

Random Copolymer: Gaussian Variational Approach

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Abstract. — We study the phase transitions of a random copolymer chain with quenched disorder. We calculate the average over the quenched disorder in replica space and apply a Gaussian variational approach based on a generic quadratic trial Hamiltonian in terms of the correlation functions of monomer Fourier coordinates. This has the advantage that it allows us to incorporate fluctuations of the density, determined self-consistently, and to study collapse, phase separation transitions and the onset of the freezing transition within the same mean field theory. The effective free energy of the system is derived analytically and analyzed numerically in the one-step Parisi scheme. Such quantities as the radius of gyration, end-to-end distance or the average value of the overlap between different replicas are treated as observables and evaluated by introducing appropriate external fields to the Hamiltonian. As a result we obtain the phase diagram in terms of model parameters, scaling for the freezing transition and the dependence of correlation functions on the chain index.

1. Introduction

Various models of random copolymers have been extensively studied using theoretical [1–6] and numerical [7–9] methods. It has been found that even simple models exhibit a rich variety of conformational states leading to quite a complicated phase diagram.

Most of the theoretical results have been obtained within the replica approach [10] for directed polymers in random media [11–13] and for self-interacting copolymers under the assumption of the ground state dominance and constant density approximations for Gaussian disorder [2, 3, 14]. Computer simulations [7–9] have qualitatively confirmed some of the theoretical predictions.

In this paper we study the complete phase diagram of a random copolymer chain with attractive and repulsive units. It is believed that such studies have application in the field of protein folding and related subjects. Thus we apply a Gaussian variational approach based on a generic quadratic trial Hamiltonian in terms of monomer Fourier coordinates of replicas, which is an alternative to the standard one using the density overlap function as the replica order parameter and constant density approximation. A similar approach was applied by Mézard and Parisi to manifolds in random media [11]. The method has the advantage that it allows us

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to incorporate fluctuations of the density, determined self-consistently, and to study collapse, phase separation and glass transitions within the same mean field theory.

Note that the self-consistent method has been applied to various other problems at equilibrium [15,16] and in kinetics [17] of homo- and block copolymers and to directed polymers in random media [12,13].

It is convenient to represent the Hamiltonian as the sum of two parts, $H = H_{\text{hom}} + H_{\text{dis}}$. The first is purely homopolymeric and the second is related to the quenched disorder. Thus,

$$\beta H_{\text{hom}} = \frac{\kappa}{2} \sum_i (\mathbf{r}_i - \mathbf{r}_{i+1})^2 + \sum_{n=1}^{\infty} \frac{u_{n+1}}{(n+1)!} \sum_{\{m_0 \dots m_n\}} \prod_{i=1}^n \delta(\mathbf{r}_{m_0} - \mathbf{r}_{m_i}), \quad (1)$$

$$H_{\text{dis}} = \frac{1}{2} \sum_{\{ij\}} u_2(\lambda_i, \lambda_j) \delta(\mathbf{r}_i - \mathbf{r}_j), \quad (2)$$

where the connectivity constant is $\kappa = 3l^{-2}$, with l being the bond length. Here the u_n denote the virial coefficients and the curly braces indicate that the terms with coinciding indices are excluded. The matrix of two-body interactions may be written [1] *via* the quenched random variables $\{\lambda_i\}$,

$$u_2(\lambda_i, \lambda_j) = v + a(\lambda_i + \lambda_j) + \chi \lambda_i \lambda_j, \quad (3)$$

where the parameters v , a and χ may be expressed in terms of, for example, u_{AA} , u_{BB} and u_{AB} in the case of only two monomer types. The average over the quenched disorder is performed by introducing replicas [10]

$$\beta F_{\text{quench}} = -\overline{\log Z(\{\lambda_i\})} = -\lim_{n \rightarrow 0} n^{-1} \left(\overline{Z^n(\{\lambda_i\})} - 1 \right), \quad (4)$$

$$\overline{Z^n(\{\lambda_i\})} = \int D\mathbf{r}_i^n \exp(-\beta H_{\text{eff}}^n) \quad (5)$$

where Z , H_{eff}^n are respectively the partition function of the system and the effective Hamiltonian in the replica space. Here the bar stands for the average over disorder.

