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Damián H. Zanette

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Damián H. Zanette **

International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

We introduce a kinetic equation for describing irreversible aggregation in the ballistic regime, including velocity distributions. The associated evolution for the macroscopic quantities is studied, and the general solution for Maxwell interaction models is obtained in the Fourier representation.

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1. INTRODUCTION

Initially introduced for describing the dynamics of colloids, aggregation is a kinetic process in which dispersed particles under interaction stick together, to build clusters which eventually undergo the same process [1]. Analogous aggregation models have then been seen to apply for studying a wide class of processes, like the dynamics of aerosols [2] and smokes [3], formation of polymers [4] and gelation [5]. They have also been extended to study electrolysis [6], filtration [7] and dielectric breakdown [8], and could provide a proper description for the formation of planets from planetesimals [9].

Aggregation processes deserve two aspects to be studied: the first one, which has received very much attention specially in the last years, regards the geometry of the clusters formed through the sticking events [10]. These aggregates are shown to have fractal structure, which characteristics depend strongly on the underlying kinetic process. The second aspect, involves the kinetic of the evolution, i.e., the quantitative description of the time dependence for the relevant magnitudes in the system (mean size of clusters, size distribution). Even when this problem was introduced very early [11], relevant results have been achieved only recently [12].

In this paper we shall deal with this second aspect, in the case of irreversible aggregation. A kinetic equation for irreversible aggregation was proposed by Smoluchowski in 1916 [11]. It reads

$$\dot{\rho}_n = \frac{1}{2} \sum_{m=1}^{n-1} K_{m,n-m} \, \rho_m \rho_{n-m} - \rho_n \sum_{m=1}^{\infty} K_{nm} \, \rho_m , \qquad (1.1)$$

where $\rho_n(t)$ is the density of clusters formed by n particles. The constants K_{nm} give the probability of interaction between clusters per unit time. Smoluchowski considered as initial condition the so-called *monodisperse case* [13], i.e.,

$$\rho_n(0) = \rho_1(0) \, \delta_{n1} , \qquad (1.2)$$

for which only single particles are present at $t = 0$. Of course, this initial condition has been fully generalized. Eq.(1.1) has received much attention both in the search for exact solutions [14] and in the study of their large time behaviour and similarity properties [12].

Regarding the transport processes to be associated with the Smoluchowski equation, previous works have mainly considered the diffusive approach, in which particles and clusters display Brownian motion. However, in view of some applications (aerosols, planetesimals), ballistic models have also been considered [15]. In these models particles and clusters behave as free particles during the time between collisions. Clusters formed through these ballistic processes are found to display severe geometrical differences with the diffusive approach [1].

For ballistic models, velocity distributions are expected to play a relevant role in the dynamics of the system. Indeed, velocity should appear explicitly in the interaction probabilities, so that the transport process would modify the evolution due to aggregation, as observed to occur

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in chemical kinetics [16]. Furthermore, velocity distributions govern the statistical evolution of the system between collisions. In this paper, we propose a kinetic equation for studying irreversible aggregation, introducing explicitly velocity distributions for particles and clusters. The underlying aggregation processes are characterized by the conservation of momentum in each collision, which determines the convolution structure of the equation. This structure is used to find a general solution in the case of Maxwell interaction models. Particular exact solutions, as well as the evolution of the relevant macroscopic quantities, are also discussed.

2. THE KINETIC EQUATION

As considered in the formulation of the Smoluchowski equation, we deal here with an infinite set of *units* (particles, microaggregates, monomers ...) able to stick together under the action of some attractive force. These events are considered to be irreversible, and the so formed clusters are supposed to undergo the same aggregation process.

