Diffusion of clusters with randomly growing masses

Jerzy Łuczka
Department of Theoretical Physics, Silesian University, 40-007 Katowice, Poland

Peter Hänggi
Department of Physics, University of Augsburg, Memminger Strasse 6, D-86135 Augsburg, Germany

Adam Gadomski
Department of Physics of Nonmetallic Materials, Silesian University, 41-200 Sosnowiec, Poland
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Diffusion of fractal clusters of dimension d_f in a three-dimensional space is investigated. The diffusion process is assumed to be modeled by a standard parabolic diffusion equation but with a random diffusion coefficient. The motivation for this assumption is provided by two pieces of evidence: (1) the cluster diffusion coefficients depend on the clusters' masses, sizes, and shapes; (2) the masses of clusters change stochastically in time due to random attachment or detachment of particles. Two models of the growing process are considered: (a) a Poisson process; (b) a simple birth-and-death process with linear rules. The mean square displacement of the cluster mass centers is analyzed and its anomalous behavior is demonstrated as a function of the fractal cluster dimension.

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I. INTRODUCTION

Diffusion processes are observed in simple as well as in complex systems. In the former, a single Brownian particle can be mentioned. The properties of the Brownian particle are described by a standard diffusion equation with a diffusion constant $D=kT/m\gamma$ [1] (k is the Boltzmann constant, T is the temperature of the surroundings in which the particle moves, m is its mass, and γ is a friction coefficient). The main features of Brownian motion are that it is a Gaussian-Markovian process and the mean square of its displacement is a linear function of time—it is called normal diffusion. If the mean-squared displacement is not a linear function of time then the process is called anomalous diffusion. Typical examples of anomalous diffusion are a random walk of particles on fractal structures and a random walk in random and disordered media [2].

As an example of diffusion processes in complex systems one can mention transport processes of clusters or aggregates (structures consisting of connected subsystems, molecules, particles, etc.) in biological systems, e.g., diffusion of proteins or protein aggregates in lipid surroundings (cf. [3] and references therein). The complexity of these systems is mostly due to a certain inhomogeneity or anisotropy (obstacles, traps, etc.) of the environment in which some particles or tracers (i.e., some "well-defined" objects) proceed in a random motion. In general, one should be aware that in biophysical systems, in which both aggregation of clusters and random walk of their centers of mass is observed, one may expect a huge variety of physicochemical phenomena. Let us recall, for example, such processes as aggregation of receptors for hormones, clustering of virus glycoproteins in the plasma membrane of an infected cell, or cation-induced phase separation of lipid or even protein domains (cf. Ref. [3] and references therein). It is known [3,4] that when observing those processes we easily notice two groups of effects, i.e., some basic ones, such as diffusion of clusters (purely random or directed, translational and/or rotational) and aggregation of them; some additional ones, such as electrostatic repulsion of clusters, hydrodynamic interactions among clusters, sticking at the interfaces, the presence of obstacles and steric hindrances in the system, lateral gel separation, etc. [3–5]. Another scenario, however, is possible as well; namely, that some complex objects, which may accidentally gain or lose their mass [6], walk at random in a rather homogeneous and isotropic medium. An example of a mass changing object is a colloid cluster (a low-density tenuous "object") which may grow in some liquids or gases and the trajectories of which are expected to be Brownian [6]. For systems like these, clusters (or particles) move via random-walk trajectories; they collide with each other and create new aggregates. This process may be fast and irreversible (diffusion-limited cluster-cluster aggregation [7]) or slow and reversible (reaction-limited cluster-cluster aggregation [8]). For such systems the diffusion coefficient is assumed to be inversely proportional to a certain power of the cluster mass. The power, in turn, takes into account the effects of cluster geometry and in typical physical systems is equal to the inverse of the fractal dimension d_f of the diffusing cluster [9–11]. It should be stressed that the above listed processes have strong support in certain practical realizations like aggregation of colloidal particles, aggregation of suspensions, gel formation or flocculation (cf. Ref. [12] for a more recent outlook). A simple model of diffusion of such (fractal) objects with changing mass has recently been proposed [13]. This model is based on the standard three-dimensional diffusion equation with a time-dependent diffusion coefficient. In the work [13], the assumption of a deterministic and linear in time increase of mass M is used, $M(t)=M_0(1+\eta t)$, where M_0 is the initial mass of the cluster and $\eta>0$ is a constant. It is shown that the diffusion process is anomalous and the mean square displacement $\langle r^2(t)\rangle$ of the cluster mass center depends on the fractal dimension d_f of the cluster. For large times, $t \gg 1$, it behaves as

$$\langle r^2(t)\rangle \propto \begin{cases} \dfrac{6d_f D_0}{(1-d_f)\eta M_0^\beta} & \text{if } d_f<1, \\ \dfrac{6D_0}{\eta M_0^\beta}\ln(\eta t) & \text{if } d_f=1, \\ \dfrac{6d_f D_0}{(d_f-1)\eta M_0^\beta}(\eta t)^{(d_f-1)/d_f} & \text{if } d_f>1, \end{cases} \tag{1}$$

where D_0 is a diffusion constant and $\beta=1/d_f$.

