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# Monte-Carlo simulation for the kinetics of collapse and phase separation in homopolymer solutions

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## Abstract

We present preliminary results from a Monte-Carlo simulation in a lattice model of homopolymer solutions at various concentrations up to the semi-dilute regime. Two main simulation routines based on the Metropolis algorithm are implemented and these control the internal and global movements of each polymer chain, respectively. We study the kinetics of conformational changes after a quench to the poor solvent region. Each chain may collapse individually as well as aggregate with others, and the competition of both types of processes determines the conformational state. We visually observe and quantitatively analyse the formation of *mesoglobules* – nearly spherical aggregates consisting of a few distinct chains, recently observed experimentally in our laboratory, as a non-equilibrium state. The time scale during which the mesoglobules are preserved is found to be rather long compared to the collapse time of an isolated chain even for large quenches considered here. Our findings agree qualitatively with the results of both experimental and theoretical work carried out in our laboratory.

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## 1. Introduction

Considering the whole polymer concentration range much theoretical and simulation work have been most successful at its extrema [1–6], whereas experimental work [7] have been carried out for all concentrations from very dilute to melts.

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Nevertheless, most fundamental ideas are probably now worked out for equilibrium polymer systems [1,3,4]. The same is not true for dynamical and general non-equilibrium phenomena for polymers. For example, the kinetics of conformational changes has gained considerable attention recently, and most notably, the question of homopolymer collapse for a single-chain [8–15] is considered to be a logical starting point with regard to the more complex problem of biopolymer folding (see e.g. [16,17] and references therein). There is growing consensus in the scientific community that the kinetics of single-chain collapse is a three-stage process consisting of: (i) rapid formation of a “necklace” of locally condensed polymer by a spinodal process [8–10]; (ii) a quasi-ideal Rouse relaxation of the “pearls” on a string [9]; and (iii) final compaction [8–10]. There may be also a final slow self-reptation stage, but in realistic polymer concentrations it would be so slow as to be, perhaps, unobservable due to competition of aggregation. Unfortunately, these single-chain results are difficult to compare to experimental work due to the limitation of dynamic light scattering (DLS) experiments at rather low concentrations [7,18,19].

With polymer melts, the other limit of the concentration range, theory, simulation [20,21] and experiment [7] have had more success in tackling similar problems. Polymer melt simulation on cubic lattices can be easily extended using the methodology of single-polymer simulations where polymer diffusion can be solely attributed to reptation [20]. However, this is not the case for polymer simulation in the dilute to semi-dilute regime. The development of a multichain extension of the Gaussian method was an important step because it makes theoretical study across the dilute up to melt regime practical, exhibiting both equilibria, long-lived metastable structures and kinetic phenomena.

Our aim in this paper, along with its two companion papers [19,22] has been to draw theory and simulation of kinetics of polymer solution into the regime where experimentalists can work with confidence. A secondary aim has been to exhibit the close collaboration possible between these different approaches in the field of soft matter [23]. Experimentally, DLS along with Electron Microscopy, gives information on particle size and distribution. One of the important observations in the experimental work [19] was the appearance of spherical aggregates with a relatively monodisperse size distribution resulting from the phase separation at relatively low dilutions.

These were interpreted in the Gaussian self-consistent method applied to the Edwards-type bead-and-spring model [22] as a long-lived kinetically arrested state. We note that initial insight into the understanding of the equilibrium aspects of the problem was made in the works [24].

We attempt in this very preliminary simulation paper to study similar effects in kinetics after a quench to the poor solvent region in a different lattice model, thereby establishing their universal character. In addition, we can now obtain visual representation of the evolving chains. Here we only consider large quenches where the mesoglobules are manifested as non-stable kinetic structures.

## 2. Method

In the theoretical work [22] we have discussed that the degrees of freedom of the system can be unambiguously decomposed into the inter-molecular and intra-molecular ones. Whilst the former describe motions of each isolated chain, the latter correspond to the motions of the centre-of-masses of distinct chains. It is natural therefore in a Monte-Carlo method to treat two types of attempted moves separately, although taking into account properly the interaction between the two. Thus, the simulation program consists of two separate Monte-Carlo routines: one controlling the internal, and the other controlling the global movements of the chain. Both use the Metropolis algorithm to calculate the transition probabilities, thereby automatically accounting for the interaction. The first routine has been previously discussed at some length in Ref. [10] dealing with the single-chain collapse and thus, shall only be briefly outlined here.

