

Kinetics at the collapse transition Gaussian self-consistent approach

E. G. Timoshenko, Yu. A. Kuznetsov, and K. A. Dawson

Theory Group, Centre for Soft Condensed Matter and Biomaterials, Department of Chemistry, University College Dublin, Dublin 4, Ireland

(Received 24 August 1994; accepted 21 October 1994)

We introduce an approximation to the Langevin equation that can be used to study the nonequilibrium dynamics and kinetics of polymer conformational transitions in dilute solution. The approach we describe involves the introduction of a time-dependent effective potential, $\Delta V_q(t)$, and effective friction ζ_q . The potential is used to generate a time-dependent Gaussian ensemble and we derive time-dependent self-consistent equations that can be analyzed numerically, or by asymptotic methods. We work out various examples of the homopolymer kinetics, including relaxation of a Flory coil and the collapse transition. For the latter we argue that there are various characteristic regimes after a fast quench that carry us from the Flory to collapsed state. We have explicitly worked out the early stage kinetics where we find a process rather like spinodal decomposition, but where the degrees of freedom are confined to the internal metric of the polymer chain. The chain evolves to produce a chain with a near-periodic arrangement of locally collapsed blobs, which is then believed to coarsen, and we have discussed this phenomenon elsewhere. © 1995 American Institute of Physics.

I. INTRODUCTION

The equilibrium properties of polymers in dilute solution have been thoroughly studied in recent years using well founded scaling¹ and statistical mechanical methods.² Although computer simulation of polymer kinetics has proved to be very fruitful,³ analytical techniques that permit us to study dynamics and kinetic phenomena^{4,5} are much less well developed, and the traditional methods of nonequilibrium statistical mechanics⁶ are not so readily applied to polymers, networks, and other such materials. For example, we would like to study the kinetic phenomena associated with various macromolecular conformational changes, such as the coil to globule, helix-to-coil, and other transitions. Thus, although these phenomena are not true phase transitions for finite-length chains in dilute solution, there is reason to believe that they possess certain generic features, characteristic laws, and even, in some circumstances, universal exponents. Furthermore, one expects many of the important motifs from such simple polymers to persist for biopolymer conformational transitions, including the protein and DNA folding transition.⁷ For these reasons, then, we see the need to develop such techniques, and to apply them to simple homopolymer phenomena. The present method has the benefit that it can be applied to any dilute polymer system with a potential interaction that can be Fourier transformed.

II. METHOD

We refer the reader to a previous paper⁴ for details of some calculations and basic notations. We shall develop equations of motion for the correlation functions using cyclic boundary conditions in which, $x_{m+N} = x_m$, $m = 0, \dots, N-1$. The appropriate Fourier series are then

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

We denote complex conjugation as $\mathbf{x}_{-q} = \mathbf{x}_q^*$. Throughout the paper we use the short hand notations

$$\begin{aligned} c_q^{nn'} &\equiv \exp \frac{i2\pi qn}{N} - \exp \frac{i2\pi qn'}{N}, \\ d_{q,n-n'} &\equiv |c_q^{nn'}|^2 = 2 - 2 \cos \frac{2\pi q(n-n')}{N}. \end{aligned} \quad (2)$$

We may note that the equations for open polymers differ from those for cyclic polymers in minor ways. The potential V for an interacting polymer may be written as follows. Firstly, the spring term is written in terms of the connectivity constant

$$k_q = Nd_{q,1} k \rightarrow \frac{(2\pi q)^2 k}{N} \left(\frac{q}{N} \rightarrow 0 \right), \quad (3)$$

with $k = 3k_B T/a^2$, where a is the microscopic length scale. In principle, the potential V also includes contributions from excluded volume effects, conveniently written as a virial expansion in density. Including up to two- and three-body interactions we find

$$\begin{aligned} V &= V_2 + V_3 = u_2 \sum_{mm'} \delta(\mathbf{x}_m - \mathbf{x}_{m'}) \\ &+ u_3 \sum_{mm'm''} \delta(\mathbf{x}_m - \mathbf{x}_{m'}) \delta(\mathbf{x}_{m'} - \mathbf{x}_{m''}), \end{aligned} \quad (4)$$

where u_2, u_3 are virial coefficients and $m \neq m' \neq m''$. Additional parts of the Hamiltonian may be studied, providing they can be written in terms of a Fourier series, since the methods that we are about to describe may then be applied.

We shall accept that the problems we study are well represented by the Langevin equation

$$\dot{x}_q^\alpha(t) = \sum_{\alpha', q'} H_{qq'}^{\alpha\alpha'} [x(t)] \left(-k_{q'} x_{q'}^{\alpha'} - \frac{\partial V}{\partial x_{-q'}^{\alpha'}} + \eta_{q'}^{\alpha'}(t) \right), \quad (5)$$

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

$$\langle \eta_q^\alpha(t) \eta_{q'}^{\alpha'}(t') \rangle = (H^{-1})_{qq'}^{\alpha\alpha'} 2k_B T \delta(t-t') \delta_{\alpha\alpha'} \delta_{-qq'}. \quad (6)$$

The explicit form of the Oseen tensor, describing the relation between generalized velocities and forces $v_n^\alpha = \sum_{\alpha' n'} H_{nn'}^{\alpha\alpha'} F_{n'}^{\alpha'}$, is

$$H_{qq'}^{\alpha\alpha'} [x(t)] = \frac{1}{\eta_s N^2} \sum_{n \neq n'} e^{(i2\pi/N)(q'n' - qn)} \times \int \frac{d\mathbf{w}}{(2\pi)^3} \frac{\mathcal{P}_{\alpha\alpha'}(\hat{\mathbf{w}})}{\mathbf{w}^2} \times \exp\left(-i\mathbf{w} \sum_p c_p^{nn'} \mathbf{x}_p(t)\right), \quad (7)$$

$$\mathcal{P}_{\alpha\alpha'}(\hat{\mathbf{w}}) \equiv \delta_{\alpha\alpha'} - \hat{w}_\alpha \hat{w}_{\alpha'}, \quad \hat{w}_\alpha = w_\alpha / w.$$