More realistic, however, is a model of mass that grows stochastically due to random attachment or detachment of particles. This process can be described by stochastic step functions. Examples are Poisson and birth-and-death processes. The Poisson and pure birth processes can model irreversible aggregation in which the cluster mass grows in time and any part of the aggregate cannot be disconnected from it. In contrast, the birth-and-death process with the death transition coefficient greater than zero corresponds to the situation when particles or ingredients can get rid of the aggregate (e.g., a reversible polymerization as in Ref. [14] where the kinetics of red blood cells in diluted human blood was considered).

In the next section, the basis of our modeling is presented. In Sec. III, the mean square displacement of the center of the diffusing aggregate is calculated for the case that a Poisson process governs the growing mass. In Sec. IV, a birth-and-death process of growing mass is considered. The analysis is carried out for a process with linear birth and death rules. Two limiting cases of this process are studied, namely, the case of equal birth and death transition coefficients and the case of a pure birth process. The summary is given in Sec. V.

II. DESCRIPTION OF MODEL

The main assumptions concerning the diffusional motion of growing objects are the same as in [13]. Let us briefly recall them. A fractal cluster of dimension d_f which diffuses in dilute solutions (or gases) is assumed to be described by a standard three-dimensional diffusion equation,

$$\frac{\partial p(\mathbf{r},t)}{\partial t}=D\Delta p(\mathbf{r},t), \quad p(\mathbf{r},0)=p(\mathbf{r}) , \tag{2}$$

where $p(\mathbf{r},t)$ is the probability density of finding a cluster mass centered at $\mathbf{r}$ at instant t and $p(\mathbf{r})$ is the initial probability distribution of the cluster. The diffusion coefficient D should depend on the structure of the clusters, in particular, on their mass, size, shape, etc. [9–11]. It is known that in generic colloidal systems the diffusion coefficient varies as the inverse of the mass and scales as

$$D=D_0/M^\beta , \tag{3}$$

where the exponent β takes into account the effects of cluster geometry. Assuming the aggregates are self-similar fractals with fractal dimension d_f, one can expect that [9–11]

$$\beta=1/d_f . \tag{4}$$

The existence of such dependence of a diffusion coefficient upon cluster mass clearly follows from the Kirkwood-Riseman theory [15] and has strong practical evidence, noticed mostly in some polymer systems [16]. The same form has been used in large-scale computer simulations of diffusion-limited cluster-cluster aggregation processes [9–11].

The mass M of the cluster changes in time due to attachment and/or detachment of particles: between collisions its mass is constant and after a reactive collision particles stick to the aggregate. The process of mass changing is obviously random in time and changes of the mass are discrete. It may be modeled by random step functions $N(t)$ as

$$M=M(t)=M_0[1+N(t)] , \tag{5}$$

where M_0 is the initial mass of the cluster. Now, the diffusion coefficient is a random function of time,

$$D=D(t)=\frac{D_0}{M_0^\beta[1+N(t)]^\beta} \tag{6}$$

and Eq. (2) with (6) becomes a stochastic partial differential equation. In this case, the probability density $P(\mathbf{r},t)$ of the cluster mass center is an averaged solution of Eq. (2),

$$P(\mathbf{r},t)=\langle p(\mathbf{r},t)\rangle^N , \tag{7}$$

where the superscript N indicates an average over all realizations of the process $N(t)$.

