

Gaussian self-consistent approach to multichain polymer systems

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Abstract

Here we extend the Gaussian self-consistent method that has been successfully applied to the single polymer collapse problem to a polymer solution of many identical chains earlier. This method permits a complete study of the equilibrium thermodynamic properties as well as of the kinetic transformations. We discuss various aspects of the aggregation and collapse phenomena paying particular attention to the interplay between the intra- and inter-molecular degrees of freedom. We show that, at equilibrium, in part of the parameter space our equations may be reduced to those of the Flory–Huggins mean field theory. In kinetics a new phenomenon, notably the existence of a long-lived metastable state of “mesoglobules”, is found.

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1. Introduction

Polymer solutions at finite concentrations have been a subject of intensive theoretical research for many years [1,2]. They are characterised by delicately balanced interactions so that for some range of conditions the polymer chains behave as Flory coils, in others the chains are quite well packed, and there are some intermediate situations. It is worth mentioning that examples of such interesting systems include polystyrene in cyclohexane and benzene, and also poly-N-isopropylacrylamide in water [3]. The former exhibits an upper consolute point, whilst the latter exhibits a lower consolute point.

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The transition between these two regimes of Flory coil and condensed collapsed state in dilute solution is of considerable interest to scholars of statistical mechanics due to its intrinsic beauty, as well as a simple model of biopolymer folding. As a consequence the transition has been well studied for a single coil and many interesting aspects of the problem have now been elucidated. However, the connection to experiment has been much more complicated largely because of the difficulties in carrying out good experiments in very dilute solutions, and at fast enough time scales. On the other hand, numerous experiments have been reported for polymer solutions where multichain effects are relevant [4]. Thus, whilst in no manner diminishing the importance of the single-chain problem, it is of most direct practical relevance to develop a clear understanding of the equilibrium and kinetic aspects of polymer solutions of finite concentrations. We have also an additional impetus for the current study to relate it to the ongoing experiment in our laboratory by Gorelov and his colleagues [3]. The current theoretical research represents our initial attempt to interpret their interesting observation of quite stable and monodisperse mesoscopic polymer globules discovered within the two-phase coexistence region.

At present there are few options for scientists wishing to interpret such systems. For purely equilibrium issues one can apply the Flory–Huggins theory [5]. However it is well known that this theory is incomplete in various regimes. Approaches based on the scaling theory [6], on the self-consistent treatments in terms of the density variables [1] and on the Lifshitz theory [7] provide interesting advances. We note that the beginning of progress in the multichain problem may be observed in the recent work based on a single-mode variational approximation [8].

The approach that we shall develop is closely related to earlier ideas for the treatment of the single chain problem discussed by us [9] and others [10]. Essentially we replace the true intra- and inter-molecular interactions by an effective harmonic interaction matrix. The set of spring constants associated with these interactions may then be adjusted to find an optimal set using some suitable criterion. The advantages of this approach include its validity for finite size systems and relative simplicity in applications to periodic and random copolymers and semiflexible polymers [11]. We emphasize that in many practical situations [3] it may be almost impossible to access true equilibrium, and it becomes important to have a single theoretical framework that can address both equilibrium and kinetics. Our main focus thus will be to construct such a theoretical approach for this problem. Exhaustive study of the implications will be deferred for further reports of our research.

2. The multichain formalism

We shall denote by \mathbf{X}_n^a the coordinates of n th monomer in the a th chain. The Langevin equation without the hydrodynamic effect is then,

$$\zeta_b \frac{d}{dt} \mathbf{X}_n^a = - \frac{\partial H}{\partial \mathbf{X}_n^a} + \boldsymbol{\eta}_n^a(t), \quad (1)$$

where ζ_b is the bare friction constant of a monomer and the Gaussian noise is characterised by the second momentum,

$$\langle (\eta_n^a)^x(t) (\eta_n^a)^y(t') \rangle = 2k_B T \zeta_b \delta^{x,y} \delta^{a,a'} \delta_{n,n'} \delta(t-t'). \quad (2)$$

