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Review

Agglomeration and Aggregation of Nanoparticles

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Abstract: Agglomeration of nanoparticles is an often-observed phenomenon. In severe cases, it may lead to a reduction in the usability of a product. Therefore, it is necessary to study the processes that lead to this undesirable phenomenon. Analyzing this phenomenon, one learns that it is necessary to distinguish between 'hard' agglomerates called aggregates and 'soft' agglomerates. Furthermore, one has to distinguish arrangements, where, potentially, each particle may collide with each other or arrangements, where collisions are possible only with the next neighbors. The first of these cases is observed in the case of synthesis, whereas the second one is typical for particles stored in a box. For the analysis of thermodynamic stability, the entropy of the mixture is the appropriate parameter described by the Gibbs equation. In the lack of sufficient data for possible materials, it was not possible to calculate the free enthalpy to give a thermodynamically valid description of the stability of the agglomerates. Furthermore, this paper indicates theoretical problems waiting for great ideas.

***Keywords*:** agglomeration, aggregation, Monte Carlo method, Markov chain, entropy

1. Introduction

Looking at agglomeration and aggregation processes, one has to distinguish two generally different phenomena.

- Possibility 1: Each particle can—earlier or later—come into contact with each other of them. This process is, e.g., typical for gas-phase processes.
- Possibility 2: The particles may touch only the neighboring particles. This is, e.g., the case where a powder is stored in a box.

Furthermore, the type of interaction between the particles may be used for differentiation. The most important ones are:

- Formation of 'soft' agglomerates, that are bonded together, e.g., by van-der-Waals interaction.
- The particles exchange surface energy. This leads to 'hard' agglomerates, called aggregates.
- The particles are interacting by additional forces acting over larger distances. A typical example is magnetic particles. In this case, additional interaction based on van-der-Waals or surface energy is possible.

Agglomeration is an important topic for scientists who apply granular material. The approach for the interpretation of the results may be from the perspective of thermodynamics or statistical considerations. One of the first models of coalescence published by Sunada et al. [1], used a two-dimensional model with 100 particles. Further papers applied structure models [2, 3], or sought a maximum of the entropy [4-7]. Other papers discuss different criteria based on theoretical considerations or experimental results that rule out agglomeration [8, 9]. A different approach

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is the application of Monte Carlo simulations based on Markov chains [10] or these calculations combined with thermodynamic considerations [11]. Results based on Monte Carlo calculations, with to estimateicle distributions obtained by different gas phase processes, were published by Vollath [12]. Later, a similar simulation process was published describing the development of raindrops or planets [13-16]. A broad review of modeling without considering Monte Carlo methods of gas phase processes was given by Eggersdorfer and Pratsinis [17].

Within this paper, the results of agglomeration processes concerning particle size distribution and entropy of the system will be discussed. For the first time, agglomerations caused by neighboring arrangements are analyzed. In this context, it is important to draw attention also to applications especially in the field of metallic nanoparticles [18-20], as this is important for additions of rocket fuels.

Sometimes, the terms agglomeration and aggregation are used as identical. This is incorrect. Agglomeration describes a process that leads to particles, which are loosely connected, whereas aggregated particles are new and stable objects. As the stability of the products is—in general—not the topic of this paper, for reasons of simplicity, within this paper describing general phenomena, the word agglomeration is applied for both processes.

2. Theoretical background

Agglomeration is a random process. Therefore, statistical methods are applied. As a first step, the case, where each particle has, in general, the possibility to touch each other particle is discussed. At the beginning of the process of interaction, we consider an ensemble consisting of N_{tot} primary particles, each one of the same size. As these particles do not have quantum features, it is possible to mark each one of these particles with a number. Furthermore, we consider a system, where these particles can interact. Therefore, at the time $t = 0$, the beginning of the process, all of the particles have size 1, this number also stands for the volume of the particles the total volume of the particles.

At $t = 0$, the total volume of the particles is described by $N(0,i) = N_{tot}$; at this time, also the number of collisions j is set to 0. At the time t, one has a distribution of particle sizes, each one of these sizes consists of $N(t,i)$ particles of the size i. In the context of this paper, the number of collisions (agglomeration steps) in between the particles is taken equivalent to the time. Quantity i describes the number of elementary particles in this group, which is equal to the volume of the particles. At each time t, the relation is valid.

$$N_{tot} = \sum_i iN(t,i), \quad N_{tot}, N, i, t \in \mathbb{N} \tag{1}$$

Taking Equation (1) as the basis, derived from the Markov chain formalism, the agglomeration of two particles of the sizes i and j may be described as [12].

