

A Cluster of Chains Can Be Smaller Than a Single Chain: New Interpretation of Kinetics of Collapse Experiments

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Despite a considerable number of theoretical and experimental studies,^{1,2} the current understanding of the collapse transition of macromolecules from the coil to the compact globular state is still far from complete. A few years ago Chu and co-workers^{3,4} reviewed the experimental situation on the most-studied homopolymer system, polystyrene in cyclohexane. In particular, they were the first to stress the importance of carrying out equilibrium chain collapse experiments within the thermodynamically stable one-phase region, to the left of the low-concentration branch of the binodal line of the polymer–solvent phase diagram. They collected the experimental results published by their and other groups and showed that those which passed the “phase-separation test”⁴ were perfectly consistent and reproducible: all data fell on a *single master curve* when plotted as $\alpha_H^3|\tau|M_w^{1/2}$ against the excluded-volume parameter $|\tau|M_w^{1/2}$, where $\alpha_H = R_H/(R_H)_0$ is the contraction ratio of the chain hydrodynamic radius over its unperturbed Θ -state value and $\tau = (T - \Theta)/\Theta \approx (T - \Theta)/T$ is the reduced temperature. In particular, Chu’s group⁵ and Vidaković and Rondelez⁶ reached a common plateau in the $\alpha_H^3|\tau|M_w^{1/2}$ plot at $|\tau|M_w^{1/2} \approx 90$, using completely different experimental techniques (quasi-elastic light scattering and analytical ultracentrifugation, respectively). The existence of this plateau can be justified theoretically by means of general scaling arguments. However the R_H values at the plateau were still rather large compared to those expected for a compact spherical object. This means that those experiments did not lead to fully collapsed chains; instead, the volume spanned by them still included a large solvent fraction.

In a subsequent set of experiments^{7,8} Chu and his group observed the appearance of much more compact objects at higher polymer concentrations, *within the thermodynamically unstable two-phase region* of the phase diagram. They were actually able to follow the *kinetics* of two concurrent processes occurring in the solution, following an abrupt temperature drop from the Θ state: (1) chain collapse and (2) formation and growth of larger aggregates, leading eventually to precipitation of a polymer-rich phase. Appearance of the small collapsed objects occurred in two subsequent and clearly distinct stages: (i) a fast but relatively modest ($\approx 30\%$) contraction of the chain hydrodynamic radius; (ii) concurrently with the formation of the larger aggregates, a further shrinkage down to an R_H value some 50% smaller than the intermediate one.

Chu *et al.*⁸ interpreted these observations on the basis of qualitative scaling theories of the kinetics of the coil-to-globule transition,^{9,10} according to which a chain undergoes a two-stage collapse: from the coil to a “crumpled globule”, which is a fast process with a characteristic time $t_1 \sim M_w^2$, followed by a slow cooperative transition to a “compact globule” with a characteristic time $t_2 \sim M_w^3$. In addition, they used Grosberg and Kuznetsov’s theory¹¹ in an attempt to model quantitatively their data on the properties of the fully

collapsed globules but acknowledged that the outcome was not fully satisfactory and some inconsistencies remained. Here we shall suggest an alternative and fundamentally different interpretation of the experimental results.

We were prompted to re-address the interpretation of the above experiments by the following observations:

(a) The intermediate “semicollapsed” hydrodynamic radii [see point i above] fall exactly^{7,8} on the previously-discussed master curve,⁴ obtained within the thermodynamically stable one-phase region of the phase diagram.

(b) The kinetic experiments were performed at $|\tau|M_w^{1/2} \approx 60$: this is much smaller than the value reached in the previous equilibrium experiments^{5,6} ($|\tau|M_w^{1/2} \approx 90$), which however failed to produce a comparable chain contraction.

(c) There is no apparent reason why the single-chain size should undergo an abrupt reduction on going from the one- to the two-phase region; indeed, according to a mean-field theory recently proposed by us¹² as well as to qualitative considerations,^{1,13} the chain radius of gyration should increase with polymer concentration, for a given temperature (*i.e.*, at fixed $|\tau|M_w^{1/2}$).