For simplicity we assume the distribution of $\{\lambda_i\}$ to be Gaussian with mean value λ_0 and variance Δ^2 ,

$$P(\{\lambda_i\}) = \prod_i \frac{1}{(2\pi\Delta^2)^{1/2}} \exp\left(-\frac{(\lambda_i - \lambda_0)^2}{2\Delta^2}\right). \quad (6)$$

However other distributions, for example the binary distribution, can be considered. Averaging over the quenched disorder produces a compact expression for the effective Hamiltonian in the replica space,

$$\begin{aligned} \beta H_{\text{eff}}^n &= \beta H_{\text{hom}}^n + \frac{1}{2} \text{Tr} \log M_{ij} + N \frac{\lambda_0^2}{2\Delta^2} \\ &\quad - \frac{1}{2\Delta^2} \sum_{ij} [\lambda_0 - \beta\Delta^2 a \sum_{a,l(\neq i)} \delta(\mathbf{r}_i^a - \mathbf{r}_l^a)] M_{ij}^{-1} [\lambda_0 - \beta\Delta^2 a \sum_{b,m(\neq j)} \delta(\mathbf{r}_j^b - \mathbf{r}_m^b)] \end{aligned} \quad (7)$$

where

$$M_{ij} = \delta_{ij} + \beta\Delta^2 \chi (1 - \delta_{ij}) \sum_a \delta(\mathbf{r}_i^a - \mathbf{r}_j^a). \quad (8)$$

Further we assume $\chi = 0$ in (3). This choice of parameters in the matrix of interactions corresponds to the amphiphilic model, in which the monomers of A-type attract each other and monomers of B-type repel each other. We note here that the case $\chi \neq 0$ requires some additional treatment, for example application of the perturbation expansion of the matrices M^{-1} and $\log M$, and return to this discussion in later sections.

2. Variational Approach

It is useful to introduce the Fourier coordinates of the monomer positions. For ring polymers the appropriate Fourier transform is defined as

$$\mathbf{r}_q^a = \frac{1}{N} \sum_{n=0}^{N-1} \exp\left(\frac{i2\pi q n}{N}\right) \mathbf{r}_n^a, \quad \mathbf{r}_n^a = \sum_{q=0}^{N-1} \exp\left(\frac{-i2\pi q n}{N}\right) \mathbf{r}_q^a, \quad (9)$$

and the generalization to the case of open chain is straightforward. The standard Gibbs-Bogoliubov variational principle gives the estimate for the free energy,

$$F_{\text{eff}}^n = F_0^n + \langle (H_{\text{eff}}^n - H_0^n) \rangle_0. \quad (10)$$

We choose the trial Hamiltonian as a quadratic form, which is standard in the polymer literature [11, 12], but with q -dependence of all variational parameters

$$\beta H_0^n = \frac{1}{2} \sum_{a,b} \sum_q V_{ab}(q) \mathbf{r}_{-q}^a \mathbf{r}_q^b, \quad (11)$$

where the effective potential matrix is to be taken non-diagonal in the replica indices and diagonal in the chain index due to the assumption of the translational invariance along the chain after integrating out the disorder. Averaging (7) over the statistical ensemble (11) we obtain the effective free energy of the following form

$$\beta F_{\text{eff}}^n = -\frac{3}{2} \sum_q \text{Tr} \log \mathcal{F}_q^{ab} + \sum_{ab} E^{ab} \quad (12)$$

where we have introduced the correlation functions $\mathcal{F}_q^{ab} = \frac{1}{3} \langle \mathbf{r}_{-q}^a \mathbf{r}_q^b \rangle_0 = (V^{-1}(q))_{ab}$ and the effective energy matrix E^{ab} , see more details in the Appendix. In the notation of equation (12) the effective free energy appears to be quite simple. The procedure of performing the limit $n \rightarrow 0$ is well-known from studies of spin glass systems [10, 11]. To do so we assume that \mathcal{F}_q^{ab} is a Parisi-type hierarchical matrix parametrised by $\{\tilde{\mathcal{F}}_q, \mathcal{F}_q(u)\}$, $u \in [0, 1]$, where $\tilde{\mathcal{F}}_q$ and $\mathcal{F}_q(u)$ are correlation functions for monomers from the same replica and from different replicas respectively. Finally, assuming that $N \gg 1$ we obtain the effective free energy per replica in the limit $n \rightarrow 0$, which is convenient to represent as a sum of two terms,

$$\lim_{n \rightarrow 0} (\beta F_{\text{eff}}/n) = \beta N \left(f_0[\tilde{\mathcal{F}}_q] + f_1[\tilde{\mathcal{F}}_q, \mathcal{F}_q(u)] \right). \quad (13)$$

