Fluctuations in discrete fragmentation processes studied by stochastic simulations

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The influence of fluctuations in discrete shattering and nonshattering fragmentation processes is studied by means of a stochastic simulation algorithm based on a master equation. For both processes, we find that the fluctuations in the total number of clusters N and the weight-averaged mass M_W are large, and that the maximum fluctuations occur at different times for N and M_W. A mean-field description is shown to be valid for nonshattering processes, whereas for shattering processes it is appropriate only in the limit of a large number of small initial clusters.

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I. INTRODUCTION

Fragmentation processes arise in a great variety of chemical and physical processes such as polymer degradation [1], droplet breakup [2], and fragmentation of colloidal aggregates [3,4]. Theoretical studies of fragmentation usually employ the continuous deterministic fragmentation equation. Two regimes of fragmentation kinetics have been identified using the fragmentation equation: shattering kinetics, and nonshattering kinetics [5,6]. In shattering processes, smaller fragments have a higher fragmentation rate than larger ones. This situation causes clusters to break apart at ever-increasing rates, leading to a phase of particles with zero-size mass. Conceptually, the shattering transition is the inverse of the gelation transition that occurs in aggregating systems. In nonshattering processes, smaller fragments have a smaller fragmentation rate than larger ones, and so no cascading breakup occurs.

Recently, a stochastic formulation of the problem has shown that fluctuations play an important role in shattering-fragmentation processes [7,8]. This suggests that the deterministic fragmentation equation, which is a mean-field theory, may not accurately model fragmentation processes in which fluctuations are large. The stochastic models investigated so far can either only account for fluctuations in the total number of clusters N [8] or only for fluctuations of the concentrations of clusters [7]. However, fluctuations and correlations of the weight-average mass M_W or of other physical quantities are also of interest.

Many studies of fragmentation use a continuous model, in which clusters can be fragmented indefinitely. It has been pointed out, however, that discrete models are more appropriate since in experimental systems there is always a smallest possible fragment [1,3,8] implying that the fragmentation stops at a certain time whereas the continuous model leads to an infinitely running process.

In this article the fluctuations of discrete shattering and nonshattering processes are investigated. We demonstrate that a stochastic simulation method based on a master equation [9,10] is well suited to study the role of fluctuations in realistic discrete fragmentation processes. This method has previously been used sucessfully to investigate aggregation processes [11–13]. The simulation algorithm is used to obtain complete information about the fragmentation process, i.e., expectation values, fluctuations, and correlations of any physical quantity. This enables us to reveal the limitations of the deterministic fragmentation equation.

Our article is organized as follows. We first describe the deterministic formulation of discrete fragmentation processes. Then we give the corresponding master equation and show its relationship to the deterministic approach. Finally, we describe results of the stochastic simulation when applied to two typical discrete fragmentation processes, one of them shattering and the other nonshattering.

II. DETERMINISTIC FRAGMENTATION MODELS

The general deterministic kinetic equation that approaches the linear binary discrete fragmentation process is the so-called mean-field fragmentation equation [1],

$$\frac{dn_k(t)}{dt} = -a_k n_k(t) + 2\sum_{j=k+1}^{L} F_{k,j-k} n_j(t), \qquad (1)$$

where $a_k \equiv \sum_{j=1}^{k-1} F_{j,k-j}$. Here $n_k(t)$ is the number of particles of size k at time t and L is the size of the largest particle. The kernel $F_{i,j}$ denotes the rate that a particle of size $i+j$ breaks into two fragments of size i and j. Consequentely, a_k is the total transition rate from a particle of size k. In the following we make the random scission assumption, i.e., $F_{i,j}$ is a function of $i+j$ only. A classification scheme of fragmentation models has been achieved for continuous fragmentation models with the total breakup rate $a(x)$ being of the homogeneous form $a(x) = x^\lambda$. Shattering transition models are characterized by $\lambda < 0$ and nonshattering models by $\lambda > 0$.

