

Theoretical and Experimental Approaches to Kinetics at the Collapse Transition of a Homopolymer

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Abstract

We discuss some recent theoretical studies of the kinetics of the collapse transition in homopolymers. An isolated polymer is modelled using computer simulation, and a time-dependent mean field theory. The mean-field theory is analysed analytically for early stages, and for short polymers the equations are studied numerically. The results of simulation and theory are compared yielding, we argue, a consistent physical picture. Quantitative comparisons are not yet given, but seem relatively promising.

1 Introduction

We here discuss some recent ideas on the kinetics of synthetic polymers and biopolymers such as proteins and DNA that have emerged as a result of simulation, theory and experiment. There are, of course, different behaviours between these different systems, but in our discussions we shall emphasize the elements that unify them.

The basic problem is well known. Thus, as a function of temperature, salinity, or some other such parameter it is possible to cause the polymer to undergo a precipitous change from an open extended state to a collapsed globular form. However the kinetic processes and laws that govern this transition have long been a subject of interest, and to a large degree, uncertainty. Various researchers have striven to elucidate the protein folding transition using spin-glass methods [1] and others [2], mainly focussing on the equilibrium aspects of the problem. Others have sought to approach the problem less directly, in the belief that a complete understanding of the collapse kinetics of homopolymers will be invaluable in elucidating the process for more complex biopolymers. Thus in the last few years, various laboratories have begun to make progress in understanding the kinetics of the simple homopolymer collapse using simulation [3, 4] and theory [5] though experimental progress [6, 7] has been slower.

In this paper we shall discuss the results of some recent calculations using simulation and theory. The basic kinetic stages are discussed at both qualitative and theoretical levels, confirming the predictions of various simulation studies. In particular we believe that there are universal kinetic exponents associated with these phenomena, and we [5] and others [4] have attempted to calculate them. We also make a brief comment on the state of the experimental work that aims to confirm these theories.

2 Method

We begin by noting that two previous papers [8, 5] contain details of some of the basic notations that we shall rely on here, and so our main focus will be on recent results.

In all our theoretical and simulation work we assume that the system may be described using the Langevin equation, possibly including hydrodynamic interactions. In addition we assume a model such as that discussed some time ago by the school of Edwards [9]. Thus, we have replaced a Kuhn length segment by a bead and spring, reflecting the statistical independence of successive units, and assumed that effective interactions between the polymer units, including solvent interactions, can be represented by van der Waals interactions for simulations and a virial expansion in the case of theoretical calculations. One may regard the virial expansion, expressed in terms of a series of delta functions, as being equivalent, at long length scales, to the van der Waals potential interactions where the virial coefficients between beads are calculated and fixed to cause a Flory coil, theta or collapsed globule to be stable. From the point of view of theory it is convenient to work in the space of the Fourier transformed variables where, we emphasize, the index refers to momenta conjugate to the internal metric of the chain, rather than the physical space in which the polymer is embedded, and moves. We define these variables using cyclic boundary conditions in which, $x_{m+N} = x_m$, $m = 0, \dots, N - 1$. This leads to the Fourier series,

$$\mathbf{x}_q = \frac{1}{N} \sum_{n=0}^{N-1} \exp \frac{i2\pi nq}{N} \mathbf{x}_n, \quad \mathbf{x}_n = \sum_{q=0}^{N-1} \exp \frac{-i2\pi nq}{N} \mathbf{x}_q. \quad (1)$$

The equations for open polymers differ from those for cyclic polymers in minor ways. In all cases we describe the connectivity of the coil in terms of a spring term which is written,

$$V^{(s)} = \frac{k}{2} \sum_n |\mathbf{r}_n - \mathbf{r}_{n-1}|^2. \quad (2)$$

To this we add the effective interactions, $V^{(b)}$, that represent polymer-unit–polymer-unit, polymer–solvent and solvent–solvent interactions. For the purposes of simulation we may represent this as the Lennard–Jones potential,

$$V^{(b)} = \sum_{nn'} \left(\frac{b_1}{|\mathbf{r}_n - \mathbf{r}_{n'}|^{12}} - \frac{b_2}{|\mathbf{r}_n - \mathbf{r}_{n'}|^6} \right) \quad (3)$$

and we have calculated the virial coefficients, u_n , for $n = 2, 3$ by integration of the appropriate expressions

$$u_2 = - \int d\mathbf{r} f(\mathbf{r}), \quad u_3 = -\frac{1}{3} \int d\mathbf{r} d\mathbf{r}' f(\mathbf{r})f(\mathbf{r} - \mathbf{r}')f(\mathbf{r}'), \quad (4)$$

$$f(\mathbf{r}) = 1 - \exp\left(-\frac{V^{(b)}(\mathbf{r})}{k_B T}\right). \quad (5)$$

