Change in the elasticity of a random heteropolymer chain induced by freezing

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Abstract. – We consider a simple model of a random heteropolymer chain that is known to undergo the freezing transition. We investigate the change in the elastic properties of the chain upon freezing. The elastic constants are evaluated and it is shown that they acquire a non-trivial contribution in the frozen phase.

The goal of this letter is to investigate the elasticity of a random heteropolymer chain and, in particular, its change upon freezing.

Macroscopic elastomeric response is one of the fundamental properties of cross-linked polymeric systems [1]. It originates from the presence of an infinite network. On a macroscopic level uncrosslinked polymeric systems exhibit a viscous flow rather than an elastic recovery behavior. However, on a microscopic level a single polymer chain is endowed with an elastic response [2]. This is a combined effect of both the chain connectivity and the huge number of possible conformations. Here we examine the elasticity of a single random heteropolymer chain that undergoes a freezing transition. This transition leads to a non-ergodic phase characterized by a highly rugged topography of the free-energy landscape with multiple multidimensional minima. Different chain conformations are separated by high-energy barriers. This effectively reduces the number of accessible chain conformations and thus should result in a change of the elastic properties of the heteropolymer chain.

It should be emphasized here that the model random heteropolymer and its freezing transition which are considered in this work are very similar to those discussed in the context of protein folding. Thus, the method we are using to investigate an emerging additional contribution to the heteropolymer chain elasticity can be used to study the elasticity or stiffness of a folded protein. In general, elastic properties may be related to the structure and the stability of the ground state (note that elastic constants are determined by the curvature of the free energy). Under certain conditions [3] elastic constants may even be considered as order

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parameters for monitoring possible structural transitions. This implies that elastic constants could play an important role in theories based on the energy landscape paradigm [4, 5].

We consider the “random bond” model (RBM) [6-9] of a random heteropolymer chain. The physics of the RBM in higher dimensions [10] is equivalent to that of the random energy model (REM) [11]. The REM plays an important role in theoretical studies of protein folding and, in this context, was first introduced by Bryngelson and Wolynes [12]. Despite the fact that the RBM has been intensively studied in higher and lower dimensions [6-8], its elastic properties have not been investigated to the best of our knowledge.

The RBM is characterized by a Hamiltonian, $H(\{\mathbf{r}_i\}, \{b_{ij}\})$ that depends on a set of independent random quenched variables $\{b_{ij}\}$,

$$H(\{\mathbf{r}_i\}, \{b_{ij}\}) = H_{\text{vol}}(\{\mathbf{r}_i\}) + \frac{v}{2} \sum_{i \neq j} b_{ij} \delta(\mathbf{r}_i - \mathbf{r}_j) + U_{\kappa}. \quad (1)$$

The set of $\{b_{ij}\}$ specifies heterogeneity of pair-wise interactions. Each variable b_{ij} has a Gaussian probability distribution with mean value b_0 and mean-square variation Δ^2 [6]. In eq. (1) H_{vol} and U_{κ} describe excluded-volume interactions and the chain connectivity,

$$\beta H_{\text{vol}} = \frac{v_0 v}{2!} \sum_{\mathbf{r}} \rho^2(\mathbf{r}) + w_3 \frac{v^2}{3!} \sum_{\mathbf{r}} \rho^3(\mathbf{r}), \quad \beta U_{\kappa} = \frac{\kappa}{2} \sum_i (\mathbf{r}_i - \mathbf{r}_{i-1})^2. \quad (2)$$

In eq. (2) v_0 , w_3 , v are the second and the third virial coefficients, and the excluded volume, respectively. The densities in eq. (2), $\rho(\mathbf{r}) = \sum_i \delta(\mathbf{r}(s) - \mathbf{r})$, are considered to have resolution v whenever it is necessary, $\delta(0) = v^{-1}$.

The RBM undergoes a freezing transition. In the frozen phase the replica overlaps $Q_{ab}(\mathbf{R})$ are localized on a microscopic spatial scale $g = v^{1/d}$, where d is the space dimensionality [6, 8, 9]. In the following we briefly outline a different derivation of this known result. Then, we use our alternative approach to investigate the elastic response of the RBM.