Since we are interested in the kinetic features of the evolution of the system, each cluster is seen as a point particle, characterized by its velocity v and the number of units that it contains, n. The only effects of size taken into account in the model determine the explicit form of the transition probability associated with the interaction. In fact, the probability per unit time for the interaction of two clusters containing, respectively, n and m units, with velocities v' and v'', and giving place to a new cluster with velocity v, will be given by a function $W(n, m; v', v'' \to v)$. This function is supposed to satisfy the symmetry [17]:

$$W(n, m; v', v'' \to v) = W(m, n; v'', v' \to v) . \tag{2.1}$$

Furthermore, because of the irreversible character of the interactions, the only conserved magnitude is the momentum. This conservation law fixes the outgoing velocity as

$$v = \frac{nv' + mv''}{n + m} , \tag{2.2}$$

and determine the transition probability to be factored as [18]

$$W(n, m; v', v'' \to v) = \sigma(n, m; |v' - v''|)\, \delta[(n + m)v - nv' - mv''] , \tag{2.3}$$

where the probability σ depends on the relative incoming velocity $|v' - v''|$.

At the kinetic level, the system is described by an infinite set of distribution functions $f_n(r, v, t)$, depending on the position r, the velocity v and the time t, and labelled with the number of units in the corresponding clusters, n. The quantity $f_n(r, v, t)\,dr\,dv$ represents then the elementary probability of finding a cluster of n units in the volume $dr\,dv$ of the phase space around the

point (r, v) at time t. According to the arguments used to propose the Smoluchowski equation, the evolution of $f_n(r, v, t)$ is given by the kinetic equation

$$D_t^{(n)} f_n(r, v, t) = \frac{1}{2} \sum_{m=1}^{n-1} \int\int dv'\, dv'' W(m, n - m; v', v'' \to v) f_m(r, v', t)\, f_{n-m}(r, v'', t) -$$
$$- f_n(r, v, t) \sum_{m=1}^{\infty} \int\int dv'\, dv'' \, W(n, m; v, v' \to v'') f_m(r, v', t) , \tag{2.4}$$

where $D_t^{(n)} = \partial_t + v \cdot \nabla_r + n^{-1} F \cdot \nabla_v$ is the material derivative, and F represents external forces. Using Eq.(2.3), this kinetic equation becomes

$$D_t^{(n)} f_n(v) = \frac{1}{2} \sum_{m=1}^{n-1} \left(\frac{n}{n-m}\right)^d \int dv'\, \sigma\left(m, n - m; \frac{n}{n-m} |v - v'|\right) f_m(v') f_{n-m}\left(\frac{nv - mv'}{n-m}\right) -$$
$$- f_n(v) \sum_{m=1}^{\infty} \int dv'\, \sigma(n, m; |v - v'|) f_m(v') , \tag{2.5}$$

where d indicates the dimension of space. For simplicity, we have only indicated the distribution dependence on velocity. Equation (2.5) must be considered as a Cauchy problem, to be solved for any initial values $f_n(r, v, 0)$, $n = 1, 2, \ldots$, and appropriate boundary conditions.

Because of the relevance of momentum as a conserved magnitude, it is worthwhile to introduce the *momentum representation* of Eq.(2.5) by defining the distribution $g_n(p)$ as

$$g_n(p) = n^{-d} f_n(p/n) , \tag{2.6}$$

so that $g_n(p)\,dp = f_n(v)\,dv$. The evolution equation for g_n reads

$$D_t g_n(p) = \frac{1}{2} \sum_{m=1}^{n-1} \int dp'\, \sigma\left(m, n - m; \frac{n}{n-m}\left|\frac{p}{n} - \frac{p'}{m}\right|\right) g_m(p') g_{n-m}(p - p') -$$
$$- g_n(p) \sum_{m=1}^{\infty} \int dp'\, \sigma\left(n, m; \left|\frac{p}{n} - \frac{p'}{m}\right|\right) g_m(p') , \tag{2.7}$$

with $D_t = \partial_t + \frac{p}{n} \cdot \nabla_r + F \cdot \nabla_p$. Both forms of the kinetic equation, (2.5) and (2.7), will be used later.

