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A DISCRETE APPROACH TO GRAIN GROWTH BASED ON PAIR INTERACTIONS

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Abstract—A discrete 3D model for normal grain growth based on pair interactions is presented where the inhibition effect due to second phase particles is also considered. A probabilistic approach has been adopted to evaluate the contact probability between neighbouring grains and the continuity equation has been reformulated and adapted to the structure of the interactions in a discrete system. The present model predicts a quasi-stationary grain size distribution more symmetrical than that by the analytical mean field theory by Hillert. As expected, its skewness is modified by the presence of inhibition by second phases.

It is demonstrated that this new approach represents a valuable alternative to the mean field models even if, at present, it gives only a small improvement in explaining the shape of the quasi-stationary grain size distribution found in experiments.

Keywords: Grain growth; Kinetics

1. INTRODUCTION

A large effort has been dedicated in the past to the comprehension of the physical basis governing grain coarsening in polycrystalline materials. The well known analytical formulation of the mean field theory by Lifshitz and Slyozov [1] and by Wagner [2] for particles (hereafter referred to as LSW theory) modified by Hillert [3], has been directly applied to describe normal grain growth.

This theory gives not only a satisfactory estimate of the overall kinetics (evolution of the average grain size) but also predicts the achievement of an asymptotically stationary state of the system after a sufficient elapsed time in isothermal conditions. The grain size distribution (GSD) becomes self-similar, i.e. its shape remains unchanged if rescaled to the average size. The analytical expression for the GSD asymptotic shape is left-skewed and has a cut-off at a reduced size $D/\langle D\rangle$ equal to 2. Conversely, experimentally measured size distributions show elongated right tails up to reduced radius values from 2.5 to 3.

An extensive literature can be found where several approaches have been proposed, starting from modified analytical treatments [4–6] to stochastic formulations [7] and, more recently, also to computer simulations [8–12]. All the mean field approaches fail in predicting the shape of the size distribution since the stationary distributions necessarily obey the Hillert's asymptotic solution.

The difficulties in applying the mean field theories are further confirmed by the introduction of empirical functions to describe the GSD [13, 14]. Among them it is worth mentioning the log-normal distribution function firstly introduced by Feltham, nowadays commonly accepted in quantitative metallographic investigations [15].

The aim of this work is to present a discrete approach for 3D grain growth which tries to overcome the above-mentioned difficulties and where the averaging operations required to describe the system statistically are carried out on the surface areas shared among grains rather than on the growth rates.

2. NORMAL GRAIN GROWTH

To formulate the normal grain growth kinetic equation for single-phase polycrystalline materials, the currently accepted hypothesis that the grain boundary velocity is proportional to the pressure difference caused by the grain curvature is considered [3, 5]. The following assumptions have been made: the average curvature of grains is calculated considering a spherical shape, the GSD is divided into discrete classes of width ΔR and the grain sizes are associated to the class centre. The growth process is expressed in terms

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of elementary matter exchanges between pairs of interacting grains. Accordingly, the relative volume change of a grain belonging to the *i*th size class and a grain in the *j*th class is proportional to the product between the grain boundary velocity and the shared surface. It can be written as:

$$\frac{\mathrm{d}v_i}{\mathrm{d}t}\Big|_j = M\gamma A_{ij}\left(\frac{2}{R_j}-\frac{2}{R_i}\right) \tag{1}$$

where R_i and R_j are the grain radii, γ is the interfacial energy (assumed constant for the whole system), A_{ij} is the effective exchange area between the grains and M is the grain boundary mobility given by [16]

$$M = \frac{D_{\mathrm{GB}}b^2}{k_{\mathrm{B}}T} \tag{2}$$

with D_{GB} representing the grain boundary diffusivity and b the magnitude of Burgers' vector.

For each pair of classes, the volume balance condition implies that

$$w_{ij}\frac{\mathrm{d}v_i}{\mathrm{d}t}\Big|_j = -w_{ji}\frac{\mathrm{d}v_j}{\mathrm{d}t}\Big|_i \tag{3}$$

where w_{ij} and w_{ji} are the number of contacts (common faces) per volume unit between the two classes. Due to the symmetry of the process:

$$A_{ij} = A_{ji} \tag{4a}$$

$$w_{ij} = w_{ji} \tag{4b}$$

which states the equivalence of shared surfaces and number of contacts whichever class i or j is considered as reference.