The effective free energy functional, H , of M identical chains consisting of N monomers each is given by,

$$H = \frac{k_B T}{2l^2} \sum_{a,n} (\mathbf{X}_n^a - \mathbf{X}_{n-1}^a)^2 + \frac{k_B T}{2L^2} \sum_a (\mathbf{Y}^a - \mathbf{Y})^2 + \sum_{J \geq 2} u_J \int d\mathbf{r} (\rho_\epsilon(\mathbf{r}))^J, \quad (3)$$

where we have written the virial expansion of the excluded volume interactions via the smoothed density², $\rho_\epsilon(\mathbf{r}) = (\pi\epsilon^2)^{-3/2} \sum_{a,n} \exp(-(\mathbf{X}_n^a - \mathbf{r})^2/\epsilon^2)$, and have introduced the radii of the centre of mass of the a th chain and the whole system respectively, $\mathbf{Y}^a \equiv (1/N) \sum_n \mathbf{X}_n^a$, $\mathbf{Y} \equiv (1/M) \sum_a \mathbf{Y}^a$. The first term in (3) represents the connectivity of a chain with l being the characteristic bond length, and the second one effectively introduces a soft spatial cut-off, L , onto the system³.

For simplicity we prefer to consider ring polymers, i.e. we shall have the condition $\mathbf{X}_{n+N}^a = \mathbf{X}_n^a$ for any n and a . We can also assume formal cyclicity for the radii of the centre of mass, $\mathbf{Y}^{a+M} = \mathbf{Y}^a$ for any a , which in fact is not an additional restriction since different chains are unconnected. This allows us to introduce the Fourier transforms as follows:

$$\bar{\mathbf{X}}_n^a \equiv \mathbf{X}_n^a - \mathbf{Y}^a = \sum_{q=0}^{N-1} f_n^{(-q)} \mathbf{x}_q^a, \quad \mathbf{x}_q^a = \frac{1}{N} \sum_{n=0}^{N-1} f_n^{(q)} \bar{\mathbf{X}}_n^a, \quad (4)$$

$$\bar{\mathbf{Y}}^a \equiv \mathbf{Y}^a - \mathbf{Y} = \sum_{Q=0}^{M-1} g_a^{(-Q)} \mathbf{y}^Q, \quad \mathbf{y}^Q = \frac{1}{M} \sum_{a=0}^{M-1} g_a^{(Q)} \bar{\mathbf{Y}}^a, \quad (5)$$

$$f_n^{(q)} \equiv \exp\left(\frac{2\pi i q n}{N}\right), \quad g_a^{(Q)} \equiv \exp\left(\frac{2\pi i Q a}{M}\right). \quad (6)$$

Henceforth we shall call \mathbf{x}_q^a ($q \neq 0$) the intra-molecular and \mathbf{y}^Q ($Q \neq 0$) the inter-molecular degrees of freedom respectively, with the zero modes being identically zero due to our earlier convention.

² This represents a natural way of introducing *thickness* of the polymer chain.

³ Without loss of generality we may assume the condition $\mathbf{Y} = 0$, i.e. we fix the reference point in the centre of mass of the whole system. As for the use of a soft Gaussian cut-off, it should not matter for sufficiently large system which type of the boundary conditions is imposed.

Now we have to take into account the symmetries in the system. There are only the following non-vanishing equal-time correlations,

$$\frac{1}{3} \langle \mathbf{x}_q^a(t) \mathbf{x}_q^{a'}(t) \rangle \equiv \delta^{a,a'} \delta_{-q,q} \mathcal{F}_q(t), \quad \frac{1}{3} \langle \mathbf{y}^Q(t) \mathbf{y}^Q(t) \rangle \equiv \delta^{-Q,Q} \Gamma^2(t)/M. \quad (7)$$

