2 \rfloor} \frac{m!}{(m-2k)! (3k-m)!} \left[ \frac{|v|}{8} \right]^{3k-m} \left[ \frac{w}{38} \right]^{m-2k} \times \delta(r_1 - r_2) \delta(r_3 - r_4) \ldots \delta(r_{6k-2m-1} - r_{6k-2m})
\]

\[
\times \delta(r_{6k-2m+1} - r_{6k-2m+2}) \delta(r_{6k-2m+1} - r_{6k-2m+3}) \ldots \delta(r_{m-2} - r_{m-1}) \delta(r_{m-2} - r_m).
\]

(B6)

In eq. (B6) the second line includes \( 3k - m \) \( \delta \)-functions with arguments successively pairwise divided between \( 6k - 2m \) points. The third line includes \( m - 2k \) \( \delta \)-functions so that in each successive pairs of them one \( r \) - point is common.

Let us consider some particular cases of eq. (B6).

i) \( m = 1 \). Then \( \{m/3\} = 1, \lfloor m/2 \rfloor = 0 \) and

\[
\overline{t(r)} = 0
\]

(B7)

ii) \( m = 2 \). Then \( \{m/3\} = 1, \lfloor m/2 \rfloor = 1 \) and eq. (B6) reads

\[
\overline{t(r_1) t(r_2)} = \frac{|v|}{4} \delta(r_1 - r_2)
\]

(B8)

iii) At \( m = 3, \{m/3\} = 1, \lfloor m/2 \rfloor = 1 \) (i.e. \( k=1 \)) and one gets

\[
\overline{t(r_1) t(r_2) t(r_3)} = \frac{w}{8} \delta(r_1 - r_2) \delta(r_1 - r_3)
\]

(B9)

iv) At \( m = 4, \{m/3\} = 2, \lfloor m/2 \rfloor = 2 \) (i.e. \( k=2 \)) and

\[
\overline{t(r_1) t(r_2) t(r_3) t(r_4)} = \frac{3}{16} |v|^2 \delta(r_1 - r_2) \delta(r_3 - r_4)
\]

(B10)

v) Finally at \( m = 5, \{m/3\} = 2, \lfloor m/2 \rfloor = 2 \) and

\[
\overline{t(r_1) t(r_2) t(r_3) t(r_4) t(r_5)} = \frac{5!}{384} |v| w \delta(r_1 - r_2) \delta(r_3 - r_4) \delta(r_3 - r_5)
\]

(B11)

The important feature of these moments is that all of them are positive, which means that \( t(r) \) is real.
APPENDIX C: SPATIAL FLUCTUATIONS FOR WEAKLY INHOMOGENEOUS GLOBULE

In this appendix we give the Landau-expansion only for the case when \( q \) and coefficients \( \Gamma^{(2)}, \Gamma^{(3)}, \Gamma^{(4)} \) are weakly \( k \) - dependent in the RS - sector. The spatial Fourier transformation in eq.(3.1) leads to the following effective Hamiltonian

\[
H_{RS}\{q(k)\} = \int \frac{d^d k}{(2\pi)^d} \Gamma^{(2)}(k)q(k)q(-k) + \int \frac{d^d k_1 d^d k_2}{(2\pi)^d} \Gamma^{(3)}(k_1, k_2)q(k_1)q(k_2)q(-k_1 - k_2) + \int \frac{d^d k_1 d^d k_2 d^d k_3}{(2\pi)^d} \Gamma^{(4)}(k_1, k_2, k_3)q(k_1)q(k_2)q(k_3)q(-k_1 - k_2 - k_3) + \ldots ,
\]

(C1)

where

\[
\Gamma^{(2)}(k) = \frac{2}{|v|} - \int \frac{d^d k}{(2\pi)^d} \frac{1}{\left[\frac{\alpha^2}{2\sigma^2} k^2 + \mu\right]\left[\frac{\alpha^2}{2\sigma^2} (\kappa - k)^2 + \mu\right]},
\]

(C2)

\[
\Gamma^{(3)}(k_1, k_2) = \frac{4}{3} \left[ \frac{w}{|v|^3} - \int \frac{d^d k}{(2\pi)^d} \frac{1}{\left[\frac{\alpha^2}{2\sigma^2} k^2 + \mu\right]\left[\frac{\alpha^2}{2\sigma^2} (\kappa - k_1)^2 + \mu\right]\left[\frac{\alpha^2}{2\sigma^2} (\kappa - k_1 - k_2)^2 + \mu\right]\left[\frac{\alpha^2}{2\sigma^2} (\kappa - k_1 - k_2 - k_3)^2 + \mu\right]} \right],
\]

(C3)

\[
\Gamma^{(4)}(k_1, k_2, k_3) = \frac{2}{|v|^4}\left(\frac{w^2}{|v|^3} + \frac{z}{3}\right) - 2 \int \frac{d^d k}{(2\pi)^d} \frac{1}{\left[\frac{\alpha^2}{2\sigma^2} k^2 + \mu\right]\left[\frac{\alpha^2}{2\sigma^2} (\kappa - k_1)^2 + \mu\right]\left[\frac{\alpha^2}{2\sigma^2} (\kappa - k_1 - k_2)^2 + \mu\right]\left[\frac{\alpha^2}{2\sigma^2} (\kappa - k_1 - k_2 - k_3)^2 + \mu\right]} \] \]