In some parts of our discussion we shall assume a diagonal mobility tensor in which

$$H_{qq'}^{\alpha\alpha'} = \zeta_q^{-1} \delta_{\alpha\alpha'} \delta_{qq'}. \quad (8)$$

In the absence of hydrodynamics $\zeta_q \equiv \zeta = N\zeta_b$ is simply a constant. If we include hydrodynamics the mobility will exhibit nontrivial q and N dependence. The present approach involves the introduction of a time-dependent effective potential⁵ via the Gaussian stochastic ensemble,

$$\zeta_q(t) \dot{x}_q^\alpha(t) = -\Delta V_q(t) x_q^\alpha + \eta_q^\alpha(t), \quad (9)$$

$$\langle \eta_q^\alpha(t) \eta_{q'}^{\alpha'}(t') \rangle = \zeta_q 2k_B T \delta(t-t') \delta_{\alpha\alpha'} \delta_{-qq'}. \quad (10)$$

Here, $\Delta V_q(t)$ and $\zeta_q(t)$ are, respectively, a time-dependent potential and friction that can be determined self-consistently. The method is somewhat reminiscent of time-dependent Hartree theory in field theory.

III. THE NONEQUILIBRIUM EQUATIONS OF MOTION

Our present purpose is to investigate the following correlation functions,

$$\mathcal{F}_q(t) = \frac{1}{3} \langle |\mathbf{x}_q(t)|^2 \rangle, \quad (11)$$

$$\mathcal{S}_q(t) = \frac{1}{3} \langle \mathbf{x}_{-q}(0) \mathbf{x}_q(t) \rangle. \quad (12)$$

We assume space-isotropic initial conditions and, consequently, all space components give equal contributions. Let us introduce the function

$$\mathcal{D}_m(t) = \frac{1}{3} \langle (\mathbf{x}_m(t) - \mathbf{x}_0(t))^2 \rangle = \sum_q d_{q,m} \mathcal{F}_q(t). \quad (13)$$

Also from the approximate dynamics (9) it follows that

$$\mathcal{F}_q(t) = \mathcal{F}_q(0) G_q^{2V}(t) + \frac{2k_B T}{\zeta_q} \int_0^t dt_2 G_q^{2V}(t-t_2), \quad (14)$$

$$\mathcal{S}_q(t) = G_q^V(t) \mathcal{F}_q(0), \quad (15)$$

where the Green function is

$$G_q^V(t) = \exp\left(-\frac{1}{\zeta_q} \int_0^t dt_2 \Delta V_q(t_2)\right). \quad (16)$$

A. Model without hydrodynamics

If one neglects the hydrodynamic interaction, the Langevin equation becomes,

$$\zeta_q \dot{\mathbf{x}}_q(t) = -k_q \mathbf{x}_q(t) - \frac{\partial V}{\partial \mathbf{x}_q(t)} + \eta_q(t) \quad (17)$$

with the noise correlation function of Eq. (10). Multiplying Eq. (17) by $\mathbf{x}_{-q}(t)$ or $\mathbf{x}_{-q}(0)$ then taking the average it is possible to derive differential equations for the functions $\mathcal{F}_q(t)$ and $\mathcal{S}_q(t)$. The time-dependent averages are calculated using the approximate dynamics (9), and may be found in the Appendix. The resulting equation for $\mathcal{S}_q(t)$, together with Eq. (15), yields the definition of the self-consistent potential,

$$-\zeta_q \frac{d}{dt} \log \mathcal{S}_q(t) = \Delta V_q(t) = k_q - \hat{u}_2 \sum_{mm'} \frac{d_{q,m-m'}}{\mathcal{S}_{m-m'}^{5/2}(t)} - \hat{u}_3 \sum_{mm'm''} \frac{d_{q,m_1} \mathcal{D}_{m_2}(t) + d_{q,m_2} \mathcal{D}_{m_1}(t) - 2e_{q,m_1 m_2} \mathcal{E}_{m_1 m_2}(t)}{[\mathcal{D}_{m_1}(t) \mathcal{D}_{m_2}(t) - \mathcal{E}_{m_1 m_2}^2(t)]^{5/2}}. \quad (18)$$

In terms of this time-dependent potential we find the non-equilibrium equations of motion,

$$\frac{\zeta_q}{2} \dot{\mathcal{F}}_q(t) = k_B T - \Delta V_q(t) \mathcal{F}_q(t), \quad (19)$$

$$\zeta_q \dot{\mathcal{S}}_q(t) = -\Delta V_q(t) \mathcal{S}_q(t), \quad (20)$$

Let us note that from Eqs. (19) and

$$\frac{\zeta_q}{2} \dot{\mathcal{F}}_q(t) = [k_B T - \Delta V_q(t) \mathcal{F}_q(0)] G_q^{2V}(t) \quad (21)$$

one can derive the relation

$$\mathcal{F}_q(t) = \frac{k_B T}{\Delta V_q(t)} + \left(\mathcal{F}_q(0) - \frac{k_B T}{\Delta V_q(t)} \right) G_q^{2V}(t). \quad (22)$$