### 2.1. Local polymer movement

The Hamiltonian of the system is defined by [10]

$$H = \frac{1}{2} \sum_{i \neq j} w(r_{ij}) \mathcal{J}_{s_i s_j}, \quad (1)$$

where  $i, j$  enumerate all lattice sites, and  $s_i$  denotes the “contents” of the  $i$ th site, which clearly could be either a monomer or solvent. Here  $\mathcal{J}_{s_i s_j}$  is a  $2 \times 2$  symmetric matrix representing the monomer–monomer,  $\mathcal{J}_{mm}$ , monomer–solvent,  $\mathcal{J}_{ms}$  and solvent–solvent,  $\mathcal{J}_{ss}$ , interaction constants, respectively. The distance between sites  $i$  and  $j$  is denoted as  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ , and  $w(r_{ij})$  is a weighting function which specifies the magnitude of the interaction between sites  $i$  and  $j$ . Since we are dealing with a short-ranged model  $w(r)$  is set equal to zero for separations  $r > 2$ . The interaction parameter  $\chi$  is defined as

$$\chi = \frac{2\mathcal{J}_{ms} - \mathcal{J}_{mm} - \mathcal{J}_{ss}}{k_B T}, \quad (2)$$

and from physical considerations [1] it is non-negative  $\chi \geq 0$ .

Local internal moves and reptations [25] are used to update the polymer conformation. Both use a “heuristic” method, determined by the structure of the Hamiltonian, to generate neighbourhood polymer structures whilst maintaining polymer connectivity and excluded volume constraints. Each move is accepted or rejected based on the transition probability,  $\eta$ , that may be written as

$$\eta = \exp\left(\chi \sum_r w(r) \Delta n_r\right), \quad (3)$$

where the summation is over all neighbouring sites with  $w(r) > 0$ , and  $\Delta n_r$  is the change in monomer environment during the course of the move at each length scale,  $r$ .

## 2.2. Global polymer movement

When there is more than one polymer in the system the diffusion can no longer be excluded from the consideration. Together with the boundary conditions it controls the concentration and thus the collision rate between polymers. The diffusion “constant”,  $D(t)$ , may obviously be measured by monitoring the change in the centre-of-mass of each polymer chain,  $\mathbf{R}_c$ , as a function of time,

$$\langle |\mathbf{R}_c(t) - \mathbf{R}_c(0)|^2 \rangle = 6D(t)t, \quad (4)$$

where the angular brackets denote an ensemble average over many evolving conformations.

It is well established that the diffusion constant increases during collapse (see, e.g. discussion in Ref. [9]) as a consequence of the Stokes law,  $D \propto 1/r$ , or remains constant if the hydrodynamic interaction is neglected. Unfortunately, due to the inherent nature of the quasi-local Monte-Carlo scheme, exacerbated by the fact that it is performed on a cubic lattice, the diffusion constant decreases dramatically when a polymer collapses. Nevertheless, this deficiency of the Monte-Carlo algorithm can be remedied quite easily.

We note that in the Langevin dynamics, without the hydrodynamic effect, the diffusion appears due to the zero Fourier component of the thermal noise. The diffusion constant there has the same form as in the Rouse model [26] and it can be related to the degree of polymerization,  $N$ , as follows:

$$D = \frac{k_B T}{\zeta_0 N}, \quad (5)$$

where  $\zeta_0$  is the friction of each bead.

Thus, we are required to maintain a constant diffusion value. This can be accomplished by decoupling the diffusion from the internal movements affecting each polymer. It is straightforward to see that  $\chi = 0$  corresponds in this model to an athermal solvent. Indeed, any attempted move that does not violate connectivity and excluded volume constraints will be accepted at  $\chi = 0$  as there is no associated energy change. The resulting Flory coil is a simple self-avoiding random walk which has the right value of the diffusion constant. We can, therefore, use the measured diffusion constant in this regime  $D(\chi = 0)$  as a convenient reference point. Without hydrodynamics, one should further ensure that  $D$  does not change with  $\chi$ .