$$\begin{aligned} N(t,i+j) &= N(t-1,i+j) - f_{i,j}\frac{N(t-1,i)}{N_{tot}}\frac{N(t-1,j)}{N_{tot}} \\ N(t,i) &= N(t-1,i) - f_{i,j}\frac{N(t-1,i)}{N_{tot}}\frac{N(t-1,j)}{N_{tot}}, \qquad f_{i,j} \in \mathbb{R}, \quad N,i,j \in \mathbb{N} \\ N(t,j) &= N(t-1,j) - f_{i,j}\frac{N(t-1,i)}{N_{tot}}\frac{N(t-1,j)}{N_{tot}} \end{aligned} \tag{2}$$

The parameter $f_{i,j}$ describes the interaction of particles with the sizes i and j; its quantity depends on the process assumed for agglomeration.

In general, to describe the basic properties of such an agglomeration process, the parameter $f_{i,j}$ is set constant. This setting helps to obtain a first insight into these phenomena. Therefore, this setting is also used to introduce these topics. Reality is more complex. Looking e.g., at gas phase processes, the probability of collision increases with increasing particle diameter. In the case where only direct neighbors are agglomerating, the same basic Markov equations are applicable, the difference is given by the selection of the reactants. In the framework of this paper, the interaction parameter is normalized $f_{i,j} = 1$. However, to describe processes of synthesis in very detail, it would be necessary to

take the increase of the particle diameter caused by agglomeration into account. For the description of plasma synthesis processes, it is also necessary to analyze the influence of electrical particle charges [12, 21].

Looking at the second possibility of agglomeration, agglomeration of powders, e.g., stored in a bag, the probability discussions as presented for the first case does not make sense. Instead, one has to look at the spatial distribution of the particles. In this case, we have to analyze three different cases.

- Aggregates, hard agglomerates; this means that the particles touching each other are stable; this means that they can grow by adding further particles; however, a reduction of the size is impossible.
- Soft agglomerates. In this case, agglomerates can lose particles if they are touched by another particle or agglomerate.
- Interacting particles, e.g., magnetic particles, not only particles touching each other but also particles in a certain distance can interact. Typical examples are magnetic particles or aggregates.

These calculations may be summarized as neighborhood analysis.

In this context, one has to ask if there are inherent limits to agglomeration. Certainly, there are two criteria the limiting agglomeration. If agglomeration is connected to an exchange of energy, there is a limit that is necessarily given by a minimum of the free enthalpy. However, the necessary data to estimate the reduction of the energy due to agglomeration are, in general, very limited. Therefore, in this paper, only the entropy of the system is used to analyze the possibility of an agglomeration. For this analysis, Gibbs's definition of the entropy of an ensemble of objects is applied.

$$S^*(t) = -\sum_i p(t,i) \ln p(t,i), \qquad p(t,i),\ S^*(t) \in \mathbb{R} \tag{3}$$

As in the context of this paper, the entropy data are used only for comparison; for the entropy, the reduced version $S^* = S/k$, where k stands for the Boltzmann constant, is applied. The probability $p(t,i)$ is derived from the particle size distribution.

$$p(t,i) = \frac{N(t,i)}{\Sigma_j N(t,j)} \tag{4a}$$

$$p(t,i) = \frac{N(t,i)}{N_{\text{tot}}} \tag{4b}$$

Equations (4a) and (4b) describe two entirely different situations. In the case of Equation (4a), it is assumed that the new particles formed in the process are stable 'hard' aggregates, whereas the idea leading to Equation (4b) starts from the condition that the agglomerated particles can re-arrange, 'soft' agglomerates.

Finally, one has to find the possibilities to solve the system of Markov chains, as shown in Equation (2). Experience has taught that the most effective route to obtaining representative solutions uses the Monte Carlo approach [12], as this route allows one to select a given number of collisions without inherent preferences. In the case of neighborhood analysis, Monte Carlo algorithms are applied, too.

3. Simulation results using Monte Carlo calculations

3.1 *Non-localized particless*

For the beginning of these calculations, particles of equal size were assumed. The basic assumption for these calculations was that, inherently, each particle can collide with each other particles. Therefore, for these calculations, the particles are not localized; they are just identified by a number. This basic assumption leads to an arrangement characterized by a maximum of entropy, provided that the probability or energy of interaction is neglected [10, 11]. As explained in the section 'Theoretical background', this arrangement allows us to consider the interaction between the

particles. This interaction may additionally depend on the sizes or electrical charges of the particles.