The physical meaning is straightforward. At infinite time $\mathcal{F}_q(t)$ tends to its equilibrium value,

$$\mathcal{F}_q^{(e)} = \frac{k_B T}{\Delta V_q^{(e)}}. \quad (23)$$

This is what one would expect from an equilibrium Gaussian ensemble. It is worth noting that with certain provisions, we can now say that both the initial and final equilibrium stages are well described by Eqs. (19) and (20). This does not establish that their nonequilibrium behavior is valid, but it is encouraging. We finally note that $\Delta V_q^{(e)}$ is determined by the equilibrium self-consistent equation

$$k_q - \Delta V_q^{(e)} = \hat{u}_2 \sum_{m'm''} \frac{d_{q,m_1} \mathcal{D}_{m_2}^{(e)} + d_{q,m_2} \mathcal{D}_{m_1}^{(e)} - 2e_{q,m_1 m_2} \mathcal{E}_{m_1 m_2}^{(e)}}{\mathcal{D}_{m_1}^{(e)} \mathcal{D}_{m_2}^{(e)} - \mathcal{E}_{m_1 m_2}^{(e)2}} + \hat{u}_3 \sum_{mm'm''} \frac{d_{q,m_1} \mathcal{D}_{m_2}^{(e)} + d_{q,m_2} \mathcal{D}_{m_1}^{(e)} - 2e_{q,m_1 m_2} \mathcal{E}_{m_1 m_2}^{(e)}}{(\mathcal{D}_{m_1}^{(e)} \mathcal{D}_{m_2}^{(e)} - \mathcal{E}_{m_1 m_2}^{(e)2})^{5/2}}, \quad (24)$$

where $m_1 = m - m'$, $m_2 = m'' - m'$ and also $\hat{u}_2 = u_2 / (2\pi)^{3/2}$, $\hat{u}_3 = u_3 / (2\pi)^3$.

B. Model with Oseen hydrodynamic tensor

In a similar fashion, from Eq. (5) we obtain up to two-body contributions:

$$\begin{aligned} \frac{1}{2} \dot{\mathcal{F}}_q(t) = & v_1 \sum_{nn'} \frac{\cos[2\pi q(n-n')/N]}{\mathcal{D}_{n-n'}^{1/2}(t)} [k_B T - k_q \mathcal{F}_q(t)] + v_2 \sum_{mm'n} \frac{\cos(2\pi q m_1/N) - \cos(2\pi q m_2/N)}{\mathcal{D}_{m_1-m_2}^2(t)} \\ & \times \{ [\mathcal{D}_{m_1-m_2}(t) \mathcal{D}_{m_1}(t) - \mathcal{E}_{m_1 m_1-m_2}^2(t)]^{-1/2} - [\mathcal{D}_{m_1-m_2}(t) \mathcal{D}_{m_2}(t) - \mathcal{E}_{m_2 m_1-m_2}^2(t)]^{-1/2} \} \mathcal{F}_q(t), \end{aligned} \quad (25)$$

$$\begin{aligned} \dot{\mathcal{F}}_q(t) = & -k_q v_1 \sum_{nn'} \frac{\cos[2\pi q(n-n')/N]}{\mathcal{D}_{n-n'}^{1/2}(t)} \mathcal{F}_q(t) + v_2 \sum_{mm'n} \frac{\cos(2\pi q m_1/N) - \cos(2\pi q m_2/N)}{\mathcal{D}_{m_1-m_2}^2(t)} \{ [\mathcal{D}_{m_1-m_2}(t) \mathcal{D}_{m_1}(t) \\ & - \mathcal{E}_{m_1 m_1-m_2}^2(t)]^{-1/2} - [\mathcal{D}_{m_1-m_2}(t) \mathcal{D}_{m_2}(t) - \mathcal{E}_{m_2 m_1-m_2}^2(t)]^{-1/2} \} \mathcal{F}_q(t), \end{aligned} \quad (26)$$

where

$$v_1 = [3(2\pi^3)^{1/2} \eta_s N^2]^{-1}$$

and $v_2 = 2u_2 / [3(2\pi)^3 \eta_s N]$. Again we can rewrite these in the same form as Eqs. (19) and (20) if we identify

$$\frac{1}{\zeta_q(t)} = v_1 \sum_{nn'} \frac{\cos[2\pi q(n-n')/N]}{\mathcal{D}_{n-n'}^{1/2}(t)}. \quad (27)$$

The equation for

$$\mathbf{D}_q(t) = \frac{1}{3} \langle |\mathbf{x}_q(t) - \mathbf{x}_q(0)|^2 \rangle = \mathcal{F}_q(t) + \mathcal{F}_q(0) - 2\mathcal{F}_q(t) \quad (28)$$

is well defined only for the $q=0$ diffusive mode when the effective potential vanishes to give

$$\dot{\mathbf{D}}_0(t) = \frac{2k_B T}{\zeta_0(t)}. \quad (29)$$

Here ζ_0 is determined by Eq. (27). This is the natural generalization of the diffusion law for kinetics where the mean size of the polymer is changing as a function of time. It is physically well defined whenever diffusion is fast compared to conformational change.

IV. RELAXATION TOWARDS EQUILIBRIUM

In this section we consider the simplest application of the kinetic equations describing a small deviation from the equilibrium. However, as important the role of hydrody-

amic interaction is, we do not consider it here for reasons of simplicity. In fact, it may be easily taken into account in our method and consequences are analyzed elsewhere.⁸ Our main purpose here is to study the method, as a preliminary to a more involved calculation outlined in Sec. V. Now let us study Eq. (19) for a good solvent when $u_2 > 0$. We then may restrict our consideration to the u_2 term. Let us consider the case when the initial condition, $\mathcal{F}_q(0)$, is different from the equilibrium one $\mathcal{F}_q^{(e)} = \mathcal{F}_q(\infty)$, but both are still Flory coils. The equilibration property of the Langevin equation guarantees that this distribution tends to equilibrium as t tends to infinity. At large t the deviation $\Delta \mathcal{F}_q(t)$, defined by

$$\mathcal{F}_q(t) = \mathcal{F}_q^{(e)} + \Delta \mathcal{F}_q(t),$$

should be small, so one may consider the linearized equation for $\Delta \mathcal{F}_q(t)$ near the final equilibrium solution. Using the equilibrium self-consistent equation, Eq. (24), we obtain

$$\frac{\zeta_q}{2} \Delta \dot{\mathcal{F}}_q(t) = -\Delta V_q^{(e)} \Delta \mathcal{F}_q(t)$$

$$- \frac{5}{2} \hat{u}_2 \sum_{mm'} \frac{d_{q,m-m'} \mathcal{F}_q^{(e)}}{(\mathcal{D}_{m-m'}^{(e)})^{7/2}} \Delta \mathcal{D}_{m-m'}(t),$$