With the help of a scaling ansatz for $n_k(t)$, the following equation can be derived for nonshattering models [6]:

$$S(t) = [\lambda\omega t + S(0)^{-\lambda}]^{-1/\lambda}, \tag{2}$$

where $S(t)$ is a measure of the mean cluster size [here taken to be $S(t) = M_W(t)$] and ω is a constant. These results also apply qualitatively to the corresponding discrete fragmentation process since the continuum model is an approximation of the discrete one in the limit of small times and large clusters [1].

III. STOCHASTIC FRAGMENTATION MODELS

A. The master equation

In the stochastic formulation of discrete fragmentation, the process is characterized by the joint probability function $P(\vec{N},t)$. It denotes the probability that the system at time t is in the state $\vec{N} = (N_1, N_2, ..., N_L)$, i.e., N_i particles of size i are present. The dynamics of the system is governed by the master equation

$$\frac{\partial P(\vec{N},t)}{\partial t} = \sum_{j=2}^{L}\Bigg[(N_j+1)\sum_{n=1}^{j-1}F_{j-n,n} \times P(\vec{N}-\vec{e}_{j-n}-\vec{e}_n+\vec{e}_j,t) - a_jN_jP(\vec{N},t)\Bigg]. \tag{3}$$

For brevity we use the notation $\vec{N}+\vec{e}_i = (N_1,...,N_{i-1},N_i+1,N_{i+1},...,N_L)$. The function $P(\vec{N},t)$ contains not only the information about average quantities but also about fluctuations and correlations of the process.

B. The macroscopic equation

We now show that the deterministic fragmentation equation (1) arises as a limiting case of the master equation (3). By taking the expectation value $\langle N_k\rangle(t) \equiv \sum_{\vec{N}} N_kP(\vec{N},t)$ of Eq. (3), the so-called macroscopic equation [14] can be derived

$$\begin{aligned}\frac{d\langle N_k\rangle}{dt} &= \left\langle \sum_{\vec{N}} N_k\left(\sum_{j=2}^{L}\left[(N_j+1)\sum_{n=1}^{j-1}F_{j-n,n}P(\vec{N}-\vec{e}_{j-n}-\vec{e}_n+\vec{e}_j,t) - a_jN_jP(\vec{N},t)\right]\right)\right\rangle \\ &= \sum_{j=2}^{L}\left[\sum_{n=1}^{j-1}\left(F_{j-n,n}\{\langle N_kN_j\rangle + [\delta_{k,j-n}+\delta_{k,n}-\delta_{k,j}]\langle N_j\rangle\}\right) - a_j\langle N_kN_j\rangle\right] \\ &= -a_k\langle N_k\rangle + 2\sum_{j=k+1}^{L}F_{k,j-k}\langle N_j\rangle. \end{aligned} \tag{4}$$

This equation corresponds to the deterministic fragmentation equation (1) provided $n_k(t)$ is set equal to $\langle N_k\rangle(t)$. Consequently, the expectation values of the stochastic simulation results should exactly obey solutions of the deterministic fragmentation equation even when fluctuations are large. It should be emphasized that when macroscopic equations are derived from a master equation, higher moments of the distribution generally appear, i.e., terms of the form $\langle N_nN_m\rangle$ with $(n,m = 1,2,...)$. This is the case for aggregation processes where the Smoluchowski equation is an approximation for the macroscopic equation of the underlying master equation [12]. Thus Eq. (4) is a nontrivial result, although the computation is simple.

C. Stochastic simulation algorithm

The treatment of a master equation as a differential equation is known to be a difficult mathematical task [7,8,14]. However, the mathematical difficulties can be overcome by using a numerical algorithm [9,10,12] to simulate the kinetics. Up until now this stochastic algorithm has been greatly underestimated as a tool in the study of fragmentation processes. With the stochastic simulation method, one generates an ensemble of exact realizations of the stochastic process and then estimates the physical quantities of interest.

