



Glass transition of an amphiphilic random copolymer and relation to the Ising model of spin-glass

To cite this article: A. Moskalenko *et al* 1997 *EPL* **40** 135

View the [article online](#) for updates and enhancements.

You may also like

- [Ultrafast dynamics of subwavelength periodic ripples induced by single femtosecond pulse: from noble to common metals](#)
Ke Cheng, Kaiqiang Cao, Yuchan Zhang et al.
- [Non-Abelian gapless and quasi-gapless excitations of vortices in condensed matter systems](#)
A J Peterson and M Shifman
- [Asymmetric nucleation processes in spontaneous mode switch of active matter](#)
Bing Yang, , Yanting Wang et al.

Glass transition of an amphiphilic random copolymer and relation to the Ising model of spin-glass

A. MOSKALENKO(*), YU. A. KUZNETSOV and K. A. DAWSON

*Irish Centre for Colloid Science and Biomaterials, Department of Chemistry
University College Dublin - Belfield, Dublin 4, Ireland*

(received 4 April 1997; accepted in final form 4 September 1997)

PACS. 36.20Ey – Conformation (statistics and dynamics).

PACS. 64.70Pf – Glass transitions.

Abstract. – We present the results of our study of the freezing transition of an amphiphilic random copolymer. We here confirm that a replica variational approach predicts a “scale”-dependent freezing transition due to the connectivity of the chain. In addition we suggest that two systems, a random copolymer and an Ising spin-glass, can be directly related to each other on the mean-field level in the vicinity of the freezing transition. Both systems have the same type of effective free energy. The properties of replica symmetrical (RS) and replica symmetry broken (RSB) solutions are discussed. The latter has larger radius of gyration and effective free energy, and is less phase separated. It might be related to a globule with more than one hydrophobic core.

Introduction. – Different models of heteropolymers have been studied recently in connection to the protein folding problem. It is believed that the studies of conformational statistics of a random copolymer chain, the simplest heteropolymer, can provide insight into the basic principles of the protein folding process [1]. It is conventional to apply spin-glass methods to investigate the property of a random copolymer because the disorder is quenched into the sequence. This approach has brought many interesting results and recently become very popular [1]-[11]. However, the relation between the random heteropolymer models and more typical Ising-type models of spin-glasses still remains unclear in many cases.

We suggest a relation between a random amphiphilic copolymer model with Gaussian distribution of disorder [10]-[13], and an Ising model of spin-glass in which each spin is coupled to z neighbours [14], and the coupling constants are independently distributed with a Gaussian probability density. In fact we shall establish that, on the mean-field level, both models have the same type of effective free energy in the vicinity of the freezing transition. The numerical analysis of the system predicts a scale-dependent freezing, which vanishes as connectivity becomes less relevant. By scale in this context we mean that groups of different numbers of monomers have effectively different freezing temperatures. This reflects the influence of connectivity on the transition.

(*) E-mail: andrei@fiachra.ucd.ie

Here we base our description on the variational approach in terms of monomer coordinates rather than density variables [15]. Recently the application of the variational approach to systems with quenched disorder has been developed, and we refer the reader to a review in ref. [7]. The Hamiltonian of the system is

$$H = H_{\text{hom}} + \frac{a}{2} \int_0^N \int_0^N ds ds' (\lambda_s + \lambda_{s'}) \delta(\mathbf{r}(s) - \mathbf{r}(s')), \quad (1)$$

$$\beta H_{\text{hom}} = \frac{\kappa}{2} \int_0^N ds \left(\frac{d\mathbf{r}(s)}{ds} \right)^2 + \sum_{m=1}^{\infty} \frac{u_{m+1}}{(m+1)!} \int_0^N \{ds_0 \dots ds_m\} \prod_{i=1}^m \delta(\mathbf{r}(s_0) - \mathbf{r}(s_i)).$$