Before analyzing the properties of Eq.(2.5), let us say a word about the possible forms of the function $\sigma(n, m; v)$, giving the probability of collision between two clusters with relative velocity v, and n and m units, respectively. Since σ is a probability per unit time, it can be factored as [19]

$$\sigma(n, m; v) = \sigma_0 v\, I(n, m; v) , \tag{2.8}$$

where I indicates the cross section for the collision, and σ_0 is an appropriate normalization constant. Furthermore, if the v-dependence of the cross section is independent of the size (or mass) of clusters, I is also factored as

$$I(n, m; v) = K_{nm}\, y(v) , \tag{2.9}$$

where in the constants K_{nm} we recognize the coefficients of the Smoluchowski equation (1.1). The function $y(v)$ is given by the interaction potential and generally has the asymptotic form $y(v) \sim v^a$ for $v \to \infty$, when the involved potential depends on the distance as $V(r) \sim r^{2(d-1)/(s-1)}$ [19]. The explicit expression of these functions will be fixed by the considered interaction model.

3. EVOLUTION OF MACROSCOPIC QUANTITIES

As a first step in the analysis of Eq.(2.5), let us determine the evolution laws for macroscopic magnitudes in terms of the distribution function. Generally, we are interested in the behaviour of the following mean values:

$$M_{ij} = \rho < n^i v^j > = \sum_{n=1}^{\infty} n^i \int dv \, v^j \, f_n(r,v,t); \quad i,j = 0,1,2,\dots; \quad (3.1)$$

supposed that sums and integrals converge. The density ρ is given by

$$\rho(r,t) = M_{00} = \sum_{n=1}^{\infty} \int dv \, f_n(r,v,t) \equiv \sum_{n=1}^{\infty} \rho_n(r,t), \quad (3.2)$$

as the sum of the partial densities ρ_n. After integration and proper symmetrization in Eq.(2.5), we obtain

$$\partial_t M_{ij} + \nabla_r \cdot J_{ij} = \frac{1}{2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \int dv \, dv' \, P_{ij}(n,m;v,v')\sigma(n,m;|v-v'|)f_n(v)f_m(v'), \quad (3.3a)$$

with

$$P_{ij}(n,m;v,v') = (n+m)^i \left(\frac{nv + mv'}{n+m} \right)^j - (n^i v^j + m^i v'^j). \quad (3.3b)$$

In the l.h.s. of Eq.(3.3a), J_{ij} represents a current associated to M_{ij}, i.e.,

$$J_{ij} = \rho < v n^i v^j > . \quad (3.4)$$

The kernel P_{ij} determines the evolution of the corresponding moment M_{ij}. In fact, because of the positivity of the functions σ and f_n, its sign indicates straightforwardly whether M_{ij} decreases or increases with time. Let us study the values of P_{ij} in some particular cases:

a) For $j = 0$, $P_{ij} = (n+m)^i - n^i - m^i$ determines the evolution for the mean values of the powers of the unit number in the clusters. We observe that $P_{00} = -1 < 0$, indicating that the density of clusters ρ decreases. For $i = 1$, $P_{10} = 0$ as expected from the conservation of the total particle number. Finally,

$$P_{i0} = \sum_{k=1}^{i-1} \binom{i-1}{k} n^k m^{i-1-k} > 0, \quad (3.5)$$

for any $i > 1$, i.e., the mean values of high-order powers of n ($i \geq 2$), increase with time. Observe that all these results coincide with known properties of the Smoluchowski equation [1].

b) With $i = j = 1$, $P_{11} = 0$. This fact states the conservation for the mean value of the momentum, as required by the corresponding microscopic conservation law. It is interesting to note that, because of the different masses of the clusters, the mean velocity $\rho < v >$ is not conserved. In fact,

$$P_{01} = \frac{mv + nv'}{n+m} \neq 0. \quad (3.6)$$

In this case, the r.h.s. of Eqs.(3.3a) measures the anistropy of the distribution functions. Indeed, it is easy to show that for an isotropic initial condition the mean velocity does not change in spite of the non vanishing value of P_{01}.