In our simulation we can therefore first equilibrate polymers in the Flory state, then change the sign of u_2 , and calculate the non-equilibrium averages representing the kinetics of collapse. These potential interactions are useful for simulations, but overly detailed for the purpose of theory, so they may be further simplified by first rewriting in terms of the density operators, and then reexpressing these in terms of the delta functions, assuming that the finite size of the beads may be neglected. The result, including up to two- and three-body interactions is,

$$V = V_2 + V_3 = u_2 \sum_{mm'} \delta(\mathbf{x}_m - \mathbf{x}_{m'}) + u_3 \sum_{mm'm''} \delta(\mathbf{x}_m - \mathbf{x}_{m'})\delta(\mathbf{x}_{m'} - \mathbf{x}_{m''}), \quad (6)$$

where u_2, u_3 are virial coefficients and $m \neq m' \neq m''$.

We accept in this work that the problems we study are well represented by the Langevin equation which may be written in terms of the transformed variables as,

$$\dot{x}_q^\alpha(t) = \sum_{\alpha', q'} H_{qq'}^{\alpha\alpha'} [x(t)] \left(-k_{q'} x_{q'}^{\alpha'} - \frac{\partial V}{\partial x_{-q'}^{\alpha'}} + \eta_{q'}^{\alpha'}(t) \right), \quad (7)$$

where hydrodynamic effects may be incorporated via $H_{qq'}^{\alpha\alpha'}$, the Oseen hydrodynamic interaction tensor, and the noise has the second order correlation function,

$$\langle \eta_q^\alpha(t) \eta_{q'}^{\alpha'}(t') \rangle = (H^{-1})_{qq'}^{\alpha\alpha'} 2k_B T \delta(t - t') \delta_{\alpha\alpha'} \delta_{-qq'}. \quad (8)$$

This mobility tensor describes the relation between generalised velocities and forces $v_n^\alpha = \sum_{\alpha' n'} H_{nn'}^{\alpha\alpha'} F_{n'}^{\alpha'}$.

We have decided to begin our studies by neglecting the hydrodynamic effects, and therefore we shall assume a diagonal mobility tensor in which,

$$H_{qq'}^{\alpha\alpha'} = \zeta_q^{-1} \delta_{\alpha\alpha'} \delta_{qq'}, \quad (9)$$

and $\zeta_q = \zeta N$. The reasons are partly practical in the sense that it is important to understand the basic phenomena for a simple chain before introducing further complications. However, there is in any case, reason to believe that the basic picture is unchanged by inclusion of the Oseen terms [3, 8, 5].

The Gaussian self-consistent approach involves introduction of a time – dependent effective potential, $\Delta V_q(t)$, via the Gaussian stochastic ensemble,

$$\zeta_q \dot{x}_q^\alpha(t) = -\Delta V_q(t)x_q^\alpha + \eta_q^\alpha(t), \quad (10)$$

$$\langle \eta_q^\alpha(t) \eta_{q'}^{\alpha'}(t') \rangle = 2k_B T \zeta_q \delta(t-t') \delta_{\alpha\alpha'} \delta_{-qq'} \quad (11)$$

that may be considered as an approximation to the exact equations (7,8).

Let us introduce the following correlation functions,

$$\mathcal{F}_q(t) = \frac{1}{3} \langle | \mathbf{x}_q(t) |^2 \rangle, \quad (12)$$

$$\mathcal{G}_q(t) = \frac{1}{3} \langle \mathbf{x}_{-q}(0) \mathbf{x}_q(t) \rangle, \quad (13)$$

and also the Fourier transformed function

$$\mathcal{D}_m(t) = \frac{1}{3} \langle (\mathbf{x}_m(t) - \mathbf{x}_0(t))^2 \rangle = \sum_q d_{q,m} \mathcal{F}_q(t) \quad (14)$$

where $d_{q,m} = 2 - 2 \cos \frac{2\pi qm}{N}$. We assume space-isotropic initial conditions and consequently all space components give equal contributions.