The two-point correlations of monomer positions, $D_{n_1, n_2}^{a_1, a_2} \equiv \frac{1}{3} \langle (\mathbf{X}_{n_1}^{a_1} - \mathbf{X}_{n_2}^{a_2})^2 \rangle$, may be reduced via,

$$D_{n_1, n_2}^{a_1, a_2} = \delta^{a_1, a_2} D_{n_1 - n_2} + 2(1 - \delta^{a_1, a_2})(R_g^2 + \Gamma^2), \quad (8)$$

where we have introduced the notations of Ref. [9] for the correlations of monomer positions, D_k , and the mean squared radius of gyration, R_g^2 , of a chain,

$$D_k \equiv \sum_{q=1}^{N-1} d_k^{(q)} \mathcal{F}_q, \quad R_g^2 \equiv \sum_{q=1}^{N-1} \mathcal{F}_q, \quad d_k^{(q)} \equiv 2 \left(1 - \cos \frac{2\pi qk}{N} \right). \quad (9)$$

Finally, the total radius of gyration is simply,

$$\mathcal{R}_g^2 \equiv \frac{1}{2N^2 M^2} \sum_{(n, a), (n', a')} \langle (\mathbf{X}_n^a - \mathbf{X}_{n'}^{a'})^2 \rangle = R_g^2 + \frac{M-1}{M} \Gamma^2. \quad (10)$$

Performing derivations analogous to those of Ref. [9] we arrive at the expression for the mean energy,

$$\mathcal{E} = \sum_{J \geq 2} \hat{u}_J \sum_{\{(a, n)\}} (\det \Delta_\varepsilon^{(J-1)})^{-3/2}, \quad \hat{u}_J \equiv (2\pi)^{-3(J-1)/2} u_J, \quad (11)$$

where we have used the shortcut notation $\{(a, n)\} \equiv \{(a_1, n_1) \neq (a_2, n_2) \neq \dots \neq (a_J, n_J)\}$. Here $\Delta^{(J-1)}$ is the matrix of size $J - 1$ with the elements

$$(\Delta_\varepsilon^{(J-1)})_{ij} = D_{n_i, n_{i+1}}^{a_i, a_{i+1}} + (1 + \delta_{ij})\varepsilon^2/2, \quad (12)$$

$$D_{n_1, n_2, n_3, n_4}^{a_1, a_2, a_3, a_4} = \frac{1}{2} (D_{n_1, n_4}^{a_1, a_4} + D_{n_2, n_3}^{a_2, a_3} - D_{n_1, n_3}^{a_1, a_3} - D_{n_2, n_4}^{a_2, a_4}). \quad (13)$$

Similar calculations for the entropy give,

$$\mathcal{S} = \frac{3}{2} k_B M \left(\sum_{q=1}^{N-1} \log \mathcal{F}_q - \frac{ND_1}{l^2} + \frac{M-1}{M} \left(\log \Gamma^2 - \frac{\Gamma^2}{L^2} \right) \right). \quad (14)$$

Keeping the excluded volume terms up to the three-body interactions and with the help of (12) and (13) we obtain the explicit expression for the mean energy,

$$\begin{aligned} \frac{\mathcal{E}}{MN} = & \hat{u}_2 \left(\sum_k (D_k + \varepsilon^2)^{-3/2} + (M-1)N(2R_g^2 + 2\Gamma^2 + \varepsilon^2)^{-3/2} \right) \\ & + \hat{u}_3 \left(\sum_{k_1 \neq k_2} (D_{k_1} + \varepsilon^2)(D_{k_2} + \varepsilon^2) - (D_{k_1, k_2} + \varepsilon^2/2)^2 \right)^{-3/2} \end{aligned}$$

$$\begin{aligned}
& + 3(M-1)N \sum_k ((D_k + \varepsilon^2)(2R_g^2 + 2\Gamma^2 + \varepsilon^2) - (D_k + \varepsilon^2)^2/4)^{-3/2} \\
& + (M-1)(M-2)N^2 (\frac{3}{4}(2R_g^2 + 2\Gamma^2 + \varepsilon^2)^2)^{-3/2}, \tag{15}
\end{aligned}$$