c) For $i = 1, j = 2$ we obtain

$$P_{12} = -\frac{nm}{n+m} |v - v'|^2 < 0, \quad (3.7)$$

whose value is directly involved in the evolution of the temperature. In fact, for our system, the temperature T is given by:

$$dk\rho T = \rho < nv^2 > -2\rho < nv > \cdot < v > + \rho < n > | < v > |^2, \quad (3.8)$$

where k is the Boltzmann constant. For isotropic systems $< v > = 0$, so that the variation of the temperature consists of two contributions:

$$dk \frac{dT}{dt} = -\frac{dkT}{\rho} \frac{d\rho}{dt} + \frac{1}{\rho} \frac{d}{dt} [\rho < nv^2 >]. \quad (3.9)$$

The first term is a positive contribution related with the decrease of the total density ρ, which increases the energy per cluster measured by T. On the other hand, according to Eq.(3.7), the second term is always negative. It is associated with a net decrease of the kinetic energy in each microscopic interaction: in the collision of two clusters with n and m units, and velocities v' and v'', respectively, the energy of the resulting cluster is

$$\varepsilon = \frac{n\varepsilon' + m\varepsilon''}{n+m} + \frac{nm}{n+m} v' \cdot v'' \leq \frac{n\varepsilon' + m\varepsilon''}{n+m} + \frac{nm}{n+m} v'v'' \leq \varepsilon' + \varepsilon''. \quad (3.10)$$

For anisotropic systems, the mean value of v depends on time, as discussed in point b). According to Eq.(3.8), this evolution contributes additionally to the temporal dependence of the temperature.

4. MAXWELL MODELS

In view of the unfortunate previous experience in finding general solutions for nonlinear kinetic equations, we cannot expect to be able to give the solution of Eq.(2.5) for arbitrary initial

values, boundary conditions and transition probabilities. Therefore, in this section we shall be restricted to consider force–free, spatially homogeneous systems (as usually done in analyzing aggregation processes) in the frame of the Maxwell interaction models [19]. Much of the exact results dealing with the solution of kinetic equations require to work with these models, which consider that the transition probability in a binary collision is independent of the velocity. This feature is provided by a potential $V(r) \sim r^{-2(d-1)}$. In the case of our equation, we introduce Maxwell models by setting

$$\sigma(n, m; v) = K_{nm} , \qquad (4.1)$$

where the constants K_{nm} can be identified as the coefficients in the Smoluchowski equation (1.1).

Now, since the transition probability does not depend on the velocity variable, the momentum representation of the kinetic equations, (2.7), proves to be a convenient tool for treating the problem. Introducing Eq.(4.1), Eq.(2.7) reads

$$\partial_t g_n(p) = \frac{1}{2} \sum_{m=1}^{n-1} K_{m,n-m} \int dp' \, g_m(p') \, g_{n-m}(p - p') - \\ - g_n(p) \sum_{m=1}^{\infty} K_{nm} \, \rho_m(t) , \qquad (4.2)$$

where ρ_m indicates the partial densities introduced in Eq.(3.2).

We observe from Eq.(4.2) that for Maxwell models the partial densities satisfy the Smoluchowski equation (1.1). This result, obtained by direct integration of Eq.(4.2) in the domain of p, is a particular case of a well–known feature in kinetic theory: Chemical rate equations exclusively involving the density of the reacting species, can be derived from kinetic equations only in the frame of Maxwell interaction models [20]. Consequently, the evolution of the partial densities can be found independently. In fact, when solving Eq.(4.2), we shall consider that the density problem has been solved.