The first term, f_0 , coincides with the annealed effective free energy,

$$\begin{aligned} \beta N f_0 &= -\frac{3}{2} \sum_q \log \tilde{\mathcal{F}}_q + 6\kappa N \sum_q \tilde{\mathcal{F}}_q \sin^2 \frac{\pi q}{N} \\ &+ \sum_{n=1}^{\infty} \frac{u_{n+1} - 3\delta_{n+1,3} \tilde{\Delta}^2}{(n+1)!(2\pi)^{3n/2}} \sum_{\{m_0 \dots m_n\}} X_1 \dots X_n^{-3/2}, \end{aligned} \quad (14)$$

where $\tilde{\Delta} = \beta a \Delta$ and $X_{1\dots m}$ are determinants of $m \times m$ -matrices

$$X_{1\dots m} = \det_{m \times m} \tilde{D}_{l:k}, \quad \tilde{D}_{l:k} = \tilde{D}_{i_1 i_0 i_k} = \sum_q d_{i_1 i_0 i_k}^{(q)} \tilde{\mathcal{F}}_q, \quad \tilde{D}_{ij} = \sum_q d_{ij}^{(q)} \tilde{\mathcal{F}}_q.$$

The second term, f_1 , is determined purely by the quenched disorder,

$$\begin{aligned} \beta N f_1 &= -\frac{3}{2} \sum_q \left[\log(1 - \langle \mathcal{R}_q \rangle) + \frac{\mathcal{R}_q(0)}{1 - \langle \mathcal{R}_q \rangle} - \int_0^1 \frac{du}{u^2} \log \frac{1 - \langle \mathcal{R}_q \rangle - [\mathcal{R}_q](u)}{1 - \langle \mathcal{R}_q \rangle} \right] \\ &+ \frac{\tilde{\Delta}^2}{2!(2\pi)^{6/2}} \sum_{\{ijk\}} \int_0^1 du [\tilde{\mathcal{D}}_{ij} \tilde{\mathcal{D}}_{jk} - \mathcal{D}_{ijk}^2(u)]^{-3/2} \end{aligned} \quad (15)$$

where by definition for any arbitrary matrix a :

$$\langle a \rangle = \int_0^1 du a(u), \quad [a](u) = - \int_0^u dv a(v) + ua(u), \quad (16)$$

and

$$\mathcal{D}_{ijk}(u) = \sum_q d_{ijk}^{(q)} \mathcal{F}_q(u), \quad 0 \leq \mathcal{R}_q(u) = \frac{\mathcal{F}_q(u)}{\tilde{\mathcal{F}}_q} < 1. \quad (17)$$

Here we introduce $\mathcal{R}_q(u)$, which gives the measure of correlations between different replicas relatively to correlations in the same replica and allows the division on “annealed” and “quenched” parts (13). The effective free energy has to be minimized with respect to $\tilde{\mathcal{F}}_q$ and maximized with respect to $\mathcal{F}_q(u)$ with the constraints $0 \leq \mathcal{R}_q(u) < 1$. The latter physically means that monomer coordinates’ correlations between different replicas are always weaker than those in the same replica. Alternatively these constraints can be derived if we require the matrices $V_{ab}(q)$ and \mathcal{F}_q^{ab} to have positive eigenvalues for arbitrary integer n , $n \geq 1$, and all non-diagonal elements of the matrices $V_{ab}(q)$ to be negative to match the sign of the corresponding non-diagonal terms in the effective Hamiltonian.

Usually one is interested in such quantities as radius of gyration R_g , end-to-end distance, phase separation order parameters or the average value Q of an overlap between different replicas Q_{ab} , for example,

$$\begin{aligned} R_g^2 &= \frac{1}{2} N^{-2} \sum_{ij} \langle \overline{(\mathbf{r}_i - \mathbf{r}_j)^2} \rangle_0, \quad Q_{ab} = l^3 N^{-1} \sum_i \langle \overline{\delta(\mathbf{r}_i^a - \mathbf{r}_i^b)} \rangle_0, \\ \delta R_g^2 &= \frac{1}{2} N^{-2} \sum_{ij} \langle \overline{(\lambda_i - \lambda_0)(\mathbf{r}_i - \mathbf{r}_j)^2} \rangle_0. \end{aligned} \quad (18)$$

All these can be treated as observables and evaluated by introducing appropriate external fields to the partition function. The model we consider exhibits a strong tendency for phase-separation. Therefore, the parameter $\Psi = \delta R_g^2 / R_g^2$ can be considered as a measure of phase separation, 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, $\delta R_g^2 = R_{gA}^2 - R_{gB}^2$. Introducing the term $\mu \delta R_g^2$ into the Hamiltonian one obtains

$$\delta R_g^2 = - \lim_{\mu, n \rightarrow 0} \frac{\partial}{\partial \mu} \frac{\partial}{\partial n} \langle Z^n(\mu) \rangle = \frac{3}{4} \frac{\tilde{\Delta} \cdot \Delta}{(2\pi)^{3/2} N^2} \sum_{\{ijk\}} \frac{\tilde{\mathcal{D}}_{ijk}^2 - \langle \mathcal{D}_{ijk}^2 \rangle}{\tilde{\mathcal{D}}_{jk}^{5/2}} \quad (19)$$