Thus, it seems clear that if the coordinates of a polymer are periodically manipulated using a translation based on some random scheme, it would be possible, in principle, to control the diffusion within the system. If the simulation space were continuous this would be essentially trivial but it is somewhat more complicated on a lattice. The required random scheme may be realised as follows:

$$\mathbf{R}_c(t + \Delta t) = \mathbf{R}_c(t) + \mathfrak{R}(\Delta \mathbf{R}_c), \quad (6)$$

where  $\mathfrak{R}$  is an auxiliary noise and  $\Delta \mathbf{R}_c$  denotes the change in the centre-of-mass coordinate during a Monte-Carlo sweep (MCS) due to the local movement algorithm

described above. Let us denote the integer and fractional parts of  $\Delta R_c$  spatial components as  $[\Delta R_c]$  and  $\{\Delta R_c\}$ , respectively. Each component of  $\mathfrak{R}$  is then determined by the expression

$$\mathfrak{R}_i(\Delta R_c) = \theta(\xi - \{\Delta R_c\}) - [\Delta R_c], \quad (7)$$

where  $\theta(z)$  is the step-function and  $\xi$  is a uniform random deviate such that  $-\alpha \leq \xi \leq \beta$  with  $\alpha, \beta > 0$ . Apparently the ratio of  $\alpha$  and  $\beta$  determines the value of the diffusion constant

$$D = \frac{\beta}{2(\alpha + \beta)} \quad (8)$$

and thus  $\mathfrak{R}$  allows the control of  $D$ . In principle, a second random number is also required to select the direction in space ( $\mathfrak{R}_i$  is always greater than zero). We remark that  $\{\Delta R_c\}$  has a Gaussian-shaped distribution centred about zero and this is one reason why it is possible to overlay it with  $\xi$  without affecting  $D$  to any grave extent.

### 2.3. Multichain algorithm

Given a system of  $M$  polymers each of size  $N$  a MCS is defined as  $MN$  Metropolis steps using the local movement algorithm. The global movement algorithm is then initiated and calculates all *connected paths* within the system. A connected path is defined as set of polymers that are in the interaction range with each other. Each connected path is termed a *clump* of polymers. Each clump consisting of  $S$  chains attempts a diffusion step with a corrected diffusion constant of  $D/S$  according to Eq. (5). If successful the transition probability is then assessed based on the change of the energy calculated in the standard way.

Following this, each polymer within the current clump is in turn diffused separately using the same procedure. In this way, polymers have the opportunity to associate and disassociate based on the Boltzmann distribution. In practice, to reduce the calculation time it might be reasonable to introduce a recursion depth  $S_0$  for attempting to translate sub-clumps of size  $S_0$  within a clump. This yields only a small error since the contribution of the large clumps to the total diffusion constant is small. A simple test shows that this procedure ensures the conservation of the diffusion constant both in time, and with a quasi-static change of  $\chi$  with any required precision depending on the recursion depth  $S_0$ .

### 2.4. Observables

The observables of interest in the multichain polymer system can be broken up into two categories: microscopic and macroscopic.

Microscopic observables that are currently of interest include the mean-squared total radius of gyration,  $R_{tot}^2$ , the mean-squared radius of gyration of a chain,  $R_{chain}^2$ , the mean-squared distances between the centre-of-masses of any two chains,  $\Gamma_{chain}^2$ , and

also similar observables defined with respect to the clumps rather than distinct chains denoted as  $R_{clump}^2$  and  $\Gamma_{clump}^2$ , respectively. The exact definition of these quantities depends on the boundary conditions imposed upon the system. For diffusion to have the appropriate properties at long times it is preferable to use periodic boundary conditions.

Among the macroscopic observables of interest is the average number of polymer clumps  $\langle N_{clump}(t) \rangle$  and the mean clump size  $\langle S_{clump}(t) \rangle$ .

### 3. Results and discussion

We do not attempt here to give an exhaustive survey of the phenomena in terms of concentrations and quench depth. We will instead focus on the concept of mesoglobules and their origins.