Let us decribe this method in more detail. Consider a system of particles at time t in the state $\vec{N} = (N_1,...,N_L)$ where N_i is the number of i-mers A_i. Let us assume that the system can change its state according to a specific fragmentation reaction

$$R_{ij}: \quad \vec{N} \to \vec{N} + \vec{e}_j + \vec{e}_i - \vec{e}_{i+j}$$

to a new state $\vec{N}'$ after a certain time interval Δt (waiting time). A simple calculation [9,10] yields that the waiting time distribution is given by

$$f(\Delta t) = u_0(\vec{N})\exp(-u_0\Delta t),$$

$$\text{where } u_0(\vec{N}) = \sum_{j=2}^{L}a_jN_j. \tag{5}$$

Here, $u_0(\vec{N})$ can be interpreted as the total transition rate from the state $\vec{N}$ to any other state $\vec{N}' \neq \vec{N}$. In order to simulate the time $t+\Delta t$ at which the next reaction occurs, a random number according to the dis-

tribution $f(\Delta t)$ has to be tossed. Random numbers Δt distributed according to $f(\Delta t)$ can be received from uniform distributed ones by the transformation

$$\Delta t = \frac{1}{u_0(\vec{N})} \ln(\eta_1), \tag{6}$$

where η_1 is uniformly distributed in $]0,1]$. A second random number η_2 also uniformly distributed in $]0,1]$ is used to determine the particle that undergoes fragmentation. Its size k is selected according to the probability $a_k N_k / (\sum_{m=2}^{L} a_m N_m)$. To specify in which specific reaction $R_{i,k-i}$ occurs, a third random number η_3 is used. It represents the number of the breaking bond. If no cycles occur, a k-mer has exactly $k-1$ bonds. If, in addition, all bonds break with equal probability, then η_3 is randomly selected out of the set $\{1, 2, ..., k-1\}$. However, in certain cases, it is supposed that bonds break more likely in the middle of the particle than at the ends [1,15]. This can also be modeled with our algorithm by tossing η_3 according to the desired fragmentation probability.

To summarize, the dynamics of the fragmentation process can be simulated by the following stochastic algorithm [9,10] :

(a) Start with the initial condition $\vec{N}(0) = \vec{N}_0$ and set time t to zero.

(b) Calculate $u_0(\vec{N})$ according to Eq. (5).

(c) Determine the time Δt after which a reaction occurs by use of Eq. (6). Replace t by $t + \Delta t$.

(d) Select the size k of the fragmenting particle and the breaking point i of the particle undergoing fragmentation as described above.

(e) Change the state of the system according to the reaction selected in (d), i.e., replace $\vec{N}$ by $\vec{N} + \vec{e}_i + \vec{e}_{k-i} - \vec{e}_k$.

(f) Go to step (b) if simulation time is less than the final time.

This procedure has to be carried out several times to generate an ensemble of realizations of the fragmentation process. From this ensemble, physical quantities of interest can be estimated. For example, the expectation value $\langle N_k \rangle$ of the number of particles of size k is estimated by

$$\frac{1}{N_R} \sum_{i=1}^{N_R} N_k^{(i)}(t) \ ,$$

where N_R is the number of realizations of the stochastic process and $N_k^{(i)}(t)$ is the number of particles of size k measured at time t in the ith realization.

The key features of the stochastic simulations presented here are the following. For the initial conditions, we assume that a single cluster of size L is present. Good statistics are achieved by generating an ensemble of 10^4 realizations of the processes. From this ensemble, averages denoted by brackets (e.g., $\langle N \rangle$) and standard deviations denoted by Δ (e.g., ΔN) are estimated. For convenience, time is measured in units of $\tau(L) = 1/a_L$, i.e., $T = t a_L$. Simulations were performed on a 486-type computer processor, and each one took less than an hour to conduct.