The evaluation of the contact area shared between two neighbouring grains i and j is carried out by a geometrical approximation (see Appendix A). It can be expressed as:

$$A_{ij} = \pi r_{ij}^2 \tag{5}$$

where

$$r_{ij} = \frac{R_iR_j(R_i + R_j)}{R_i\sqrt{R_i(R_i + 2R_j)} + R_j\sqrt{R_j(R_j + 2R_i)}} \tag{6}$$

Hence, as $r_{ij} = r_{ji}$, equation (5) fulfils the symmetry requirement (4a).

The number of contacts per unit volume between any pair of classes, w_{ij}, is calculated by a purely probabilistic model taking into account each size class, both the discrete GSD (number of grains per unit volume, n_i) and their average number of faces m_i (grain co-ordination number). Assuming a spherical shape of the grains, for any given size class the latter is defined as the ratio between the grain boundary surface and the average area of the faces, $\langle A_i\rangle$, as:

$$m_i = \frac{4\pi R_i^2}{\langle A_i\rangle} \tag{7}$$

The total number of contacts (faces) per volume unit, counted only once, can be expressed as:

$$m_{\mathrm{V}} = \frac{1}{2}\sum_i n_i m_i \tag{8}$$

The probability of finding a common face between the size classes i and j is proportional to the product of the occurrence probabilities of their respective faces in the system:

$$p_{ij} = \left(\frac{n_i m_i}{\sum_k n_k m_k}\right)\left(\frac{n_j m_j}{\sum_k n_k m_k}\right) \tag{9}$$

Therefore, the number of contacts per volume unit between the classes i and j is:

$$w_{ij} = m_{\mathrm{V}}p_{ij} = \frac{n_i m_i\, n_j m_j}{2\sum_2 n_k m_k} \tag{10}$$

Clearly, equation (10) fulfils the condition (4b) and the sum of w_{ij} over i and j gives m_{V}.

At this point, the quantity $\langle A_i\rangle$ must be evaluated. It is assumed that a reasonable estimate can be calculated by a weighted average of the individual surfaces A_{ij} on the fraction of contacts:

$$\langle A_i\rangle = \sum_j\left(\frac{n_j m_j}{\sum_k n_k m_k}\right)A_{ij} \tag{11}$$

By substituting equation (7) into (11) the following implicit form is obtained for the average contact area:

$$\langle A_i \rangle = \frac{\sum_j n_j R_j^2 A_{ij} / \langle A_j \rangle}{\sum_k n_k R_k^2 / \langle A_k \rangle} \tag{12}$$

which can be solved by an iterative procedure rapidly converging to the complete set of $\langle A_i \rangle$.

It has to be observed that the average surfaces from equation (12) are related to the grain boundary area of each size class and to the overall grain boundary surface per volume unit in the system through the following relationships:

$$\sum_j w_{ij} \langle A_i \rangle = \frac{4\pi n_i R_i^2}{2} \tag{13a}$$

$$\sum_i \sum_j w_{ij} \langle A_i \rangle = S_V \tag{13b}$$

Finally, the average number of faces per grain in the system, $\langle m \rangle$, can be calculated as:

$$\langle m \rangle = \frac{2m_V}{N_V} = \sum_i \frac{n_i}{N_V} m_i \tag{14}$$

where N_V is the total number of grains per volume unit:

$$N_V = \sum_i n_i \tag{15}$$

3. THE MODIFIED CONTINUITY EQUATION

In the analytical approach of the LSW and Hillert theories [1–3] the mass conservation in the system is imposed through the continuity equation

$$\frac{\partial n(v)}{\partial t} + \frac{\partial}{\partial v}\left(n(v) \frac{\mathrm{d}v}{\mathrm{d}t} \right) = 0 \tag{16}$$

where $n(v)$ is the GSD and $\mathrm{d}v/\mathrm{d}t$ the growth rate, a function of grain volume. In discrete models based on the mean field hypothesis, a single and constant value of the growth rate is associated to each size class. As expected, the numerical integration with respect to time of the kinetic equations recovers the analytical asymptotic solution after an initial transient.