A number of multichain systems of varying concentration,  $M = 10, 25, 40, 55$  with an ensemble size  $Q = 50$  for two separate quenches  $\Delta\chi_1 = 0.5$  and  $\Delta\chi_2 = 1.0$  were studied for polymers with a degree of polymerisation  $N = 50$  on a lattice of size  $L = 50$ . Each system was allowed to run for 2000 MCS, once the quench had been initiated. Two of these simulations of ensemble size  $Q = 50, 20$  for  $M = 10, 25$  and  $\Delta\chi_1$  were allowed to run for longer times 35 000 and 20 000 MCS, respectively.<sup>2</sup>

When  $\chi$  is greater than  $\chi_c$ , the polymer tends to minimise its contact with the solvent. In order to do this the system adopts conformations which minimise the polymer surface area to volume ratio. It is clear that this corresponds to a system with only one globule or clump where all the polymers interpenetrate each other. For a large globule the polymer environment inside the globule is similar to a polymer melt. According to the standard Flory–Huggins theory [3] due to the entropic contribution the actual equilibrium state could be a gas of single-chain globules, a coexistence of those globules with pieces of the macroscopic aggregate, or the pure state aggregate in the form of one unique large globule.

However, the non-equilibrium states that appear in kinetics usually have rather more complex conformations. We mention here the appearance of the “necklace” of locally collapsed globules in the kinetics of single coil collapse [9]. These are local structures predominantly formed by the near-neighbours and they simply reflect the quasi-local character of the early stage of the process. However, there is a strong coupling effect resulting in a nearly periodic array of clusters along the chain.

We believe that formation of the “mesoglobules” in Ref. [22] is also a non-equilibrium manifestation of the quasi-local character in 3-D space of the collapse process. Further aggregation may occur, but it is impeded due to the entropic barriers resulting in a rather long kinetically arrested state. In real experiment the steric and more specific interaction may render the unification of distinct globules even harder

<sup>2</sup> The Monte-Carlo acceptance rate on average was about 0.32 giving a successful Metropolis transition every three attempts. This is quite high considering the high density of the polymer clumps. For this reason, it seems likely that the system is not stuck in some small region of phase space and the results may be trusted.

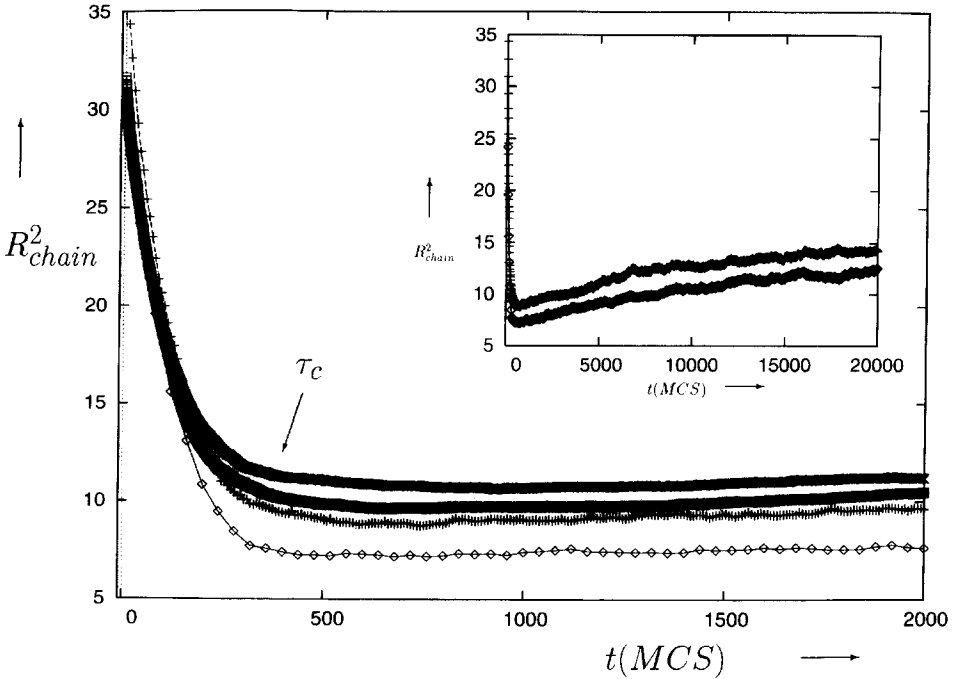


Fig. 1. The mean-squared radius of gyration of a single chain, whether isolated or in an aggregate,  $R_{chain}^2$  is plotted as a function of time after the quench has been initiated. Here  $L = 50$ ,  $N = 50$  and  $\Delta\chi_1 = 0.5$ . Over the short time scale,  $t_{max} = 2000$ , the number of polymers in the simulation are 55, 40, 25 and 10 from top to bottom, respectively.  $\tau_c$  is labelled to indicate the characteristic timescale for one polymer to collapse. Over the longer time scale,  $t_{max} = 20000$ , the number of polymers in the simulation are 25 and 10 (from top to bottom, respectively). This insert illustrates the rapid collapse-aggregation process followed by an expansion of a chain in the globule as it feels near-ideal melt-like environment.

resulting in much longer metastability time-scales and perhaps monodispersity of the mesoglobules.

