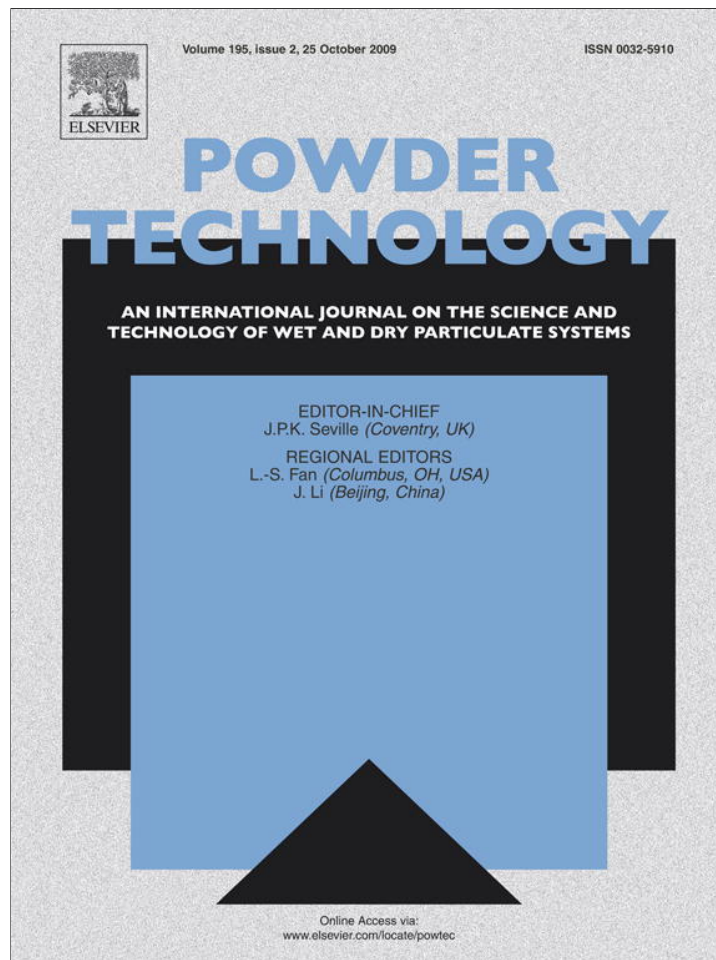


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Short communication

Qualitative models of particle de-agglomeration

Dominique Chu^{a,*}, Shih-Chi Chu^b, Mostafa Barigou^b^a Computing Laboratory, University of Kent, CT2 7NF, Canterbury, UK^b School of Chemical Engineering, University of Birmingham, B15 2TT Birmingham, UK

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ABSTRACT

We present a differential equation model and a computer simulation of particle de-agglomeration in suspensions. The models are qualitative in nature, that is they do not assume specific parameters. Instead, this article investigates whether qualitative features of a series of transient volume–size distributions can give an insight into the underlying dynamics of particle de-agglomeration. We find that this is indeed possible and provide a table summarizing how various breakdown processes can be distinguished by considering the qualitative features of the transient volume–size distributions only.

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1. Introduction

De-agglomeration of particles in solutions has important applications in scientific and industrial contexts. Correspondingly, there have been some significant experimental efforts [1–4] to understand the specifics of how agglomerates of particles (the *secondary* particles) can be broken down into smaller units, possibly even into their constituent particles (usually called the *primary* particles). Breakdown of particles is either a fragmentation process (i.e. a particular secondary particle is broken down into many much smaller fragments) or an erosion process (i.e. a secondary is asymmetrically split into two particles of unequal size). The process of breaking down particles usually involves some kind of energy input into the dispersion that causes the de-agglomeration process. The efficiency of this process and its details depend on the conditions of the medium (temperature, pH-value, etc...), the nature of the particles to be dispersed and the source of the dispersion energy (mechanical input, or sonification) [6]. In this article, we will not be concerned with these details, but rather investigate the dynamics of de-agglomeration processes, independent of the detailed circumstances that cause them. Also, we will not report any experimental data, but exclusively concentrate on modeling the dispersion process.