(C4)

For weak fluctuations around MF - solution \( q_m \) to be investigated one should estimate Hessian

\[
\frac{\delta^2 H_{RS}}{\delta q(r_1)\delta q(r_2)} \bigg|_{q=q_m} = 2\Gamma^{(2)}(r_1 - r_2) + 6q_m \int d^d r_3 \Gamma^{(3)}(r_2 - r_1, r_3 - r_1) + 12q_m^2 \int d^d r_3 d^d r_4 \Gamma^{(4)}(r_2 - r_1, r_3 - r_1, r_4 - r_1) + \ldots ,
\]

(C5)

or in the Fourier space

\[
\frac{\delta^2 H_{RS}}{\delta q(r_1)\delta q(r_2)} \bigg|_{q=q_m} = 2\Gamma^{(2)}(k) + 6q_m \Gamma^{(3)}(k, k = 0) + 12q_m^2 \Gamma^{(4)}(k, k = 0, k = 0) + \ldots .
\]

(C6)

The resulting effective Hamiltonian expansion around the MF - solution takes the following form

\[
H_{RS}\{q_m, \Delta q(k)\} = H_{RS}\{q_m\} + \frac{1}{2} \int \frac{d^d k}{(2\pi)^d} \frac{\delta^2 H_{RS}}{\delta q(k)\delta q(-k)} \bigg|_{q=q_m} \Delta q(k)\Delta q(-k)
\]

\[
= Aq_m^2 + Bq_m^3 + Cq_m^4 + \int \frac{d^d k}{(2\pi)^d} \left[ \Gamma^{(2)}(k) + 3q_m \Gamma^{(3)}(k, k = 0) + 6q_m^2 \Gamma^{(4)}(k, k = 0, k = 0) \right] \times \Delta q(k)\Delta q(-k),
\]

(C7)

where

\[
\Delta q(k) = q(k) - q_m
\]

(C8)

and

\[
A = \Gamma^{(2)}(0) , \quad B = \Gamma^{(3)}(0, 0) , \quad C = \Gamma^{(4)}(0, 0, 0) .
\]

(C9)

The expressions for \( A, B \) and \( C \) are given by eqs. (3.7) - (3.9). It is easy to estimate the integrand in eq.(C7) at small \( k \) (weak inhomogeneity). The straightforward calculations yields
\[ H_{\text{RS}}\{q_m, \Delta q(k)\} = H_{\text{RS}}\{q_m\} + \int \frac{d^d k}{(2\pi)^d} \left\{ X(|v|, w) + (ka)^2 Y(|v|, w) \right\} \Delta q(k) \Delta q(-k), \tag{C10} \]

where

\[ X = A + 3q_mB + 6q^2_mC \tag{C11} \]

and

\[ Y = \left( \frac{1}{2\pi da^2} \right)^{d/2} \frac{2d - 3}{12\mu \frac{d - 2}{d}} \Gamma \left( \frac{6 - d}{2} \right) + q_m \left( \frac{1}{2\pi da^2} \right)^{d/2} \frac{3d - 4}{9\mu \frac{d - 2}{d}} \Gamma \left( \frac{8 - d}{2} \right) \]
\[ + q^2_m \left( \frac{1}{2\pi da^2} \right)^{d/2} \frac{4d - 5}{20\mu \frac{d - 2}{d}} \Gamma \left( \frac{10 - d}{2} \right). \tag{C12} \]

From (C10) it is obvious that the corresponding correlation function

\[ \left\langle |\Delta q(k)|^2 \right\rangle = \frac{1}{X(|v|, w) + (ka)^2 Y(|v|, w)}. \tag{C13} \]
[31] D. Jasnow and M. Fisher, Phys. Rev. B13 (1976) 1112.
[32] S.V. Panyukov and Y. Rabin, Phys. Rep. 269 (1996) 1.
[33] T. Ohta and K. Kawasaki, Macromol. 19, 2621 (1986).
[34] G. Fredrickson and E. Helfand, J. Chem. Phys. 93, 2048 (1990).
[35] J. Zinn-Justin, Quantum field theory and critical phenomena (Clarendon press, Oxford, 1989).
[36] A.Yu. Grosberg and A.R. Khokhlov Statistical Physics of Macromolecules (AIP, New York), 1994.
[37] T.A. Vilgis and P. Haronska, Macromol. 27 (1994) 6465.
[38] B. Derrida, Phys. Rev. B24 (1981) 2613.
[39] M. Mézard and G. Parisi, J. Phys. I 1 (1991) 809.
[40] Yu.L. Klimontovich, Statistical Physics (Harwood Academic Publishers, New York, 1986)
[41] R.G. Palmer, Adv. Phys. 31 (1982) 669.
[42] D.J. Gross and M. Mézard, Nucl. Phys. B 240 [FS12] (1984) 431.
[43] S. Ramanathan and E. Shakhnovich, Phys. Rev. E50 (1994) 1303.
[44] S. Takada and P. Wolynes, J. Chem. Phys. 107 (1997) 9585.