Here κ is the connectivity constant, u_m are virial coefficients, a is a parameter of interaction and $\{\lambda_s\}$ are quenched random variables. We assume that the chemical composition is fixed, but monomers of A and B types can appear in random sequences. Therefore we are dealing with quenched disorder and the average over random variables $\{\lambda_s\}$ can be handled by introducing replicas [16]. The partition function of the replicated system is

$$\overline{Z^n(\{\lambda_s\})} = \int D\{\mathbf{r}^a(s)\} \exp[-\beta H_n], \quad (2)$$

where Z and H_n are, respectively, the partition function of the system and the effective Hamiltonian in the replica space, and the bar stands for the average over disorder. We assume here that the Hamiltonian is regularized at short distances by introduction of an appropriate cut-off. For simplicity we assume that all $\{\lambda_s\}$ have a Gaussian density distribution with mean value $\lambda_0 = 0$ and variance Δ^2 . Therefore, the effective Hamiltonian has the form

$$\beta H_n = \beta H_{\text{hom}}^n - \frac{\tilde{\Delta}^2}{2!} \int_0^N ds ds_1 ds_2 \sum_{ab} \delta(\mathbf{r}^a(s, s_1)) \delta(\mathbf{r}^b(s, s_2)), \quad (3)$$

$$\mathbf{r}^a(s, s_1) \equiv \mathbf{r}^a(s) - \mathbf{r}^a(s_1), \quad (4)$$

where we have introduced $\tilde{\Delta} \equiv \beta \Delta a$.

We exploit the Gibbs-Bogoliubov estimate for the free energy, F_n , in the replica space [5] and choose the Gaussian trial Hamiltonian in terms of monomer Fourier coordinates [7], [11]:

$$F_n = F_0 + \langle (H_n - H_0) \rangle_0, \quad (5)$$

$$\beta H_0 = \frac{1}{2} \sum_{a,b} \sum_q V_{ab}^{(q)} \mathbf{r}_{-q}^a \mathbf{r}_q^b. \quad (6)$$

We have also used the following definition of Fourier transform for a closed polymer chain:

$$\mathbf{r}_q = \frac{1}{N} \int_0^N ds \exp \left[\frac{-i2\pi s q}{N} \right] \mathbf{r}(s), \quad \mathbf{r}(s) = \mathbf{r}_0 + \sum_{q=1}^{\infty} \exp \left[\frac{i2\pi s q}{N} \right] \mathbf{r}_q. \quad (7)$$

Here one has to introduce a mass term $\mu \delta_{ab}$ to the effective potential $V_{ab}^{(q)}$ in (6) for regularization [5]. The limit $\mu \rightarrow 0$ is assumed to be taken at the final stage of calculation. Performing an average over the Gaussian ensemble (6), one arrives at the following result:

$$\beta F_n = -\frac{3}{2} \sum_q \text{Tr} \log \hat{\mathcal{F}}_q + \frac{6\kappa\pi^2}{N} \sum_a \sum_q q^2 \mathcal{F}_q^{aa} +$$

$$\begin{aligned}
& + \sum_{m=1}^{\infty} \frac{u_{m+1} - 3\delta_{m,2}\tilde{\Delta}^2}{(m+1)!(2\pi)^{3m/2}} \sum_a \int \{ds_0 \dots ds_m\} (X_{1\dots m}^{a\dots a})^{-3/2} - \\
& - \frac{\tilde{\Delta}^2}{2(2\pi)^3} \int ds_1 ds_2 ds_3 \sum_{a \neq b} (D_{s_1 s_2}^{aa} D_{s_2 s_3}^{bb} - (D_{s_1 s_2 s_3}^{ab})^2)^{-3/2}.
\end{aligned} \tag{8}$$