where $D_{k_1, k_2} \equiv \frac{1}{2}(D_{k_1} + D_{k_2} - D_{k_1 - k_2})$. Thus, we have derived the variational free energy, $\mathcal{A} = \mathcal{E} - T\mathcal{S}$, as a function of the variables \mathcal{F}_q and Γ . Its minimisation with respect to them gives the equilibrium free energy \mathcal{A}_{eq} . It is also straightforward to extract the equilibrium thermodynamic functions such as the chemical potential and the osmotic pressure,

$$\mu_{eq} = \left(\frac{\partial \mathcal{A}}{\partial M} \right)_{eq}, \quad \Pi_{eq} = - \left(\frac{\partial \mathcal{A}}{\partial L^3} \right)_{eq} = k_B T \frac{M}{L^5} \Gamma^2. \tag{16}$$

Proceeding from the Langevin equation (1) in the way described in detail in Refs. [9,11] it is possible to derive the kinetic equations for our dynamic variables (7). These may be written as follows:

$$\frac{\zeta}{2} \frac{d}{dt} \mathcal{F}_q = - \frac{2}{3} \mathcal{F}_q \frac{\partial \mathcal{A}}{\partial \mathcal{F}_q}, \quad \zeta \frac{d}{dt} \Gamma = - \frac{1}{3} \frac{\delta \mathcal{A}}{\delta \Gamma}, \quad \zeta \equiv NM\zeta_b. \tag{17}$$

These equations represent, along with Eqs. (15) and (14), some of the key results of our treatment.

3. Thermodynamic limit

Now we consider the thermodynamic limit $M, L \rightarrow \infty$, $M/L^3 = const$. The free energy may be decomposed into the three parts,

$$a \equiv \lim_{L, M \rightarrow \infty} \frac{\mathcal{A}}{L^3} = a_{inter}[\Gamma] + a_{inter-intra}[\Gamma, \mathcal{F}_q] + a_{intra}[\mathcal{F}_q]. \tag{18}$$

To obtain a finite answer we should keep the concentration, $c = NM/L^3$, and the ratio $\gamma \equiv L^{-2}\Gamma^2$ finite. The inter-intramolecular term non-trivially renormalizes the interaction parameters in a_{inter} , and we obtain

$$\frac{a'_{inter}}{k_B T} = - \frac{3}{2} \frac{c}{N} \log((MN/c)^{2/3} \gamma) + \frac{3}{2} \frac{c\gamma}{N} + v_2 c^2 \gamma^{-3/2} + v_3 c^3 \gamma^{-3}, \tag{19}$$

where we have introduced the rescaled variables

$$v_J \equiv J^{-3/2} \frac{\hat{u}_J}{k_B T} \alpha_J, \quad \alpha_2 \equiv \left(1 + 3 \frac{\hat{u}_3}{\hat{u}_2} \sum_k (D_k + \varepsilon^2)^{-3/2} + \dots \right), \quad \alpha_3 = 1. \tag{20}$$

Minimisation of (19) with respect to γ yields

$$\frac{1}{N\gamma} = \frac{1}{N} - v_2 \frac{c}{\gamma^{5/2}} - 2v_3 \frac{c^2}{\gamma^4}. \tag{21}$$

We can consider two simple limiting regimes:

(a) If $|v_2|c \ll 1/N, v_3c^2 \ll 1/N$ we obtain the solution $\gamma \simeq 1 + N(v_2c + 2v_3c^2)$. In this regime we can solve the equations for \mathcal{F}_q first, ignoring the coupling with Γ , and substitute the result into (20).⁴ Then we obtain the Flory–Huggins expressions for the osmotic pressure and the free energy:

$$\frac{\Pi_{FH}}{k_B T} = \frac{c}{N} \gamma = \frac{c}{N} + v_2 c^2 + 2v_3 c^3, \tag{22}$$

$$\frac{a_{FH}}{k_B T} = \frac{c}{N} \log \frac{c}{c_0} + v_2 c^2 + v_3 c^3, \tag{23}$$

where $c_0 = MN e^{-3/2}$ is an irrelevant constant removed by consideration of the free energy of mixing. Now let us go back to the equations for \mathcal{F}_q for a moment. These have the same form as the equations for one chain with the substitution $\hat{u}_2 \rightarrow \hat{u}_2 + 2^{-3/2} 3\hat{u}_3 c \gamma^{-3/2}$. Since we have $c\hat{v}_2 \ll \hat{v}_3$ the coupling between both types of the variables indeed may be neglected there.