It is found that the size of a chain  $R_{chain}^2$  (see Fig. 1) for the system reaches a minimum value at the collapse time,  $\tau_c$  (roughly equal to the collapse time of a single polymer), and then slowly increases until the system has reached its final state. The latter reflects the fact that the polymers are exploring phase space within the globules changing their fractal dimension towards that of the nearly ideal coil [22].

The process of globules interpenetrating each other is initially slow because it is difficult for the two colliding globules to begin mixing with each other. The average clump size  $R_{clump}^2$  was found to initially decrease over a very short time scale  $\tau_c$ , corresponding to the Flory coils collapsing, and increases from then on. The total system size  $R_{tot}^2$  decreases slowly reflecting the overall compaction. When  $R_{clump}^2$  and  $R_{tot}^2$  eventually become equal the system has reached its final state (see Fig. 2).

Practically  $\Gamma_{clump}^2$  and  $\Gamma_{chain}^2$  were found, quite reasonably, to be very similar until there is only one clump remaining (at which point  $\Gamma_{clump}^2$  becomes undefined). The

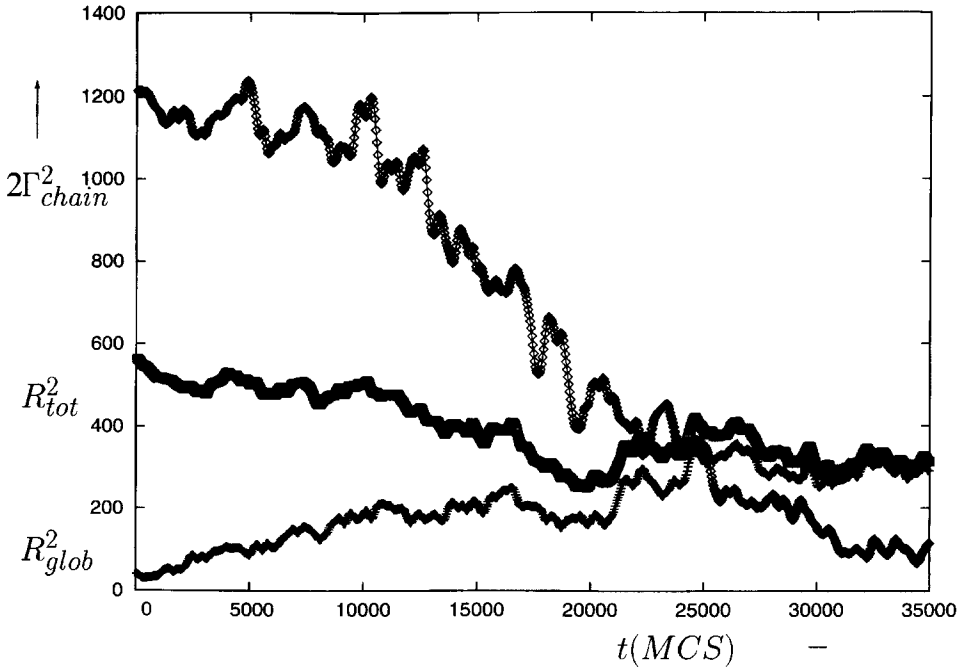


Fig. 2. Plots of the observables  $2\Gamma_{chain}^2$ ,  $R_{tot}^2$  and  $R_{glob}^2$  versus time after the quench. Here  $L = 50$ ,  $N = 50$  and  $\Delta\chi_1 = 0.5$  for the simulation has 10 polymers averaged over an ensemble size of  $Q = 50$ .

inter-chain distance  $\Gamma_{chain}^2$  (see Fig. 2) decreases slowly over short times and then finally falls dramatically to its equilibrium value, in agreement with a companion theory paper [22]. This moment roughly coincides with the overlap of  $R_{tot}^2$  and  $R_{glob}^2$ .