The size distribution of secondary particles is normally well modeled by a log-normal distribution (this distribution is either the number of particles of size x or the proportion of total dry-mass volume contained in secondary particles of size x versus the size) with some distribution parameters μ and σ (the precise numbers depend

on the experimental conditions and the particles used). Input of dispersion energy will eventually result in a dispersion with particles being distributed according to a different μ and σ (the new μ typically being significantly smaller). This final distribution is reached via a transient bi-modal particle size distribution that can be described as the sum of two log-normal distributions with different parameters. The first (or small) mode can be approximated by a log-normal distribution around a median value (given by e^μ in log normal distributions) that is significantly smaller than the median around the second (or large) mode that is at or near the median of the original distribution before energy input started. The small mode indicates the part of the particle mix that has been broken down by the energy input; given sufficient energy input, the large mode will eventually disappear restoring the mono-modal nature of the distribution.

In experimental setups it is possible to take snapshots of the transient particle-size distributions. These snapshots hold information about the underlying processes that lead to the breakdown of secondary particles. However, interpreting these by mere verbal reasoning is difficult and prone to errors. For this reason, formal modeling methods have been proposed to describe the process of breaking down particles (see for example [5]). A fairly general model has been described by Kusters et al. [7]; this model is formulated as an integro-differential equation. Kuster's model is sufficiently general to represent most scenarios likely to be of practical relevance; however, integro-differential equations are technically very difficult to analyze, and can normally not be solved analytically. Solving such equations is possible but requires significant knowledge of numerical solution techniques (see for example Sommer et al. [8]).

The aim of the present contribution is twofold. Firstly, in Section 2 we present a simplified version of Kuster's model (along with an analytical solution) that covers a limited (but arguably important) set

* Corresponding author.

E-mail addresses: D.F.Chu@kent.ac.uk (D. Chu), S.Chu@bham.ac.uk (S.C. Chu), M.Barigou@bham.ac.uk (M. Barigou).

of cases, namely fragmentation of secondary particles. Secondly, we present a stochastic simulation model of particle de-agglomeration that directly models the breakdown of secondary particles in a simulation model. This model is described in Section 3. The main focus of this article is on qualitative models that aid the interpretation of sequences of transient volume distributions as they arise in de-agglomeration processes, rather than model a specific set of experiments. We will therefore not make any attempt to relate the input parameters of the models to any specific system parameters (e.g. energy input, particle size, charge, pH-value and the like). Instead, in this contribution we are mainly concerned with the qualitative features of the transient particle size distributions and what they reveal about the underlying processes.

2. Differential equation model

The original model by Kusters [7] describes both fragmentation and erosion in a single integro-differential equation model. While very descriptive, this original model is rather complicated, analytically not solvable and non-trivial to solve numerically. The difficulty when modeling erosion (or fragmentation) of particles using differential equations is that the breakup of a secondary particle into two fragments results in particles that are significantly different in size to the original. For example, a newly created particle of size x_1 can be the fragment of a particle of any size $x_2 > x_1$. Hence, in order to model the change of the number (or “concentration”) of particles of size x_1 one needs to sum (or integrate) over the probabilities of any of the larger particles to be broken down into a fragment of size x_1 . This is a source of complication of the full Kusters model. Reducing the complexity of the model to include only decay of the large mode, but not the small mode removes this difficulty and can significantly simplify the model. However, this comes at the cost of a reduced generality of the model. As will become clear in this section the simplified model can still be useful to interpret data from particle de-agglomeration experiments, under some circumstances. In this section we will formulate the model, derive an analytic solution and present some numerical examples that give insight into the qualitative behavior of the system.

Assume $n(x,t)$ is the number (or rather “concentration”) of agglomerates of size x at time t . If we ignore particles of sizes that are typical of the fragments (i.e. the small mode) and if we further assume that fragments are typically much smaller than the particles of the original distribution, then we can ignore the addition of fragments. This simplifies the Kusters model significantly and leads to a differential equation of a decay process:

$$\dot{n}(x,t) = -n(x,t) \cdot f(x). \quad (1)$$

Here $f(x)$ is a function that determines how the fragmentation of secondary particles depends on their size x ; note that we assume $f(x)$ to be independent of the time t . Such a differential equation is for many choices of $f(x)$ solvable by separating the variables, i.e. rewriting Eq. (1) as:

$$\int \frac{1}{-nf} dn = \int dt \quad (2)$$

Here we omitted the functional dependencies of n and f to improve readability. For the special case of $f(x) = c$, where c is some constant, one obtains:

$$n = \exp(-tc - Kc). \quad (3)$$

Here K is an arbitrary integration constant arising from the integration over t in Eq. (2). At this point only the time dependence of $n(x,t)$ is determined. The dependence on the particle size enters

the solution via the initial condition. This can be done by assuming $K = K(x)$ and forcing Eq. (3) to fulfill the initial condition

$$n(x,0) = \exp(-cK(x)) = F(x). \quad (4)$$

Here $F(x)$ is the initial distribution of particles sizes before the fragmentation process started. In what follows we assumed it to be a log-normal distribution with parameters μ and σ .