(b) If on the contrary $|v_2|c > 1/N$, i.e. N is large, we can solve (21) first ignoring the coupling in (20). The solution is $\gamma \simeq (2(v_3/|v_2|c)^{2/3})$. This corresponds to the formation of an insoluble precipitate with the free energy and osmotic pressure,

$$\frac{a_{prec}}{k_B T} = -\frac{|v_2|^2}{4v_3} c + O\left(\frac{1}{N}\right), \quad \frac{\Pi_{prec}}{k_B T} = \frac{c^{5/3}}{N} \left(\frac{2v_3}{|v_2|}\right)^{2/3} + O\left(\frac{1}{N^2}\right). \tag{24}$$

If we substitute the above γ back to the equations for \mathcal{F}_q we shall see that the inter-chain repulsion is noticeably weakened.

4. Discussion

We refer the reader to our earlier works [9,11] for the details⁵ of the numerical procedure adopted for solving Eqs. (17).

⁴It is interesting to note here that at $\varepsilon = 0$ in the repulsive regime there is a strong cancellation of the two-body attraction by the inter–intra-chain three-body repulsion. Indeed for large N we have the nearly constant solution [9], $D \simeq \frac{2}{3} (|\hat{u}_2|/2\hat{u}_3 N)^{-2/3}$, that gives rise to the result $\alpha_2(\varepsilon) = \alpha_2(0) + \alpha'_2 \varepsilon^2 + \dots$ with the coefficients $\alpha_2(0) \simeq 0.025$ and $\alpha'_2 \simeq 0.35 (|\hat{u}_2|/N\hat{u}_3)^{2/3}$. Thus, only about 2.5% of the original attraction remains in the absence of the chain thickness.

⁵We shall use the following choice of units of measurement: $k_B T = 1, l = 1$ and $\zeta_b = 1$. Also the third virial coefficient is taken equal to $u_3 = 10$.