It is interesting to note that the observable  $\langle S_{clump}(t) \rangle$  (see Fig. 3) increases linearly in accordance with the Lifshitz–Slyozov theory since mesoglobules are unstable for large quenches. The clump polydispersity,  $\Omega(t)$ , which is the ensemble average of the fluctuation in clump size, is well defined only for large systems ( $M$  large) and ensemble sizes.

There seems to be a number of processes involved here (see Figs. 4). Firstly, intermolecular polymer collisions prior to full single-polymer collapse (Fig. 4(a)) lead to mesoglobule structures of a few polymers inter-mingled with each other (Fig. 4(b)). The size of these mesoglobules is determined by a careful balance between the intramolecular characteristic collapse time  $\tau_c$  and the diffusion time determined by the diffusion constant  $D$ . Having formed quite rapidly these mesoglobules exist for a reasonable fraction of the overall collapse process. Barriers to intermingling, including entanglements, make it difficult for the overall separation process to occur quickly after  $\tau_c$ . Even so, the polymers continue to aggregate, obeying finally the Lifshitz–Slyozov law. This might have been expected due to the analogy with the gas–liquid transition where liquid droplets coalesce and grow linearly with time for quenches beyond the spinodal.



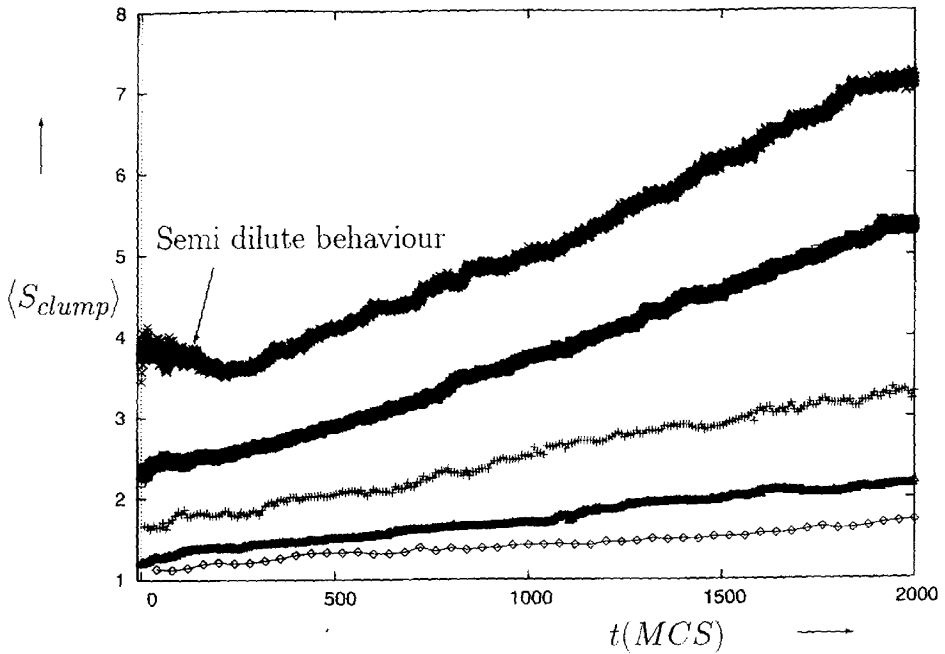


Fig. 3. The average clump size  $\langle S_{clump} \rangle$ , is plotted as a function of time after the quench. Here  $L = 50$ ,  $N = 50$  and  $Q = 50$ ; ( $\times$ ) represents  $M = 55$  and  $\Delta\chi_1 = 0.5$ ; ( $\square$ ) represents  $M = 40$  and  $\Delta\chi_1 = 0.5$ ; (+) represents  $M = 25$  and  $\Delta\chi_1 = 0.5$ ; ( $\triangle$ ) represents  $M = 10$  and  $\Delta\chi_2 = 1.0$ ; ( $\diamond$ ) represents  $M = 10$  and  $\Delta\chi_1 = 0.5$ .

