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Influence of the chain mobility on the dynamic scaling of chain-chain aggregation in three dimensions

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The dynamical scaling of the chain-chain aggregation model is investigated in three dimensions. Monte Carlo simulations are performed on a cubic lattice with a diffusion coefficient proportional to k^{γ} for a chain of mass k. At large times the mean chain mass grows like t^{z} and the mean-square radius of gyration like $t^{2z/D}$, where D is the fractal dimension of the chains. The relation $z=(1-1/D+\varphi-\gamma)^{-1}$, obtained when one assumes that the sticking probability between two chains of mass k is proportional to $k^{-\varphi}$, is checked numerically with $\varphi(3D)\approx 0.72$.

A model for linear polycondensation in which the chemical reaction is simulated on a lattice by the aggregation of randomly diffusing chains has been recently introduced.[1] In two dimensions (2D) the dynamic scaling of this model with a diffusivity coefficient proportional to k^{γ} for a chain of mass k has been investigated[2] with the result that the chain-mass distribution function changes from monodisperse to polydisperse at a value $\gamma_{ch}(2D)\approx 0$ when γ is increased. This change is also observed for the aggregation of ramified clusters with $\gamma_{cl}(2D)\approx -0.25$ and $\gamma_{cl}(3D)\approx -0.5$ (Ref. 3) although there exists a qualitative difference between the two models: chain-chain aggregation is not only diffusion limited but also reaction limited because two chains stick only when their two tips meet. In 2D, our numerical results support the assumption that the sticking probability is a homogeneous function of degree $-\varphi$ so that two chains of mass k stick with a probability proportional to $k^{-\varphi}$; we got $\varphi(2D)=0.36\pm 0.02$, independent of γ. We present here a series of 3D simulations for six values of the mobility exponent γ in the range $-1.8\leq\gamma\leq 0.25$. The results are analyzed in close analogy with the 2D case[2] to which the reader is referred for further details.

A simulation is started with 8000 monomers of unit mass (one-particle chains) randomly distributed on nonadjacent sites of a $100\times 100\times 100$ cubic lattice with periodic boundary conditions. Each Monte Carlo step is performed as follows.

(1) Randomly select a k-particle chain with a probability proportional to $k^{-\gamma}$ and increment the physical time.

(2) Choose at random one of the six possible directions on the lattice and translate the selected chain by one lattice unit in this direction, only when the new position is free.

(3) If the tips of two different chains arrive on first-neighbor sites, make the two chains merge.

For fifty values t_i of the physical time, regularly distributed on a logarithmic scale, the number of k-particle chains per unit volume $n(k,t_i)$ and their mean-square radius of gyration $R^2(k,t_i)$ are stored; the results presented here are averages over fifty simulations for each γ value considered.

The scaling assumption that both $n(k,t)$ and $R^2(k,t)$ are generalized homogeneous functions of the chain mass k and the time t has been checked numerically for chain-chain aggregation in 2D (Ref. 2) and also for cluster-cluster aggregation in 2D (Ref. 4) and 3D (Refs. 3, 5, and 6). From this assumption, the following relations result:

$$n(k,t)=t^{-2z}g(x)=k^{-2}f(x)\,, \tag{1a}$$

$$R^2(k,t)=t^{2z/D}r(x)=k^{2/D}q(x)\,, \tag{1b}$$

where D is the fractal dimension of the chains and z the dynamic exponent entering the scaling parameter $x=k/t^{z}$. The asymptotic behavior of the two scaling functions $f(x)$ and $g(x)$ may be predicted[7] in the framework of the Smoluchowski theory:[8] when $x\gg 1$, both functions decrease exponentially and when $x\ll 1$, three classes of kinetics are possible. In classes I and II we have

$$f(x)\sim x^{2-\tau};\quad g(x)\sim x^{w/z-2}\,, \tag{2}$$

with the scaling relation $w=(2-\tau)z$, and in class III, f and g are both exponentially decreasing functions of x. Defining the mth moment of the distribution function as

$$M_m(t)=\sum_{k=1}^{k=\infty}k^{m}n(k,t) \tag{3}$$

and introducing the asymptotic form of $g(x)$ for $x\ll 1$, we obtain the large-time behavior of the total number of

chains

$$N(t)\sim t^{-z}, \text{ class III or } \tau\leq 1,$$
$$N(t)\sim t^{-w}, \quad \tau>1, \tag{4}$$

and the mean chain mass

$$\langle k\rangle = M_2(t)/M_1(t)\sim t^{z}. \tag{5}$$

At large times $\ln N$ and $\ln\langle k\rangle$ become linear functions of $\ln t$ and the slopes of both curves have the same absolute value within the error bars so that we always have $\tau\leq 1$ or a class-III kinetics for $-1.8\leq\gamma\leq 0.25$. We also define a mean square radius of gyration, averaging $R^2(k,t)$ over all the chains present at time t, with the following asymptotic behavior:

$$\langle R^2\rangle\sim t^{2z/D}\sim\langle k\rangle^{2/D}. \tag{6}$$

Plotting $\ln\langle k\rangle$ as a function of $\ln\langle R^2\rangle^{1/2}$, we get straight lines at large $\langle k\rangle$ whose slopes give the chain fractal dimension D near to the self-avoiding walk value. These estimates, together with those of the dynamic exponent z, are given in Table I. Larger chains are obtained when γ is increased and the variation of D with γ is essentially due to finite-size effects.