For a general discussion, agglomeration phenomena neglecting the influence of particle size and electrical charges were analyzed. To obtain statistically relevant results, the number of particles used for these calculations was selected in the range between 10^7 and 10^9. The number of iteration steps was selected up to the range of 10^9. The number of collisions, which is certainly smaller, is, at this stage of the analysis, not known. These large numbers ensured that the results are statistically significant. Figure 1 shows the particle size distribution obtained after 10^9 iterations of 108 primary particles. In this figure, the abscissa is on a logarithmic scale. There is a strict exponential relationship between the particle size and the number of particles. It can be shown that this relationship is related to a maximum of entropy [10, 11].

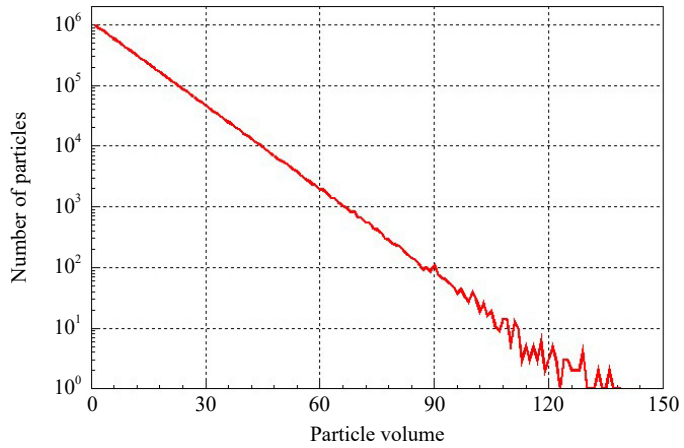

Figure 1. Number of particles as a function of particle size after 10^7 iterations as a function of the particle volume. The starting arrangement consisted of 10^8 particles. As long as the number of particles is sufficiently large, there is a perfect exponential relation.

This exponential relation is valid regardless of the number of iterations. Figure 2 displays this fact in the range of 10^7 to 9.5×10^7 iterations. Again, like in Figure 1, one realizes, independent of the number of iterations, a perfect exponential relationship. Due to the large number of particles, the statistical significance of these results is perfect. However, at particle numbers less than 100, due to statistical scattering, one realizes scattering of the particle in the vicinity of the ideal straight line.

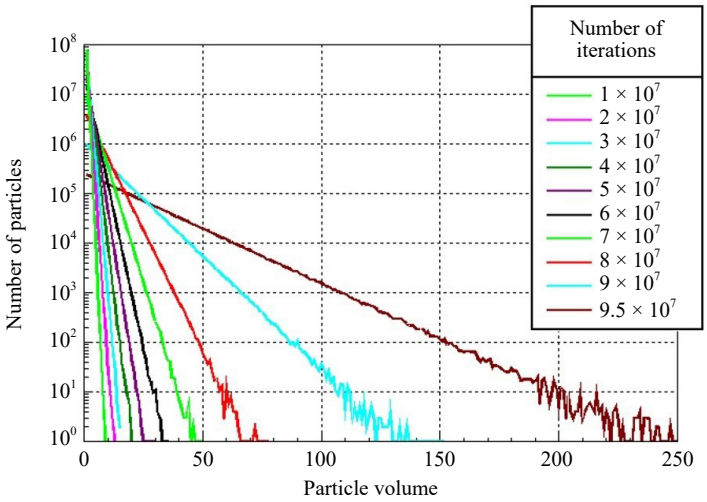

Figure 2. Distribution of particle sizes as a function of the number of iterations displayed in a semi-logarithmic system. For particle numbers less than 100, one realizes some scattering caused by statistical uncertainty.

The exponential course of the number of particles as a function of the particle volume can be described by the following equation.

$$N_i = N_0 \exp(-ib), \quad b \in \mathbb{R} \tag{5}$$

In Equation (5), N_i stands for the number of particles with volume i; N_0 represents the number of particles with volume 1 after n_{iter} iterations; b is a parameter to be determined by fitting to data obtained by the simulation process. To obtain additional information about this parameter, the inclination of the straight lines in Figure 2 was determined and plotted. The result of this action is displayed in Figure 3. This plot displays the inclination as a function of the number of iterations (it is important to realize that these results were obtained in a semi-logarithmic system).