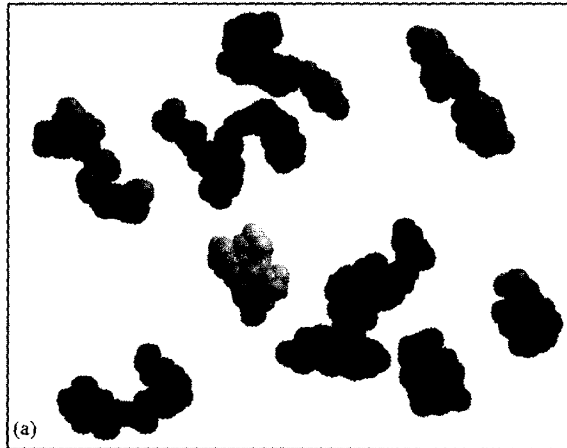


Fig. 4. A visual representation of a configuration with  $L = 50$ ,  $N = 50$  and  $M = 10$  at three different stages after a quench  $\Delta\chi = 0.5$ : (a) after 40 MCS, the configurations are still asymmetric and the polymers have not associated with other; (b) after 4 000 MCS, the polymers are in separate clumps and are kinetically arrested for long times; (c) after 40 000 MCS, the system has reached the final state with one clump remaining with all the polymers strongly interpenetrating one another.

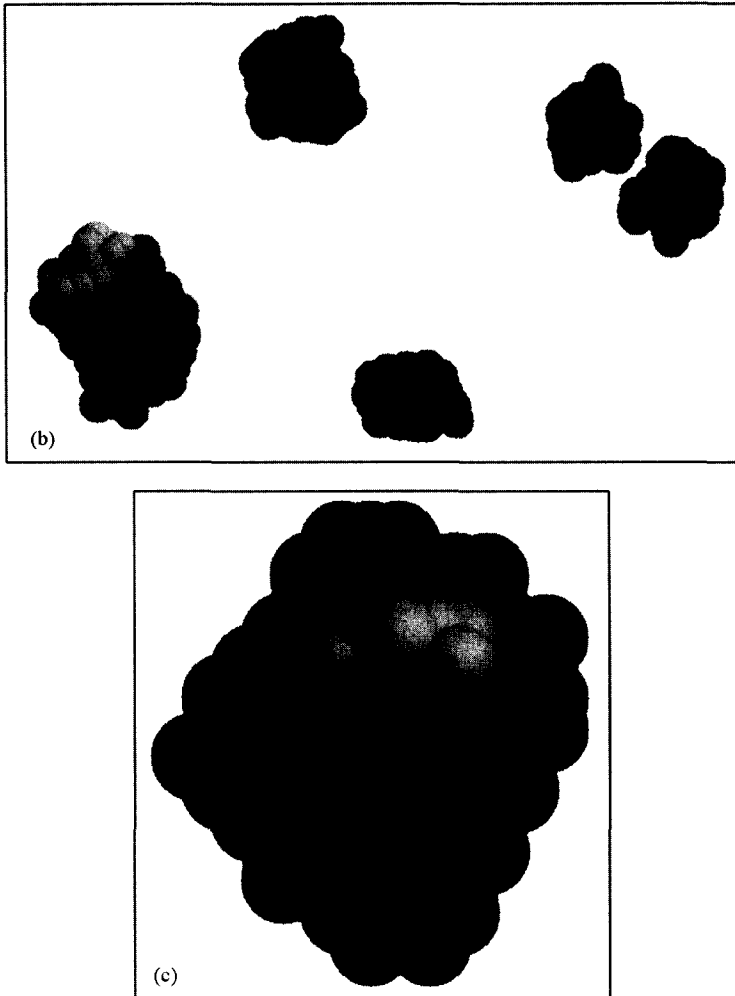


Fig. 4. Continued.

Obviously this process of aggregation, for large systems, will ultimately produce large macroscopic globules (Fig. 4(c)) that scatter light resulting in what would appear to be a milky looking appearance, finally leading to a powdery precipitate.

Thus, the overall understanding that has been developed of kinetic phenomena in polymer solutions now extends from single-coil kinetics, to mesoglobules and to macroscopic phase separation. We can now identify a number of distinct kinetic processes and envisage the laws beginning from single-chain limit [22] to multichain systems. As we have mentioned in the introduction, there is growing consensus that the single-chain collapse is a multistage process [9,10,15], but there is no such general view for the regime studied in this work. The kinetic processes for semi-dilute and more dense systems are now being intensively studied [27], and we hope that elegant and interesting results will emerge.

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