We follow a replica version [13] of the variational approach [14] and approximate the free energy F of the system by the Gibbs-Bogoliubov estimate F_n of the effective free energy of the replicated system,

$$F = \lim_{n \rightarrow 0} \frac{1}{n} \min_{\hat{\Psi}_q} F_n[\{\hat{\Psi}\}], \quad F_n = F_{\text{ref}} + \langle (H_{\text{eff}} - H_{\text{ref}}) \rangle_{\text{ref}}, \quad (3)$$

where F_{ref} and H_{ref} are the free energy and the Hamiltonian of a Gaussian reference system. The average $\langle \cdot \rangle_{\text{ref}}$ is taken with respect to H_{ref} . H_{eff} denotes the effective Hamiltonian of the replicated system,

$$-\beta H_{\text{eff}} = \ln \int d\{b_{ij}\} \prod_{i < j} P(b_{ij}) \exp \left[-\beta \sum_a H^{(a)} \right]. \quad (4)$$

The Gibbs-Bogoliubov estimate F_n depends on a set of variational order parameters, $\hat{\Psi}(q)$. Here $\hat{\Psi}(q)$ is a $nd \times nd$ matrix. Its elements, $\Psi_{\mu\nu}^{ab}(q)$, are the Fourier transformations of spatial monomer position correlation functions $\langle (\mathbf{r}_{i,\mu}^a - \mathbf{r}_{j,\mu}^a)(\mathbf{r}_{i,\nu}^b - \mathbf{r}_{j,\nu}^b) \rangle$ of the reference system [15]. Note that in $\Psi_{\mu\nu}^{ab}(q)$ the superscripts stand for replica indices and the subscripts stand for spatial indices. In contrast to [15] we include order parameters that are non-diagonal in spatial indices $\mu \neq \nu$ in order to be able to describe a strained system. Omitting trivial terms, the free energy of the system can be written as

$$\beta F_n = -\frac{1}{2} \sum_q \text{tr} \log \hat{\Psi}(q) + \sum_{a=1}^n \langle \beta U_{\kappa}^{(a)} \rangle_{\text{ref}} + \sum_{s=2}^3 \sum_{a=1}^n u_s N^s (\det \hat{\Phi}^{(aa)})^{(1-s)/2} + \langle \beta H_X \rangle_{\text{ref}}, \quad (5)$$

$$\langle \beta H_X \rangle_{\text{ref}} = -N^2 \frac{(g^d \beta \Delta)^2}{8(2\pi)^d} \sum_{a \neq b} (\det \hat{M}^{(ab)})^{-1/2}. \quad (6)$$

Here $\hat{\Phi}^{(ab)}$ is $d \times d$ matrix, $[\hat{\Phi}^{(ab)}]_{\mu\nu} = G_{\mu\nu}^{ab}$, where $G_{\mu\nu}^{ab}$ denote generalized mean-square radii of gyration, $G_{\mu\nu}^{ab} = \langle \mathbf{r}_{i,\mu}^a \mathbf{r}_{i,\nu}^b \rangle = \sum_{q=1}^{N-1} \Psi_{\mu\nu}^{ab}(q)$. Furthermore, $\hat{M}^{(ab)}$ is $d \times d$ block matrix of 2×2 matrices $\hat{B}_{(\mu\nu)}^{(ab)}$,

$$\hat{B}_{(\mu\nu)}^{(ab)} = \begin{bmatrix} G_{\mu\nu}^{aa} + g^2 \delta_{\mu\nu} & G_{\mu\nu}^{ab} \\ G_{\mu\nu}^{ba} & G_{\mu\nu}^{bb} + g^2 \delta_{\mu\nu} \end{bmatrix}. \quad (7)$$

Renormalized virial coefficients are given by $u_2 = (v/2!)(v_0 + \beta b_0 - (\beta \Delta)^2/2)/(4\pi)^{d/2}$, $u_3 = (w_3 v^2/3!)/(3^{1/2} 2\pi)^d$. In the following we assume that upon freezing the chain is in a compact state corresponding to a large, negative u_2 . Our results are, strictly speaking, only applicable to the case of higher dimensions [6] due to approximations involved in the evaluation of the Hamiltonian: we use $\langle \exp[ik_1 r_i^a + ik_2 r_j^b] \rangle = \langle \exp[ik_1 r_i^a] \rangle \langle \exp[ik_2 r_j^b] \rangle$, if $i \neq j$. The relation to the formalism exploiting replica overlaps [6, 8, 10] is discussed in ref. [9].