Point a strongly suggests that *the intermediate “crumpled globule” stage of collapse actually corresponds to the final equilibrium state, as far as the single-chain degrees of freedom are concerned*. Of course, this is not an equilibrium state with respect to every other degree of freedom of the polymer solution: there is a slower ongoing phase separation process, which is controlled by chain diffusion and aggregation. Thus we are immediately led to the following question: having ruled out a further *single-chain* contraction, what could possibly give rise to the much smaller objects observed in the second stage of collapse [point ii above]? As we discuss below, it can be argued that *the “compact globules” observed under kinetic conditions are actually macromolecular clusters resulting from aggregation of a small number of polymer chains*.

In a recent paper¹² we proposed a simple free-energy expression for a cluster of ν chains, each consisting of N statistical segments. This is a function of the chain radii of gyration, which are assumed to be all identical, and of the mean-square distance between their centers of mass. The equilibrium values of these variables are obtained by free energy minimization, at each reduced temperature τ . The driving force for collapse and aggregation is provided by the negative segment cluster integral,^{1,11,12} proportional to the adimensional quantity τB (B is a positive constant, which increases with the monomer covolume). In the first paper¹² we carried out the numerical calculations only for the $\nu \rightarrow \infty$ thermodynamic limit: this allowed us to study the interplay between the conformational and the phase behavior of the polymer chains in solution. Here we present our first numerical results of the small- ν case: a more complete and detailed report is currently under preparation.¹⁴ In Figure 1 we have plotted the normalized root-mean-square radii of gyration [$\alpha_S(\nu)$, see the figure caption for its definition] of a single chain and of the clusters of 2, 3, 5, and 10 chains. The plots are limited to the poor-solvent regime, $T < \Theta$. It can be seen that the curves for $\nu \geq 2$ only appear below certain ν -dependent negative values of $\tau BN^{1/2}$, which increase with the number of chains. Above its characteristic “formation temperature” a cluster is unstable against dissociation into isolated chains: in the neighborhood of the Θ

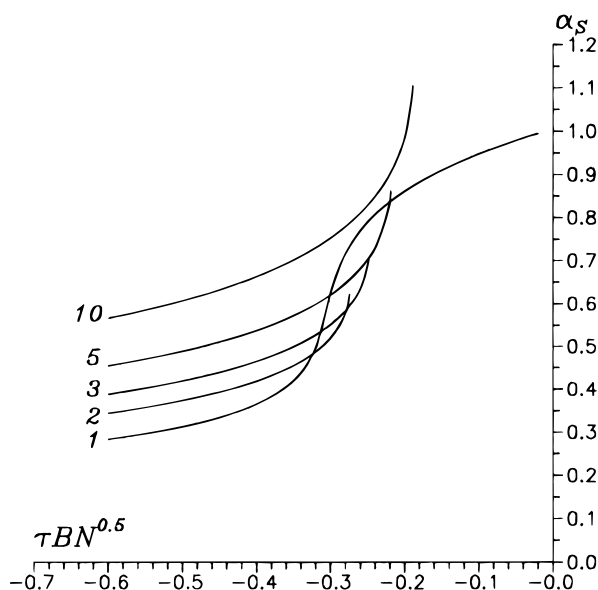


Figure 1. Normalized root-mean-square radii of gyration of a single chain and of the clusters of $\nu = 2, 3, 5, 10$ chains: $\alpha_S(\nu) = (\langle S_\nu^2 \rangle / \langle S_1^2 \rangle_0)^{1/2}$, where $\langle S_\nu^2 \rangle$ is the mean-square radius of gyration of a cluster and $\langle S_1^2 \rangle_0$ is that of an unperturbed single chain. Here $\tau BN^{1/2}$ is the excluded volume parameter, where N is the number of statistical segments in a chain, $\tau = (T - \Theta)/T$, and τB ($B > 0$) is proportional to the two-body cluster integral between statistical segments.¹² The plots have been obtained with the adimensional three-body parameter¹² $K_1 = 0.0019$.