The convolution structure of the positive term in the r.h.s. of Eq.(4.2) suggests the application of a d–dimensional Fourier transform in the momentum space. Defining:

$$\xi_n(k,t) = \int e^{-ik \cdot p} g_n(p,t) dp , \qquad (4.3)$$

we find

$$\partial_t \xi_n(k,t) = \frac{1}{2} \sum_{m=1}^{n-1} K_{m,n-m} \, \xi_m(k,t) \xi_{n-m}(k,t) - \xi_n(k,t) \sum_{m=1}^{\infty} K_{nm} \, \rho_m(t) , \qquad (4.4)$$

which is a local equation in the Fourier variable k. Now,

$$\rho_m(t) = \xi_m(0,t) . \qquad (4.5)$$

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Before considering the general solution of Eq.(4.4), let us analyze a class of exact solutions. As said previously, for Maxwell models the partial densities $\rho_m(t)$ satisfy the Smoluchowski equation. Then, from a comparison between Eqs.(4.4) and (1.1) it is clear that a particular solution for the former is given by

$$\xi_n(k,t) = \rho_n(t) . \qquad (4.6)$$

However, in the original p–space these distributions correspond to the irrelevant case of vanishing velocities. In any case, the solution (4.6) is immediately generalized observing that

$$\xi_n(k,t) = \Xi^n(k) \, \rho_n(t) , \qquad (4.7)$$

also satisfies Eq.(4.4), for an arbitrary function $\Xi(k)$ in the $\mathcal{L}_2(\mathbb{R}^d)$ space. In view of Eq.(4.5), we must impose $\Xi(0) = 1$. For this separable solution, the momentum distributions are given by

$$g_n(p,t) = (2\pi)^{-d} \int e^{ik \cdot p} \Xi^n(k) \, \rho_n(t) \, dk = \\ = \rho_n(t) \int dp_1 \ldots dp_n \, G(p_1) \ldots G(p_n) \, \delta(p - p_1 \ldots - p_n) , \qquad (4.8)$$

where $G(p)$ is the Fourier anti–transform of $\Xi(k)$, and determines the momentum distribution of units, i.e., $g_1(p,t)$. Therefore, it is clear that Eq.(4.8) gives a particular solution of Eq.(4.2) as a superposition of all possible contributions to $g_n(p,t)$ from combinations of n units satisfying momentum conservation.

It is important to observe that, by virtue of the central–limit theorem of statistics [21], $\Xi^n(k)$ approaches a (scaled) Gaussian as $n \to \infty$. This fact implies that, for arbitrary $\Xi(k)$, the kinetic process determines the momentum distributions of large–n clusters to display a Maxwellian (i.e. equilibrium) profile. In particular, note the case

$$\Xi(k) = \exp(-k^2/2\beta); \quad \beta > 0 . \qquad (4.9)$$

In the p–space we obtain

$$g_n(p,t) = N(n,\beta) \rho_n(t) \exp\left[-\frac{p^2 \beta}{2n}\right] = N(n,\beta) \rho_n(t) \exp[-\varepsilon/kT] , \qquad (4.10)$$

with $kT = \beta^{-1}, \varepsilon = p^2/2n$ and $N(n,\beta)$ a proper normalization constant. It is then clear that this particular choice of $\Xi(k)$, Eq.(4.9), describes a system in thermal equilibrium with temperature T, so that the interaction between cluster with different unit numbers does not modify the energy distributions.

Certainly, the particular solution Eq.(4.7) corresponds to a very special initial condition for the momentum distribution, namely

$$\xi_n(k,0) = \Xi^n(k) \, \rho_n(0) , \qquad (4.11)$$

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in the Fourier variable. However, it becomes particularly interesting when noting that it provides the general solution for Maxwell models for the initial condition considered by Smoluchowski, Eq.(1.2). In fact, since $\rho_n(0) = 0$ $(n = 2, 3, \ldots)$, the corresponding initial momentum distributions are irrelevant. The solution Eq.(4.7) is then properly written as

$$\xi_n(k,t) = [\xi_1(k,0)/\rho_1(0)]^n \rho_n(t) . \tag{4.12}$$

5. GENERAL SOLUTION FOR MAXWELL MODELS

In this section we present the general solution of Eq.(4.4) in a one–dimensional space. The arguments can be straightforwardly extended to more dimensions, and we treat here only the case with $d = 1$ because of its relative simplicity.