To determine the freezing transition one may study the change of the average overlap among replicas Q as well as the eigenvalues of the matrix \hat{T} of the second derivatives of the free energy (13) with respect to all $\tilde{\mathcal{F}}_q$ and $\mathcal{F}_q(u)$. The solution we are looking for is a saddle point with the positive eigenvalues of \hat{T} corresponding to $\tilde{\mathcal{F}}_q$ and negative ones corresponding to $\mathcal{F}_q(u)$. As one can see from the numerical analysis, the solution with all $\mathcal{F}_q(u) = 0$, no correlations among replicas, is not a saddle point of the type mentioned above for the variance of the disorder $\tilde{\Delta}$ larger than some particular critical value $\tilde{\Delta}_f$. The latter can vary with a change in the values of the virial coefficients.

3. Numerical Analysis

In principle we can evaluate the effective free energy for any finite number of steps in the Parisi scheme. In practice this means the introduction of a large number of variational parameters. If one has a polymer of length N monomers and applies the k -step Parisi scheme, then one has to analyze a set of approximately $N(k+1)$ nonlinear algebraic equations. Therefore, we apply a minimal one-step Parisi scheme, which still incorporates all the main features of the exact solution and allows one to locate the onset of the transition to phases with broken replica symmetry if such exists. Thus we approximate $\mathcal{F}_q(u)$ by the step function

$$\mathcal{F}_q(u) = \begin{cases} \mathcal{F}_q^{(0)} & u < x, \text{ correlations between replicas from different groups,} \\ \mathcal{F}_q^{(1)} & u > x, \text{ correlations between replicas from the same group.} \end{cases} \quad (20)$$

in one-step approximation:

$$\begin{aligned} \beta N f_1 &= -\frac{3}{2} \sum_q \left[\frac{1}{x} \log \left(1 - (1-x)\mathcal{R}_q^{(1)} - x\mathcal{R}_q^{(0)} \right) \right] \\ &\quad - \frac{3}{2} \sum_q \left[\frac{x-1}{x} \log \left(1 - \mathcal{R}_q^{(1)} \right) + \frac{\mathcal{R}_q^{(0)}}{1 - (1-x)\mathcal{R}_q^{(1)} - x\mathcal{R}_q^{(0)}} \right] \\ &\quad + \frac{\tilde{\Delta}^2}{2!(2\pi)^{6/2}} \sum_{\{ijk\}} \left[(1-x)Q_{ijk}^{(1)-3/2} + xQ_{ijk}^{(0)-3/2} \right], \end{aligned} \quad (21)$$

$$Q_{ijk}^{(s)} = \tilde{D}_{ij}\tilde{D}_{jk} - \mathcal{D}_{ijk}^{(s)2}, \quad \mathcal{D}_{ijk}^{(s)} = \sum_q d_{ijk}^{(q)} \mathcal{F}_q^{(s)}, \quad s = 0, 1. \quad (22)$$

In the following we restrict ourselves to the choice of parameters: $k_B T = 1$, $l = 1$, which provide the scaling units of energy and length; and we set $u_m = 0$ for $m \geq 5$. Note that the zero-modes $\tilde{\mathcal{F}}_0$ and $\mathcal{R}_0^{(0,1)}$ do not contribute to the mean energy of the system describing diffusion of the center of mass of the polymer chain.

The system exhibits two different types of behaviour above and below the freezing transition. Above the freezing temperature, the monomer coordinates correlation function for monomers from the same replica, $\tilde{\mathcal{F}}_q$, closely coincides with that for annealed disorder, whilst the monomer coordinates correlation functions for monomer from different replicas, $\mathcal{R}_q^{(0)}$ and $\mathcal{R}_q^{(1)}$, possess only trivial solutions, namely: $\mathcal{R}_q^{(0)} = \mathcal{R}_q^{(1)} = 0$. The coil and globular states are similar to the homopolymer coil and liquid-like globule states respectively. The trial Hamiltonian is diagonal in the replica space and the free energy differs from the annealed one by the term

$$\beta N f_1 = \frac{\tilde{\Delta}^2}{2!(2\pi)^{6/2}} \sum_{\{m_0 m_1 m_2\}} (\tilde{D}_{m_0 m_1} \tilde{D}_{m_0 m_2})^{-3/2},$$