Let us mention that the diffusion process is now *non-Gaussian* and *non-Markovian*. In particular, this means that higher-order moments or multitime correlation functions do not factorize and cannot be expressed by lower-order characteristics. Assuming that at $t=0$ the initial state of the system does not depend upon the process $N(0)$, solving (2) and using (7) yields

$$P(\mathbf{r},t)=\int_{-\infty}^{\infty}\langle G(\mathbf{r}-\mathbf{r}_0,t)\rangle^N p(\mathbf{r}_0)d^3\mathbf{r}_0 , \tag{8}$$

where

$$G(\mathbf{r},t)=[4\pi F(t)]^{-3/2}\exp[-r^2/4F(t)] , \tag{9}$$

$$F(t)=\int_0^t ds\, D(s)=\frac{D_0}{M_0^\beta}\int_0^t ds[1+N(s)]^{-\beta} , \tag{10}$$

and $r^2=\mathbf{r}\cdot\mathbf{r}$. Generally, it is impossible to obtain a compact and tractable form of the propagator $\langle G(\mathbf{r}-\mathbf{r}_0,t)\rangle^N$. But simple characteristics of the process (as, e.g., its moments) can be analyzed. In particular, the mean square displacement $\langle r^2(t)\rangle$ of the aggregate mass center reads

$$\langle r^2(t)\rangle=\langle r^2(0)\rangle+6\langle F(t)\rangle \ . \tag{11}$$

For convenience we take $\langle r^2(0)\rangle=0$ and then

$$\langle r^2(t)\rangle=\frac{6D_0}{M_0^\beta}\int_0^t ds \sum_{k=0}^{\infty}(1+k)^{-\beta}P_k(s) \ , \tag{12}$$

where

$$P_k(t)=\text{Prob}\{N(t)=k\} \tag{13}$$

is the probability that at instant t the process $N(t)$ takes the value k. Below we consider two models of the growing process $N(t)$.

III. POISSON GROWTH MODEL

As a consequence of Eq. (5), increments of the aggregate mass occur in units of its starting mass, i.e., M_0, but the moment of sticking is random. The probability that k-unit particles attach to the cluster during the time interval $(0,t)$ is given by the Poisson distribution [17]

$$P_k(t)=\frac{(\lambda t)^k}{k!}e^{-\lambda t} \ , \tag{14}$$

where λ is the mean number of unit particles attached to the cluster per unit time. It is the only process for which the mean number and fluctuations of attached particles increase linearly in time,

$$\langle N(t)\rangle=\lambda t \ , \tag{15}$$

$$\langle N^2(t)\rangle-\langle N(t)\rangle^2=\lambda t \ . \tag{16}$$

Realizations of this process can be represented by nondecreasing step functions with unit increments and random length of steps (see Fig. 1). For an arbitrary value of the cluster dimension d_f, Eq. (12) for this model can be represented by the expression

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0^\beta \Gamma(\beta)}\int_0^\infty dy \frac{y^{\beta-1}}{e^y-1}[1-e^{-\lambda t(1-e^{-y})}] \ , \tag{17}$$

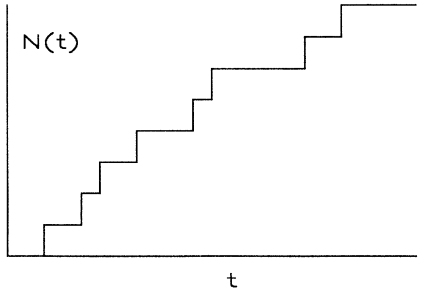

FIG. 1. Sketch of a possible realization of the Poisson process $N(t)$ with the initial value $N(0)=0$ and unit steps at random instants t_i, $i=0,1,2,\ldots,$. $N(t_{i+1})-N(t_i)=1$.

where $\Gamma(\beta)$ is the gamma function. To obtain the representation (17) we have utilized the identity [18]

$$\Gamma(\beta)a^{-\beta}=\int_0^\infty dy\, y^{\beta-1}e^{-ay} \ , \tag{18}$$

which is valid for any $\text{Re}(\beta)>0$ and $\text{Re}(a)>0$.

If the fractal dimension of the cluster is less than 1, $d_f<1(\beta>1)$, then the integral in (17) converges for any $t>0$ and for $t\to\infty$ it tends to a constant value [18],

$$\lim_{t\to\infty}\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0^\beta}\zeta(\beta), \quad \beta=1/d_f>1 \ , \tag{19}$$

where $\zeta(\beta)$ is the Riemann zeta function [19]. In this case, saturation effects of fluctuations of the cluster mass center should be observed. The dependence of (19) on the fractal dimension d_f is qualitatively the same as for the deterministic model in (1) for $d_f<1$. If β in (19) is close to 1 then in the neighborhood of the point $\beta=1$ the Laurent series for the Riemann zeta function reads [19]

$$\zeta(\beta)\cong\frac{1}{\beta-1}+\gamma=\frac{d_f}{1-d_f}+\gamma \ , \tag{20}$$

where γ is the Euler constant ($\gamma\cong 1.781$). Using (20) in Eq. (19) gives exactly the same d_f dependence of the mean squared displacement as in the first expression of Eq. (1).