$$F(x) = \frac{1}{x\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln(x)-\mu)^2}{2\sigma^2}\right) \quad (5)$$

Solving Eq. (4) for $K(x)$ and substituting the relevant expression in Eq. (3) then leads to the sought solution for the time evolution of the particle size distribution $n(x,t)$. In the particular case of $f(x) = c$ this yields:

$$n(x,t) = \frac{1}{\sqrt{2\pi}x\sigma} \exp\left(-\frac{1}{2}\sigma^{-2}\ln^2(x) + \sigma^{-2}\ln(x)\mu - \frac{1}{2}\sigma^{-2}\mu^2 - tc\right) \quad (6)$$

For this particular choice of $f(x)$ the solution has the rather interesting property that the position of the peak of the distribution (and hence the median value) does not change over time. This can be seen by determining the maximum of the distribution, i.e. solving the following equation for x :

$$\frac{\partial n(x,t)}{\partial x} = 0 \quad (7)$$

Using $n(x,t)$ from Eq. (6) this leads to the following expression for the peak of the distribution:

$$x_{\max}(t) = \exp(\mu - \sigma^2). \quad (8)$$

Note that this expression is independent of time; translated into the language of transient volume distributions this means that the position of the peak of the large mode does not change as the system evolves. This conclusion changes when $f(x)$ depends on x . We consider as an example the case of $f(x) = cx$, i.e. a linear dependence of the fragmentation rate on the particle size leads to:

$$n(x,t) = \frac{1}{\sqrt{2\pi}x\sigma} \exp\left(-\frac{1}{2}\sigma^{-2}(\ln(x))^2 + \sigma^{-2}\ln(x)\mu - \frac{1}{2}\sigma^{-2}\mu^2 - tcx\right) \quad (9)$$

$$x_{\max}(t) = \frac{\sigma^{-2} \text{LambertW}(tce^{-\sigma^2} + \mu\sigma^2)}{tc}.$$

Here $\text{LambertW}(x)$ is the Lambert W function.

We can also get solutions for more complicated cases; the fragmentation rate might depend on the size in a number of ways. Restricting our attention to the case of proportionality to some power of x , i.e. $f(x) = cx^j$, we get the following solution:

$$n(x,t) = \frac{1}{\sqrt{2\pi}x\sigma} \exp\left(-\frac{1}{2}\sigma^{-2}\ln^2(x) + \sigma^{-2}\ln(x)\mu - \frac{1}{2}\sigma^{-2}\mu^2 - tcx^j\right) \quad (10)$$

$$x_{\max} = \exp\left(-\frac{j\sigma^2 - j\mu + \text{LambertW}(tcj^2e^{-j(\sigma^2-\mu)\sigma^2})}{j}\right)$$

2.1. Numerical examples

Fig. 1 shows the position of the peak of the large mode as a function of time. The graph indicates that the higher the dependence of the fragmentation rate on the particle size, the faster the displacement of the peak of the large mode over time. In the special case of no