We first consider an isotropic unstrained system in equilibrium. In this case only order parameters that are diagonal in spatial indices have non-trivial values $\Psi_{\mu\mu}^{ab}(q) \equiv \Psi^{ab}(q)$ ($G_{\mu\mu}^{ab} \equiv G^{ab}$), and $\Psi_{\mu\nu}^{ab}(q) = 0$ for $\mu \neq \nu$. The last term in the free-energy expression (5) (*i.e.* the term given by eq. (6)) is responsible for replica symmetry breaking (RSB). In the absence of stress it is determined by the equilibrium values of $\det \hat{B}_{(\mu\mu)}^{(ab)}$. Simple analysis of $\det \hat{B}_{(\mu\mu)}^{(ab)}$ shows that in the large- N limit term (6) is irrelevant everywhere except for the glass phase. Indeed, one has the following estimate of (6):

$$\frac{\langle \beta H_X \rangle}{N} = -\rho \frac{(v\beta\Delta)^2}{8(2\pi)^d} \begin{cases} (2^d v)^{-1} \sum_{\{ab\}} \Xi_N^{ab}, & \text{if } G^{ab} \neq 0, \\ n(n-1) (G^{aa})^{-d/2} \sim 0, & \text{otherwise,} \end{cases} \quad (8)$$

where Ξ_N^{ab} is a very sharp function with the following properties:

$$\Xi_N^{ab} \sim \begin{cases} 1, & \text{if } (a, b) \text{ such that } G^{ab} \approx G_{\text{max}}^{ab} \approx G^{aa}, \\ O(N^{-1}), & \text{otherwise.} \end{cases} \quad (9)$$

The values of the order parameters are, in principle, determined by the optimization of the free energy. The substantial contribution to (8), however, comes only from the pairs of replicas that are maximally correlated $G^{ab} \approx G_{\text{max}}^{ab}$, $G^{ab} \in [0, G_{\text{max}}^{ab}]$. Assuming that in the glassy phase the globule is frozen down to the micro scale g , one finds an estimate for G_{max}^{ab} : $G_{\text{max}}^{ab} = \max \langle \mathbf{r}_{i,\mu}^a \mathbf{r}_{i,\mu}^b \rangle = \langle \mathbf{r}_{i,\mu}^a \mathbf{r}_{i,\mu}^a \rangle - g^2 = G^{aa} - g^2$ for $a \neq b$.

Thus, in the frozen phase in the limit $n \rightarrow 0$ [16], $G^{ab} \rightarrow [\tilde{G}, G(s)]$, one has

$$\lim_{n \rightarrow 0} \frac{\langle \beta H_X \rangle}{nN} = \frac{(\beta\Delta)^2 \rho g^d}{8(4\pi)^d} \int_0^1 ds \Xi_N(\tilde{G} - g^2 - G(s)), \quad (10)$$

where $\Xi_N(y)$ is a sharp function for $N \gg 1$ and $\rho = N/\tilde{G}^{d/2}$. The optimization of the free energy with respect to inter-replica order parameters yields two phases: liquid-like phase with zero inter-replica correlations and the frozen phase. The maximization of the free energy with respect to correlations between replicas from different groups in one step RSB ansatz,

G_0 , yields $G_0 = 0$ in the large- N limit. If one considers higher orders of RSB, the result persists and the optimization yields zero for all correlations for replicas from different groups. This represents the fact that only one step of RSB is relevant in the thermodynamic limit. Furthermore, the replica-overlap order parameter G_1 (*i.e.* correlations between replicas from the same group) has a discontinuous jump upon transition to the frozen phase [7].

Let us therefore consider only one step RSB solution with $G_0 = 0$. If N is relatively small the order parameter G_1 exhibits a small discontinuity upon freezing. As N increases the jump in the value of inter-replica order parameter G_1 at the transition increases. Both for small and large N the density remains approximately constant ($\rho \approx \rho^*$) in the vicinity of the transition. Due to the peculiar structure of term (8) for sufficiently large N , G_1 changes upon freezing from zero to $G_{1,\max}$. Thus, in the limit $N \rightarrow \infty$ one finds that the correlations between the replicas from the same group, G_1 , are not determined variationally, but by the requirement that the replica coupling term survives the thermodynamic limit, see eqs. (8), (9), (10). Summarizing, one can write that in the glassy phase

$$\tilde{G} - g^2 - G(s) \approx 0, \quad \forall G(s) \neq 0, \quad \text{for } N \gg 1. \quad (11)$$

Equation (11) can be viewed as a constraint restricting the range of parameter space available for variation. The existence of such a constraint suggests that in the frozen phase the density should be treated as a model parameter rather than as a variational parameter [17]. Indeed, if the density were a variational parameter in the frozen phase, then one would still have to minimize the free energy with respect to the density ρ (or $\tilde{G}$) and maximize it with respect to G_1 . However, eq. (11) relates one variable to the other for $N \gg 1$. Along the line given by (11) the mini-max procedure loses its meaning. Thus, in the frozen phase we set $\rho = \rho^* = \rho(T_c)$ and the free energy becomes a function of only one variational parameter x , which is the fraction of replicas that belong to the same group.