We note that the results presented below are qualitatively unaffected by contribution from u_4 and higher terms. Here we have introduced matrices of spatial $D_{s_1 s_2}^{ab} = \frac{1}{3} \langle (\mathbf{r}^a(s_1) - \mathbf{r}^b(s_2))^2 \rangle_0$ and Fourier $\mathcal{F}_q^{ab} = \frac{1}{3} \langle \mathbf{r}_{-q}^a \mathbf{r}_q^b \rangle_0$ monomer correlations

$$X_{1\dots n} = \det_{n \times n} D_{l:k}, \quad D_{l:k} = D_{s_l s_0 s_k}^{aa}, \quad 2D_{s_1 s_2 s_3}^{ab} = D_{s_1 s_2}^{ab} + D_{s_2 s_3}^{ab} - D_{s_1 s_3}^{ab}.$$

At this stage the limit $n \rightarrow 0$ in (8) can be evaluated exactly using the Parisi parameterization, $\mathcal{F}_q^{ab} \rightarrow \{\tilde{\mathcal{F}}_q, \mathcal{F}_q(u)\}$, and the resulting effective free energy has to be minimized with respect to $\tilde{\mathcal{F}}_q$, correlations within the same replica, and maximized with respect to $\mathcal{F}_q(u)$, correlations between different replicas. This allows one to study numerically the collapse, phase separation and freezing transition. An interesting discussion on a possibility of numerical solution of the saddle point equations for directed polymers with various forms of correlations of the random potential can be found in ref. [6]. To pursue this direction, one has to discretize all functions, substitute the integrations by the summations over non-coinciding indices,

$$\int_0^N d\{s_1 s_2 \dots s_m\} \leftrightarrow \sum_{\{i_1, i_2, \dots, i_m\}=0}^{N-1}, \quad \frac{6\kappa\pi^2}{N} \sum_q q^2 \tilde{\mathcal{F}}_q \rightarrow 6\kappa N \sum_{q=1}^{N-1} \tilde{\mathcal{F}}_q \sin^2 \frac{\pi q}{N}, \tag{9}$$

and use K -step approximations for $\mathcal{F}_q(u)$. This has been carried out for $K = 0, 1$ and we briefly summarize the results here. We shall use the notations $u_2^{(\theta)}$ and $u_2^{(f)}$, respectively, as the values of the second virial coefficient for the collapse and the onset of freezing. i) Collapse occurs, as normal, when u_2 is negative. However, it is also possible for small positive u_2 , but large values of the variance of the second-virial coefficient $\tilde{\Delta}$. The latter can be viewed as an effective three-body effect since, for $m = 2$, the bare u_3 term (8) is replaced by an effective three-body term, with coefficient $u_3 - 3\tilde{\Delta}^2$. ii) Two types of globule are possible, liquid-like and glassy. However, the chain always collapses into liquid-like globule first, as $u_2^{(\theta)} > u_2^{(f)}$ for arbitrary $\tilde{\Delta} > 0$ and fixed positive u_3 . iii) $|u_2^{(f)}/u_2^{(\theta)}| \gg 1$ in the limit of small disorder, $\tilde{\Delta} \sim 0$ and $u_2^{(\theta)} \approx u_2^{(f)}$ in the limit of large disorder. iv) Beyond the glass transition the correlations between different replicas appear at different “scales”. Thus, there are no correlations for large q between replicas in the vicinity of the freezing transition, but these grow as $\tilde{\Delta}$ increases. For a ring polymer this situation also pertains, providing the limit $q < N/2$, as $\mathcal{F}_q = \mathcal{F}_{N-q}$. The profiles of the replica correlation functions for the replicas from the same group in the one-step RSB scheme are presented in fig. 1 to illustrate this point, $\mathcal{R}_q^{(1)} = \mathcal{F}_q^{(1)}/\tilde{\mathcal{F}}_q$. Both $\mathcal{R}_q^{(0)}$, correlations between replicas from different groups, and $\mathcal{R}_q^{(\text{rs})}$, correlations for RS solution, exhibit behaviour similar to that of $\mathcal{R}_q^{(1)}$ in fig. 1: $\mathcal{R}_q^{(1)} > \mathcal{R}_q^{(\text{rs})} > \mathcal{R}_q^{(0)}$.