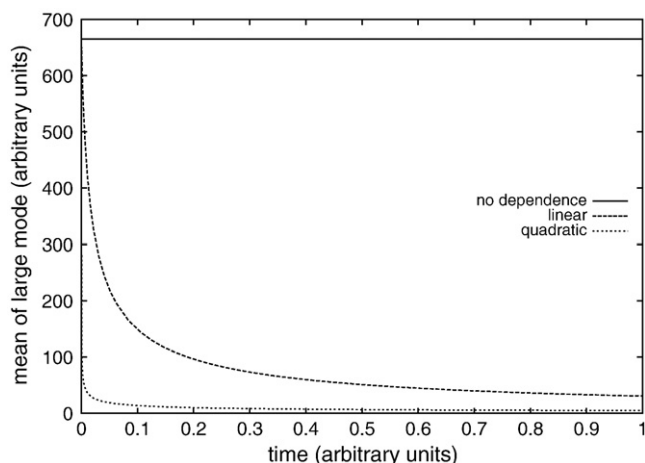


Fig. 1. The position of the peak of the large mode as predicted by the differential equation model Eq. (1) as a function of time. We are not attempting to fit the model to any specific data, so the graph here is to be understood as a numerical example only. The figure shows three cases corresponding to an unbiased model, a linear and a quadratic dependence of the fragmentation rate on the particle size. For the unbiased case, the position of the peak does not change, as predicted above. For the linear and quadratic case the graph shows what resembles an exponential fall of the peak of the large mode. Here we assumed the following parameters: $\mu = 7.5$, $\sigma = 1$, $s = 0.3$, $m = 2.0$, $c = 0.1$.

dependence, the peak is not displaced at all; once the dependence is inverted, i.e. smaller particles are more likely to be fragmented, the mean displacement would accelerate again, but in the opposite direction (i.e. the peak would be shifted towards larger secondary particle sizes). In the linear and quadratic case, the speed of peak displacement is not constant but fast at first and decelerating as time progresses.

Fig. 2 shows the size of the peak (so essentially the volume percentage contained in the peak) over time. In the unbiased case there is a linear dependence, whereas the linear and the quadratic cases show a much faster decay of the peak; on the graph in Fig. 2 the decay curve for the quadratic case is barely visible because of the fast pace of decay. The observation that the size of the large mode decays very fast when the dependence on the particle size is strong suggests that real data would appear somewhat different to the results of the differential equation model. One must assume that the measurement device cannot detect very small peaks. In practice, one can therefore assume that even in the quadratic (or higher order) case the speed of mean displacement would appear to be constant; the area where the displacement of the peak decelerates would most likely be undetectable. The shape of the peak-displacement curve therefore contains only limited information about the power of the size dependence on the fragmentation, except in the case of a static peak which is a conclusive indicator for a fragmentation curve that is independent of the size.

3. Computer model

In this section we present a computer simulation of the particle de-agglomeration process. Unlike the differential equation model, the computational model represents both the large and the small mode and it can easily be used to model fragmentation and erosion of particles. The main difference between the computer model and the differential equation model is that the former assumes discrete populations, i.e. every single secondary particle is explicitly counted. In terms of its computational cost (and in consequence the feasibility of it being fitted to real data) the computational model is clearly inferior to formal mathematical approaches. However, its main benefit is that it can easily be adapted to model a number of approaches that would be very difficult to model using equation-based approaches.

The initial particle distribution is chosen according to a log-normal distribution around a user-specified peak. The simulation model is updated in discrete time steps. At every time-step the model updates the number of secondary particles of a given size (as measured by the number of primary particles); for example, a secondary particle of size 100 is the agglomerate of 100 primary particles. At every time-step the particle numbers are updated according to the following algorithm:

- (1) Initialise time to $T = -1$.
- (2) Set the secondary particle size to be considered next to $n = 1$ and set $T = T + 1$.
- (3) For secondary particles of size n determine the base rate of fragmentation/erosion:
 - (a) Determine the base probability $p(n)$ of a single secondary particle of size n to be fragmented/eroded. In this article we consider 3 functions, namely $p(n) = c$ (henceforth referred to as *unbiased*), and $p(n) = c_1 n + c_2$ (henceforth *linear*) and $p(n) = c_1 n^2 + c_2$ (henceforth *quadratic*); here c , c_1 , c_2 are constants to be set by the user.
 - (b) Calculate the number S of particles of size n to be fragmented/eroded: $S = p(n) \cdot n$.
 - (c) If $S < 1$ then draw a random number f between 0 and 1 from a uniform distribution. If $f < S$ then set $S = 1$, otherwise $S = 0$.
 - (d) If S is not an integer, round S to the next lowest integer to determine the number of particles to be eroded/fragmented.
- (4) Fragment/erode simultaneously S particles of size n using the fragmentation/erosion subroutine described below.
- (5) Increment n by 1.
- (6) If n has reached a maximum number (determined by the user in relation to the initial distribution), then go to step 3; otherwise go to step 3.