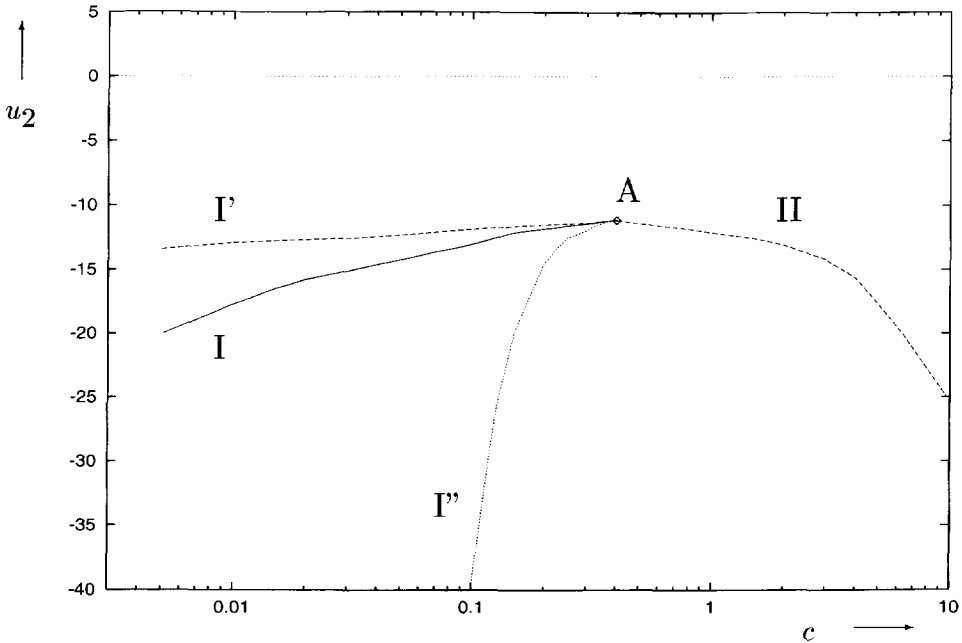


Fig. 1. The phase diagram of a homopolymer solution in variables of the concentration c and the second virial coefficient u_2 . Curve I corresponds to first-order phase transition and curve II to continuous transition. Point A is a critical point. Curves I' and I'' are "spinodals". The region of phase coexistence lies below curves I' and II. Here $N = 100$ and $L = 100$.

At equilibrium we obtain the phase diagram presented in Fig. 1. For positive u_2 chains exist in the extended coil state. In the attractive regime, $u_2 < 0$, in a very narrow region at low concentrations (above and to the left of curve I' in Fig. 1) chains collapse individually, forming a gas of non-interacting globules. The narrowness of this region is responsible for the difficulties in experimental observation of the single polymer collapse. The area below the curves I' and II corresponds to the two-phase coexistence region where $\partial^2 \mathcal{A} / \partial c^2$ is negative, and point A denotes the critical point. We agree with the Flory–Huggins theory with respect to the laws describing the boundary of the coexistence region for sufficiently small thickness parameter ε .

We may remark that the variational method allows one to obtain only pure thermodynamically dominant states which could correspond either to stable (global minimum of \mathcal{A}) or metastable (local minima) states. Thus, we have two such states here: a gas of globules above curve I, and a dense macroscopic precipitate of aggregated chains below and to the right of the first order transition curve I. Beyond curve II only the macroscopic precipitate can exist which may be viewed simply as a macroscopic dense globular state filling most of the available space. In the region between I and the "spinodal" I'' at the same concentration the gas may exist as a metastable state, as well the metastable precipitate may exist between I and I'. The crucial observation is that $\partial^2 \mathcal{A} / \partial c^2$ is negative at all of these branches in

the coexistence region. Thus, we should use the Maxwell construction that joins the concave part of the free energy by a straight line. In doing so we separately treat the thermodynamically stable branches and metastable ones. This procedure results in the following picture of the two-phase coexistence region.

At equilibrium there is a coexistence of the low-density gas of globules and the high-density precipitate just as in the Flory–Huggins theory. However, in the region between I and I' there appears a metastable state formed by an interacting gas of “mesoglobules” obtained by collapse of a few distinct chains, in principle, coexisting with a gas of single chain globules. For the mesoglobules to coalesce to a macroscopic aggregate, a potential barrier must be overcome. Thus, there should be a critical size of the mesoglobules associated with the nucleation process accompanying this first-order transition. Similarly, between I and I' there is a metastable very high-density precipitate coexisting with a very low-density precipitate.

In Fig. 2 we draw the quantities Γ^2 and R_g^2 across the transition curve I at different free energy branches. At I the inter-chain distance, Γ , drops dramatically from the magnitude of order L to a much smaller value corresponding to the dense precipitate. In Fig. 3 we present $L^{-2}\Gamma^2$ as function of the concentration. This figure confirms that the two limits discussed at the end of Section 3 are satisfactory, and also that for the precipitate $\gamma \sim c^{2/3}$ reaffirming the idea of the macroscopic dense state. On the