In the present discrete model, the formulation of the continuity equation (16) cannot be applied due to the structure of the kinetic equations and to the cross-links among the number of common faces shared by couples of grain classes. Therefore, the volume balance has been guaranteed by introducing the following continuity equation:

$$\frac{\partial n(v)}{\partial t} = \int_0^v \frac{\partial}{\partial v}\left(w(v, \tilde{v}) \frac{\mathrm{d}v}{\mathrm{d}t}\Big|_{\tilde{v}} \right) \mathrm{d}\tilde{v} - \int_v^\infty \frac{\partial}{\partial \tilde{v}}\left(w(\tilde{v}, v) \frac{\mathrm{d}\tilde{v}}{\mathrm{d}t}\Big|_{v} \right) \mathrm{d}\tilde{v} \tag{17}$$

A detailed description of the procedure adopted to calculate the evolution of the discrete GSD is reported in Appendix B together with the derivation of the mass balance equation (17) in the continuous domain.

4. INHIBITION OF GRAIN GROWTH BY SECOND PHASE PARTICLES

The pinning effect exerted by second phase particles on the grain boundary can be directly accounted for in the growth equation. Assuming $R_i > R_j$, equation (1) can be rewritten as [3–6, 16]:

$$\left. \frac{\mathrm{d}v_i}{\mathrm{d}t} \right|_j = M\gamma A_{ij} \left(\frac{2}{R_j} - \frac{2}{R_i} - Z \right) \tag{18}$$

where Z is the inhibition contribution which is always opposed to the boundary motion. In these conditions, the volume growth rate must be ≥ 0. A negative balance implies that in any case, exchange occurs between the interacting grains and the value of growth rate is imposed to be zero.

5. RESULTS

Simulations have been carried out on an ideal system to check the model behaviour. The mobility of austenite from Ref. [16] at 1073°C ($M = 9.03 \times 10^{-11}$ m^4 J^{-1} s^{-1}) and an average grain boundary energy of 0.5 J m^{-2} have been used. Different levels of inhibition have also been considered with Z having values 0, 50, 100 and 200/mm. An initial Gaussian GSD with average size 5 μm and standard deviation 2.5 μm has been used in all cases with $\Delta R = 1$ μm and the calculations have been extended up to 200 s.

The calculated evolution of the average grain size is shown in Fig. 1 on a log–log scale. As expected, an increase in the inhibition level retards the coarsening process.

A quasi-stationary state, characterised by a linear behaviour in the double logarithmic plot, is correctly

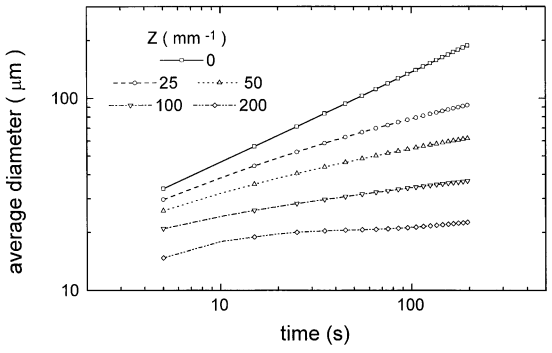

Fig. 1. Double-logarithmic plot of the grain coarsening kinetics at different levels of inhibition.

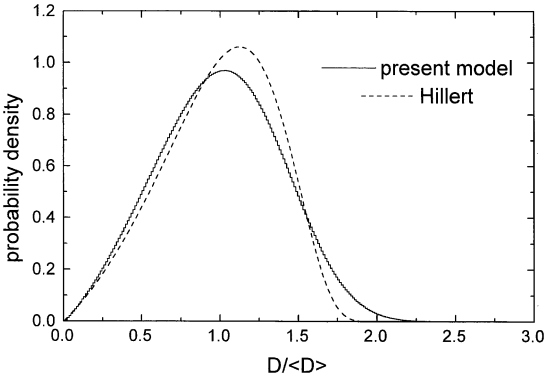

Fig. 2. Quasi-stationary grain size distribution in reduced form ($\sigma_D = 0.39$) and comparison with the asymptotic solution by the Hillert's model ($\sigma_D = 0.35$).

predicted by the model after the initial transient depending on the inhibition level. This behaviour is also confirmed by the evolution of the variation coefficient k_{GSD} (ratio between the standard deviation of the GSD and the average size), which reaches an almost constant level after the initial transient.

The growth exponent is equal to 0.48 in the absence of inhibition (and close to the expected theoretical value of 0.5) and decreases continuously with increasing inhibition level. In Table 1 some relevant parameters of the quasi-stationary GSD and the growth exponents are reported as a function of *Z*. These values have been obtained from simulations extended up to 200 s and must be considered only as an indication of the general trend and not as an absolute reference, being slightly dependent on the width of size classes.