Erosion is implemented using the following algorithm:

- (1) To erode a particle of size n draw a random number f from an exponential distribution around some user-determined parameters μ and σ .
- (2) To determine the fragment size round f to the next integer $i < f$.
- (3) If $f \geq n$ abort.
- (4) Otherwise, remove a secondary particle of size n and add one particle of size f and one of size $n - f$.

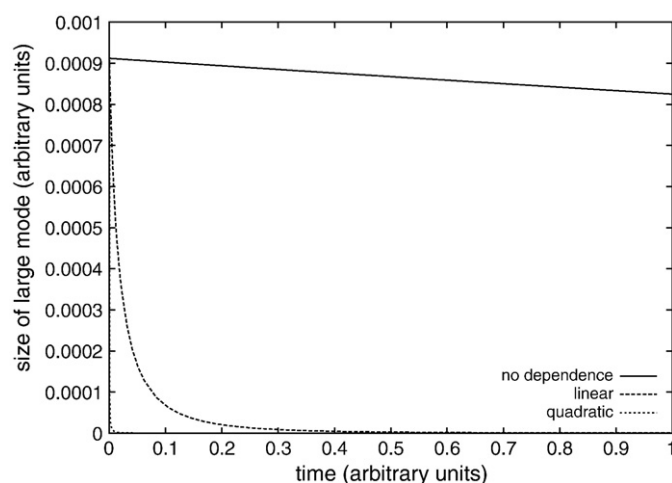


Fig. 2. The height of the peak of the large mode as predicted by the differential equation model Eq. (1) as a function of time. These are example solutions of Eq. (1) for the same parameters as those shown in Fig. 1. The graphs clearly show that a stronger dependence on the particle size leads to a faster decay of the maximum. The quadratic case is barely visible and only appears in the lower right corner of the graph; this means that in the case of quadratic dependence the large mode is very quickly reduced if compared to weaker dependencies.

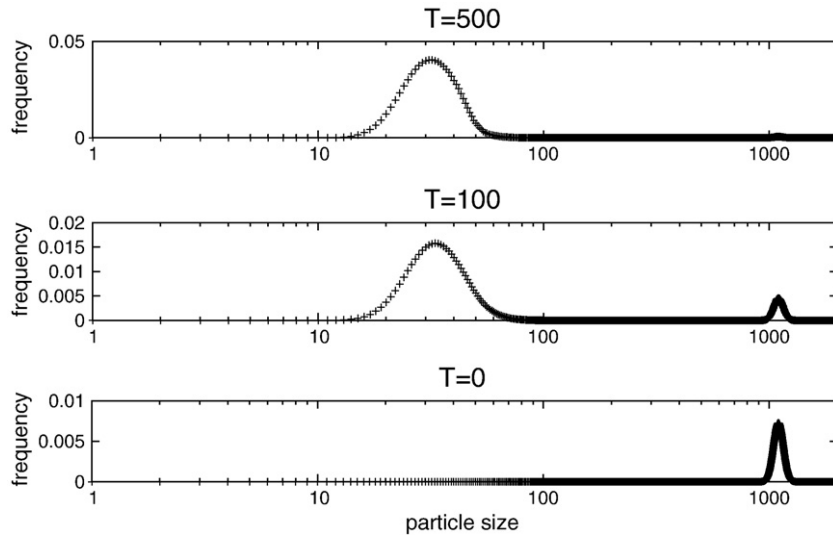


Fig. 3. An example simulation run of the computational mode. The lowest graph shows the initial distribution of secondary particles around a mean of about 1100. At time step 100 (middle graph) the distribution has become bi-modal; the small mode peaks at around 30. In the top graph ($T=500$) the large mode has disappeared and the small mode now peaks at about 20. The simulation shown here used an unbiased fragmentation algorithm described in Section 3. The fragmentation rate for each particle is 0.01; the initial distribution contained about 10 million secondary particles.

Fragmentation is implemented as follows:

- (1) To fragment a particle of size n use the erosion algorithm to create two particles of size f and $n - f$.
- (2) Set $n = n - f$ and go to step 3. (the procedure will stop when the abort condition in step 3 in the erosion subroutine is encountered.)