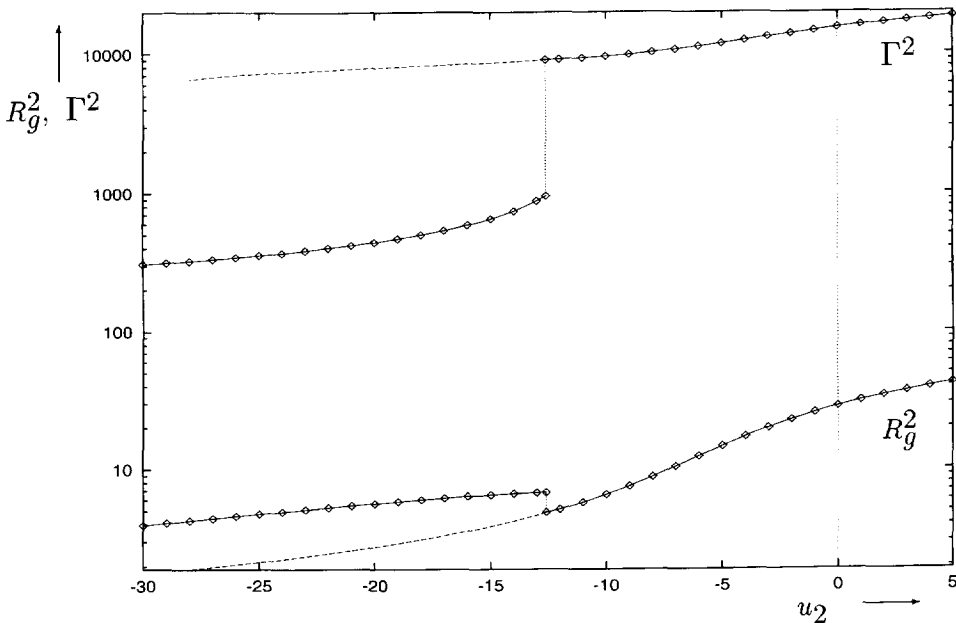


Fig. 2. Plots of the mean squared inter-chain distance Γ^2 and the mean squared radius of gyration of a chain R_g^2 vs. the second virial coefficient u_2 . Here and below solid curves represent observables in the global free energy minimum and dashed curves, in metastable minima. Here $N = 100$, $L = 100$ and $c = 0.12$.

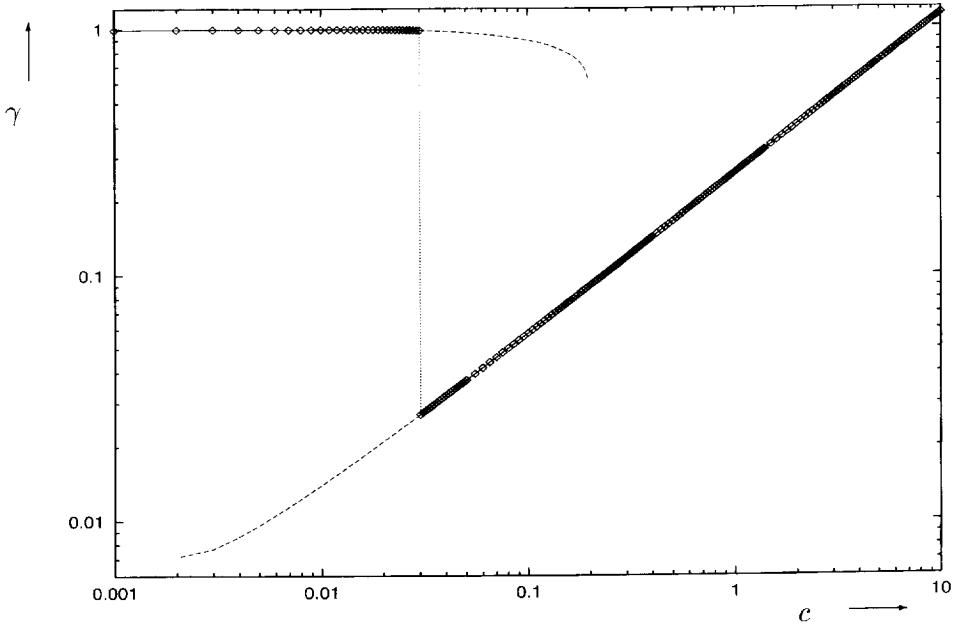


Fig. 3. Plot of the quantity γ vs. the concentration c for $N = 100$, $L = 100$ and $u_2 = -15$. For the aggregate, in the right-hand side of the figure, γ scales as, $\gamma \sim c^{2/3}$, corresponding to space filling.