We would like to remark at this point that in other approaches [8,9] the density is usually excluded from the variational treatment of the frozen phase. This is based on the incompressibility approximation that can be used for sufficiently large, negative u_2 .

Thus, from the analysis of the free energy in the thermodynamic limit one finds that above freezing

$$F = \min_{\rho} F(\rho), \quad (12)$$

where $F(\rho)$ is given by the replica diagonal part of eq. (5). Below freezing one finds

$$F = F(\rho^*) + \max_x \delta F(x, \rho^*), \quad (13)$$

where x is the fraction of replicas that belong to the same group. The part of the free energy subjected to maximization, $\delta F(x, \rho^*)$, is similar to that derived by Takada and Wolynes [9]. Consequentially, optimization yields the transition temperature T_c that is proportional to the variation of disorder Δ and that is inversely proportional to the square root of the entropy loss s_{loss} : $k_B T_c \sim \Delta(v\rho^*/s_{\text{loss}})^{1/2}$.

Let us now turn to the elasticity of the system. Elasticity is defined as a specific response of the system to an external deformation. The change in the free energy upon an arbitrary deformation is accommodated through the change in the order parameters, $F_n(\hat{\Psi}')$ (for examples of similar calculations, see, *e.g.*, [18] and references therein). Parameterizing the effect of the deformation by a strain tensor $\hat{u}$, we relate the order parameters of the strained and original unstrained systems: $\hat{\Psi} \rightarrow \hat{\Psi}' = \hat{\Psi} + \delta\hat{\Psi}(\hat{u})$. If V is the volume occupied by the chain,

one has the following definition for the second-order elastic constants (ECs):

$$V\Theta_{\mu\nu,\gamma\delta} = \lim_{\hat{u} \rightarrow 0} \frac{\partial^2}{\partial u_{\mu\nu} \partial u_{\gamma\delta}} \lim_{n \rightarrow 0} n^{-1} (F_n(\hat{\Psi}') - F_n(\hat{\Psi})). \quad (14)$$

Equation (14) can be easily generalized for higher-order ECs. One can relate the definition of the second-order ECs and the Hessian of the free energy, $\mathbf{H}_{ab,cd}^{\mu\nu,\delta\gamma}$,

$$V\Theta_{\mu\nu,\gamma\delta} = \lim_{u,n \rightarrow 0} \frac{1}{n} \frac{\partial^2}{\partial u_{\mu\nu} \partial u_{\gamma\delta}} F_n(\hat{\Psi}') = \lim_{\hat{u}, n \rightarrow 0} \frac{1}{n} \sum_{qq'} \frac{\partial \delta \hat{\Psi}(q, \hat{u})}{\partial u_{\mu\nu}} \cdot \overset{\leftrightarrow}{\mathbf{H}}(q, q') \cdot \frac{\partial \delta \hat{\Psi}(q', \hat{u})}{\partial u_{\gamma\delta}}. \quad (15)$$

Note that the limits $\lim_{u \rightarrow 0}$ and $\lim_{n \rightarrow 0}$ are interchangeable in eq. (15) for the free energy (5) as can be checked by the explicit calculation.

Let us consider a shear deformation, given by an affine transformation $\mathbf{r}_i \rightarrow \mathbf{r}'_i = \mathbf{r}_i + \hat{u} \cdot \mathbf{r}_i$ with the diagonal elements of the strain tensor being equal to zero, $u_{\mu\mu} = 0$. To evaluate ECs of higher orders, one needs to consider the exact expression for $\delta \Psi_{\mu\nu}^{ab}(q, \hat{u})$, that is straightforward for the given affine deformation and it depends only on linear and quadratic in $\hat{u}$ terms. As follows from eq. (15), only the linear term in $\hat{u}$ is required to evaluate the second-order ECs.