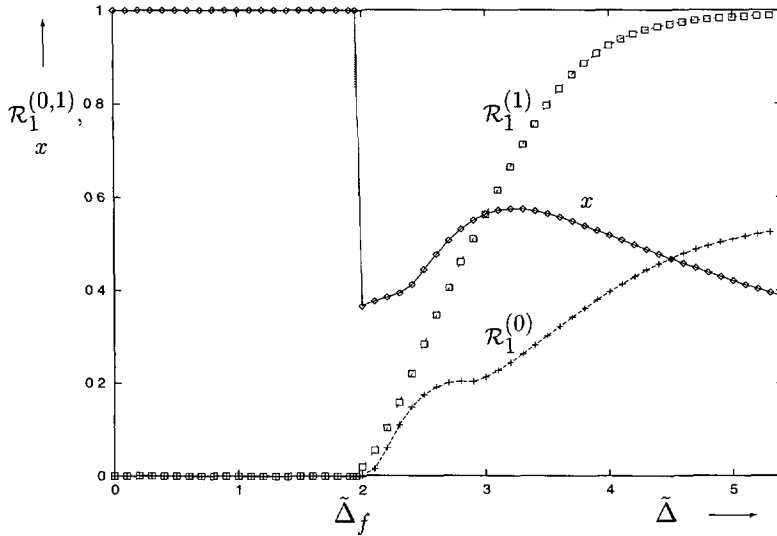


Fig. 1. — Plot of the correlation functions $\mathcal{R}_1^{(0,1)}$ and the replica symmetry breaking parameter x vs. the dispersion of disorder $\tilde{\Delta}$ for polymer with the degree of polymerization $N = 50$. Here $u_2 l^{-3} = -50$, $u_3 l^{-6} = 60$, $u_4 l^{-9} = 48$. The dispersion $\tilde{\Delta}_f$ denotes the point of the freezing transition.

which remains regular in the whole range of the parameter space and becomes negligibly small in the region of small $\tilde{\Delta}$.

The situation changes around some critical value of the dispersion of disorder $\tilde{\Delta}_f$, at which point the solution yields nontrivial values for the correlation functions $\mathcal{R}_q^{(0)}$ and $\mathcal{R}_q^{(1)}$ and the parameter x . Thus, the onset of the freezing transition can be seen clearly from the behaviour of both x and the set of $\mathcal{R}_q^{(0,1)}$, where they start to change rapidly. The typical behaviour of the correlation functions for monomers from different replicas can be seen in Figures 1 and 2.

Figure 1 presents the correlation function for monomers from the same group of replicas, $\mathcal{R}_1^{(1)}$, and from different groups of replicas, $\mathcal{R}_1^{(0)}$, and the parameter x versus the dispersion of disorder $\tilde{\Delta}$ at fixed values of the other parameters in the free energy (13). Strictly speaking the solution below freezing is valid only in the vicinity of the transition line, though we draw it for a wide range of the dispersion of disorder, keeping in mind that more steps in the Parisi scheme are required to describe the properties of the frozen phase. After the freezing transition the coordinates of monomers from different replicas become correlated which results in a decrease of the entropy of the system. The symmetry among replicas is spontaneously broken, the correlations between the positions of the monomers from the same group of replicas are higher than those between the positions of the monomers from different groups.

Figure 2 presents the profile of the replica's correlation functions $\mathcal{R}_q^{(0)}$ and $\mathcal{R}_q^{(1)}$ in the chain index q . There are no short-range correlations between different replicas in the vicinity of the freezing transition although these become non-zero deeper in the frozen phase. Therefore to locate the onset of the freezing transition only correlations on the first mode, $\mathcal{R}_1^{(0)}$ and $\mathcal{R}_1^{(1)}$, and the parameter x are needed.

The resulting phase diagram of the random copolymer is represented in Figure 3. It shows that the collapse can occur in two different ways. For small values of the variance of the two body interaction, $\tilde{\Delta}$, the coil collapses to the liquid-like globule as the effective two body