It can be readily seen that low inhibition levels, as experimentally observed [16], cause a sharpening of the GSD with respect to uninhibited normal grain growth, whereas the broadening increases at higher inhibition values.

The quasi-stationary GSD for normal grain growth without inhibition is shown in Fig. 2 in reduced form together with the asymptotic analytical solution [3]. The present model predicts a GSD with a right tail extending beyond the cut-off value of the Hillert's distribution. Consequently, its standard deviation is slightly increased. The effect of different inhibition levels on the reduced shape of the stationary GSD is reported in Fig. 3.

Concerning the topological features of the model for the quasi-stationary normal grain growth regime, the distribution of the number of faces per grain in the uninhibited quasi-stationary GSD is shown in Fig. 4 and the relationship between the average number of faces per size class and the reduced grain size is reported in Fig. 5.

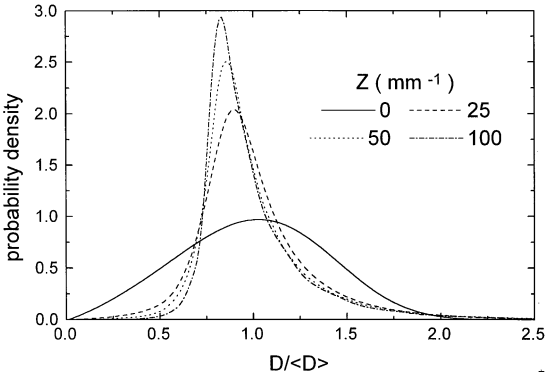

Fig. 3. Shape of the quasi-stationary reduced GSD as a function of the inhibition level.

It is worth noting that, as expected on the basis of theoretical arguments, for the latter case, a parabolic dependence of m_i on the reduced size $D/\langle D\rangle$ is obtained. A very good fit is calculated even imposing the theoretical value of four (minimum number of faces per grain) to the intercept. In addition, this relationship has been found to be invariant during the evolution of the system and independent of the inhibition level. The analytical expression of the curve (correlation coefficient >0.9999) is shown below:

Table 1. Indicative values of the parameters of the quasi-stationary GSDs and kinetic exponents after 200 s of simulated grain growth as a function of the inhibition level

Z (mm^{-1})	k_{GSD}	$\langle m\rangle$	Growth exponent
0	0.387	11.43	0.477
25	0.304	11.63	0.245
50	0.313	11.62	0.181
100	0.316	11.61	0.120
200	0.360	11.52	0.095

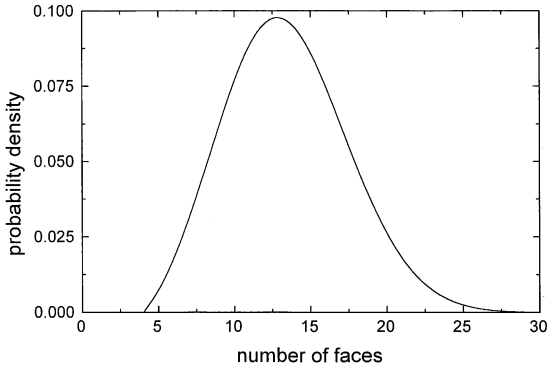

Fig. 4. Distribution of the number of faces per grain in the quasi-stationary GSD without inhibition.

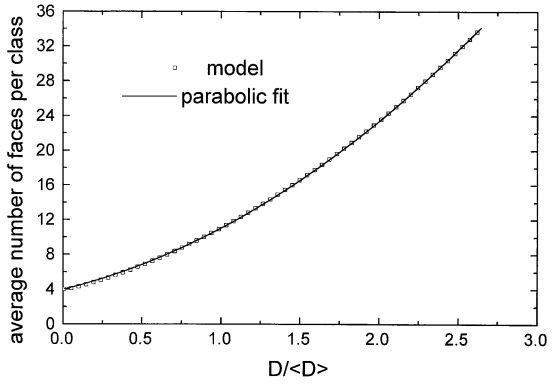

Fig. 5. Average number of faces per size class, m_i, in the quasi-stationary GSD without inhibition (squares) as a function of grain size and the corresponding parabolic fit (solid curve).

$$m = 4 + 4.37\left(\frac{D}{\langle D\rangle}\right) + 2.664\left(\frac{D}{\langle D\rangle}\right)^2 \qquad (19)$$

Finally, it is interesting to observe that the reduced quasi-stationary distribution of the proposed model is very similar to the computer simulation result obtained by the sophisticated Surface Evolver program [17] based on the evolution of grain boundaries towards a minimum energy.