If $d_f=1$ then the integration in Eq. (17) can be carried out analytically [18]. As a result we obtain

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0}[\mathcal{C}+\ln(\lambda t)-\text{Ei}(-\lambda t)] \ , \tag{21}$$

where $\mathcal{C}$ is Euler's constant ($\mathcal{C}\cong 0.577$) and $\text{Ei}(x)$ is the exponential integral function [19]. For $x\to 0$ it behaves as $\text{Ei}(-x)\approx\mathcal{C}+\ln(x)$ and for $x\to\infty$ it has the asymptot-

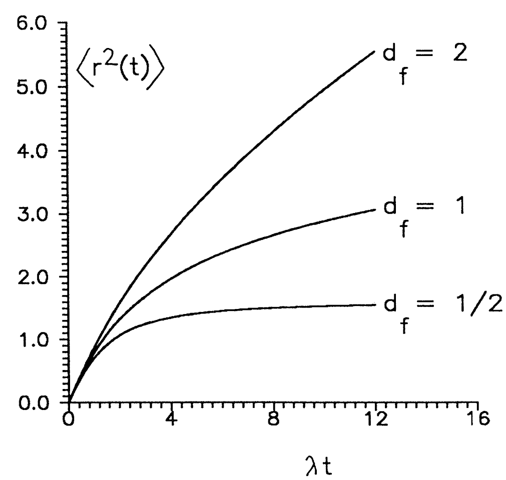

FIG. 2. The mean square displacement (17) of the cluster mass center for the Poisson growth model as a function of rescaled time λt and for three selected values of the cluster dimension $d_f=\frac{1}{2},1,2$. The remaining parameters are fixed in such a way that $6D_0/\lambda M_0^\beta=1$.

ics $\mathrm{Ei}(-x)\approx -\exp(-x)/x$. Hence for long times the mean square displacement diverges logarithmically,

$$\langle r^2(t)\rangle \propto \ln(\lambda t) \ . \tag{22}$$

For this case, the function $\langle r^2(t)\rangle$ behaves asymptotically in the same way as the deterministic counterpart in Eq. (1).

Unfortunately, for $d_f>1$, the integral in (17) cannot be expressed by literature-known functions. We have not been able to evaluate the asymptotics of (17) for $d_f>1$ for long times $t\to\infty$. The graphical representation of Eq. (17) is shown in Fig. 2 for three representative values of the dimension d_f. From the above and from the numerical analysis it follows that for any d_f the diffusion process is anomalously slower than the normal diffusion.

IV. LINEAR BIRTH-AND-DEATH GROWTH MODEL

Let us designate again a discrete set of states by $k=0,1,2,\ldots$. The probability for a birth transition $k\to k+1$ (attachment of a particle to the aggregate) in the time interval $(t,t+\Delta t)$ is denoted by $\lambda_k\Delta t$; likewise, one has $\mu_k\Delta t$ for the probability of a death transition $k\to k-1$ (detachment of a particle from the aggregate) in $(t,t+\Delta t)$. The probability of staying in the state k (no changes of mass) during the same interval is equal to $1-(\lambda_k+\mu_k)\Delta t$. The parameters λ_k and μ_k are assumed to be dependent on k but independent of t and on how the system got to that state. This latter circumstance signifies that the process is Markovian. A master equation for the probabilities $P_k(t)$ in (13) has the form [20]

$$\begin{aligned}&\frac{d}{dt}P_0(t)=\mu_1P_1(t)\ ,\\ &\frac{d}{dt}P_k(t)=\lambda_{k-1}(t)P_{k-1}(t)-(\lambda_k+\mu_k)P_k(t)\\ &\qquad\qquad +\mu_{k+1}P_{k+1}(t),\quad k=1,2,3,\ldots\ .\end{aligned}\tag{23}$$

We shall now consider a process with *linear* birth and death rules (a so called simple birth-and-death process [20]), i.e.,

$$\lambda_k=\lambda k,\quad \mu_k=\mu k,\quad k=0,1,2,\ldots\ , \tag{24}$$

where λ and μ are the probabilistic rates per individual for attachment and detachment of particles to and from the aggregate, respectively. We note that $\lambda_0=\mu_0=0$ so that $k=0$ is an absorbing state, i.e., once the process, which originally started out at a positive k value, reaches the state $k=0$ it is trapped forever (the aggregate is dissolved). For the following we shall assume that $\lambda>\mu$ which implies that on the average the cluster is *growing* with increasing time. A representative realization of the process is shown in Fig. 3.