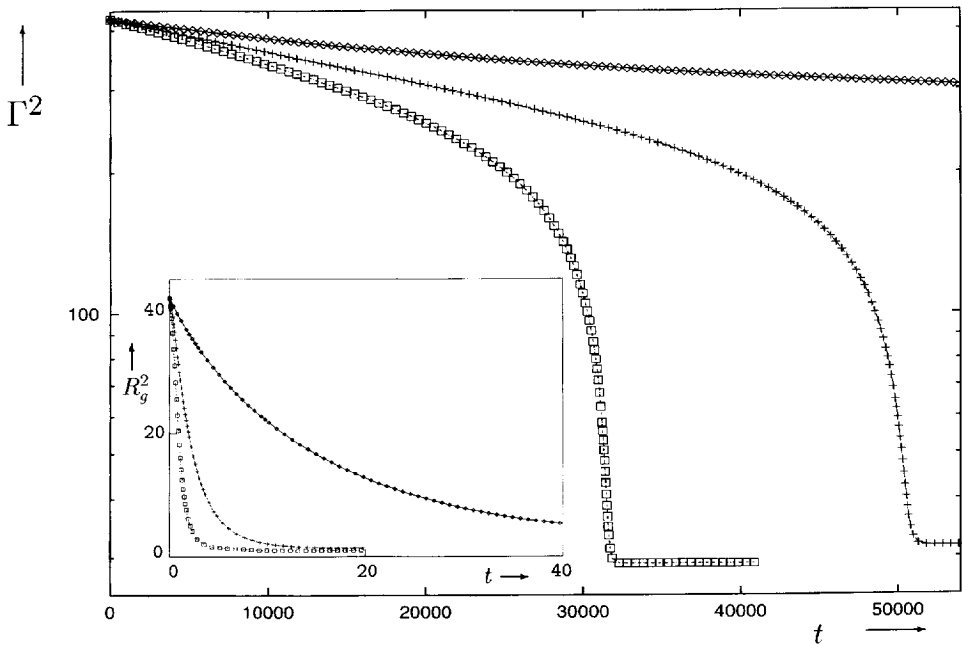


Fig. 4. Evolution of the mean squared inter-chain distance Γ^2 and the mean squared radius of gyration of a chain R_g^2 in kinetics after the quench from $u_2^{(i)} = 5$ to $u_2^{(f)} = -17$ (diamonds), -40 (pluses) and -60 (quadrangles) respectively. Here $N = 100$, $L = 20$ and $c = 0.2$.

contrary, the intra-chain distance, R_g , grows markedly at the transition curve I. Really, chains tend to swell once they have formed a larger globule approaching a nearly ideal coil conformation. It is interesting to comment that R_g is very weakly dependent of the concentration c at both branches as may be established from our analysis in section 3.

Finally, in Fig. 4 two kinetic processes after an instantaneous quench from the extended coil to the two-phase coexistence region are depicted. It can be seen from Eqs. (17) and (18) that the characteristic time-scale of inter-chain conformational changes is of order $\zeta_b c L^2$. In our particular example the kinetics of aggregation is about 10^4 times slower than that of a single chain collapse. This may explain very long time-scales observed in some of recent experiments [4]. Also we note that the “mesoglobules” always appear in kinetics as a transient non-equilibrium state, and moreover the system may be trapped in that metastable state for a long time in kinetics after quenches to a point above “spinodal” I’.

5. Conclusion

The general conclusion of this work is clear. Thus, it is now possible to construct a fundamental theory of multichain systems for both good and poor solvent conditions. This approach permits us to study the microstructure and kinetic phenomena. In some case our method leads to the well known Flory–Huggins theory of polymer solutions, thereby providing a rational route to that set of results. However, we can find more rich phenomena that are of considerable interest in experiment. For example in some conditions it is possible to form metastable very long-lived aggregates of a fairly fixed size [3]. These phenomena have not yet been investigated in a systematic manner and we hope to return to their study at a later date.

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