Another test of the scaling assumption is directly provided by the time and mass dependence of the distribution function (1a). Because of mass conservation, the curves $\ln n(k,t_i)$ against $\ln k$ obtained at different times t_i all have a common tangent with slope -2. On the other hand, fixing the chain mass at given values k_i, the set of curves $\ln n(k_i,t)$ against $\ln t$ have an envelope with a slope $-2z$, when $\tau<0$ or in class III only. Such sets of curves are displayed in Figs. 1 and 2 for three typical values of γ. It can be seen in Fig. 1 that the chain-mass distribution function which is monodisperse for $\gamma<0$ becomes polydisperse above $\gamma_{ch}(3D)\approx 0$ like in 2D (Ref. 2) to be compared with $\gamma_{cl}(3D)\approx = -0.5$ for the aggregation of clusters.[3] For the same γ value we also observe that the common tangent of the curves in Fig. 2 disappears, suggesting a qualitative change for the scaling function $g(x)$ at small x: for $\gamma\gtrsim 0$ we expect a power law with $0\leq\tau\leq 1$

TABLE I. The chain fractal dimension D and the dynamic exponents z and τ for the different γ values considered here. A slight increase of D with γ is observed and z^{-1} appears to be a linear function of γ. The exponent τ has been estimated for $\gamma\geq 0$ only, when the scaling function $g(x)$ is monotonic.

γ	D	z	τ
−1.8	1.58	0.35	. . .
−1.2	1.59	0.45	. . .
−0.6	1.63	0.57	. . .
−0.25	1.64	0.77	. . .
0	1.66	0.90	0
0.25	1.71	1.10	0.2

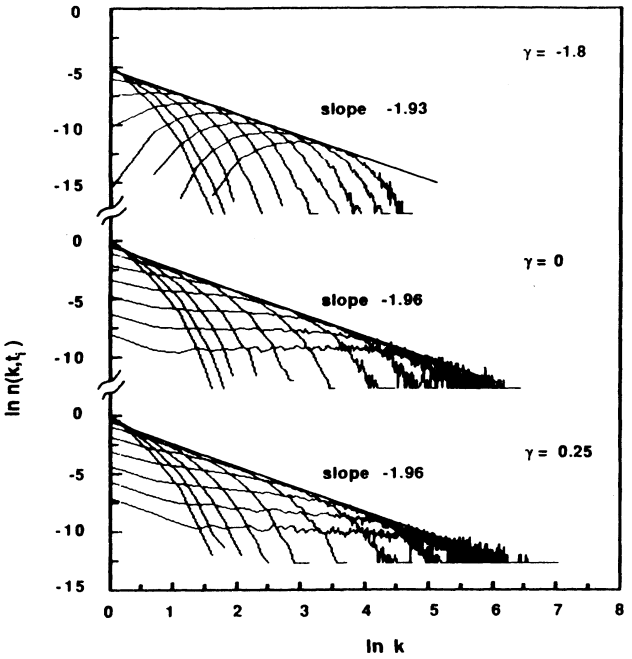

FIG. 1. Log-log plot of the distribution function $n(k,t_i)$ as a function of the chain mass k for three values of the mobility exponent γ. For a given γ value all the curves obtained at different times t_i have a common tangent with a slope close to -2. The mass distribution is monodisperse when $\gamma<0$ and polydisperse when $\gamma\gtrsim 0$.

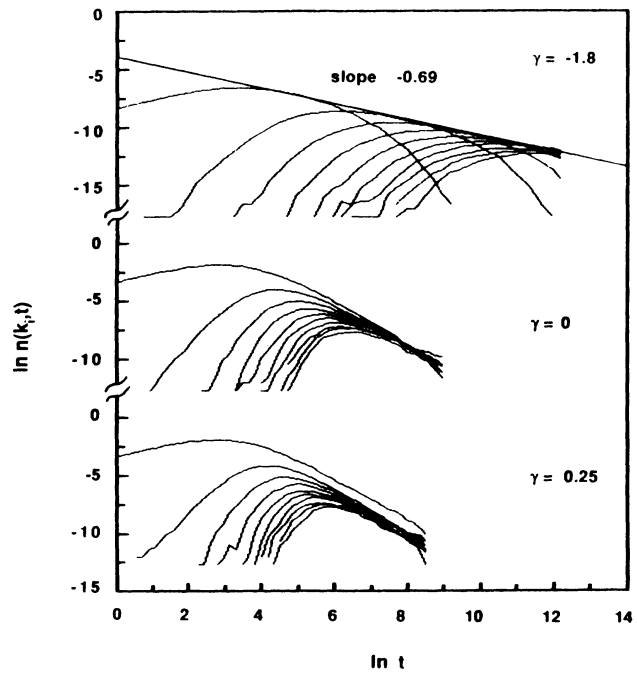

FIG. 2. Log-log plot of the distribution function $n(k_i,t)$ as a function of the time t for three values of γ. When $\gamma<0$ the curves for the different values k_i of the chain mass have a common tangent with a slope $-2z$ and when $\gamma\gtrsim 0$ this envelope disappears.