Let us emphasize once more that this phenomenon is clearly exhibited in fig. 1 where we have carried out numerical calculations. One may view the results as defining a transition temperature (or $\tilde{\Delta}_f(q)$) appropriate for the characteristic group of beads $N_{\text{char}} \sim N/q$ or the effective number of degrees of freedoms. By this we mean the following. $\tilde{\Delta}$ is proportional to the inverse temperature. Since $\tilde{\Delta}_f$ depends on q , we observe the presence of a q -dependence on the freezing temperature. Indeed, note that q is a conjugate to the chain index, and therefore is inversely proportional to the number of beads under consideration. One way of viewing this result is that, effectively, groups of beads of different numbers freeze at different temperatures.

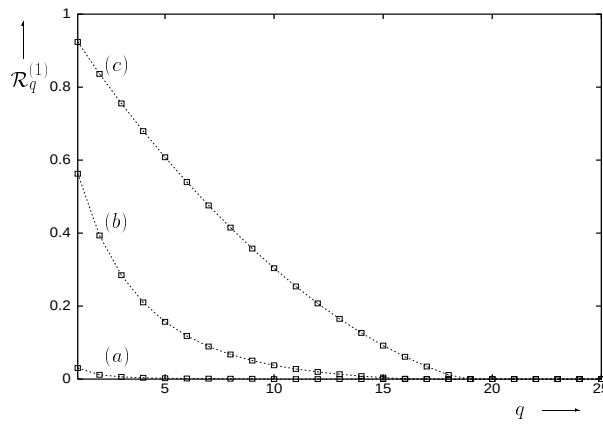


Fig. 1. – Plot of the correlation functions $\mathcal{R}_q^{(1)}$ (replicas from the same group) *vs.* the chain index q for polymer with the degree of polymerization $N = 50$. Here $u_2 l^{-3} = -50$, $u_3 l^{-6} = 60$, $u_4 l^{-9} = 48$. Lines (a)-(c) correspond, respectively, to the values of the dispersion of disorder $\tilde{\Delta} = 2$ (near the freezing transition line), 3 and 4. For convenience we have drawn the plots only for half of the space of the periodic ring polymer, and the correlation functions may be extended to the other half by the symmetry property: $\mathcal{R}_q^{(0,1)} = \mathcal{R}_{N-q}^{(0,1)}$.

Whilst groups of beads may be related to characteristic lengths in the real space, we are not yet ready to take this step. Thus, a relation between our work and that of ref. [13] may exist, but we are not yet clear about that relation. One connection we can make in a phenomenological manner. The successive freezing of different modes or reduction in the effective number of degrees of freedom is possibly related to the narrowing or “bottleneck” in the free-energy landscape, discussed by some authors [1].

The replica approach may have an advantage because it allows us to study, by standard methods [6], [14], [16], [17], the stability of both replica symmetrical and replica symmetry broken solutions in the glassy phase.

However, there are two major difficulties. The introduction of a large number of variational parameters is required to study higher steps of RSB. It is difficult to analyze the stability of the RS solution as the Hessian is non-diagonal in the q -space. Therefore, we use an addition approximation which allows us to overcome these difficulties at least for the globular state.

Here we are interested in a simpler description of the transition from the liquid-like globule to the glassy globule. The numerical analysis shows that in the vicinity of transition only correlations on the first mode are essential, $\mathcal{F}_1^{ab}$, $a \neq b$. In the globular state the density of the globule is mainly determined by the balance between two- and three-body terms, and the spring term can be neglected to the first approximation [18]. Therefore, we neglect the spring term $\kappa \sin^2(\pi q/N)$ in the set of saddle point equations,

$$\partial F_n / \partial \mathcal{F}_q^{ab} = 0, \quad a, b = 1 \dots n. \quad (10)$$

Admittedly we then lose details of the scale dependence of the transition, but the main phenomenon persists and is then described by a simple Flory-type theory. Thus, the set of equations (10) has q -independent solution,

$$\mathcal{F}_q^{ab} \equiv \mathcal{F}_1^{ab}, \quad D_{ij}^{ab} \equiv D^{ab} = 2N\mathcal{F}_1^{ab}, \quad X_{1\dots m}^{a\dots a} = (D^{aa}/2)^m (m+1).$$