In reference [5] we have derived the non-equilibrium equations of motion,

$$\frac{\zeta_q}{2} \dot{\mathcal{F}}_q(t) = k_B T - \Delta V_q(t) \mathcal{F}_q(t), \quad (15)$$

$$\zeta_q \dot{\mathcal{G}}_q(t) = -\Delta V_q(t) \mathcal{G}_q(t). \quad (16)$$

The self-consistent potential is determined from the equation

$$-\zeta_q \Delta V_q(t) = k_q - \hat{u}_2 \sum_{mm'} \frac{d_{q,m-m'}}{\mathcal{D}_{m-m'}^{5/2}(t)} - \hat{u}_3 \sum_{mm'm''} \frac{d_{q,m_1} \mathcal{D}_{m_2}(t) + d_{q,m_2} \mathcal{D}_{m_1}(t) - 2e_{q,m_1 m_2} \mathcal{E}_{m_1 m_2}(t)}{(\mathcal{D}_{m_1}(t) \mathcal{D}_{m_2}(t) - \mathcal{E}_{m_1 m_2}^2(t))^{5/2}}, \quad (17)$$

where $m_1 = m - m'$, $m_2 = m'' - m'$ and $\hat{u}_2 = u_2/(2\pi)^{3/2}$, $\hat{u}_3 = u_3/(2\pi)^3$, and we have used the notations,

$$\mathcal{E}_{m_1 m_2} = \frac{1}{2}(\mathcal{D}_{m_1 - m_2} - \mathcal{D}_{m_1} - \mathcal{D}_{m_2}), \quad (18)$$

$$e_{q, m_1 m_2} = \frac{1}{2}(d_{q, m_1 - m_2} - d_{q, m_1} - d_{q, m_2}). \quad (19)$$

One can derive a relation that is equivalent to the differential equation (15),

$$\mathcal{F}_q(t) = \frac{k_B T}{\Delta V_q(t)} + \left(\mathcal{F}_q(0) - \frac{k_B T}{\Delta V_q(t)} \right) G_q^{2V}(t), \quad (20)$$

where the Green function is defined as,

$$G_q^V(t) = \exp \left(-\frac{1}{\zeta_q} \int_0^t dt_2 \Delta V_q(t_2) \right). \quad (21)$$

Equations (17) and (20) may be solved numerically and are analysed later in this paper.

3 Kinetics across the collapse transition from simulation and theory

Here we intend to present some results that have been obtained from simulation and theory, and discuss the degree of correspondence between them. Let us begin by saying that, so far, the only agreement that we have established between the two approaches is of a qualitative nature. We shall comment on this later, and give reasons for it.

Firstly, the simulations indicate that there may be at least two kinetic stages following a rapid quench into the collapsed globule region of the phase diagram. Thus, at early stages we find spontaneous formation of small locally collapsed globules, in agreement with the works of references [3, 4]. We believe that these globules, possess some average period along the metric of the chain that depends on the depth of the quench and other parameters of the system. This picture originates from a short-time analysis of the equations (15,17) where we find that a sort of spinodal decomposition in the metric of the chain is predicted. This is an interesting and novel phenomenon because,

here, the unstable modes correspond to a range of q -values, where q is the momentum index conjugate to the residue number, n . In the simulations these globules grow rapidly, consuming the slack chain that constitutes the Flory coil, that is distributed around about them. In Fig. 1 we exhibit an instantaneous configuration from the simulation for an open polymer. The slack polymer of the Flory coil state has been gathered into locally collapsed globules that grow as a function of time, as the overall radius of the polymer chain decreases. However, when the excess chain is consumed, and indeed this occurs quite rapidly, we find that the small collapsed globules must now grow against the tension of the chain, including restraining terms that arise from the chain entropy. This produces a slowing in the rate of collapse, observable as the commencement of the second regime. We may also note that this “tense” chain of locally collapsed beads may be expected to have an effective Flory exponent at short distances ($\nu = 1/3$) and another exponent, reflecting a more linear state (probably $\nu = 1$) at longer distances along the chain. Besides the simulation results in the theory we may see many of these basic phenomena in our study of the self-consistent equations, (17,20).