temperature the two-body attractions between the polymer segments are not strong enough to counterbalance the entropy loss resulting from chain association. However, the most interesting feature of the plots is that there is a range of the excluded volume parameter ($-0.3 < \tau BN^{1/2} < -0.2$) wherein clusters with $\nu = 2-5$ have a smaller radius of gyration than a single chain. Indeed, at $\tau BN^{1/2} \approx -0.25$ even a cluster of 10 chains has a size comparable to that of a single polymer molecule. The upper and lower limits for $\tau BN^{1/2}$ indicated above correspond to an average cluster formation temperature and to the single-chain collapse temperature, respectively. The possibility of anomalous single-chain/cluster volume ratios had been hinted by us in another recent publication,¹⁵ where we argued that in a cluster of ν chains the effective driving force to collapse is proportional to $\tau B(\nu N)^{1/2}$, to be compared with $\tau BN^{1/2}$ for a single chain. The proportionality between the overall number of segments in a cluster or an isolated chain and their volume is re-established only below the single-chain collapse temperature: for $\tau BN^{1/2} < -0.4$ we have $\alpha_S(\nu) \propto \nu^{1/3}$, where $\nu \geq 1$. On the other hand, an important difference between the $\nu = 1$ and the $\nu \geq 2$ cases is that the equilibrium state of a macromolecular cluster is always rather compact, except for a very narrow range of $\tau BN^{1/2}$ immediately below their formation temperature. This compactness might slow down significantly the further aggregation of the clusters into larger objects.^{15,16}

Notice that the plots presented in Figure 1 are N - and B -independent but are influenced by the value of the repulsive three-body parameter^{1,2,11,12} K_1 . Thus they are not universal and depend on the chemical identity of the polymer and possibly also of the solvent. Here we have chosen $K_1 = 0.0019$, which was obtained¹⁷ by fitting previous experimental results¹⁸ on the collapse of polystyrene in dioctyl phthalate. Reducing the value of K_1 produces a sharper single-chain collapse transi-

tion^{1,2} but at the same time widens the range of $\tau BN^{1/2}$ wherein the clusters are smaller than the isolated chains and decreases the $\alpha_S(\nu)/\alpha_S(1)$ ratio ($\nu = 2, 3, \dots$) in this range.¹⁴ On the other hand, for a sufficiently large three-body parameter the clusters only appear below the (smoother) single-chain collapse transition: in this case, we always find¹⁴ $\alpha_S(1) < \alpha_S(\nu)$.

It would be desirable to have some direct experimental proof of our interpretation of the nature of Chu's compact globules. The most obvious one would be to measure their molecular mass. Unfortunately, the quasi-elastic light scattering technique only provides the M_z/M_w ratio,^{3,8} but not M_w itself. Application of static light scattering³ to the determination of M_w is also problematic since it requires extrapolation to zero polymer concentrations: besides being technically difficult, this would bring the polymer solution from the two-phase to the one-phase region. As an alternative to the determination of the molecular mass, it might be possible to perform neutron scattering experiments on mixtures of hydrogenated (H) and deuterated (D) chains: admitting for simplicity that the compact globules only consist of two-chain aggregates, neutron scattering should reveal the existence of two distinct D-containing globules, namely the DD and the HD clusters. Computer simulations of macromolecular clusters under poor-solvent conditions should also be useful as an independent check of the results presented in Figure 1.

As a final remark, we point out that the present re-interpretation of the experiments by Chu and co-workers does not rule out the possibility of a two-stage kinetics of single-chain collapse. Besides the already-mentioned scaling arguments,^{9,10} independent theoretical suggestions of a two-stage transition have been put forward on the basis of a numerical integration of the Langevin equations of motions for the chain normal modes¹⁹ or, in the context of protein folding, Monte Carlo simulations of lattice polymer models.²⁰ Instead, we suggest that the single-chain contraction observed in those experiments is probably not strong enough for the fully-fledged two-stage process to occur. Its observation might require much more negative values of the excluded volume parameter.

At present, the experimental situation on nonequilibrium collapse is indeed very complicated. We do not claim to have a straightforward explanation for every single experimental observation: this goes beyond the purpose of a short Communication. But we can confidently argue that the possibility of chain clustering during the second stage of collapse should be seriously taken into consideration.

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