(30)

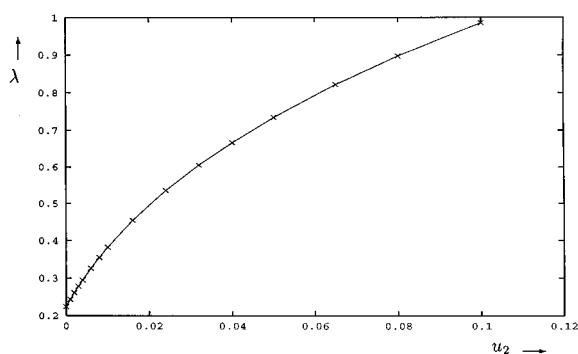


FIG. 1. Plot of the inverse decay rate λ vs the second virial coefficient u_2 for degree of polymerization $N=1000$.

$$\Delta \mathcal{D}_m(t) = \sum_p d_{p,m} \Delta \mathcal{F}_p(t), \quad \mathcal{D}_m^{(e)} = \sum_p d_{p,m} \mathcal{F}_p^{(e)}. \quad (31)$$

This equation, although linear, is quite complicated because of the mode coupling. However, as we shall presently show, the latter leads all modes to decay with the same rate. Indeed, suppose that the q th mode decays with an inverse rate λ_q , i.e., $\Delta V_q(t) \sim \mathcal{A}_q e^{-\lambda_q t}$ as t tends to infinity. Then the leading term on the right-hand side of Eq. (31) will be proportional to $e^{-\lambda_1 t}$, where $1/\lambda_1$ is the largest rate. Thus, the only way in which the equation may be satisfied asymptotically is to have $\lambda_q = \lambda_1$. Now, the inverse decay rate λ_1 and the amplitude \mathcal{A}_q may be found as the lowest eigenvalue and appropriate eigenvector of the following matrix $\Lambda_{qq'}$,

$$\Lambda_{qq'} \equiv \Delta V_q^{(e)} \delta_{qq'} + \frac{5}{2} \hat{u}_2 k_B T \sum_{mm'} \frac{d_{q,m-m'} d_{q',m-m'}}{(\mathcal{D}_{m-m'}^{(e)})^{7/2} (\Delta V_q^{(e)} \Delta V_{q'}^{(e)})^{1/2}}, \quad (32)$$

$$\sum_{qq'} \Lambda_{qq'} A_{q'} = \frac{\zeta}{2} \lambda_1 A_q, \quad (33)$$

where we have rescaled the amplitude $A_q \equiv (\Delta V_q^{(e)})^{1/2} \mathcal{A}_q$ in order to have a symmetric matrix. Let us recall that

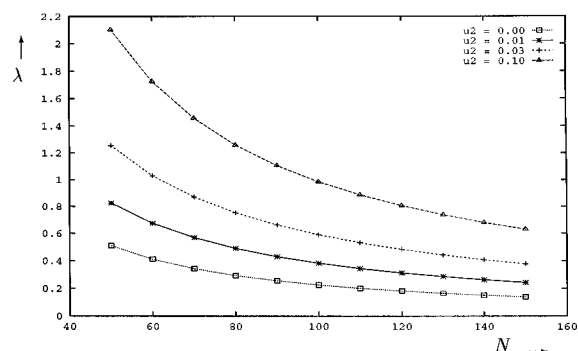


FIG. 2. Plot of the inverse decay rates λ vs the degree of polymerization N at various virial coefficients u_2 .

TABLE I. Exponent ζ values vs virial coefficient u_2 .

u_2	0.01	0.03	0.05	0.1	0.2	0.7
ζ	1.113	1.093	1.092	1.095	1.098	1.098

$\zeta_q = \zeta = N \zeta_b$ is constant in the absence of the hydrodynamic interaction. Equation (33) may be analyzed numerically. Let us introduce the dimensionless parameters $\lambda = (b^2 N \zeta_b / 2 k_B T) \lambda_1$ and $u_2 = (10/b^3 k_B T) \hat{u}_2$. From Fig. 1 it is clear that λ is an increasing function of u_2 . In Fig. 2 we show λ vs N for various values of the virial coefficient u_2 . These plots appear to be consistent with a power law, $\lambda_1 \propto N^{-1-\zeta}$. Values of the exponent, ζ , found from the least-square fit are presented in Table I. Now, for very small values of u_2 , the exponent tends to $\zeta=2\nu$. The exponent decreases as u_2 grows, then begins to increase again. Note that at zero u_2 we have instead the θ point exponent $\nu=\frac{1}{2}$, and account of hydrodynamic interaction changes the scaling law to $\lambda_1 \propto (\Delta V_1 / \zeta_1) \propto N^{-3\nu}$. Therefore, for very small u_2 we recover the results of the Rouse and Zimm models. Figures 3 and 4, respectively, contain plots of the decay amplitude A_q as a function of q at various u_2 and N values. Note that A_q is defined only at integer points $q=1,2,\dots$, and that it decreases and oscillates as a function of q . The smaller u_2 , the sharper the A_q peak becomes. This implies that at zero u_2 we would have $A_q \propto \delta_{q1}$, corresponding to the decoupling limit of an ideal coil—when all modes decay with their own inverse rate $\lambda_q \propto \Delta V_q^{(e)}$. Evidently an increase of u_2 implies stronger coupling, and the distribution grows wider. One can see that the absolute value of A_q depends very weakly on polymerization degree N , whereas the sign depends on N more sensitively. The peak of the distribution at lower values of q has a straightforward physical meaning. Long length-scale fluctuations take longer to equilibrate, so at large t these modes are still in a nonequilibrium state, while short length-scale modes have already attained equilibrium.