To understand the early time phenomena we may consider linearization of equation (15), with parameters $\hat{u}'_2 < 0$, $\hat{u}_3 > 0$ appropriate for a collapsed state, around the initial Flory state with $\hat{u}_2 > 0$, $\hat{u}_3 > 0$. This sort of analysis has been discussed in more detail in reference [5], which the interested reader may consult for mathematical details. We assume that the initial state before the quench is at equilibrium, and therefore \mathcal{F}_q satisfies the equilibrium equation. Then we suddenly change the second virial coefficient by the amount $\Delta\hat{u}_2 = \hat{u}'_2 - \hat{u}_2 < 0$. As a consequence of the quench, the system begins to evolve away from the equilibrium Flory coil. At small times the deviation $\Delta\mathcal{F}_q(t)$ from the initial value $\mathcal{F}_q^{(e)}[\hat{u}_2, \hat{u}_3]$ is small and one may linearize the equation near the initial equilibrium state. The resulting linear equation may then be analysed to determine the early stages of kinetics. For small t the solution may be sought for in the form

$$\Delta\mathcal{F}_q = \mathcal{A}_q(1 - e^{-\lambda_q t}) \simeq B_q t + C_q \frac{t^2}{2} + \dots, \quad \lambda_q \simeq -C_q/B_q \quad (22)$$

because the deviation at the initial moment $\Delta\mathcal{F}_q(0)$ must vanish. We find the following expressions

$$\frac{\zeta}{2} B_q = \Delta\hat{u}_2 \mathcal{F}_q^{(e)} \sum_{mm'} \frac{d_{qm_1}}{\mathcal{D}_{m_1}^{(e) 5/2}}, \quad (23)$$

$$\begin{aligned}
\frac{\zeta}{2}C_q &= -\Delta V_q^{(e)}B_q + \Delta\hat{u}_2B_q \sum_{mm'} \frac{d_{qm_1}}{\mathcal{D}_{m_1}^{(e)5/2}} - \frac{5}{2}\hat{u}'_2\mathcal{F}_q^{(e)} \sum_{mm'} \frac{d_{qm_1}B_{m_1}}{\mathcal{D}_{m_1}^{(e)7/2}} \\
&- \hat{u}_3\mathcal{F}_q^{(e)} \left[\frac{5}{2} \sum_{mm'm''} \frac{d_{qm_1}\mathcal{D}_{m_2}^{(e)} + d_{qm_2}\mathcal{D}_{m_1}^{(e)} - 2e_{qm_1m_2}\mathcal{E}_{m_1m_2}^{(e)}}{(\mathcal{D}_{m_1}^{(e)}\mathcal{D}_{m_2}^{(e)} - \mathcal{E}_{m_1m_2}^{(e)2})^{7/2}} \right. \\
&\quad \left. (\mathcal{D}_{m_2}^{(e)}B_{m_1} + \mathcal{D}_{m_1}^{(e)}B_{m_2} - 2\mathcal{E}_{m_1m_2}^{(e)}B_{m_1m_2}) \right. \\
&\quad \left. - \sum_{mm'm''} \frac{d_{qm_1}B_{m_2} + d_{qm_2}B_{m_1} - 2e_{qm_1m_2}B_{m_1m_2}}{(\mathcal{D}_{m_1}^{(e)}\mathcal{D}_{m_2}^{(e)} - \mathcal{E}_{m_1m_2}^{(e)2})^{5/2}} \right], \tag{24}
\end{aligned}$$

where the standard notations

$$B_m = \sum_q d_{qm} B_q, \quad B_{m_1m_2} = \sum_q e_{qm_1m_2} B_q$$

have been used.

These formulae may be subjected to straightforward numerical study. We work in terms of dimensionless variables. The plot of the first correction, B_q , is presented in the Fig. 2. This quantity is always negative indicating that the size of the system decreases during the collapse transition. The second correction C_q however changes sign for some range of q for given \hat{u}'_2, \hat{u}_3 . The negative region corresponds to an instability where the appropriate modes grow exponentially fast. The only term in (24) that contributes to the instability at sufficiently small q is the one that is linear in u'_2 . A separate and positive, 2-body contribution, comes from the term proportional to $-\Delta u_2$ though it is much smaller in magnitude in this region of q . In Fig. 3 we present a typical plot of the λ_q dependence. One can see that the instability disappears if u'_2 is sufficiently small or u_3 is sufficiently large compared to u'_2 .