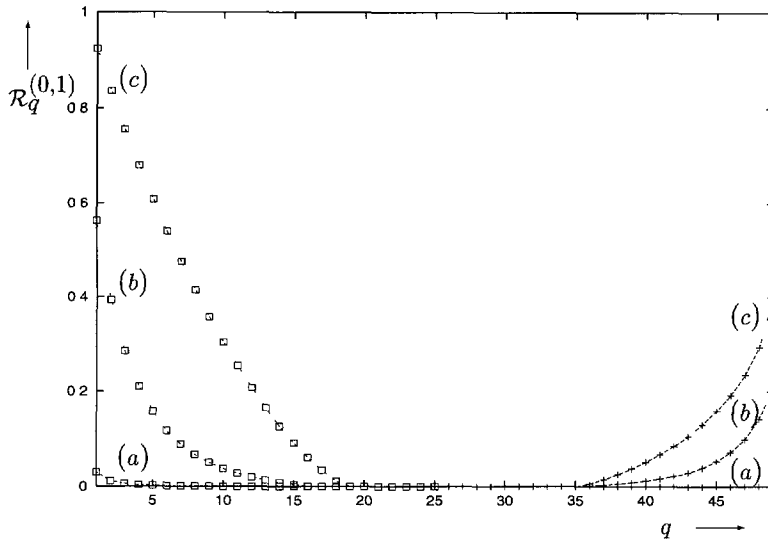


Fig. 2. — Plot of the correlation functions $\mathcal{R}_q^{(1)}$ (left-hand side of the picture) and $\mathcal{R}_q^{(0)}$ (right-hand side) vs. the chain index q for polymer with the degree of polymerization $N = 50$. Here $u_2 l^{-3} = -50$, $u_3 l^{-6} = 60$, $u_4 l^{-9} = 48$. Lines (a)–(c) correspond 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 on one of the sides, and the correlation functions may be extended to the other one by the symmetry property: $\mathcal{R}_q^{(0,1)} = \mathcal{R}_{N-q}^{(0,1)}$.

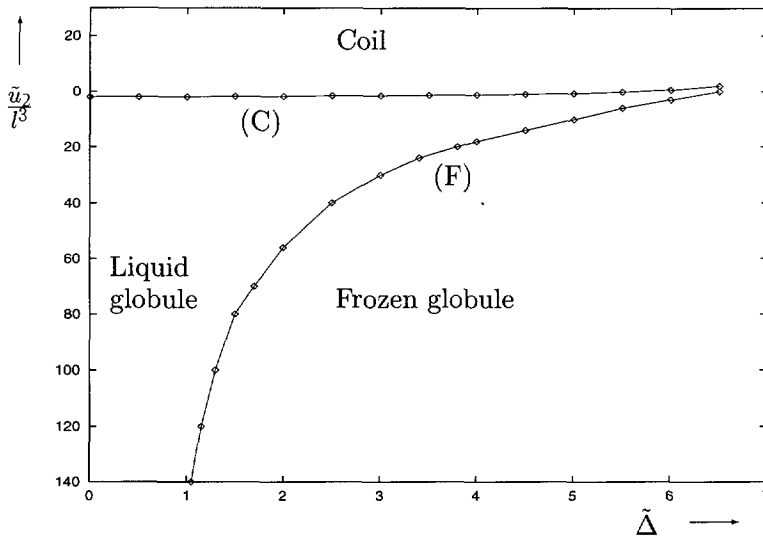


Fig. 3. — The phase diagram of a random copolymer in variables of the dispersion, $\tilde{\Delta}$, and mean value, $\tilde{u}_2 l^{-3}$, of the second virial coefficient. Lines (C) and (F) correspond to collapse and freezing transitions respectively. This diagram has been obtained from the data for a polymer with the degree of polymerization $N = 20$, the third and the fourth virial coefficients are equal to $u_3 l^{-6} = 60$, $u_4 l^{-9} = 48$. No substantial qualitative changes are observed for larger N . Due to finite width of the collapse transition for finite-size systems the line (C) is drawn by the maximal descent of the squared radius of gyration.

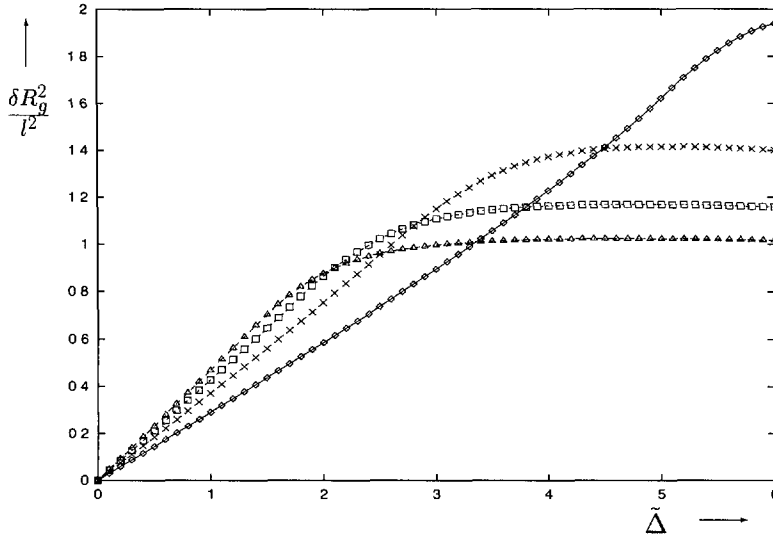


Fig. 4. — Plots of the phase separation parameter, $\delta R_g^2 l^{-2}$, vs. the dispersion of the second virial coefficient, $\tilde{\Delta}$, for polymer with $N = 20$, $u_3 l^{-6} = 60$, $u_4 l^{-9} = 48$, $\lambda_0 = 0$, $\Delta = 5$ and the values of second virial coefficient $u_2 l^{-3} = -10$ (diamonds), -40 (crosses), -70 (quadrangles) and -100 (triangles).

interaction changes from repulsion to attraction and \tilde{u}_2 becomes negative. For large $\tilde{\Delta}$ the effective three body interaction, $(u_3)_{\text{eff}} = u_3 - 3\tilde{\Delta}^2$, changes sign from positive to negative and collapse occurs due to the three body effects [6], even when \tilde{u}_2 remains positive, but small. There is also a transition from the liquid-like globule to the frozen globule (line (F) in Fig. 3). For very large $\tilde{\Delta}$ there is an indication that the copolymer chain collapses directly to the frozen phase and that the phase diagram may exhibit a multi-critical point where all three phases, coil, liquid-like and frozen globule coexist.