3.1. Simulation results

Fig. 3 shows the time evolution of the simulation. At time $T=0$ (bottom) the distribution is mono-modal. Here the peak of the large mode is at around 1000. (Note that the parameters of the initial particle distribution are user-defined). By time $T=100$ a second mode has appeared. Both the small and the large mode co-exist for a period of time, but at time step $T=500$ the large mode has disappeared and only the small mode is left. At this point the distribution does not change any more. An example of the time evolution of an erosion process is given by Fig. 4.

The particular position of the peak values can be varied by changing the parameter settings of the simulation model. We consider here the speed of the displacement of the peak positions over time because this can give insight into the underlying processes of the particle de-agglomeration. We performed a number of simulations with different assumptions about the bias of the de-agglomeration process corresponding to complete independence of the de-agglomeration probability of the secondary particle on its size, a linear dependence and a quadratic dependence.

We consider fragmentation first. In this case one would expect that the peak of the large mode does not shift over time when particles are fragmented and the fragmentation process is not biased. This is indeed confirmed by Fig. 5. However, if there is a bias in the sense that larger particles are more likely to be fragmented than smaller ones, then the large mode will shift to the left over time. The figure shows clearly that the speed of peak displacement depends on the nature of the bias. If the bias is merely linear, then the speed of displacement of the peak is lower than if the dependence is quadratic. For more extreme biases the speed of change will correspondingly increase (data not shown).

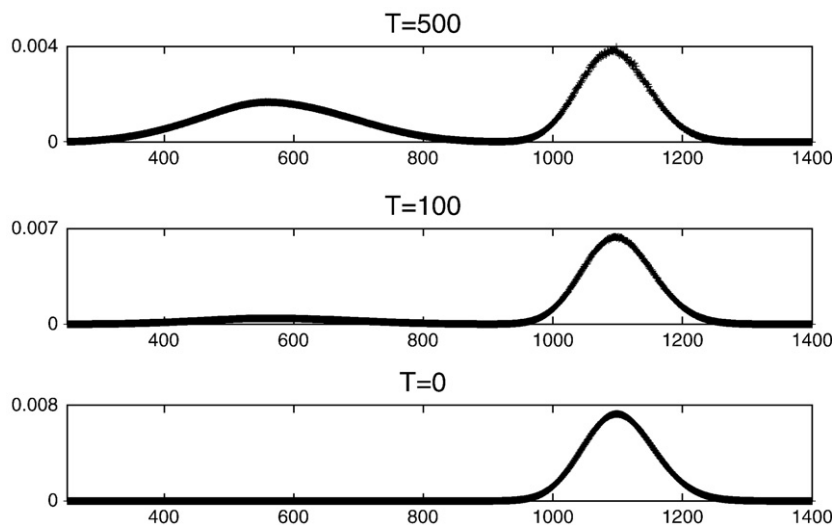


Fig. 4. As in Fig. 3 but with different parameters. The simulation shown here used a biased erosion algorithm described in Section 3. The fragmentation rate for each particle is 0.1.

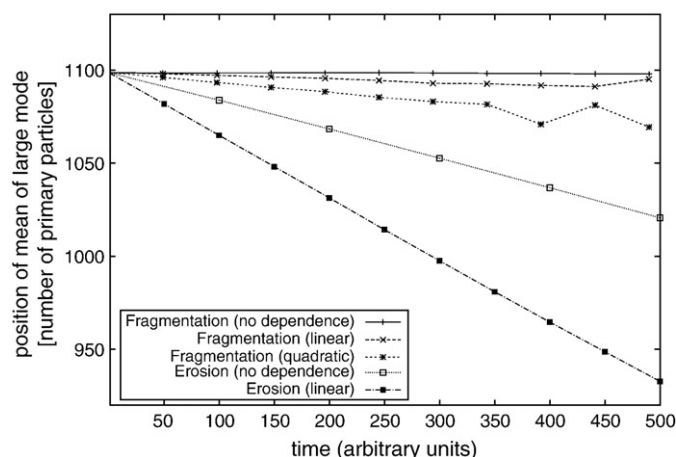


Fig. 5. The position of the peak of the large modes for fragmentation and erosion of secondary particles and various assumptions about the dependence of the de-agglomeration probability per time step on the particle size. “No dependence” denotes the case where the de-agglomeration rate is independent of the particle size. The linear and quadratic dependences are labeled accordingly. See Section 5 for numerical details of the parameters.