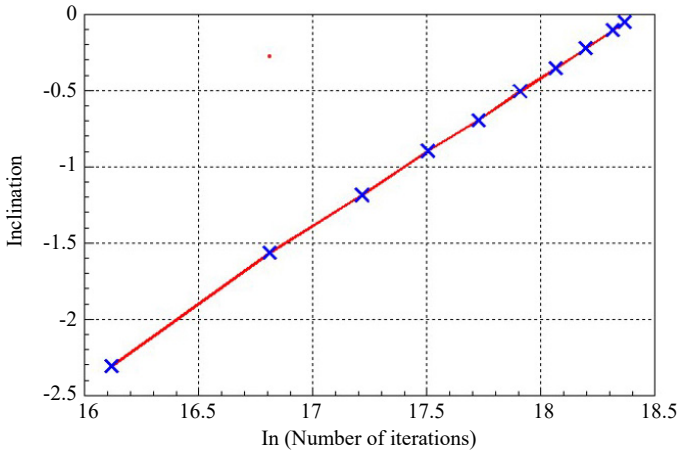

Figure 3. Inclination $\partial N/\partial \ln(n_{\text{iter}})$ of the straight lines displayed in Figure 2. Again, the combination of these results leads to a straight line in a semi-logarithmic plot.

The plot of the inclination of the straight lines in Figure 2 denoted as the quantity b in Equation (5) led to the diagram displayed in Figure 3. Again, in this semi-logarithmic plot, one realizes a straight line leading to the relation

$$b = -\ln(N_{\text{tot}}) + \ln(n_{\text{iter}}) = \ln\left(\frac{n_{\text{coll}}}{N_{\text{tot}}}\right) \tag{6a}$$

finally resulting in

$$N_i = N_0 \exp\left(-i \ln\left(\frac{n_{\text{iter}}}{N_{\text{tot}}}\right)\right) \tag{6b}$$

The quantity N_0 is certainly dependent on the number of iterations. This is visualized using a three-dimensional plot (Figure 4) of the data shown in Figure 2.

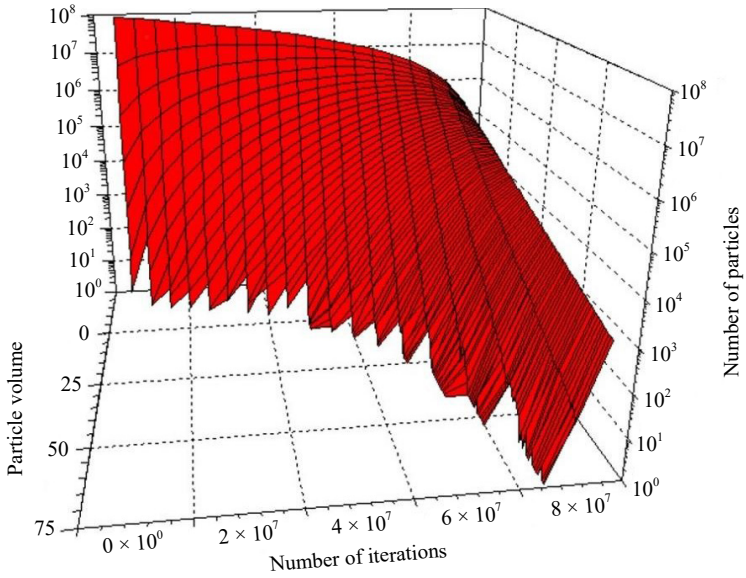

Figure 4. A three-dimensional re-plot of the data obtained by simulations is displayed in Figure 2. In this case, it is important to realize the course of the quantity N_0 from the number of iterations, represented by the upper rim of the curved surface in this figure.

The quantity N_0 as a function of the number of iterations obtained from the simulations is plotted in Figure 5. These calculations were performed with 10^8 particles in the starting arrangement in the range of up to 109 iterations. Figure 5 displays the diagram showing the function $N_0(n_{iter})$. In contrast to the expected relation $N_0 = N_{tot} - n_{iter}$, an entirely different function was found. The results of this analysis are shown in Figure 4.

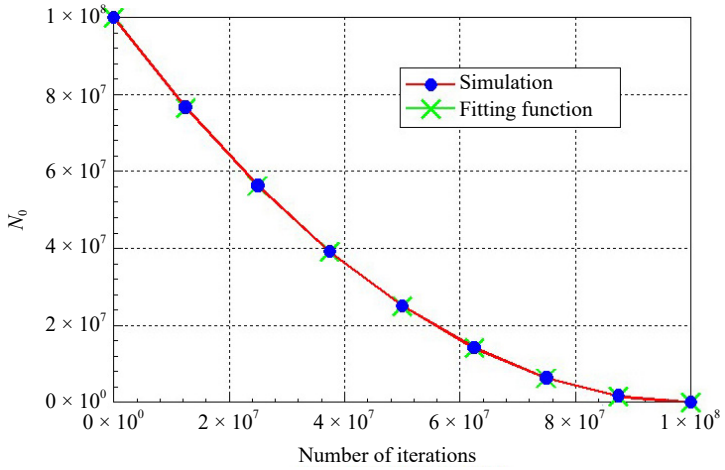

Figure 5. The course of the quantity N_0 is a function of the number of iterations. Again, these are the results of simulations that started with 10^8 particles and performed up to 10^8 iterations

The function $N_0(n_{iter})$ can be described as:

$$N_0 = \frac{(N_{tot} - n_{iter})^2}{N_{tot}} \tag{7}$$

By the combination of Equations (6b) and (7), one has all the necessary equations to describe the process of agglomeration. An open question is the theoretical interpretation of these equations obtained from simulation

experiments.