The freezing transition line in the Figure 3 scales approximately as $\tilde{\Delta}_f \sim |u_2|^{-\gamma}$ for large negative \tilde{u}_2 , where $\gamma \simeq 0.66 \pm 0.03$. The freezing transition line is nearly independent of the third virial coefficient in the region where $u_3 \ll u_4$ and increases linearly in u_3 when $u_3 \gtrsim u_4$. In a more dense globule, *i.e.* given a bigger negative u_2 or smaller \tilde{u}_3 , chains undergo a transition from a liquid-like to a frozen globule at smaller values of $\tilde{\Delta}$. Both the collapse transition and the freezing transition lines are essentially independent of the size of the chain for sufficiently large degree of polymerization N .

In Figure 4 we present the phase separation parameter δR_g^2 versus the dispersion $\tilde{\Delta}$,

$$\delta R_g^2 = \frac{3}{4} \frac{\tilde{\Delta} \cdot \Delta}{(2\pi)^{3/2} N^2} \sum_{\{j k\}} \frac{\tilde{D}_{ijk}^2 - x D_{ijk}^{(0)2} - (1-x) D_{ijk}^{(1)2}}{\tilde{D}_{jk}^{5/2}}$$

This parameter increases linearly in $\tilde{\Delta}$ in the liquid-like globule phase, but remains constant in the frozen phase, whilst Ψ reaches a maximum at the freezing transition and starts to decrease slowly in the frozen phase due to the increase in the radius of gyration R_g . This means that freezing prevents the system from further phase separation and therefore, for example, the observable δR_g^2 and its first derivative with respect to $\tilde{\Delta}$ can also be used to locate the onset of the freezing transition.

4. Discussion and Conclusions

In this paper we have applied a Gaussian variational approach to study the phase transitions of random copolymers. The essential feature of this approach is that it is based on a trial Hamiltonian in terms of the monomer coordinates rather than density variables. For this reason it may be used to describe a polymer with arbitrary Gaussian disorder across the whole range of the collapse transition. Our equations reduce to the self-consistency equations for a homopolymer at equilibrium as the variance of the second virial coefficient vanishes.

Here we discuss some simplification that were made while performing the analysis.

Firstly, the generalization to the case $\chi \neq 0$ requires application of the perturbation expansion of the effective Hamiltonian (7) in terms of $\beta\Delta^2\chi$. For $\beta\Delta^2\chi \ll 1$, such a description yields non-trivial results only for very large negative u_2 (see Fig. 3). If in this case we keep the terms up to and including Δ^2 in the effective Hamiltonian, then the results obtained are valid with the generalization $\tilde{\Delta} = \beta\Delta(a + \lambda_0\chi)$. This is analogous to the result for the freezing transition temperature for a dense globule [18]. An attempt to keep terms of Δ^4 order requires at least the evaluation of the overlaps of three replicas. The evaluation of such overlaps can be performed, but this is beyond the scope of the present paper.

Secondly, we have performed the numerical analysis of the free energy in the one-step Parisi scheme. To estimate the effect of higher steps of RSB on the onset of the freezing transition we have studied this system analytically in the limit of a very dense globule, $|u_2 l^3 / u_3| \gg 1, N \rightarrow \infty$. In this limit the spring term becomes less important [19] and we can assume that $k \rightarrow 0$. That in turn leads to a q -independent solution for all correlation functions and allows one to make some analytical predictions. It appears that in this case the replica symmetry after freezing transition is continuously broken. The transition line is independent of the number of steps in the Parisi scheme and determined by the equation

$$5 + u_2/\tilde{\Delta} + (4/3)^{5/2} (u_3 - 3\tilde{\Delta}^2)/\tilde{\Delta}^2 + 2^{3/2} u_4/\tilde{\Delta}^3 = 0. \quad (23)$$

This correctly reproduces the transition lines, u_2 vs. $\tilde{\Delta}$ and u_3 vs. $\tilde{\Delta}$, obtained by numerical analysis but shifts them to higher $\tilde{\Delta}$ due to the overestimation of the modes with large q 's. Therefore, we expect that more steps of RSB should be present in a complete scheme, $k \neq 0$. Including the higher steps of RSB brings a smoother solution for $\mathcal{F}_q(u)$ and allows one to study not only the onset of the freezing transition, but also the frozen phase itself. This does not change the profiles the freezing transition line, Figure 3, and brings some minor correction to the the phase separation parameter δR^2 for $\tilde{\Delta} \sim \tilde{\Delta}_f$, but does not change its behaviour qualitatively (Fig. 4).