The general solution to the Fourier–transformed equation (4.4) can be introduced as a direct generalization of the particular solution (4.7). In fact, in order to relax the restriction on the k–distribution of the solution, we propose the following *ansatz*:

$$\xi_n(k,t) = \Xi^n(k) \sum_{j=0}^{\infty} c_n^{(j)}(t) \frac{(ik)^j}{j!} . \tag{5.1}$$

As done for the solution (4.7) we require $\Xi(0) = 1$. Apart from this condition, $\Xi(k)$ is arbitrary, and its choice will be determined later on. Introducing the series (5.1) in Eq.(4.4) we find a set of nonlinear ordinary differential equations for the coefficients $c_n^{(j)}(t)$:

$$\dot{c}_1^{(j)} + c_1^{(j)} \sum_{m=1}^{\infty} K_{1m} \rho_m = 0 , \tag{5.2a}$$

$$\dot{c}_n^{(j)} + c_n^{(j)} \sum_{m=1}^{\infty} K_{nm} \rho_m = \frac{1}{2} \sum_{r=0}^{j} \binom{j}{r} \sum_{m=1}^{n-1} K_{m,n-m} c_m^{(r)} c_{n-m}^{(j-r)} \quad (n \geq 2) . \tag{5.2b}$$

The main property of the system (5.2) is its recursive character. Indeed, once appropriate initial values are provided, one can find successively the exact solution up to an arbitrary order. Moreover, when the lower–order coefficients have been calculated, the equation for each $c_n^{(j)}(t)$ becomes linear.

Three inital conditions are necessary for solving the recursive system (5.2): one of them is related with the solution of the differential problem, and fixes the initial values $c_n^{(j)}(0)$. The other two correspond to the recursive scheme, i.e., determine the value of the coefficients for $n = 1$ and $j = 0$. As for the first condition, we note that $c_n^{(j)}(0)$ is determined by the expansion of the initial distribution. In fact,

$$\Xi^{-n}(k)\xi_n(k,0) = \sum_{j=0}^{\infty} \frac{(ik)^j}{j!} c_n^{(j)}(0) . \tag{5.3}$$

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The recursion in the index n initiates with the solution of Eq.(5.2a), i.e.,

$$c_1^{(j)}(t) = c_1^{(j)}(0) \exp\left[-\int_0^t \sum_{m=1}^{\infty} K_{1m} \rho_m(t') dt' \right] . \tag{5.4}$$

Finally, the initial condition for the recursion in the index j is given by Eq.(4.5), which determines

$$c_n^{(0)}(t) = \rho_n(t) . \tag{5.5}$$

The solution is then found by fixing a value for n and, taking into account condition (5.5), calculating $c_n^{(j)}(t)$ for successive values of j up to the desired order, as a function of $c_m^{(r)}(t)$ $(m < n, r < j)$. Then, the value of n is indexed.

A particularly convenient choice for the function $\Xi(k)$ is the following: Supposed that $\rho_1(0) \neq 0$, take

$$\Xi(k) = \xi_1(k,0)/\rho_1(0) , \tag{5.6}$$

which indeed satisfied $\Xi(0) = 1$. From Eq.(5.3) it is clear that

$$c_1^{(j)}(0) = \rho_1(0) \, \delta_{j0} . \tag{5.7}$$

According to (5.4) and (5.5) we find the exact solution for the distribution of units to be

$$\xi_1(k,t) = \rho_1(t)\Xi(k) = \rho_1(t)\xi_1(k,0)/\rho_1(0) . \tag{5.8}$$

Observe that $\xi_1(k,t)$ preserves the profile of its k–distribution. This is a direct consequence of the independence on velocity in the transition probabilities for Maxwell models and the fact that no new units appear for $t > 0$. The choice (5.6) enables also an explicit calculation for $\xi_2(k,t)$, namely

$$\xi_2(k,t) = \rho_1(t)\xi_2(k,0)/\rho_1(0) + \Xi^2(k)[\rho_2(t) - \rho_2(0)] , \tag{5.9}$$

which presents a more complex k–dependence. For $n > 2$, general solutions for ξ_n can only be given through formal expressions.