With the initial conditions $P_k(0)=\delta_{k,1}$, the master equation (23) with the coefficients (24) can be analytically solved [20] and the probabilities $P_k(t)$, $k=0,1,2,\ldots$, explicitly read

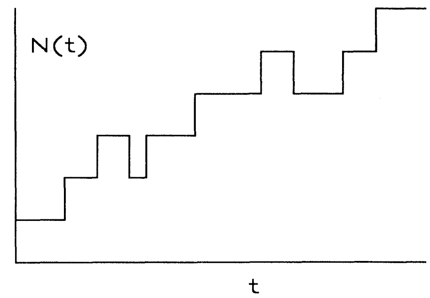

FIG. 3. Sketch of a possible realization of the linear birth-and-death process $N(t)$ with the initial value $N(0)=1$, probabilistic rates $\lambda>\mu>0$, and unit up and down steps $N(t_{i+1})-N(t_i)=\pm 1$.

$$\begin{aligned}&P_0(t)=\alpha(t)\ ,\\ &P_k(t)=[1-\alpha(t)][1-\eta(t)]\eta^{k-1}(t)\ ,\quad k=1,2,3,\ldots\ ,\end{aligned}\tag{25}$$

where

$$\alpha(t)=\mu\frac{e^{(\lambda-\mu)t}-1}{\lambda e^{(\lambda-\mu)t}-\mu},\quad \eta(t)=\lambda\frac{e^{(\lambda-\mu)t}-1}{\lambda e^{(\lambda-\mu)t}-\mu}\ . \tag{26}$$

In the asymptotic state,

$$\begin{aligned}&P_0^{\mathrm{st}}=\lim_{t\to\infty}P_0(t)=\begin{cases}1 & \text{if } \lambda<\mu,\\ \mu/\lambda & \text{if } \lambda>\mu,\end{cases}\\ &P_k^{\mathrm{st}}=\lim_{t\to\infty}P_k(t)=0\quad \text{for } k=1,2,3,\ldots\ .\end{aligned}\tag{27}$$

Let us pay attention to the fact that in the general case the normalization condition for the probabilities $P_k(t)$ need not be satisfied [21]. Here, this is the case for the stationary state when the birth transition coefficient λ is greater than the death transition coefficient μ. Then the probability that the aggregate will dissolve is not equal to 1.

The first two moments of the process are given by the relations [20]

$$\begin{aligned}&\langle N(t)\rangle=e^{(\lambda-\mu)t}\ ,\\ &\langle N^2(t)\rangle-\langle N(t)\rangle^2=\frac{\lambda+\mu}{\lambda-\mu}e^{(\lambda-\mu)t}[e^{(\lambda-\mu)t}-1]\ .\end{aligned}\tag{28}$$

So on the average the cluster mass and its fluctuations grow in time exponentially fast. Equation (12) for this model can be rewritten in the form

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0^\beta}\left[\lambda t-\ln\frac{\lambda e^{(\lambda-\mu)t}-\mu}{\lambda-\mu}+\sum_{k=1}^{\infty}\frac{\lambda^k}{k(1+k)^\beta}\left[\frac{e^{(\lambda-\mu)t}-1}{\lambda e^{(\lambda-\mu)t}-\mu}\right]^k\right]\ . \tag{29}$$

It can be simplified for two cases. For fractal clusters of dimension $d_f=\frac{1}{2}$, Eq. (29) can be expressed in the following way [see Ref. [18], Eq. 5.2.6(2)]:

$$\langle r^2(t)\rangle = \frac{6D_0}{\lambda M_0^2}\left\{2+\lambda t - \frac{\lambda e^{(\lambda-\mu)t}-\mu}{\lambda(e^{(\lambda-\mu)t}-1)} \times \left[\ln\frac{\lambda e^{(\lambda-\mu)t}-\mu}{\lambda-\mu} + \mathrm{Li}_2\frac{\lambda(e^{(\lambda-\mu)t}-1)}{\lambda e^{(\lambda-\mu)t}-\mu}\right]\right\}, \quad (30)$$

where $\mathrm{Li}_2(x)$ is the Euler dilogarithm function [18,19].