In the linear order with respect to $\hat{u}$, the correlation functions, which are diagonal in the spatial indices, do not change; on the other hand, the off-diagonal correlation functions, which are equal to zero in an unstrained system, are proportional to the degree of deformation,

$$\delta \Psi_{\mu\nu}^{ab}(q) = \begin{cases} 0 + o(\hat{u}), & \mu = \nu, \\ u_{\mu\nu} \Psi_{\nu\nu}^{ab}(q) + \Psi_{\mu\mu}^{ab}(q) u_{\mu\nu} + o(\hat{u}) = (u_{\mu\nu} + u_{\nu\mu}) \Psi^{ab}(q) + o(\hat{u}), & \mu \neq \nu. \end{cases} \quad (16)$$

Note that in eq. (16) we do not assume the Einstein summation convention for repeated indices.

Expansion of the free energy (5) up to the second order with respect to the correlation functions that are non-diagonal in spatial indices yields

$$\begin{aligned} \beta(F_n(\hat{u}) - F_n(\hat{0})) &= \frac{1}{4} \sum_q \sum_{\{\mu\nu\}} \text{tr} \left([\hat{A}_q^{(\mu\mu)}]^{-1} \hat{A}_q^{(\mu\nu)} [\hat{A}_q^{(\nu\nu)}]^{-1} \hat{A}_q^{(\nu\mu)} \right) + \\ &+ \sum_{s=2}^3 \frac{s-1}{4} u_s N^s \sum_{a=1}^n \left[\prod_{\mu=1}^d G_{\mu\mu}^{aa} \right]^{(1-s)/2} \cdot \left(\sum_{\{\mu\nu\}} [\hat{\Phi}^{(aa)}]_{\mu\mu}^{-1} [\hat{\Phi}^{(aa)}]_{\mu\nu} [\hat{\Phi}^{(aa)}]_{\nu\nu}^{-1} [\hat{\Phi}^{(aa)}]_{\nu\mu} \right) - \\ &- N^2 \frac{(g^d \beta \Delta)^2}{8(2\pi)^d} \frac{1}{4} \sum_{\{ab\}} \left[\prod_{\mu=1}^d \det \hat{B}_{(\mu\mu)}^{(ab)} \right]^{-1/2} \cdot \sum_{\{\mu\nu\}} \text{tr} \left([\hat{B}_{(\mu\mu)}^{(ab)}]^{-1} \hat{B}_{(\mu\nu)}^{(ab)} [\hat{B}_{(\nu\nu)}^{(ab)}]^{-1} \hat{B}_{(\nu\mu)}^{(ab)} \right), \end{aligned} \quad (17)$$

where $n \times n$ matrix $\hat{A}_q^{(\mu\nu)}$ defined as $[\hat{A}_q^{(\mu\nu)}]^{ab} \equiv \Psi_{\mu\nu}^{ab}(q)$. In the first and the last terms the trace is taken on $n \times n$ and 2×2 matrices, respectively. The first term in eq. (17) comes from the expansion of the free energy of the reference system. For the deformation defined by eq. (16), its contribution to the second-order ECs is the same in any phase. This is due to the fact that $[\hat{A}_q^{(\mu\mu)}]^{-1} \hat{A}_q^{(\mu\nu)} = \hat{I}_{n \times n} (u_{\mu\nu} + u_{\nu\mu})$. The second term is the contribution to the ECs from excluded-volume terms. The last term of eq. (16) is only relevant in the frozen phase and it is the only term that produces an additional elastic response upon freezing.

Taking into account the stationary condition of the free energy with respect to $\tilde{G}_{\mu\mu} (= \tilde{G})$,

$$\frac{1}{d} \langle \beta U_\kappa \rangle = \sum_q \frac{1}{2} + \sum_{s=2}^{\infty} \frac{s-1}{2} u_s N^s \tilde{G}^{d(1-s)/2}, \quad (18)$$

one finds the following expansion of the free energy in the liquid-like phase:

$$(F' - F) = \frac{1}{2d} \langle U_\kappa \rangle \sum_{\{\mu\nu\}} \mathcal{R}_{\mu\nu} \mathcal{R}_{\nu\mu} + o(\hat{u}^2), \quad (19)$$

where $\mathcal{R}_{\mu\nu}$ is a normalized inter-replica correlation function. Here we have taken into account eq. (16), according to which one has $\mathcal{R}_{\mu\nu} \equiv \delta\Psi_{\mu\nu}^{aa}(q)/\Psi^{aa}(q) = \delta G_{\mu\nu}^{aa}/G^{aa}$ and $\mathcal{R}_{\mu\nu} = u_{\mu\nu} + u_{\nu\mu}$. Finally, from eq. (19) one finds the expression for the second-order ECs outside the frozen phase,

$$\Theta_{\{\mu\nu\},\{\nu\mu\}} = \Theta_{\{\mu\nu\},\{\mu\nu\}} = \frac{2}{d} \frac{\langle U_\kappa \rangle}{V}. \quad (20)$$

Curly brackets indicate here that $\mu \neq \nu$. According to eq. (20), above the freezing transition the elastic constants originate from the chain connectivity. Note that this result is applicable to both a homopolymer chain [2] and a heteropolymer chain in the random coil and liquid-like phases.