For the quench regime with unstable growth we can see that there is a process akin to spinodal decomposition. Thus, at this early stage of exponential growth we find that, with increasing time, the modes with wavelengths between the shortest and the least unstable contribute increasingly to the configuration of the collapsing polymer leading, finally, to a chain of locally collapsed globules.

Another approach is to numerically solve the self-consistent equations (20,17). This has an obvious advantage that it is valid for arbitrary times, and thus allows one to probe all stages of the collapse. However the solution of such nonlinear equations is a significant computational task for polymers with realistic degree of polymerization.

To begin with we take a positive u_2 and find $\Delta V_q(0)$ and $\mathcal{F}_q(0) = k_B T / \Delta V_q(0)$ as solutions of the equilibrium self-consistency equation. Then at the next time step we change to a new negative value of the second virial coefficient, u_2' , and evaluate the functions $\Delta V_q(t)$ and $\mathcal{F}_q(t)$ iteratively at each further time step as solutions of the time-dependent equations. Finally, after some number of steps the system tends to the new equilibrium state corresponding to a collapsed globule. In Fig. 4 we present both the initial and the final distributions of ΔV_q . From the scaling $\Delta V_q \propto (q/N)^{2\beta}$ at small q one can extract the exponent ν that is connected with β as $\nu = \beta - 1/2$. Initially we find a fair ¹ agreement with the Flory value $\nu = 3/5$ for sufficiently large polymers, but the final value is somewhat larger than the expected $\nu = 1/3$ for the degrees of polymerization that we consider.

In Fig. 5 we plot the radius of gyration square $R_g^2(t) = \frac{1}{2N^2} \sum_{nn'} \langle (\mathbf{x}_n(t) - \mathbf{x}_{n'}(t))^2 \rangle$ against time. The overall change of this quantity may be roughly estimated as $R_g^2(0)/R_g^2(\infty) \propto N^{2(3/5-1/3)}$. The time evolution of the correlation function $\mathcal{D}_m(t)$ is shown in Fig. 6. For a quantitative analysis it is more appropriate to consider the correlation function of the Fourier modes. Let us define the time dependent exponents, $\beta(t)$, by the scaling law $\mathcal{F}_q(t) \propto q^{-2\beta(t)}$ and calculate $\beta(t)$ independently for small and large values of q [10]. We know that the small- q limit gives the chain conformation at large distances along the chain, whilst large- q determines the conformation of beads that are close to each other on the chain. For the large- q modes the exponent, presented in Fig. 7, very rapidly reaches a value smaller than the θ -point one. This corresponds to a rapid local collapse. The behaviour at small q , which we draw in Fig. 8, is quite different. Firstly, the exponent quickly increases from the Flory value up to a maximum, and only then gradually tends to the collapsed limit. Note that these changes proceed rather quickly compared to the total collapse time. This may be interpreted as formation of the blobs during the first kinetic stage. The blobs rapidly become quasi-collapsed within (large q) and at large distances (small q) the chain has the appearance of an extended, nearly linear object. This picture is consistent

¹There are reasons to believe that the present model is not physically well motivated at the latest stages of the collapse. The most obvious problem is that the self-entanglements effects become significant at late stages and also higher orders of the density operators must be included in the potential. We may also note (see reference [10]) that the Gaussian ensemble itself has problems representing a true Flory coil for $N \rightarrow \infty$, in the absence of a cut-off.

with both the results of simulation (see Fig. 1) and analysis of the linearized equation, but for better numerical determination of the exponents one would need to consider much larger polymers.

We see that further relaxation of the “tense” state must now proceed more slowly involving motions of rather large objects towards each other. We call this the coarsening stage, by analogy with the processes accompanying a classical first-order phase-transition. This phenomenon is represented in the self-consistent equations by the slow convergence of the effective short- and long-distance chain exponents to the collapsed values of $\nu = 1/3$.

Also, during this kinetic stage, in the simulation it is possible to calculate local properties of the chain with relatively good statistics. In particular the growth of the locally collapsed globules (containing S units) as a function of time appears to be well represented by a power law, $S = At^z$, with z a universal exponent. We have not yet been able to calculate this property from the self-consistent equations, but it is probably possible to do so. Thus, we believe that the crossover from small to large- q behaviour should be relatively sharp for long chains, and that this crossover sets the scale for the blob size [10]. This blob size is essentially s , and one should be able to calculate its time dependence.