If $d_f=1$ then the last term in (29) can be summed up, leading to the result [see Ref. [18], Eq. 5.2.5(5)]

$$\langle r^2(t)\rangle = \frac{6D_0}{\lambda M_0}\left[1+\lambda t - \frac{\lambda e^{(\lambda-\mu)t}-\mu}{\lambda(e^{(\lambda-\mu)t}-1)} \times \ln\frac{\lambda e^{(\lambda-\mu)t}-\mu}{\lambda-\mu}\right]. \quad (31)$$

If $\mu>0$ (and $\lambda>\mu$ as we assumed) then the long-time asymptotics is similar to the normal diffusion. Indeed, from (29) it follows that for all values of $\beta>0$

$$\langle r^2(t)\rangle \propto \frac{6D_0\mu}{\lambda M_0^\beta}t \quad \text{for } t \gg 1 . \quad (32)$$

Some examples of the time dependence of (29) are depicted in Figs. 4–6.

A. Limiting case $\lambda=\mu$

The case of equal probabilistic rate per individual for attachment and detachment of particles to and from the cluster is interesting because the cluster mass (5) stays constant on average but its fluctuations grow linearly with increasing time,

$$\langle N(t)\rangle = 1, \quad \langle N^2(t)\rangle - \langle N(t)\rangle^2 = 2\lambda t . \quad (33)$$

Let us notice that these characteristics are similar to those for a Brownian particle (the Wiener process). The probabilities $P_k(t)$ now have the form

$$P_0(t) = \frac{\lambda t}{1+\lambda t}, \qquad P_k(t) = \frac{(\lambda t)^{k-1}}{(1+\lambda t)^{k+1}}, \quad k=1,2,3,\ldots \quad (34)$$

and the mean square displacement is given by the relation

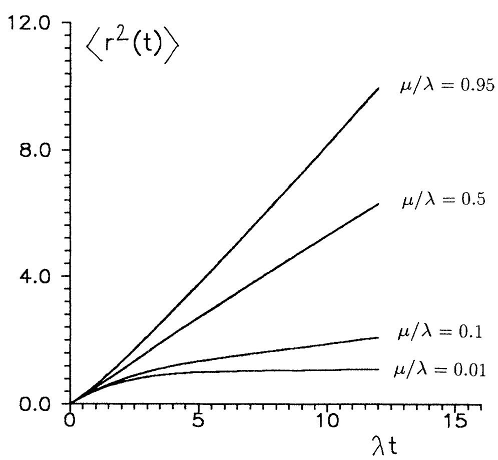

FIG. 4. The mean square displacement (29) of the cluster mass center for the birth-and-death growth model (25)–(28) as a function of rescaled time λt, the cluster dimension $d_f=1$, and four values of the quotient of death to birth rates, μ/λ. The remaining parameters are fixed in such a way that $6D_0/\lambda M_0=1$. The smaller μ/λ, the faster the increments of the aggregate mass, cf. Eq. (28), and the slower the increase of the mean square displacement.

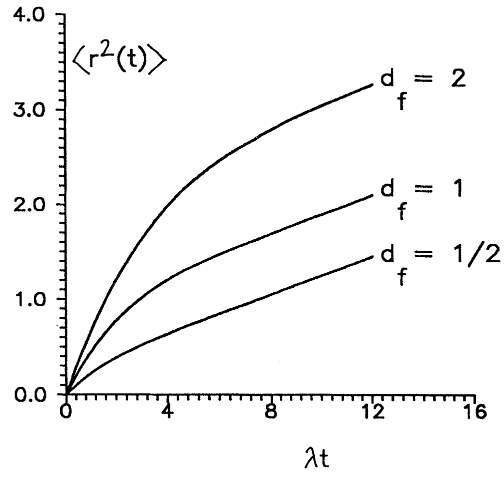

FIG. 5. Same as in Fig. 4 but for the fixed quotient of death to birth rates $\mu/\lambda=0.1$ (weak detachment of particles from the cluster), $6D_0/\lambda M_0^\beta=1$, and three values of the cluster dimension $d_f=\frac{1}{2},1,2$.

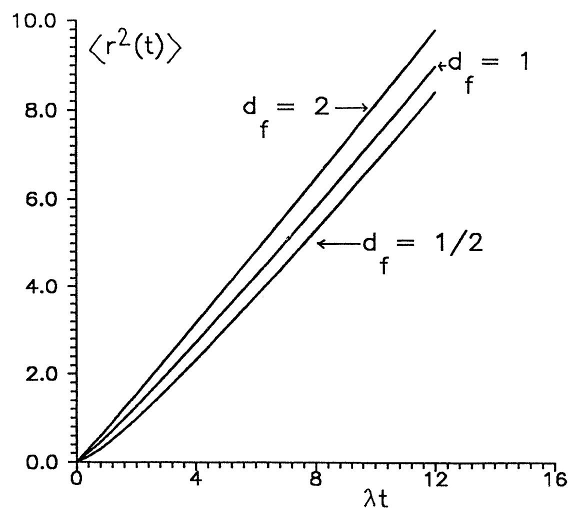

FIG. 6. Same as in Fig. 5 but for the strong detachment of particles from the cluster, $\mu/\lambda=0.8$.