IV. SIMULATION RESULTS AND DISCUSSION

A. Nonshattering model

In Fig. 1 the stochastic simulation results for the nonshattering model with $a_k = (k-1)^2$ are presented. In Fig. 1(a) the temporal evolution of the weight-average mass $\langle M_W \rangle$ and of the total number of particles $\langle N \rangle$ is shown. It is clearly seen that the fragmentation process stops at a certain time where the system consists solely of monomers. The range where the continuous fragmentation model approximates the discrete one can be estimated by comparing the evolution of M_W obtained by the stochastic simulation with the prediction of the scaling theory of the deterministic continuum fragmentation equation [6]. It is seen that for $T \leq 10^2$ for the model with $L = 10^2$ and for $T \leq 10^5$ for $L = 10^4$ the continuum and the discrete model yield equivalent results.

The temporal evolution of the relative rms fluctuations of $\Delta N / \langle N \rangle$ and of $\Delta M_W / \langle M_W \rangle$ is presented in Fig. 1(b). This plot has several interesting features. First, the relative rms fluctuations are of the order of 0.45, a remarkably high value. Second, the time at which the fluctuations are maximum depends on the quantity $\Delta N / \langle N \rangle$ has a maximum at $T \approx 0.8$ whereas $\Delta M_W / \langle M_W \rangle$ has a maximum at $T \approx 3$. Third, the fluctuations are independent of the size L of the initial cluster for $T \leq 10^2$. Thus, in this time range, the fluctuations are a function of T only. This suggests that the fluctuations obey a simple scaling law.

Let us now look at the distribution of a single physical quantity measured at an intermediate time as obtained from 10^4 realizations of the stochastic process. We expect this distribution to be peaked around its mean value. We demonstrate this in Fig. 1(c), which is a histogram plot of the total number of particles N at time $T = 10^3$. It is seen that the quantity N has a Gaussian distribution. For comparison, we fitted a Gaussian function of the form $A \exp(-[x-\bar{x}]^2/(2\sigma^2))/[(2\pi)^{1/2}\sigma]$ to the data points. A histogram plot of the weight-average mass is also Gaussian. Our simulations demonstrate that the deterministic description of fragmentation is reasonable for nonshattering models, since the distribution of any physical quantity is sharply peaked around its mean value.

B. Shattering model

The situation is quite different when a shattering-fragmentation model is investigated. We demonstrate this by showing the stochastic simulation results corresponding to the model $a_k = (k-1)^{-2}$. From the temporal evolution of the weight-average mass $\langle M_W \rangle$ and of the total number of particles $\langle N \rangle$ shown in Fig. 2(a) it is seen that the decay is much more rapid than in the nonshattering model.

The temporal evolution of the relative rms fluctuations of $\Delta N / \langle N \rangle$ and of $\Delta M_W / \langle M_W \rangle$ is presented in Fig. 2(b). It can be seen that the fluctuations are enormous, larger than the mean. In contrast to the nonshattering pro-