In the frozen phase, along with the regular part (20) one has an extra response $\delta\Theta_{\{\mu\nu\},\{\nu\mu\}}$ to the external deformation. Such extra response originates in the last term of eq. (17) that we denote as $\beta\Omega(\hat{u})$. Performing $n \rightarrow 0$ limit one finds

$$\begin{aligned} \beta\Omega(\hat{u}) &= N \frac{v\rho^*(\beta\Delta)^2}{2^4(4\pi)^d} \Upsilon_N \sum_{\{\mu\nu\}} \mathcal{R}_{\mu\nu} \mathcal{R}_{\nu\mu} + o(\hat{u}^2), \\ \Upsilon_N &= \int_0^1 ds \Xi_N(\tilde{G} - g^2 - G(s)) \frac{[(\tilde{G} + g^2)\tilde{G} - G^2(s)]^2 + [g^2 G(s)]^2}{[(\tilde{G} + g^2)^2 - G^2(s)]^2}. \end{aligned} \quad (21)$$

Taking into account one-step RSB solution, eq. (21) yields the following change in the second-order ECs induced by freezing:

$$\delta\Theta_{\{\mu\nu\},\{\nu\mu\}} = \lim_{\hat{u} \rightarrow 0} \frac{\partial^2 \Omega(\hat{u})}{\partial u_{\mu\nu} \partial u_{\nu\mu}} = \frac{N}{V} \frac{5}{32} \frac{v\beta\Delta^2 \rho^*}{(4\pi)^d} (1-x) = cv\beta(\Delta\rho^*)^2(1-x). \quad (22)$$

Here c is a positive numerical coefficient. Recall that from the free-energy optimization one finds that in the vicinity of the transition $x = T/T_c$, $x \leq 1$ [8]. The additional contribution to the elastic constants given by eq. (22) is the main result of this paper. Though (22) is determined by the replica coupling term in the effective Hamiltonian (6), the existence of constraint (11) suggests that an additional elasticity (22) induced by freezing has an entropic origin. Indeed, taking into account the stationary condition for the free energy with respect to x , one finds that the elasticity gain is determined by the freezing-induced entropy loss, $\delta\Theta_{\{\mu\nu\},\{\nu\mu\}} = ck_B T_c \rho^* s_{\text{loss}}(1-x)/x$.

We would like to point out here that a certain care is required when one considers elasticity of a disordered system. Above freezing the examined system is similar to a homopolymer with the second virial coefficient renormalized by disorder average. Therefore our calculation of the second-order ECs is analogous to earlier ones for various homopolymer systems [1, 2]. Below freezing, additional contribution to the elasticity arises from correlations between replicas. However, in the frozen phase the system is expected to remain stable upon small deformation due to the structure of the ground state. One-step symmetry breaking is related to the fact that all replicas within the same group reside in the same minima, while limit $N \gg 1$ ensures that the barriers between minima are large.

Let us make some concluding remarks. We have examined the elastic properties of a simple model heteropolymer across the complete phase diagram and found that the change in elastic

constants can be related to the entropy loss (or the entropy gain). In the case of the coil-globule transition the entropy change results simply from the reduction of the volume occupied by the chain. In the case of freezing, however, the entropy loss is not accompanied by any significant changes in the the radius of gyration. Therefore this effect appears to be somewhat reminiscent of solidification of a fluid. One therefore may speculate that freezing occurs due to the formation of “frozen” contacts that are analogous to the permanent cross-links in networks. The number of the frozen contacts should gradually increase upon the transition into the glassy phase.

The present work is somewhat close to the paper by Takada and Wolynes [9]. However, we are interested in elastic properties of the RBM rather than in phase behavior of a more complicated model for protein folding [9]. In view of the recent interest in the elastic properties of biomolecules in general and DNA in particular [19], it may be beneficial to examine the elasticity of more realistic models for protein folding, for example [9, 20].

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