V. KINETICS OF THE COLLAPSE OF A HOMOPOLYMER

We shall analyze the equations of Sec. III in an attempt to understand one of the kinetic regimes for the process that

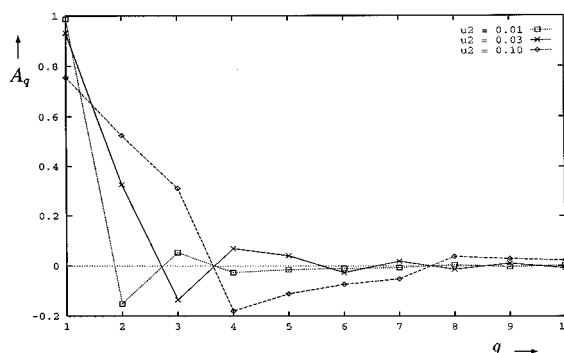


FIG. 3. The dependence of the decay amplitude A_q on the internal modes index q at various virial coefficients u_2 for $N=100$.

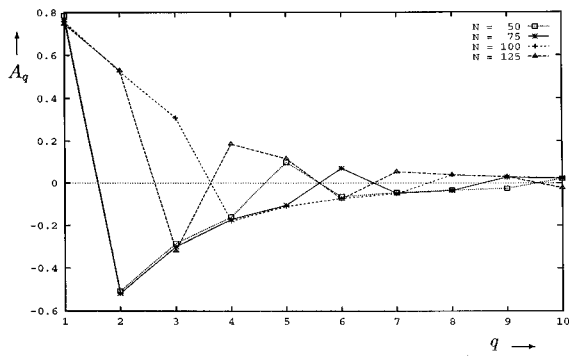


FIG. 4. Dependence of the decay amplitude A_q on the internal mode index q at various degrees of polymerization N for $u_2=0.1$.

carries us from the Flory to collapsed state. In fact, we believe that there are at least three such regimes that can be identified, although only the first of these is studied in the present paper. The last stage corresponds to a very long time-scale process lasting, perhaps, hours in which a compacted globular state equilibrates by developing the appropriate numbers of knots, perhaps even finally forming a frozen microcrystallite. We shall not discuss this stage further in the present work. For realistic systems all the processes we discuss would be complete well within a second, and should more properly be sought within the millisecond time scale.

We imagine quenching from the equilibrium Flory coil region to parameters for which the equilibrium state would be a collapsed globule. At early stages we find a process akin to spinodal decomposition. There are important differences, however. Here we find that the modes that become unstable

are typically shorter-wavelength ones, and in any case they are modes that are described in the internal metric of the chain. Physically this has important ramifications, the most obvious being that the collapse process will be driven by growth from the short length scale, and the state that is produced prior to coarsening will be a periodic array of small collapsed globules in the internal metric of the chain, not in the complete space in which the polymer chain is embedded.

After a transient period of growth of unstable modes we find mode coupling causes mode dominance, and all modes begin to relax in the same way as the fastest mode. This leads to the next stage where the effect of the chain connectivity is becoming more relevant, until finally the slack chain is all absorbed into collapsed globules distributed along the chain.

In what follows we shall only study the earliest stage. Later stages have been described by simulation,⁹ and will also be the subject of future study. We believe that the hydrodynamic interaction is not yet important at these stages, and therefore restrict ourselves by the diagonal mobility tensor.⁸

We begin by linearizing Eq. (19), with parameters $\hat{u}'_2 < 0$, $\hat{u}'_3 > 0$ appropriate for a collapsed state, around the initial Flory state with $\hat{u}_2 > 0$, $\hat{u}_3 > 0$. We assume that the initial state before the quench is at equilibrium and therefore \mathcal{F}_q satisfies Eq. (24). Then we suddenly change the second virial coefficient by a value $\Delta\hat{u}_2 = \hat{u}'_2 - \hat{u}_2 < 0$. 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 analyzed to determine the early stages of kinetics. We find

$$\begin{aligned} \frac{\xi}{2} \Delta\dot{\mathcal{F}}_q(t) = & \Delta\hat{u}_2 \mathcal{F}_q^{(e)} \sum_{mm'} \frac{d_{qm_1}}{\mathcal{D}_{m_1}^{(e)5/2}} - \Delta V_q^{(e)} \Delta\mathcal{F}_q + \Delta\hat{u}_2 \Delta\mathcal{F}_q \sum_{mm'} \frac{d_{qm_1}}{\mathcal{D}_{m_1}^{(e)5/2}} - \frac{\xi}{2} \hat{u}'_2 \mathcal{F}_q^{(e)} \sum_{mm'} \frac{d_{qm_1} \Delta\mathcal{E}_{m_1}}{\mathcal{D}_{m_1}^{(e)7/2}} - \hat{u}'_3 \mathcal{F}_q^{(e)} \\ & \times \left(\frac{5}{2} \sum_{mm'm''} \frac{d_{qm_1} \mathcal{E}_{m_2}^{(e)} + d_{qm_2} \mathcal{E}_{m_1}^{(e)} - 2e_{qm_1 m_2} \mathcal{E}_{m_1 m_2}^{(e)}}{(\mathcal{D}_{m_1}^{(e)} \mathcal{D}_{m_2}^{(e)} - \mathcal{E}_{m_1 m_2}^{(e)2})^{7/2}} (\mathcal{D}_{m_2}^{(e)} \Delta\mathcal{E}_{m_1} + \mathcal{D}_{m_1}^{(e)} \Delta\mathcal{E}_{m_2} - 2\mathcal{E}_{m_1 m_2}^{(e)} \Delta\mathcal{E}_{m_1 m_2}) \right. \\ & \left. - \sum_{mm'm''} \frac{d_{qm_1} \Delta\mathcal{E}_{m_2} + d_{qm_2} \Delta\mathcal{E}_{m_1} - 2e_{qm_1 m_2} \Delta\mathcal{E}_{m_1 m_2}}{(\mathcal{D}_{m_1}^{(e)} \mathcal{D}_{m_2}^{(e)} - \mathcal{E}_{m_1 m_2}^{(e)2})^{5/2}} \right). \end{aligned} \quad (34)$$