These simulation results are consistent with the observations from the differential equation model. However, while the differential equation model predicted a deceleration of the displacement of the peak as time progresses, it also suggested a rapid decrease of the large mode. Other than in the differential equation model, in the simulation secondary particles are represented as integer units (and not as concentrations). Hence, there is a minimum peak size (2 particles). Given rapid decay finite elements can reduce to zero fast at which point the large mode ceases to exist. In a continuous model (such as the differential model above) a zero-height of the peak of the large mode is only reached asymptotically. In this case, the deceleration of the displacement of the large peak was only noticeable in the regions where the peak size was very low as well; yet such small peak sizes do not occur in the simulation model because of the discrete nature of secondary particles. Hence, in stochastic models one observes a constant displacement speed for the peak of the large mode even in the quadratic case.

In the case of erosion the large mode moves even if there is no bias. The process of erosion creates smaller agglomerates from larger ones thus leading to an overall shift of the peak of the large mode to the left. In this case, as in the case of fragmentation, the speed of the peak displacement increases as the size bias of the fragmentation process increases.

The dynamics of peak displacement of the small mode is quite different from that of the large mode, namely opposite: For example, Fig. 6 shows that in the case of unbiased fragmentation the peak of the small mode moves to the left. This effect is reduced by introducing a bias, which can be immediately explained by considering that a bias will make it less likely that small secondary particles are further fragmented resulting in an overall lower speed of displacement of the small mode. A similar dynamics is observed in the case of erosion.

4. Discussion and conclusion

While differential equation models (such as the one proposed by Kusters) potentially describe the dynamics of both the large and the small mode, complete mathematical models are normally difficult to formulate, solve and even harder to extend. We proposed a simplified model that is amenable to analytic solutions, but only provides a partial description of the system. We also presented a computational model that is more general in its scope, and more direct in its representation, but also much more demanding in terms of computational costs. Results obtained with this model show a qualitative

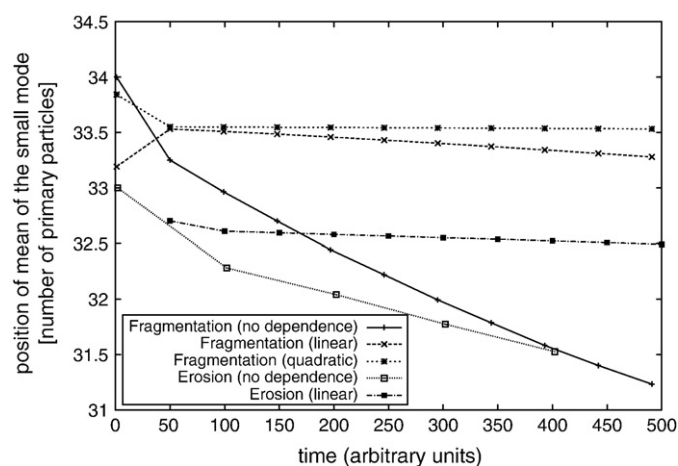


Fig. 6. As Fig. 5 but for the small mode.

agreement with the differential equation model but also highlight a crucial difference between discrete and continuous systems. The former consist of a number of discrete particles whereas the latter assumes “concentrations” of particles. In practice this will make a difference in the case of very small peaks, i.e. when the distribution is relatively flat. In continuous models very small peaks can still be represented, but in reality they would be irrelevant. Peaks consisting of a few hundreds of secondary particles are undetectable and perhaps in a statistical sense non-existing in the context of the noise inherent to the stochastic breakdown process. Given that computing power is cheap, on balance, the computational cost of explicit computer models is outweighed by their intuitive appeal and their relative ease of extension compared to differential equation models.

Considering the simulation results as a whole it is possible to derive some qualitative features of the de-agglomeration process that can help classify its underlying physical processes. Firstly, a large mode that only decays but does not change the position of its peak over time is a clear indication of a fragmentation process and is not compatible with erosion. However, displacement of the large mode is not in itself incompatible with fragmentation processes but could indicate that the fragmentation rate depends on the size of the secondary particles. Significant displacement of the large mode would, in this case, correspond to a static small mode. Hence the combination of a static and non-static small/large mode respectively points to a size dependent fragmentation process.