6. DISCUSSION

Mean field models commonly found in the literature are generally based on the calculation of an average value of the growth rate for each size class as a function of the grain surrounding. This permits the continuity equation (16) to be used to calculate the GSD evolution. This averaging operation on the growth is responsible for the sharp cut-off of the GSD due to the fact that the largest particles are restricted to grow only with the average rate of their class. Actually, some grains can grow faster than the average, due to a favourable surrounding, thus determining the elongated right tail of the GSD.

The present model tries to overcome this problem by treating grain growth in terms of pair interactions instead of a mean field. Averaging operations over the system are used only to evaluate the co-ordination number m_i for each size class from the corresponding average area of the grain faces ($\langle A_i\rangle$) through an internally coherent formalism, as confirmed by equations (13a) and (13b). Thus, the growth rates of the grain couples are only indirectly affected by system averages and can exhibit a certain spread, depending on the size of the possible neighbouring grains, leading to a quasi-stationary GSD shape which is more symmetrical than that of Hillert's model.

This result demonstrates that the pair interaction model describes grain growth with comparable predicting capabilities with respect to the mean field model, although being substantially different from it. On the other hand, it has to be observed that the shape of the asymptotic PSD, which is similar to that by Hillert, is not completely satisfactory in terms of both extension of the tail and position of the maximum. The reason for this can be sought in the fact that the distribution of contacts of a given grain is taken into account only as far as the estimation of the probability of a common boundary with a neighbour is concerned. Then, each contact is treated as if it were independent of the others. In contrast, the behaviour of each grain strongly depends on its actual surrounding considered as a whole. Although at present the model does not include this fundamental aspect, its structure makes it possible to easily introduce this further improvement, as all the main topological features of the system are directly accessible.

7. CONCLUSIONS

The proposed pair interaction model predicts a slightly right-tailed GSD in normal grain growth conditions. The model represents only a limited improvement to the mean field approach, being the shape of the asymptotic grain size distribution yet close to that by Hillert.

A new formulation of the continuity equation has been introduced which is consistent with the pair interaction approach. The model gives a correct prediction of the main topological features of a 3D polycrystal and its behaviour in the case of inhibition is similar to that exhibited by the mean field approaches.

The present approach can be easily improved to treat the grain growth process in a really statistical way.

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APPENDIX A

A.1. Estimate of the effective contact area between grains

Let us consider two tangent spheres of radius R_i and R_j, as shown in Fig. A1. The intersections of the common tangents drawn to one another from their respective centres identify a segment which can be viewed as the diameter of the circle representing their effective contact area. The radius of this circle, r_{ij}, is given by the following relationship:

$$r_{ij} = \frac{R_i R_j (R_i + R_j)}{R_i\sqrt{R_i(R_i + 2R_j)} + R_j\sqrt{R_j(R_j + 2R_i)}} \quad \text{(A1)}$$

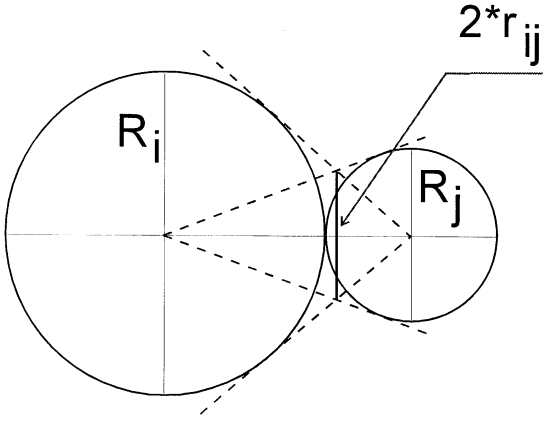

Fig. 6. Geometric construction for the evaluation of the contact area between neighbouring grains.

and its area will be:

$$A_{ij} = \pi r_{ij}^2 \quad \text{(A2)}$$

Although this is an extremely raw approximation of the real surface shared by two grains, nevertheless it has some interesting properties.