For small t the solution may be sought for in the form

$$\Delta\mathcal{F}_q = \mathcal{A}_q (1 - e^{-\lambda_q t}) \approx B_q t + C_q \frac{t^2}{2} + \dots, \quad \lambda_q \approx -C_q/B_q \quad (35)$$

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

$$\frac{\xi}{2} B_q = \Delta\hat{u}_2 \mathcal{F}_q^{(e)} \sum_{mm'} \frac{d_{qm_1}}{\mathcal{D}_{m_1}^{(e)5/2}}, \quad (36)$$

$$\begin{aligned} \frac{\zeta}{2} C_q = & -\Delta V_q^{(e)} B_q + \Delta \hat{u}_2 B_q \sum_{mm'} \frac{d_{qm_1}}{\mathcal{D}_{m_1}^{(e)5/2}} - \frac{5}{2} \hat{u}_2' \mathcal{F}_q^{(e)} \sum_{mm'} \frac{d_{qm_1} B_{m_1}}{\mathcal{D}_{m_1}^{(e)7/2}} - \hat{u}_3 \mathcal{F}_q^{(e)} \\ & \times \left(\frac{5}{2} \sum_{mm'm''} \frac{d_{qm_1} \mathcal{E}_{m_2}^{(e)} + d_{qm_2} \mathcal{E}_{m_1}^{(e)} - 2e_{qm_1 m_2} \mathcal{E}_{m_1 m_2}^{(e)}}{(\mathcal{D}_{m_1}^{(e)} \mathcal{D}_{m_2}^{(e)} - \mathcal{E}_{m_1 m_2}^{(e)2})^{7/2}} (\mathcal{E}_{m_2}^{(e)} B_{m_1} + \mathcal{E}_{m_1}^{(e)} B_{m_2} - 2\mathcal{E}_{m_1 m_2}^{(e)} B_{m_1 m_2}) \right. \\ & \left. - \sum_{mm'm''} \frac{d_{qm_1} B_{m_2} + d_{qm_2} B_{m_1} - 2e_{qm_1 m_2} B_{m_1 m_2}}{(\mathcal{D}_{m_1}^{(e)} \mathcal{D}_{m_2}^{(e)} - \mathcal{E}_{m_1 m_2}^{(e)2})^{5/2}} \right). \end{aligned} \quad (37)$$

where the standard notations

$$B_m = \sum_q d_{qm} B_q, \quad B_{m_1 m_2} = \sum_q e_{qm_1 m_2} B_q$$

have been used.

These formulas may be subjected to a straightforward numerical study. Again, we work in terms of dimensionless variables. The plot of the first correction, B_q , is presented in the Fig. 5. This quantity is always negative indicating that the size of the system decreases during the collapse transition. Least squares fit to a power yields the dependence $B_q \propto q^{-0.5}$ at $N=1000$, while the naive power counting arguments lead to the exponent -0.2 . The reason for this discrepancy will be discussed later in this section. The second correction C_q , however, changes sign for some region of q, \hat{u}_2', \hat{u}_3 . The negative region corresponds to an instability where appropriate modes grow exponentially fast. The only term in Eq. (37) that contributes to the instability at sufficiently small q is the one that is linear in u_2' . A separate and positive, two-body contribution, comes from the term proportional to $-\Delta u_2$ although it is much smaller in magnitude in this region of q . In Fig. 6 we present a typical plot of the λ_q dependence. It is interesting to consider two special points: q_c —the last unstable mode—and the extremal point

q_{\max} corresponding to the most unstable mode, which grows as $e^{\lambda_{q_{\max}} t}$. These values of q vs u_2' and u_3 are drawn in Figs. 7 and 8. One can see that the instability disappears if u_2' is sufficiently small or u_3 is sufficiently large compared to u_2' . The power fit gives the exponents $q_{\max} \propto |u_2'|^{0.8}$ and $q_{\max} \propto u_3^{-0.2}$ at $N=1000$.

At this point we note that, in many cases, it is possible to choose the unstable range to fall at relatively small q , and it is then possible to make a crude estimate of the asymptotic behavior at small q from power counting. The advantage of this is that it exhibits plainly the competing terms that compose the spectrum of modes, and aids in the physical understanding the problem. We obtain

$$\frac{\zeta}{2} B_q \propto \frac{\Delta \hat{u}_2}{b^3 N} q^{3\nu-2}, \quad (38)$$

where $\nu=3/5$ is the Flory exponent and for the inverse decay rate, λ_q , up to some numerical constants I, I' , we find

$$\lambda_q = k_B T b^{-2} \underline{q}^{2\nu+1} - I' |u_2'| b^{-5} \underline{q}^{5\nu-1} + I \hat{u}_3 b^{-8} \underline{q}^{8\nu-2}. \quad (39)$$

Again presence of attractive two-body interactions causes the instability at q for values that are smaller than a critical value q_c . This value q_c may be most easily found in the case of very large $-\Delta \hat{u}_2'$

$$q_c \propto \left(-\frac{\hat{u}_2'}{\hat{u}_3} b^3 \right)^{5/4}. \quad (40)$$

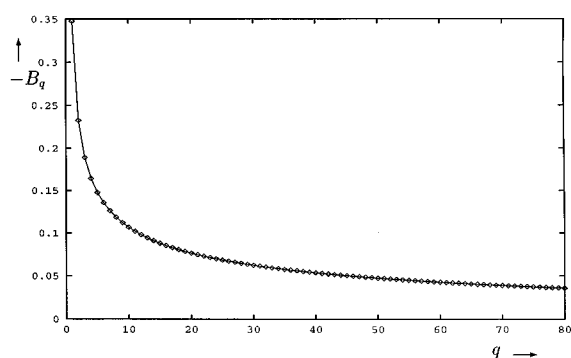


FIG. 5. Plot of the coefficient of the first correction B_q to the equilibrium expectation value \mathcal{F}_q in arbitrary units for degree of polymerization $N=1000$.