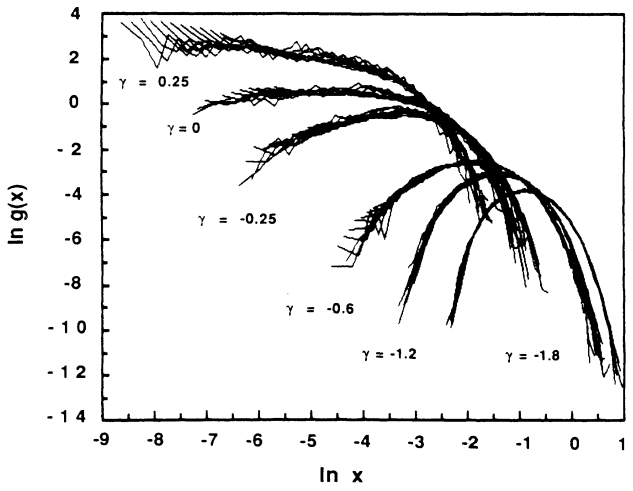

FIG. 3. Log-log plot of the scaling function $g(x)$ against the scaling variable $x=k/t^{z}$. This function is monotonic when $\gamma \gtrsim 0$ and the slope at small x gives the exponent τ; it is bell-shaped when $\gamma<0$.

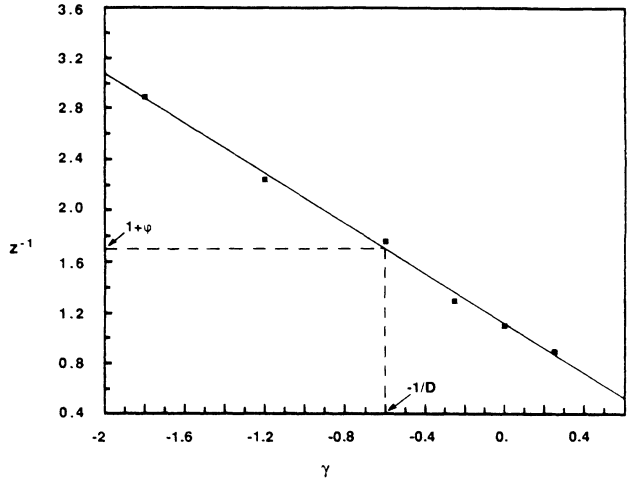

FIG. 4. Inverse of the dynamic exponent z as a function of the mobility exponent γ. The straight line is a least-squares fit of the numerical data (black squares) with a slope -0.97. The sticking exponent φ is deduced from $z^{-1}(-1/D)=1+\varphi$.

and for $\gamma \lesssim 0$ either a decreasing exponential or a power law with $\tau<0$. Figure 3 gives a log-log plot of $g(x)$ as a function of x for all the γ values studied; the reasonable dispersion of the results supports the scaling assumption. On the small x side, the slopes of the curves for $\gamma \geq 0$ give the exponent τ (see Table I) but when $\gamma<0$ the mean-square fits do not allow to discriminate between an exponential decrease or a negative τ value. To decide requires the knowledge of the reaction kernel $K(i,j)$ (Ref. 7) entering the Smoluchowski equation[8]

$$\frac{\partial n(k,t)}{\partial t}=\frac{1}{2}\sum_{i+j=k}K(i,j)n(i,t)n(j,t) -n(k,t)\sum_{i=1}^{\infty}K(k,i)n(i,t)\,, \tag{7}$$

which gives the time variation of the k-mers. For chain-chain aggregation $K(i,j)$ is obtained multiplying the kernel valid for cluster-cluster aggregation[2,9] by the sticking probability $h(i,j)$ between two chains of mass i and j which is not known. We intend to determine this quantity numerically, which requires much more extensive simulations than we have done here. Finally, let us consider the variation of the dynamic exponent z with the mobility exponent γ. For the cluster-cluster aggregation model the relation

$$z^{-1}=(2-d)/D+1-\gamma \tag{8}$$

has been proposed[5,6] and verified by numerical simulations.[3] Since in our case two chains stick only when their two tips meet this relation has to be modified, and assuming that the sticking probability between two chains of mass k is proportional to $k^{-\varphi}$ one gets the following linear relation:[2]

$$z^{-1}=(2-d)/D+1+\varphi-\gamma\,. \tag{9}$$

A straight line with a slope close to -1 is effectively obtained when z^{-1} is plotted as a function of γ (Fig. 4) and we find $\varphi(3D)=0.72\pm0.04$ for the sticking exponent, to be compared to the value $\varphi=2(1-1/D)=0.78\pm0.05$ predicted by a simple scaling argument based on the mutual transparency of the chains.[2]

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