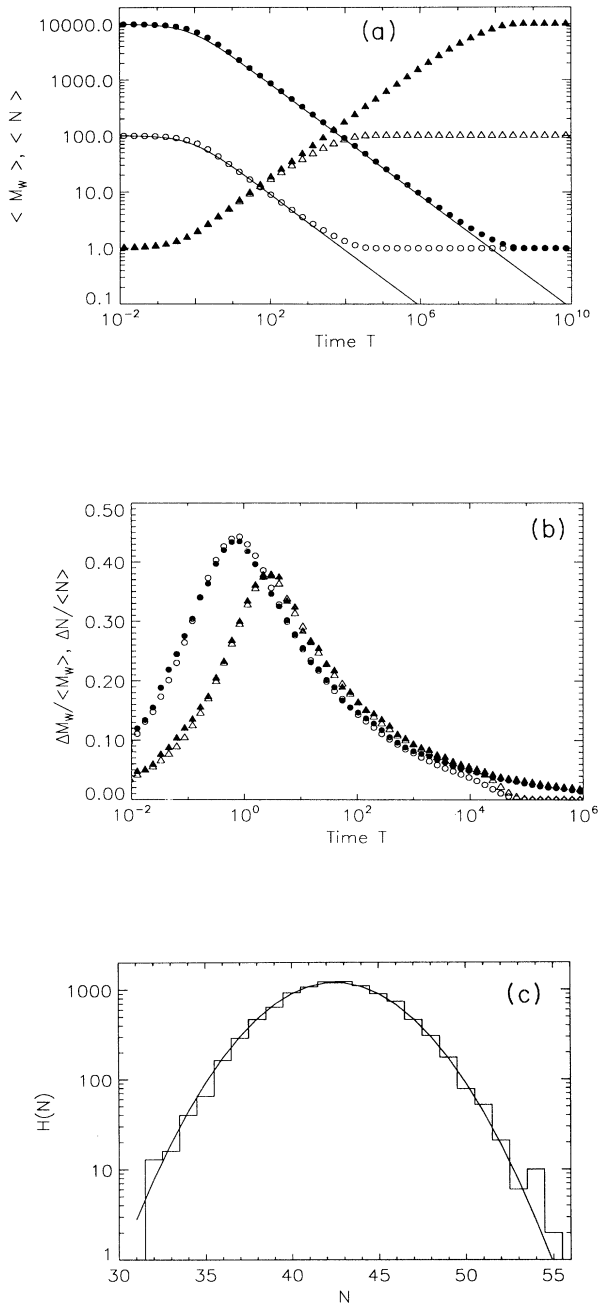

FIG. 1. Nonshattering model: (a) Weight-average mass $\langle M_W \rangle$ (circles) and total number of particles $\langle N \rangle$ (triangles) over time T with a single initial cluster of size $L = 10^2$ (unfilled symbols) and $L = 10^4$ (filled symbols). The lines are the corresponding predictions of $S(t)$ from the scaling theory of the continuous fragmentation equation (2) with $\omega = 6 \times 10^{-3}$ and $\omega = 7 \times 10^{-9}$. (b) Relative rms fluctuations of $\Delta N/\langle N \rangle$ (triangles) and $\Delta M_W/\langle M_W \rangle$ (circles) over time T with a single initial cluster of size $L = 10^2$ (unfilled symbols) and $L = 10^4$ (filled symbols). (c) Histogram plot for the total number of particles measured at time $T = 10^3$ when the initial cluster has size $L = 10^2$. The frequency distribution $H(N)$, obtained from 10^4 realizations, can be fitted by a Gaussian distribution with parameters $\bar{x} = 42.5$, $\sigma = 3.3$ and prefactor $A = 996$ as shown by the line.