It is believed that the model we have considered can provide a basis for understanding conformational states of biomolecules such as proteins. The results for the freezing transition and the phase separation are in agreement with those obtained for this model by other methods [21]. We note that the results we have obtained are valid also for binary distribution of disorder, providing higher virial coefficients remain positive. However, the whole diagram in this case will incorporate new features, for example the explicit dependence of the freezing transition on the chemical composition.

We also note that one of the important drawbacks of the theory is that Gaussian method yields an incorrect Flory exponent for a chain in a good solvent. However, this problem can be resolved in different ways and we refer the reader to the discussion of this point in [20].

Finally, we may comment that, despite the limitations, the current approach offers one of the few consistent approaches to the global "phase" diagrams of random amphiphilic copolymer chain [21, 22].

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Appendix

Here we set $\chi = 0$ in (7) and consider the simpler Hamiltonian,

$$\beta H_{\text{eff}}^n = \beta H_{\text{hom}}^n - \frac{(\beta \Delta a)^2}{2!} \sum_{\{ij\}\{jk\}} \sum_{a \neq b} \delta(\mathbf{r}_i^a - \mathbf{r}_j^a) \delta(\mathbf{r}_j^b - \mathbf{r}_k^b), \quad (\text{A.1})$$

where we have absorbed in the definition of u_2 the terms which renormalized the second virial coefficient after integrating out the disorder part (2, 3) and have made a substitution, $u_3 \rightarrow u_3 - 3(\beta \Delta a)^2$. Performing an average over the Gaussian ensemble (11) one arrives at the following result,

$$\begin{aligned} \beta F_{\text{eff}}^n &= -\frac{3}{2} \sum_q \text{Tr} \log \mathcal{F}^{ab}(q) + \frac{3\kappa N}{2} \sum_a D_{0i}^{aa} \\ &+ \sum_{n=1}^{\infty} \frac{u_{n+1} - 3(\beta \Delta a)^2 \delta_{n,2}}{(n+1)!(2\pi)^{3n/2}} \sum_{\{m_0 \dots m_n\}} (X_{1 \dots n}^{a \dots a})^{-3/2} \\ &- \frac{\beta^2 a^2 \Delta^2}{2(2\pi)^3} \sum_{\{ij\}\{jk\}} \sum_{a \neq b} (D_{ij}^{aa} D_{jk}^{bb} - (D_{ijk}^{ab})^2)^{-3/2} + n \cdot \text{const.} \end{aligned} \quad (\text{A.2})$$

Here we have introduced spatial D_{ij}^{ab} and Fourier $\mathcal{F}^{ab}(q)$ monomer correlations

$$\mathcal{F}^{ab}(q) = \frac{1}{3} \langle \mathbf{r}_{-q}^a \mathbf{r}_q^b \rangle_0, \quad D_{ij}^{ab} = \sum_q d_{ij}^{(q)} \mathcal{F}^{ab}(q), \quad D_{ijk}^{ab} = \sum_q d_{ijk}^{(q)} \mathcal{F}^{ab}(q) \quad (\text{A.3})$$

with the following two-body coefficients,

$$d_{ij}^{(q)} = 2 \left(1 - \cos \frac{2\pi q(i-j)}{N} \right), \quad (\text{A.4})$$

and the three-body coefficients factorized as

$$d_{ijk}^{(q)} = \frac{1}{2} \left(d_{ij}^{(q)} + d_{jk}^{(q)} - d_{ik}^{(q)} \right). \quad (\text{A.5})$$

The effective free energy has to be minimized with respect to all correlation functions $\mathcal{F}^{ab}(q)$ with the physical condition that the correlations for monomers from different replicas are smaller than those for monomers from the same replica,

$$0 \leq \tilde{\mathcal{F}}^{ab}(q) < \mathcal{F}^{aa}(q), \quad \text{for any } b \neq a, \quad a, b = 1 \dots n.$$

Alternatively this condition can be attained if one requires the trial matrices $V_{ab}(q)$ and $\mathcal{F}^{ab}(q)$ to be positively defined for an arbitrary positive integer n and taking into account that all non-diagonal terms of $V_{ab}(q)$ have to be negative to match the sign of corresponding terms in (A.1). Practically, we expect that the correlations between different replicas are always weaker than those in the same replica for finite variance of disorder $\tilde{\Delta}$.

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