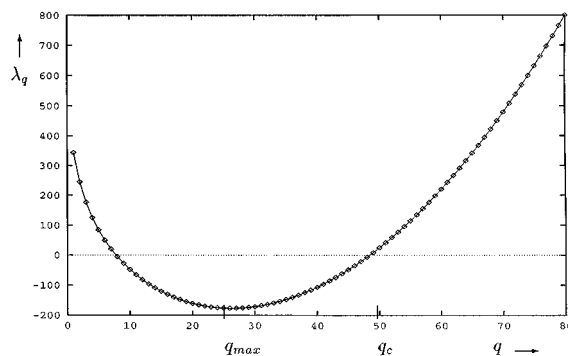


FIG. 6. Plot of the inverse decay rate λ_q vs q for degree of polymerization $N=1000$. Negative values correspond to a region of instability in which modes grow exponentially.

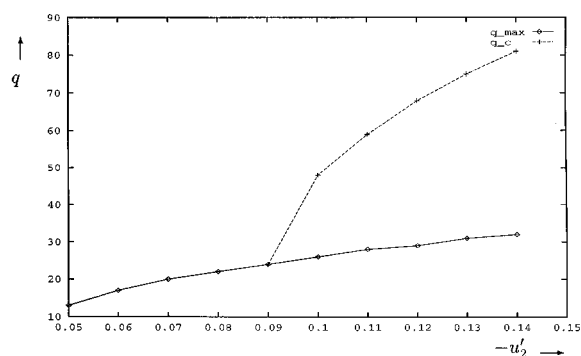


FIG. 7. Plots of the critical q_c and maximal q_{\max} values of the internal mode indices vs the final second virial coefficient u'_2 . The degree of polymerization is $N=1000$ and $u_3=0.0015$.

Evidently, the value q_{\max} at which $|\lambda_q|$ is maximal and the critical value q_c are related in this small q limit as follows $q_{\max} = (5/7)^{5/4} \hat{u}_{q_c}$. Now we may examine Eq. (39) more closely. It is possible to show that the first term originates in entropic effects for the chain. This may be checked by using the trial distribution to calculate the equilibrium entropy. In the present asymptotic regime, this term opposes the unstable behavior. The second and third terms are due to two- and three-body effects, the former driving the instability, the latter opposing it. Thus, even in the asymptotic regime there are competing effects that lead to different balances of the physical effects, depending on the depth of the quench, and so forth.

The plots in Fig. 7 and 8 are obtained in the case where \hat{u}'_2 and \hat{u}'_3 give almost equal contributions and we are close to the point when q_c disappears, and there is no exponentially growing instability. Of course, in all cases the polymer is still collapsing, since B_q is negative.

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, Eq. (40), contribute increasingly to the configuration of the collapsing polymer, leading, finally to a chain of locally collapsed globules. This type of

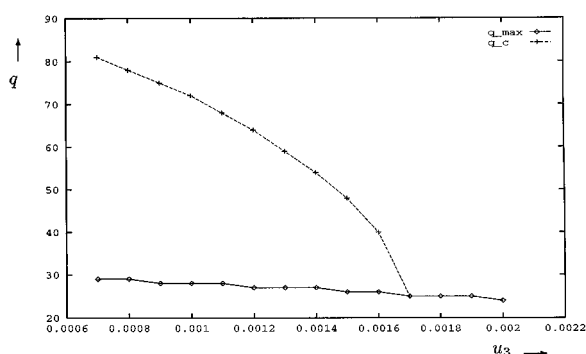


FIG. 8. Plots of the critical q_c and maximal q_{\max} values of the internal mode indices vs the final virial coefficient u_3 . The degree of polymerization is $N=1000$ and $u'_2 = -0.1$.

constrained spinodal decomposition is, we believe, the first stage of collapse kinetics, for quenches that are sufficiently deep to cause instability, but where the third virial coefficient is still positive.

It is important to emphasize at this stage that we have used an approximate method which is not yet well characterized. A potential source of concern is the fact that for infinitely repulsive forces it is known that one must apply some sensible cutoff on the equilibrium equations in order to obtain the correct behavior. This is easy to do when one works analytically in the asymptotic regime, but for the numerical calculations it is not. Thus, we may expect for instabilities that lead to a large critical wave number, and for which we therefore numerically calculate, the spectrum will be quantitatively incorrect. This is a problem that can only be solved by choosing a more complex trial dynamic⁸ which we believe gives accurate numerical answers, but which is then very difficult to analyze analytically. However, the essential features outlined earlier may be confirmed by visual observation of simulations and one finds that, indeed, the spinodal type regime does appear to exist and evolve according to the qualitative picture given earlier.

VI. CONCLUSION

In this paper we have shown that it is possible to generalize the equilibrium method of variational approximation by a Gaussian ensemble to the realm of dynamics and kinetic phenomena, although the problems that beset the equilibrium approaches to infinite repulsive potentials are also present in our generalization. It is possible to avoid these problems by inclusion of an explicit cutoff, but the equations then become considerably more cumbersome for analytical analysis.

The simplicity of the equations presented here, leads us to be able to analyze them for a few examples of relaxational processes. The relaxation to a Flory coil can be studied readily, and we find that the mode coupling is important, leading to all modes relaxing at the same rate at late stages. We have opened discussions on the kinetics of homopolymer collapse and although we believe there to be a number of distinct stages in the overall process, we have presented results for only the earliest stage. The main conclusion there, is that at early times for isolated chains there is a process rather like bulk spinodal decomposition, but with some essential differences. In particular, entropic and different parts of the potential compete, to cause rapid collapse on short length scales, where, again, mode coupling leads to mode dominance.

In the future it will be of interest to analyze these equations in more detail to exhibit the other stages of collapse, along with studying problems with a range of conformational states. There is no intrinsic reason that more complex potentials cannot be accommodated, and indeed it seems clear that simple models of proteins can be treated and analyzed by these methods. Evidently, this holds promise for the study of protein folding kinetics and other biopolymers. It will be of some interest to see such ideas unfold.