As for the form of the distributions in the p–space, by anti–transforming series (5.1) we obtain

$$g_n(p,t) = \sum_{j=0}^{\infty} \frac{1}{j!} c_n^{(j)}(t) \frac{d^j}{dp^j} \int dp_1 \ldots dp_n \, G(p_1) \ldots G(p_n) \, \delta(p - p_1 - \ldots - p_n) , \tag{5.10}$$

where, as in Eq.(4.8), $G(p)$ is the Fourier anti–transform of $\Xi(k)$. With an appropriate choice of $\Xi(k)$, the series (5.10) becomes an expansion in orthogonal functions. The general solution introduced in this section is then restricted to the corresponding Hilbert space. In this sense, a relevant example is provided by a Gaussian distribution $\Xi(k) = \exp[-k^2/2\beta]$, which in the p–space produces an expansion in Hermite polynomials [22].

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The generalization of this solution to more dimensions is straightforward, but the notation becomes complex and the relevant calculations result highly tedious. Nevertheless, the recursive character of the equation for the time–dependent coefficients is fully preserved. In order to illustrate the form in which the method is generalized, we write here the extension of the *ansatz* (5.1) to three dimensions:

$$\xi_n(k,t) = \Xi^n(k) \sum_{j_1,j_2,j_3} c_n^{(j_1 j_2 j_3)}(t) \frac{(ik_x)^{j_1}}{j_1!} \frac{(ik_y)^{j_2}}{j_2!} \frac{(ik_z)^{j_3}}{j_3!}. \qquad (5.11)$$

This is an expansion in the Cartesian coordinates (k_x, k_y, k_z). Alternative systems of coordinates (spherical, cylindric) can also be applied, as done for solving other kinetic equations [23].

6. CONCLUSION

We have introduced a kinetic equation for describing irreversible aggregation in the ballistic regime. This equation governs the evolution of the velocity distribution function for aggregation clusters, which are considered as point particles moving freely up to the moment in which they become involved in an aggregation event. In general, a sticking process like aggregation does not conserve energy, so that only the momentum is preserved in the evolution. Consequently, two relevant representations were introduced for the kinetic equation: The first one involves the distribution functions as depending on the velocity; the second representation, which results more convenient for treating some particular interaction models, is expressed in terms of the momentum distributions.

As for the evolution of the macroscopic quantities implied by the kinetic equation, we observed that the mean values of the powers of the unit number reproduce the behaviour described by the Smoluchowski equation. Among the mean values of the velocity powers, it is interesting to discuss further the evolution of temperature. In fact, in the diffusive regime, the temperature (and consequently the entropy) is shown to grow as a consequence of the decrease in the number of clusters. For the ballistic regime instead, we found a negative contribution to the temporal derivative of the temperature, originated in the diminution of energy in each microscopic event. Since in the diffusive limit there is an interchange of energy with the background through which clusters diffuse, such contribution is not present. The question of whether it can cause a decrease in temperature or not, requires a more detailed analysis.

Interaction models with velocity–independent transition probabilities provide a strong simplification to the kinetic equation. In the first place, we observed that for such models the evolution of the partial densities can be solved independently. In fact, it was shown that these densities are the solutions of the Smoluchowski equation. Once the density problem is solved, it is possible to formulate a recursive scheme for finding the general solution of the kinetic equation, through an expansion in functions of the velocity variable whose coefficients depend on time. This solution is restricted to the spatially homogeneous case, which is, however, a situation often considered in the analysis of aggregation processes.

The proposed kinetic equation is expected to describe correctly aggregating systems for situations of high dilution, in which the effects of size can be neglected or entirely charged to the transition probabilities. In particular, it should not apply in the description of a gelation regime, in the presence of an infinite cluster, acting as a sink in the system. However, since the Smoluchowski equation is able to describe gelation and explicitly appears in our model by governing the evolution of the densities, the gel transition is expected to occur for particular forms of the transition probabilities. This aspect of the kinetic problem is included in the wider task of studying the competence between transport and aggregation which, in the present theory, deserves future consideration.

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