The effective free energy now takes the form

$$\begin{aligned} \beta F_n/N = & -\frac{3}{2} \text{Tr} \log \hat{\mathcal{F}}_1 + \hat{u}_2 \sum_a \rho_a + \hat{u}_3 \left(\frac{4}{3}\right)^{3/2} \sum_a \rho_a^2 + \\ & + \hat{u}_4 2^{3/2} \sum_a \rho_a^3 - B \sum_{a,b} \rho_a \rho_b (1 - (R^{ab}/2)^2)^{-3/2}, \end{aligned} \quad (11)$$

where $\hat{u}_m = u_m/(m!(2\pi)^{3m/2})$, $B = \tilde{\Delta}^2/(2!(2\pi)^3)$, $R^{ab} = D^{ab}/(D^{aa}D^{bb})^{1/2}$ and $\rho_a \equiv N/D^{aa3/2}$, ρ_a is proportional to the density of the globule. Here we have omitted some irrelevant constants and kept terms up to the forth virial coefficient. We note that eq. (11) can be studied numerically, and that the results are comparable to full studies of eq. (8) in the limit $N \gg 1$. This provides us with an opportunity to pursue a numerical study of the complete phase behaviour [18] by solving the set of equations (10) in the limit $n \rightarrow 0$.

In comparison with RSB solutions of (10), RS solutions have lower free energy and smaller radius of gyration, but are characterized by a higher degree of phase separation. The analysis of the phase separation in the system is based upon the consideration of a corresponding order parameter,

$$\delta R_g^2 = 1/2N^{-2} \int ds ds' \langle \overline{\lambda_s(\mathbf{r}(s) - \mathbf{r}(s'))^2} \rangle_0, \quad (12)$$

where δR_g^2 is the difference of the square radii of gyration in the case of two letter copolymers with equal concentrations of both monomer types, $\delta R_g^2 = R_{gA}^2 - R_{gB}^2$. In the liquid-like globule phase δR_g^2 is proportional to $\tilde{\Delta}$ and is rapidly increasing until the freezing transition takes place. In the vicinity of the transition in the glassy phase δR_g^2 remains practically constant for both RSB and RS solutions. We may speculate here that the RS solution probably corresponds to a globule with a hydrophobic core and hydrophilic shell, whilst the RSB solutions correspond to metastable globules with more than one hydrophobic core. We point out that the effect of the scale-dependent freezing disappears as the connectivity term is excluded from the consideration. We leave the details and more extensive discussion for a later publication and proceed to establish a relation between the model of random copolymer and conventional spin-glass models.

We assume that correlations between different replicas are small in the vicinity of the glass transition and that the density of globule remains constant, $\rho^a \equiv \rho$. Then, expanding (11) around $\hat{R} = 0$ and omitting irrelevant constants, the effective free-energy density of a dense copolymer globule can be rewritten in a form well known from the studies of the Ising model of spin-glass [14],

$$\beta F_n/3N = \frac{r}{4} \text{Tr} \hat{\mathcal{R}}^2 - \frac{w}{6} \text{Tr} \hat{\mathcal{R}}^3 - \frac{y}{8} \sum_{a,b} (\mathcal{R}^{ab})^4 - \frac{u}{8} \text{Tr} \hat{\mathcal{R}}^4 + O(\hat{\mathcal{R}}^5), \quad (13)$$

where $w = 1$, $y = (5/16)B\rho^2$, $u = -1$, $R^{aa} = 0$ and $0 \leq \mathcal{R}^{ab} < 1$. The transition temperature is given by the equation $r = 1 - B\rho^2/2 = 0$. Here we use the notation of ref. [14]. In this approximation all parameters of the model, $u_{2,3,4}$ and Δ , are present in (13) through the combination $B\rho^2$, $\rho = \rho(u_2, u_3, u_4, B)$. This defines only one coupling which is consistent with the previous statement that eq. (13) is only able to describe the transition to a glassy state.