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0^\beta}\left[\lambda t-\ln(1+\lambda t)+\sum_{k=1}^{\infty}\frac{1}{k(1+k)^\beta}\left[\frac{\lambda t}{1+\lambda t}\right]^k\right]. \quad (35)$$

As in the previous case, this expression can be simplified for the cluster dimensions $d_f=\frac{1}{2}$ and 1. In the former ($\beta=2$),

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0^2}\left\{2+\lambda t-\frac{1+\lambda t}{\lambda t}\left[\ln(1+\lambda t)+\mathrm{Li}_2\left[\frac{\lambda t}{1+\lambda t}\right]\right]\right\}, \quad (36)$$

where Li_2 is the dilogarithm function. In the latter ($\beta=1$),

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0}\left[1+\lambda t-\frac{1+\lambda t}{\lambda t}\ln(1+\lambda t)\right]. \quad (37)$$

One can state that in this case

$$\langle r^2(t)\rangle\propto\frac{6D_0}{M_0^\beta}t \quad \text{for } t\gg 1 \quad (38)$$

and, independently of the fractal cluster dimension $d_f=1/\beta$ and values of the parameter λ, the diffusion process is asymptotically normal.

B. Pure birth process

For a pure birth process, when $\mu=0$, the process $N(t)$ becomes a Yule-Furry process [22] and then the probabilities read

$$P_0(t)=0,\quad P_k(t)=e^{-\lambda t}(1-e^{-\lambda t})^{k-1},\quad k=1,2,3,\ldots . \quad (39)$$

The first two moments grow exponentially fast,

$$\langle N(t)\rangle=e^{\lambda t},\quad \langle N^2(t)\rangle-\langle N(t)\rangle^2=2e^{2\lambda t}-e^{\lambda t}. \quad (40)$$

In this case Eq. (29) reduces to the form

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0^\beta}\sum_{k=1}^{\infty}\frac{(1-e^{-\lambda t})^k}{k(1+k)^\beta}. \quad (41)$$

For $d_f=\frac{1}{2}$, it can be rewritten as

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0^2}\left[2-\frac{\lambda t}{e^{\lambda t}-1}-\frac{\mathrm{Li}_2(1-e^{-\lambda t})}{1-e^{-\lambda t}}\right], \quad (42)$$

In the long-time limit, for $t\to\infty$, the function $\mathrm{Li}_2(1)$ reduces to the Riemann zeta function $\zeta(2)=\pi^2/6$ [19] and (42) tends to a constant value. For $d_f=1$, Eq. (41) can be expressed by elementary functions [cf. Eq. (31)],

$$\langle r^2(t)\rangle=\frac{6D_0}{\lambda M_0}\left[1-\frac{\lambda t}{e^{\lambda t}-1}\right]. \quad (43)$$

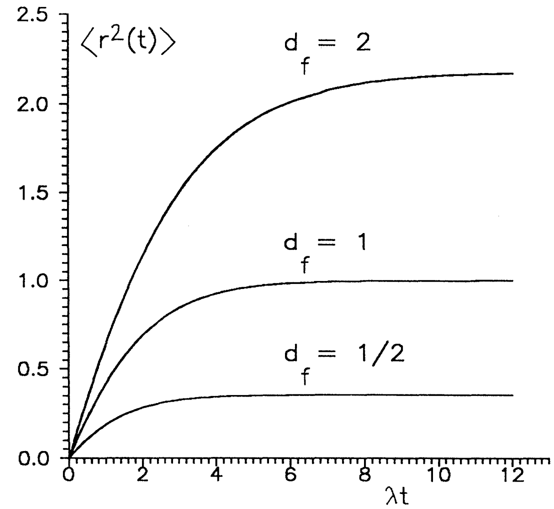

FIG. 7. The mean square displacement (41) of the cluster mass center as a function of rescaled time λt for the pure birth growth model ($\mu=0$) with a linear birth rate and $6D_0/\lambda M_0^\beta=1$. If $t\to\infty$ then all curves tend to constant values (saturation).

For long times, it tends to a constant value. For $d_f>1$, $\langle r^2(t)\rangle$ goes to a constant as well and it is demonstrated in Fig. 7.