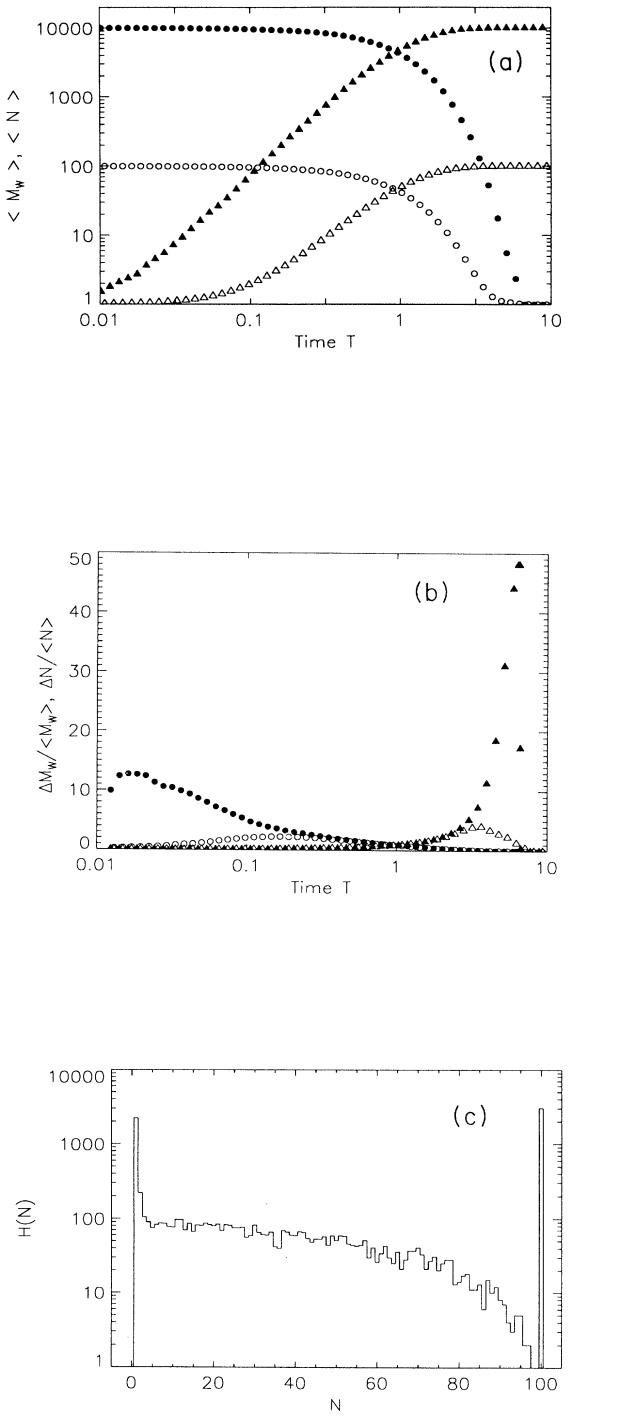

FIG. 2. Shattering model: (a) Weight-average mass $\langle M_W \rangle$ (circles) and total number of particles $\langle N \rangle$ (triangles) over time T with a single initial cluster of size $L = 10^2$ (unfilled symbols) and $L = 10^4$ (filled symbols). (b) Relative rms fluctuations of $\Delta N/\langle N \rangle$ (triangles) and $\Delta M_W/\langle M_W \rangle$ (circles) over time T with a single initial cluster of size $L = 10^2$ (unfilled symbols) and $L = 10^4$ (filled symbols). (c) Histogram plot for the total number of particles measured at time $T = 1.5$ when the initial cluster has size $L = 10^2$. Here, $H(N)$ is the frequency distribution obtained from 10^4 realizations of the process.

cess, the relative order of the fluctuations reaches a value that clearly depends on the size L of the initial cluster. Our simulation results for $\Delta N/\langle N\rangle$ agree well with those obtained by Maslov [8] presented in Fig. 1 of his paper (Maslov could not obtain the evolution of $\Delta M_W/\langle M_W\rangle$ and of other physical quantities). Since the rms fluctuations are dependent on the considered physical quantity we conclude that there exists no universal "shattering-onset" time in discrete shattering processes.

Figure 2(c) shows that the distribution of the total number of particles N at time $T = 1.5$ is U shaped. Thus, the expectation value which is described mathematically by the solution of the deterministic fragmentation equation (1) does *not* represent the result of a typical realization of the process. There are about 2000 realizations yielding just one particle and about 3000 realizations yielding 10^2 particles, that is all particles are monomers. The remaining 5000 realizations yielding particle numbers between 1 and 100. Note that the discontinuity in the distribution function at $N = 99$ is caused by the fact that the system with 98 monomers and one dimer has a very high transition rate to convert to the state where all particles are monomers.

C. Discussion of U shape

We observed the same qualitative behavior also for other models such as $a_k = 1/k$ or an "extremely shattering" process defined by $a_k = \exp(-k)$. Also other variables such as the z-average mass or the number of monomers N_1 show qualitatively the same non-Gaussian distribution. In addition we observed that the same qualitative form of the distribution function also holds for discrete shattering models with nonrandom scission.