On the other hand, if the small mode is static, then this indicates a dependence of the underlying de-agglomeration process; coupled with a static (or very slowly moving) large mode this could indicate a weakly (linearly) biased fragmentation process. If the large mode moves, however, then this would indicate either a strongly biased fragmentation or a biased erosion process. The two processes cannot be distinguished qualitatively, but require numerical modeling.

This suggests a simple scheme to gain insight into the underlying mechanisms of particle de-agglomeration from qualitative features of

Table 1

This table summarizes the qualitative features of the transient volume distributions caused by various de-agglomeration dynamics.

	Large mode static	Large mode moves
Small mode static	(Weakly) biased fragmentation	Biased erosion; strongly biased fragmentation
Small mode moves	Unbiased fragmentation	Unbiased erosion

From these qualitative features it is possible to reach conclusions about the underlying dynamics of the de-agglomeration process. The row labeled “static large row” contains the features of experiments where the peak of the large mode in transient volume distributions does not change position over time. The other rows and column have respective interpretations.

the time evolution of the small and large modes. Table 1 summarizes what can be learned from a mere qualitative assessment of the transient volume distributions in de-agglomeration processes about the dynamics of the underlying erosion/fragmentation processes. For example, from the table it is clear that if the peak of the large mode does not change position, but the peak of the small mode does, then this suggests that the underlying process was a fragmentation process without size-bias.

It is conceivable that in practice de-agglomeration processes are mixtures of both fragmentation and erosion processes. This is an additional complication that can only be clearly recognized if the two processes happen on different time-scales. For example, data from particle de-agglomeration with a shear mixer reported by Pacek et al. [1] indicates two fragmentation phases. In a first phase, large secondary particles are fragmented into smaller ones, which are then fragmented into even smaller ones in a second step. In this particular case, the two steps are clearly visible from the data. In general, if fragmentation and erosion occur concurrently, then the two methods might not be easily separated by qualitative methods only. Detailed numerical models are then necessary.

Our main interest in this contribution is to understand qualitative features of particle de-agglomeration as indicators of the underlying processes. We have therefore not made any attempts to fit our models to real data. However, at least for the differential equation model this can be relatively easily done. Fitting of the computational model is much more involved and requires good knowledge of the underlying parameters. The model presented here represents a minimal base-model that focuses on the core-features of the system. It is, however, fully possible to modify this model to include more physically relevant parameters, such as hydrophobicity and the pH value to make specific predictions about particular systems; in the context of the current model such changes would mainly enter the model via the parameter that determines the fragmentation/erosion rate of secondary particles. One could also include other types of interactions, particularly chemical reactions, in the simulation. Extending the algorithms to represent this is beyond the scope of this contribution, but otherwise straightforward. The possibility of extension also points to an advantage of computational modeling over differential equation models.

5. Methods

The simulation program was written in C++ and compiled using the open source Gnu C++ compiler (v. 4.0.1) under Mac OS 10.5. As a random number generator we used the implementation of the Mersenne Twister by Lendl from the University of Salzburg, Austria. This implementation is freely available at <http://random.mat.sbg.ac.at/ftp/pub/software/gen/>. For exponentially distributed random numbers we used the Gnu Scientific Library (<http://www.gnu.org/software/gsl>).

The initial distribution was generated by creating n secondary particles of size x . Here n was calculated as a function of x according to:

$$n(x) = N \frac{1}{x\sigma\sqrt{2\pi}} \exp\left(-\frac{(\log(x)-\mu)^2}{2\sigma^2}\right) \quad (11)$$

For all simulations reported here we used $N = 100,000,000$ as the approximate number of secondary particles, $\mu = 7$ and $\sigma = 0.05$ determine the shape and median of the initial distribution. In the fragmentation/erosion steps described in Section 3 we chose the fragment sizes by drawing random numbers from an exponential distribution with scale parameter 3.5 and exponent 0.3. The source code can be obtained from the authors upon request.

The points in Figs. 5 and 6 were generated as follows: For each point in the figure the relevant transient distribution was fitted to a log-normal distribution using the Matlab curve-fitting tool. We only considered the relevant data, that is for the large mode we disregarded the parts of the data that belonged to the small mode and vice-versa. The parameters in the simulation model were chosen such that the large and the small mode were clearly separated; hence choosing the separation was unproblematic: for the large mode we considered secondary particles of sizes between 500 and 1200; the small mode we defined as being between 0 and 150. The values in the figures were then taken from the curve fitting results.

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