ACKNOWLEDGMENTS

The authors acknowledge interesting discussions with Professor P.-G. de Gennes, Professor A. R. Khokhlov, Professor A. L. Kholodenko, Professor Y. Rabin, Dr. M. Barbosa, Dr. A. Gorelov, and Dr. O. Vasiliev. This work was supported by the DEC corporation and the Irish Government.

APPENDIX

Evaluation of necessary averages was, in fact, carried out for the general case of any initial condition in our previous work.⁴ Here, for convenience and in order to introduce basic notations, we present some basic results. One can find explicitly the contribution from the two-body interaction

$$\left\langle x_{-q}^{\alpha}(t) \frac{\partial V_2}{\partial x_{-q}^{\alpha}(t_1)} \right\rangle = -\hat{u}_2 \sum_{mm'} \frac{d_{q,m-m'}}{\mathcal{D}_{m-m'}(t_1)^{5/2}} \left[\langle |x_q^{\alpha}|^2(0) \rangle G_q^V(t) G_q^V(t_1) + \frac{2k_B T}{\zeta_q} \left(\theta(t-t_1) \int_0^{t_1} dt_2 + \theta(t_1-t) \int_0^t dt_2 \right) \right. \\ \left. \times G_q^V(t_1-t_2) G_q^V(t-t_2) \right], \quad (\text{A1})$$

with $\hat{u}_2 = u_2 / (2\pi)^{3/2}$. Using regularization for Langevin equation one can prove that one should take the symmetric prescription $\theta(0) = 1/2$. In analogy, for three-body contributions we find

$$\left\langle \left(\frac{x_{-q}^{\alpha}(t)}{x_{-q}^{\alpha}(0)} \right) \frac{\partial V_3}{\partial x_{-q}^{\alpha}(t)} \right\rangle = -\hat{u}_3 \left(\frac{\langle |x_q^{\alpha}|^2(t) \rangle}{\langle x_{-q}^{\alpha}(0) x_q^{\alpha}(t) \rangle} \right) \sum_{mm'm''} \frac{d_{q,m_1} \mathcal{D}_{m_2}(t) + d_{q,m_2} \mathcal{D}_{m_1}(t) - 2e_{q,m_1 m_2} \mathcal{E}_{m_1 m_2}(t)}{[\mathcal{D}_{m_1}(t) \mathcal{D}_{m_2}(t) - \mathcal{E}_{m_1 m_2}^2(t)]^{5/2}} \quad (\text{A2})$$

with notations

$$\mathcal{E}_{m_1 m_2} = \frac{1}{2} (\mathcal{D}_{m_1 - m_2} - \mathcal{D}_{m_1} - \mathcal{D}_{m_2}). \quad (\text{A3})$$

$$e_{q,m_1 m_2} = \frac{1}{2} (d_{q,m_1 - m_2} - d_{q,m_1} - d_{q,m_2}). \quad (\text{A4})$$

Here we have introduced relative coordinates $m_1 = m' - m$, $m_2 = m' - m''$, and $\hat{u}_3 = u_3 / (2\pi)^3$.

¹ P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, N.Y., 1979).

² M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford Science, New York, 1989); J. des Cloizeaux, G. Jannink, *Polymers in Solution* (Clarendon, Oxford, 1990); A. R. Khokhlov (unpublished); B. H. Zimm, *J. Chem. Phys.* **24**, 269 (1956); B. H. Zimm, G. M. Roe, and L. F. Epstein, *ibid.* **37**, 2547 (1962); H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971); S. F. Edwards and K. F. Freed, *J. Chem. Phys.* **61**, 1189 (1974); S. F. Edwards and M. Muthukumar, *Macromolecules* **17**, 586 (1984); A. J. Peterlin, *J. Chem. Phys.* **23**, 2464 (1955); Y. Oono and M. Kohmoto, *ibid.* **78**, 520 (1983).

³ B. Ostrovsky and Y. Bar-Yam, *Europhys. Lett.* **25**, 409 (1994).

⁴ E. G. Timoshenko and K. A. Dawson, *Phys. Rev. E* (in press).

⁵ H. C. Öttinger and Y. Rabin, *J. Non-Newt. Fluid Mech.* **33**, 53 (1989).

⁶ S.-K. Ma, *Modern Theory of Critical Phenomena* (Addison Wesley, New York, 1976).

⁷ H. A. Scheraga, *Pure Appl. Chem.* **36**, 1 (1973); N. Go and H. Taketomi, *Proc. Natl. Acad. Sci. USA* **75**(2), 559 (1978); O. Ptitsyn and A. Finkelstein, *Q. Rev. Biophys.* **13**, 339 (1980); P. Privalov, *Adv. Protein Chem.* **35**, 1 (1982); J. Bryngelson and P. Wolynes, *Proc. Natl. Acad. Sci. USA* **84**, 7524 (1987); O. Ptitsyn, *J. Protein Chem.* **6**(4), 273 (1987); T. Garel and H. Orland, *Europhys. Lett.* **6**, 307 (1988); H. Frauenfelder, F. Parak, and R. Young, *Annu. Rev. Biophys. Biophys. Chem.* **17**, 451 (1988); E. Shakhnovich and A. Gutin, *Nature (London)* **346**, 773 (1990); E. Shakhnovich, G. Farztdinov, A. M. Gutin, and M. Karplus, *Phys. Rev. Lett.* **67**(12), 1665 (1991); M. Matsumoto, T. Sakaguchi, and H. Kimura *et al.*, *J. Polym. Science B* **30**, 779 (1992); K. Minagawa, Y. Matsuzawa, Y. Yoshikawa, A. R. Khokhlov, and M. Doi, *Biopolymers* **34**, 555 (1994).

⁸ E. G. Timoshenko and K. A. Dawson (unpublished).

⁹ P. Kiernan, A. Byrne, D. Green, and K. A. Dawson, *J. Chem. Phys.* (in press).