If $\mu>0$ then the contribution to the long-time asymptotics comes exclusively from the term $P_0(t)$ in (25). The remainder $P_k(t)$ ($k=1,2,3,\ldots$) tends to zero as $t\to\infty$. On the other hand, for $\mu=0$, $P_0(t)\equiv 0$ and $P_k(t), k=1,2,3,\ldots$, contribute to the long-time asymptotics.

V. SUMMARY

In this paper we have considered the diffusion process of growing clusters. One should note that the model presented is different from the model [13]. In the latter model, the growth process of aggregates is deterministic. Here, it is modeled by a stochastic process and is much more realistic. A general formula for the mean square displacement of the cluster mass center is given by Eq. (12). For the Poisson growth model, the basic equation is (17). If the cluster dimension $d_f<1$, its long-time asymptotics saturates, cf. Eq. (19), while for $d_f=1$ the mean square displacement grows logarithmically, cf. Eq. (21). Unfortunately, for $d_f>1$ we have not succeeded in evaluating its asymptotics analytically for $t\to\infty$ [we suspect that the function (17) diverges as a power function of time but we have not been able to prove it]. Nevertheless, numerical results have been presented. It is interesting to note that the results (19) and (21) are similar to those for the deterministic model (1). It is correct for long times and is a reflection of the fact that on the average the mass grows linearly in time as given by Eq. (15). But at an early stage of evolution the two models lead to different time dynamics.

Essentially different properties are observed for the birth-and-death growth model. The most important factor determining the diffusional properties is the relation between the birth transition coefficient λ and the death transition coefficient μ. If $\lambda=\mu>0$ then the mean cluster mass is constant in time, cf. Eq. (33), its fluctuations grow linearly, and diffusion is asymptotically normal, $\langle r^2(t)\rangle \propto t$. It is rather conceivable because of the average mass constancy. For a pure linear birth process, i.e., $\lambda>0$ and $\mu=0$, the average cluster mass and its fluctuations are exponential functions of time, cf. Eq. (40). In this case $\langle r^2(t)\rangle$ tends to a constant value, fluctuations of the position of the cluster mass center are smaller and smaller, and ultraslow diffusion takes place. This result is comprehensible because the cluster mass grows very fast and the cluster becomes immobile. If $\lambda>\mu>0$, then the probability of mass increments is greater than the probability of mass decrements. As a result, the mean value of the mass increases exponentially in time, cf. Eq. (28). Fluctuations are also exponentially large. In spite of these, the mean square displacement increases linearly in time and the diffusion process is asymptotically normal as well. This result is indeed surprising because in this case the cluster mass grows on the average exponentially as in the previous case ($\lambda>\mu>0$). But one can observe an essential difference between these two cases. If $\mu=0$ then the probability $P_0(t)\equiv 0$, the remainder $P_k(t)$, $k=1,2,3,\ldots$, tend to zero as $t\to\infty$, and the probability of the particle's detachment from the aggregate is zero. For arbitrary realizations of the process the cluster mass is a nondecreasing step function of time and the cluster indeed grows. On the other hand, if $\mu>0$ then $P_0(t)\neq 0$, $t>0$, and it is an increasing function of time, $P_0(t)\nearrow\mu/\lambda$ as $t\to\infty$. Now there are realizations for which the cluster mass decreases (locally or globally) in time and with the probability μ/λ the aggregate can finally dissolve. We are of the opinion that this is the main reason of asymptotically normal diffusion for the case $\lambda>\mu>0$. One should realize that the behavior of systems under stochastic perturbations (here random attachments or/and detachments of particles) in large time intervals can be quite sensitive to low-probability events and in some cases vanishingly small fluctuations play a dominant role in formation of the system asymptotics [23].

It is worth stressing that the models presented here do not couple the aggregation kinetics to the fractal geometry itself. It was shown [24] that there is no dependence of the aggregation rate on the geometry of the fractal surface. Further, in Ref. [24] a crossover was predicted from reaction-limited to diffusion-limited cluster-cluster aggregation due to an increase in the reactive surface area as the clusters grow. Moreover, as the clusters grew they would deplete the aggregating species in their immediate vicinity. This would be reasonable if the time scale for relaxing the concentration fluctuations of the aggregating species was much faster than the diffusion of the cluster. We do not consider this effect. On the contrary, we assume the opposite case. Finally, we wish to mention the next basic restriction of our approach: we examine the diffusion process of aggregates of sizes for which the (fractal) dimension d_f is a properly determined characteristic. We consider finite times although these can be asymptotically large and when clusters become too large our approximation simply fails.

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