As the ratio R_i/R_j approaches zero, r_{ij} tends to R_i. This means that as the radius of the smaller grain i is reduced, the contact area approaches its diametrical section and the minimum allowable number of its faces tends to

$$m_i \approx \frac{4\pi R_i^2}{\pi R_i^2} = 4 \quad \text{(A3)}$$

On the other hand, in a monodisperse system where all grains have the same size R ($R_i = R_j = R$), $r_{ij} = R/\sqrt{3}$ and each grain will have a number of faces given by

$$m_{3D} = \frac{4\pi R^2}{\pi r_{ij}^2} = 12 \quad \text{(A4)}$$

which is the exact geometric value theoretically expected on the basis of the topological requirements for a regular 3D structure [18].

In the 2D case, the number of nearest neighbours is:

$$m_{2D} = \frac{2\pi R}{2r_{ij}} = \pi\sqrt{3} \approx 5.44 \quad \text{(A5)}$$

which is lower than the theoretical value of six corresponding to a hexagonal tessellation of the plane.

APPENDIX B

B.1. Algorithm for the volume conservation and reformulation of the continuity equation

In this appendix the algorithm for the conservation of the volume and number of grains in a discrete form suitable for a direct calculation is presented. This has been originally developed on the basis of simple heuristic considerations. An equivalent synthetic equation in the continuous domain, corresponding to the commonly used continuity equation (16), is also derived a posteriori.

Multiplying equation (1) by the integration time step Δt, the overall volume exchange per unit volume, ΔV_{ij} is obtained for each interacting pair as:

$$\Delta V_{ij} = w_{ij}\left.\frac{dv_i}{dt}\right|_j \Delta t = -\Delta V_{ji} \quad \text{(B1)}$$

Let us conventionally assume that in the pair, the grain in the ith class is greater than that in the jth class ($R_i > R_j$) so that the grain i always grows and ΔV_{ij} in equation (B1) is always positive. The movement of grains along the distribution is treated separately for the growing and the shrinking sides. In the case of growth, grains in the class i move to the class k which, in principle, is not adjacent to the ith. Similarly, the shrinking grains move from the jth class to the sth class, not necessarily contiguous with respect to j.

In order to allow for the total volume and the number of grains to be conserved, another auxiliary class must be introduced which, instead, is adjacent to the destination class defined above. Thus, for growing grains this auxiliary class will be the $(k + 1)$ - th, whereas for the shrinking grains it will be the $(s-1)$ - th.

Owing to the symmetry properties expressed by equations (4b) and (14), in the following derivation the quantities ΔV_{ij} and w_{ij} will be used in both cases to avoid possible confusion, taking into account the correct algebraic sign where necessary.

Let us consider the growing side first. In a time step, the volume increase ΔV_{ij} of the w_{ij} interacting particles in the ith class must be partitioned between the classes k and $k + 1$ with $k \geq i$. The index of the destination class is calculated through the final volume v_k^*

$$v_k^* = v_i + \frac{\Delta V_{ij}}{w_{ij}} \tag{B2}$$

from which the corresponding radius R_k^* is

$$R_k^* = \left(\frac{3v_k^*}{4\pi}\right)^{1/3} \tag{B3}$$

and finally the class index is given by:

$$k = \left[\frac{R_k^*}{\Delta R}\right] \tag{B4}$$

where ΔR is the class width and the square brackets denote the integer part. Now the volume conservation condition must be coupled with that for the conservation of the number of grains. The following system of linear equations is obtained where the unknowns, Δn_k and Δn_{k+1}, represent the variation in the number of elements in the destination classes:

$$v_k \Delta n_k + v_{k+1} \Delta n_{k+1} = w_{ij} v_i + \Delta V_{ij} \tag{B5a}$$

$$\Delta n_k + \Delta n_{k+1} = w_{ij} \tag{B5b}$$

The solution is:

$$\Delta n_k = \frac{w_{ij}(v_{k+1} - v_i) - \Delta V_{ij}}{v_{k+1} - v_k} \tag{B6a}$$

$$\Delta n_{k+1} = w_{ij} - \Delta n_k \tag{B6b}$$

and the updated distribution at the time $t + \Delta t$ is:

$$n_i(t + \Delta t) = n_i(t) - w_{ij} \tag{B7a}$$

$$n_k(t + \Delta t) = n_k(t) + \Delta n_k \tag{B7b}$$

$$n_{k+1}(t + \Delta t) = n_{k+1}(t) + \Delta n_{k+1} \tag{B7c}$$

Similarly, for the shrinking side, the volume decrease ΔV_{ij} of the w_{ij} interacting grains in the jth class must be partitioned between the classes s and $s-1$ with $1 < s \leq j$. Thus, as before one obtains:

$$v_s^* = v_j - \frac{\Delta V_{ij}}{w_{ij}} \tag{B8}$$

$$R_S^* = \left(\frac{3v_s^*}{4\pi}\right)^{1/3} \tag{B9}$$

$$s = \left[\frac{R_s^*}{\Delta R}\right] + 1 \tag{B10}$$

Then the volume conservation constraints are:

$$v_s \Delta n_s + v_{s-1} \Delta n_{s-1} = w_{ij} v_j - \Delta V_{ij} \tag{B11a}$$

$$\Delta n_s + \Delta n_{s-1} = w_{ij} \tag{B11b}$$

and the solution is:

$$\Delta n_s = \frac{w_{ij}(v_j - v_{s-1}) - \Delta V_{ij}}{v_s - v_{s-1}} \tag{B12a}$$

$$\Delta n_{s-1} = w_{ij} - \Delta n_s \tag{B12b}$$

so that the updated GSD is calculated as:

$$n_j(t + \Delta t) = n_j(t) - w_{ij} \tag{B13a}$$

$$n_{s-1}(t + \Delta t) = n_{s-1}(t) + \Delta n_{s-1} \qquad \text{(B13b)}$$

$$n_s(t + \Delta t) = n_s(t) + \Delta n_s \qquad \text{(B13c)}$$

Only when $s = 1$ is the number of particles not conserved due to the complete disappearance of the involved grains. Thus, as the volume of the 0th class $v_0 = 0$, the only relevant quantity, Δn_1, is directly obtained from equation (B12a):

$$\Delta n_1 = n_{i1} - \frac{\Delta V_{i1}}{v_1} \qquad \text{(B14)}$$

The final equations (B7) and (B13) for updating the GSD are used to control the integration time step Δt. This is chosen as the largest value which produces a non-negative number of elements in the size classes.

The calculation is carried out through two nested cycles. The outer one, on the index i representing the larger grain, spans the whole distribution, the inner one, on the smaller grain j, ranges from the first class up to the $(i-1)$ - th class in order to count each possible interacting pair only once.

Now it is possible to recover the expression that, in the continuous range, is equivalent to the discrete continuity equation here formulated and to compare it with equation (16).

As the integration time step $\Delta t \to 0$, also $\Delta V_{ij} \to 0$ and therefore it can be expected that $k = i$ and $s = j$ in the above equations. Thus, from equations (B6) and (B7), writing in explicit form ΔV_{ij} according to equation (17) and rearranging, the following result is obtained:

$$\left.\frac{n_i(t + \Delta t) - n_i(t)}{\Delta t}\right|_j = -\left.\frac{w_{ij}}{v_{i+1} - v_i}\frac{\mathrm{d}v_i}{\mathrm{d}t}\right|_j \qquad \text{(B15a)}$$

$$\left.\frac{n_{i+1}(t + \Delta t) - n_{i+1}(t)}{\Delta t}\right|_j = +\left.\frac{w_{ij}}{v_{i+1} - v_i}\frac{\mathrm{d}v_i}{\mathrm{d}t}\right|_j \qquad \text{(B15b)}$$

where the rate of change of grains in classes i and $i + 1$ are referred to the interactions with j grains only. A similar result is obtained for the shrinking side.

Referring to a generic size class i, the overall rate of change of n_i due to all the possible interactions will result from the balance between the positive contributions deriving from smaller grains $j \le i$ and the negative contributions from larger grains $j \ge i$. By summing up all the terms, the overall rate of change of grain number in class i becomes:

$$\left.\frac{n_i(t + \Delta t) - n_i(t)}{\Delta t}\right| = \sum_{j=1}^{n_c} \left.\frac{n_i(t + \Delta t) - n_i(t)}{\Delta t}\right|_j \qquad \text{(B16)}$$

$$= \sum_{j=1}^{i} \left.\frac{w_{ij}}{v_i - v_{i-1}}\frac{\mathrm{d}v_i}{\mathrm{d}t}\right|_j - \sum_{j=1}^{n_c} \left.\frac{w_{ij}}{v_{j+1} - v_j}\frac{\mathrm{d}v_j}{\mathrm{d}t}\right|_i$$

where n_c is the total number of classes in the discrete GSD.