In fact, it is clear that simulation is rather reliable for local chain properties because the sample statistics is relatively good, whereas it is not as satisfactory for gross properties. On the other hand the self-consistent method does not suffer from these limitations, though until now it has only been solved for relatively short chain-lengths. Given this it is difficult to make a firm quantitative connection between all aspects of the theories. However the rapid collapse at short length-scales and strightening on long lengths exhibited by the effective exponents of Figs. 7, 8 is very encouraging, since it implies the same physical picture as that given by simulation (see Fig. 1).

4 Conclusion

We have argued that there are two identifiable kinetic for an isolated Flory coil undergoing collapse to a globular state. In the early stages the chain collapses at short lengths very rapidly exhibiting a form of spinodal decomposition. This causes formation of locally collapsed globules, distributed along a relatively rigid rod-like structure. After this early stage a much

slower coarsening process commences and it is believed that the kinetics has a power-law dependence.

From ours, and calculations of other groups one believes that there are still longer time processes, not discussed here [11]. The question of whether we are likely to be able to observe the process described in the present work in experiments is not yet answered. Some preliminary observations, and comments are given in another paper presented at this conference, [12], but more work is required to make the picture clear. We may note that the initial stage of collapse is expected to take many microseconds, and the second stage may occur over a period of one second, for long polymer chains. However, there are numerous complications. Firstly, interpolymer interactions at moderate concentration may cause aggregation, or weaker associations. The growth of these may complicate any kinetic pulse-probe experiment [7, 12, 13]. Nevertheless, it seems likely that the matter can be fully elucidated by the varied efforts of a number of groups. This accomplished, the way would be opened for a direct attack on the kinetic laws of biopolymers if, indeed, there are general law to be determined. This promises to be a most interesting field of study.

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Figure Captions

Fig. 1.

Single configuration of a polymer undergoing collapse from Langevin simulation. Further collapse is occurring by a cluster–cluster coarsening mechanism.

Fig. 2.

Plot of the coefficient of the first correction, B_q , to the equilibrium expectation value \mathcal{F}_q in arbitrary units for degree of polymerization $N = 1000$.

Fig. 3.

Plot of the inverse decay rate λ_q versus q for degree of polymerization $N = 1000$. Negative values correspond to a region of instability in which modes grow exponentially.

Fig. 4.

Plots of the self-consistent potential $\Delta V_q(t)$ versus q at the Flory state (solid line) with $\nu \simeq 0.62$ and after collapse (dashed line) with $\nu \simeq 0.43$ for the degree of polymerization $N = 30$. Values of the virial coefficients in dimensionless units are $u_2 = 50$, $u_3 = 0.5$ and $u'_2 = -5$.

Fig. 5.

Time dependence of the radius of gyration square during the collapse transition for the degree of polymerization $N = 30$. Values of the virial coefficients in dimensionless units are $u_2 = 50$, $u_3 = 0.5$ and $u'_2 = -5$.

Fig. 6.

Plots of the correlation function $D_m(t)$ versus m at various time steps: $t = 0$ (solid line), $t = 100$, $t = 1000$ and $t = 3864$ (fully collapsed) for a ring polymer of the degree of polymerization $N = 30$. Values of the virial coefficients in dimensionless units are $u_2 = 50$, $u_3 = 0.5$ and $u'_2 = -5$.

Fig. 7.

Time dependence of the exponent $2\beta(t)$ found from a power fitting of the correlation function $\mathcal{F}_q(t) \propto q^{-2\beta(t)}$ at the large q region. Degree of polymerization is $N = 80$ and values of the virial coefficients in dimensionless units are $u_2 = 50$, $u_3 = 0.1$ and $u'_2 = -5$.

Fig. 8.

Time dependence of the exponent $2\beta(t)$ found from a power fitting of the correlation function $\mathcal{F}_q(t) \propto q^{-2\beta(t)}$ at the small q region. Degree of polymerization is $N = 80$ and values of the virial coefficients in dimensionless units are $u_2 = 50$, $u_3 = 0.1$ and $u'_2 = -5$.