We point out that eq. (13) may help clarify the relation between glass transition of a random copolymer and Ising spin-glass. It was earlier noted [13] that there were also some similarities in the dynamical properties. Deeper relations between these transitions, and dynamical phenomena, may emerge in time. At this stage, however, we have succeeded only

in outlining a suggestive relationship between two theories. If a true or approximate mapping does exist near the transition, then it may be best found by examining the Hamiltonians.

Finally we note that the scale-dependent freezing can be indeed deduced from a replica variational approach.

REFERENCES

- [1] For example: BRYNGELSON J. D. and WOLYNES P. G., *J. Phys. Chem.*, **93** (1989) 6902; *Proc. Natl. Acad. Sci. USA*, **84** (1987) 7524; WOLYNES P. G., ONUCHIC J. N. and THIRUMALAI D., *Science*, **267** (1995) 1619.
- [2] GAREL T. and ORLAND H., *Europhys. Lett.*, **6** (1988) 307.
- [3] EDWARDS S. F. and MUTHUKUMAR M., *J. Chem. Phys.*, **89** (1988) 2435.
- [4] SHAKHNOVICH E. I. and GUTIN A. M., *J. Phys. A*, **22** (1989) 1647.
- [5] MÉZARD M. and PARISI G., *J. Phys. I*, **1** (1991) 809.
- [6] FRANZ S., MÉZARD M. and PARISI G., *Int. J. Neural Systems (Suppl.)*, **3** (1992) 195.
- [7] MÉZARD M., in *Fluctuating Geometries in Statistical Mechanics and Field Theory* (Elsevier Science B.V.) 1996.
- [8] KANTOR Y. and KARDAR M., *Europhys. Lett.*, **14** (1991) 421.
- [9] VILGIS T. A. and HARONSKA P., *Macromolecules*, **27** (1994) 6465.
- [10] GAREL T., LEIBLER L. and ORLAND H., *J. Phys. II*, **4** (1994) 2139.
- [11] MOSKALENKO A., KUZNETSOV YU. A. and DAWSON K. A., Sissa preprint cond-mat/9702175 (1997).
- [12] TIMOSHENKO E. G., KUZNETSOV YU. A. and DAWSON K. A., *Phys. Rev. E*, **54** (1996) 4071.
- [13] THIRUMALAI D., ASHWIN V. and BHATTACHARJEE J. K., *Phys. Rev. Lett.*, **77** (1996) 5385.
- [14] BRAY A. J. and MOORE M. A., *Phys. Rev. Lett.*, **41** (1978) 1068; DE DOMINICIS C. and KONDOR I., *Phys. Rev. B*, **27** (1983) 606.
- [15] DES CLOIZEAUX J., *J. Phys. (Paris)*, **31** (1970) 715; EDWARDS S. F. and SINGH P., *J. Chem. Soc. Faraday Trans.*, **2** (1979) 1001; ALLEGRA G. and GANAZZOLI F., *J. Chem. Phys.*, **87** (1987) 1817; BOUCHAUD J.-P., MÉZARD M., PARISI G. and YEDIDIA J. S., *J. Phys. A*, **24** (1991) L1025; BRATKO D. and DAWSON K. A., *J. Chem. Phys.*, **99** (1993) 5352; ORLAND H. and SHAPIR Y., *Europhys. Lett.*, **30** (1995) 203.
- [16] MÉZARD M., PARISI G. and VIRASORO M., *Spin Glass Theory and Beyond* (World Scientific, Singapore) 1987.
- [17] DE ALMEIDA J. R. L. and THOULESS D. J., *J. Phys. A*, **11** (1978) 983.
- [18] MOSKALENKO A., KUZNETSOV YU. A. and DAWSON K. A., *Glass Transition in Random Copolymers*, *The 5-th Bar-Ilan Conference on Frontiers in Condensed Matter Physics*, to be published in *Physica A*.