Thus, the U-shaped distribution may be a universal characteristic of the discrete shattering process. This can be explained qualitatively as follows. Consider an extremely shattering model with an initial particle of size L. At small times, essentially nothing will happen, i.e, the system will stay in the state with just one particle of size L. At large times, however, the system will consist of exactly L monomers. Thus, at small times and at large times, the distributions will have a single peak. At intermediate times the distribution function is U shaped [Fig. 2(c)]. The transition between these different states of the distribution function is very fast and in fact nearly instantaneous because of the shattering kinetics. In other words, an observer measuring the total number of particles at an intermediate time will see either one particle or L particles.

Such U-shaped, or bimodal, distributions are known also in other fields of chemical kinetics. In [16] a model of combustion in a closed vessel is investigated. The solution of the master equation yields the appearance of multiple humps in the probability distribution. In [17] it is shown that a model describing explosive chemical systems exhibits a bimodal distribution of the probability function. There, the bimodality is caused by random initial conditions in connection with a nonlinear evolution equation where two time scales can be easily separated.

Finally, we have calculated distributions of the quantities N and M_W when the shattering fragmentation process starts with two clusters. These distributions are W shaped which should be clear after the discussion above. The left peak comes from the state where measurements yield two particles whereas the right peak represents the situation where $2L$ monomers are present. The peak in the middle is caused by realizations where $L+1$ particles are present. The generalization of this picture to more than two initial clusters is straightforward. For a large number of initial clusters the fluctuations of N are Gaussian distributed with a width depending sensitively on L and on the number of initial clusters. Thus, for experimental systems, averages can be measured precisely only for a large number of small initial clusters, and the deterministic description is physically meaningful only in this limit.

To conclude, discrete shattering processes are interesting model systems to investigate the influence of fluctuations on the mean-field kinetics. The stochastic simulation algorithm used here is an efficient tool to study these fluctuations. It can be tuned to study any initial condition or breakup kinetics as necessary.

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[1] R.M. Ziff and E.D. McGrady, J. Phys. A **18**, 3027 (1985); Macromolecules **19**, 2513 (1986).
[2] R. Shinnar, J. Fluid Mech. **10**, 259 (1961).
[3] L. Quali and E. Pefferkorn, J. Colloid Interface Sci. **161**, 237 (1993).
[4] D. Beysens, J.-M. Petit, T. Narayanan, A. Kumar, and M.L. Broide, Ber. Bunsenges. Phys. Chem. **98**, 382 (1994).
[5] A.F. Filipov, Theory Probab. Its Appl. **4**, 275 (1961); E.D. McGrady and Robert M. Ziff, Phys. Rev. Lett. **58**, 892 (1987).
[6] Z. Cheng and S. Redner, Phys. Rev. Lett. **60**, 2450 (1988); J. Phys. A **23**, 1233 (1989).
[7] S.E. Esipov, L.P. Gor'kov, and T.J. Newman, J. Phys. A **26**, 787 (1993).
[8] D.L. Maslov, Phys. Rev. Lett. **71**, 1268 (1993).
[9] D.T. Gillespie, J. Comput. Phys. **22**, 403 (1976); J. Phys. Chem. **81**, 2340 (1977).
[10] J. Honerkamp, *Stochastic Dynamical Systems* (VCH, Weinheim, 1994).
[11] H.P. Breuer, J. Honerkamp, and F. Petruccione, Comp. Polym. Sci. **1**, 233 (1991); Chem. Phys. Lett. **190**, 199

(1992).
[12] M. Thorn, H.P. Breuer, F. Petruccione, and J. Honerkamp, Macromol. Theory Simul. **3**, 585 (1994).
[13] M. Thorn and M. Seeßelberg, Phys. Rev. Lett. **72**, 3622 (1994).
[14] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North–Holland, Amsterdam, 1992).
[15] M. Ballauff and B.A. Wolf, Macromolecules **14**, 654 (1981).
[16] F. Baras, G. Nicolis, M. Malek Mansour, and J.W. Turner, J. Stat. Phys. **32**, 1 (1983).
[17] M. Frankowicz, M. Malek Mansour, and F. Baras, Physica A **146**, 650 (1987).