The above equation can be converted in continuous form by letting the class width $\Delta v = (v_i - v_{i-1}) \to 0$, by substituting n_i and w_{ij} with the dimensionally equivalent $n(v)\,\mathrm{d}v$ and $w(v, \tilde{v})\,\mathrm{d}v\,\mathrm{d}\tilde{v}$, respectively, and by changing the sums in the right-hand side into the corresponding integrals. Then, the net rate of formation of grains in the range $\mathrm{d}v$ is given by:

$$\frac{\partial[n(v)\,\mathrm{d}v]}{\partial t} = \left[\int_0^v \frac{\partial}{\partial v}\left(w(v, \tilde{v})\left.\frac{\mathrm{d}v}{\mathrm{d}t}\right|_{\tilde{v}}\right)\mathrm{d}\tilde{v}\right]\mathrm{d}v \qquad \text{(B17)}$$

$$-\left[\int_v^\infty \frac{\partial}{\partial \tilde{v}}\left(w(\tilde{v}, v)\left.\frac{\partial \tilde{v}}{\mathrm{d}t}\right|_v\right)\mathrm{d}\tilde{v}\right]\mathrm{d}v$$

Dividing through by $\mathrm{d}v$, the final form of the continuity equation is obtained:

$$\frac{\partial n(v)}{\partial t} = \int_0^v \frac{\partial}{\partial v}\left(w(v, \tilde{v})\left.\frac{\mathrm{d}v}{\mathrm{d}t}\right|_{\tilde{v}}\right)\mathrm{d}\tilde{v} \qquad \text{(B18)}$$

$$-\int_v^\infty \frac{\partial}{\partial \tilde{v}}\left(w(\tilde{v}, v)\left.\frac{\partial \tilde{v}}{\mathrm{d}t}\right|_v\right)\mathrm{d}\tilde{v}$$

Thus, for the present model, the integro-differential equation (B18) is the proper continuity equation. Its structure is similar to that used to describe aerosol coagulation [19] and the integrands have the same form as the continuity equation (16) used in the mean field approaches.

APPENDIX C

C. 1. Nomenclature

A_{ij}	contact area between grains in the size classes i and j [m^2]
$\langle A_i \rangle$	average area of the grain faces in the size class i [m^2]
b	magnitude of Burgers' vector [m]
D	grain diameter [m]
$\langle D \rangle$	average grain diameter [m]
D_{GB}	grain boundary diffusivity [m^2 s^{-1}]
k_B	Boltzmann constant [J K^{-1}]

k_{GSD}	variation coefficient of the GSD [dimensionless]	R_i^*	final radius of a growing/shrinking grain after the mass exchange event [m]
m_i	average number of faces of grains in the ith size class [dimensionless]	S_V	grain boundary surface per unit volume [m^{-1}]
m_V	total number of grain faces per unit volume [m^{-3}]	t	time [s]
$\langle m \rangle$	average number of faces of grains in the whole system [dimensionless]	T	temperature [K]
M	grain boundary mobility [$m^4\ J^{-1}\ s^{-1}$]	v_i	volume of a grain in the ith size class [m^3]
n_i	number of grains per unit volume in the ith size class [m^{-3}]	v_i^*	final volume of a growing/shrinking grain after the mass exchange event [m^3]
$n(v)$	continuous GSD as a function of grain volumes [m^{-6}]	w_{ij}	number of contacts between the size classes i and j per unit volume [m^{-3}]
n_c	total number of classes in the discrete GSD [dimensionless]	$w(v, \tilde{v})$	continuous distribution of the number of contacts between grains [m^{-9}]
N_V	number of grains per unit volume [m^{-3}]	Z	inhibition by second phase particles [m^{-1}]
p_{ij}	probability of a common face between the size classes i and j [dimensionless]	γ	grain boundary interfacial energy [$J\ m^{-2}$]
r_{ij}	radius of the circular contact surface between grains in the size classes i and j [m]	Δn_i	variation of number of grains per unit volume in the ith size class [m^{-3}]
R	grain radius [m]	ΔR	width of size classes in radius [m]
R_i	radius of a grain in the ith size class [m]	Δv	width of size classes in volume [m^3]
		ΔV_{ij}	volume exchanged per unit volume between grains in the classes i and j [dimensionless]
		σ_D	standard deviation of the GSD [m]