The question now arises whether these results are thermodynamically possible. The answer is given by the course of the entropy. In this context, it is important to realize that there are two possible ways to calculate these values. As shown in Equations (6a) and (6b), the entropy may be based on the actual number of particles—aggregates—or the initial number of particles—agglomerates—before agglomeration starts. The results of these calculations are displayed in Figure 6.

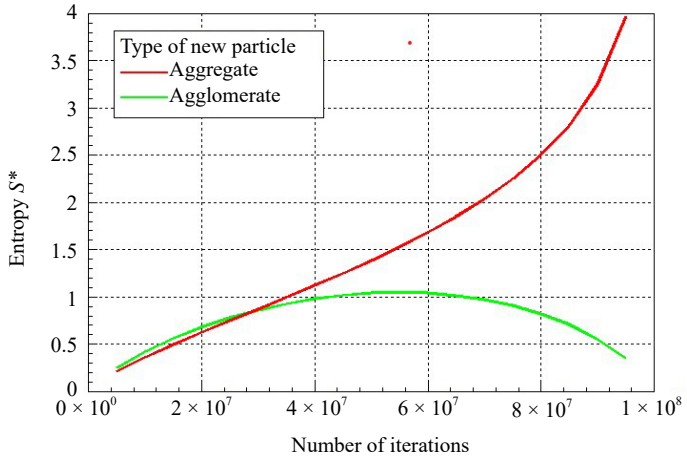

Figure 6. The course of the entropy is a function of the number of iterations. This figure shows the course of the entropy for 'hard' aggregates and 'soft' agglomerates. It is obvious that, for agglomerates, the entropy shows a maximum in the range of approximately 5×10^7 iterations.

Figure 6 shows the relation between the number of collisions and the entropy for agglomerates and aggregates. The two courses are entirely different. The function describing the entropy of aggregates shows—more or less—the expected course, increasing with increasing number of iterations. This is different for the entropy of agglomerates. This function shows a maximum in the range of 5×10^7 iterations. From the standpoint of the second law of thermodynamics, this is impossible. Therefore, in the case of agglomerates, one has to conclude that either the growth of these particles is limited or—more probable—one obtains *a priori* only a mixture of aggregates and agglomerates. Assuming that agglomerates are limited in size, one has to expect fluctuations of entropy in the vicinity of the maximum. Such fluctuations of the entropy are often described [2, 3].

One must be aware of the fact that the two cases displayed in Figure 5 are extreme ones. In reality, one will observe less distinct courses.

3.2 *Neighborhood analysis—localized particles*

For this analysis, the primary particles are randomly arranged in a three-dimensional space. Within this space, a plane is inserted. In this plane, the neighborhood of each particle is analyzed. Using random access, within this plane, a particle is selected and the neighborhood is analyzed at a distance of one or more points. In the case of a close neighbor, agglomeration is assumed. The calculations are performed using a plane consisting of 2^{20} points up to 10^{14} iterations. The starting arrangement consisted of randomly distributed particles within a field with a size of $(2^{20})/2$ objects. This means that an occupation of 50% was assumed. The particle size was determined within a field with an edge length of 9 points.

For these calculations, three basic assumptions were applied.

- Iterations in the 'soft' mode, leading to agglomerates. In this case, it was assumed that, in case of a collision, a cleavage of one of the colliding particles is possible.
- Iterations in the 'hard' mode, formation of aggregates, this means that the colliding particles are stable and just add their mass.
- Iterations with additional magnetic interaction. Lastly, these are iterations in the 'hard' mode; however, the

interaction distance was assumed to be larger following a 1/distance^2 rule.

The first example shows the agglomeration in the 'soft' mode. Figure 7 displays the particle size distribution. In this figure, the size distribution is plotted twice: once with linear (Plate a) and once with logarithmic (Plate b) ordinates. In both cases, the particle size distribution of the starting arrangement and after 6.6×10^{11} iterations. In contrast to the former case, where each particle may collide with each other, a special distribution function cannot be deduced.

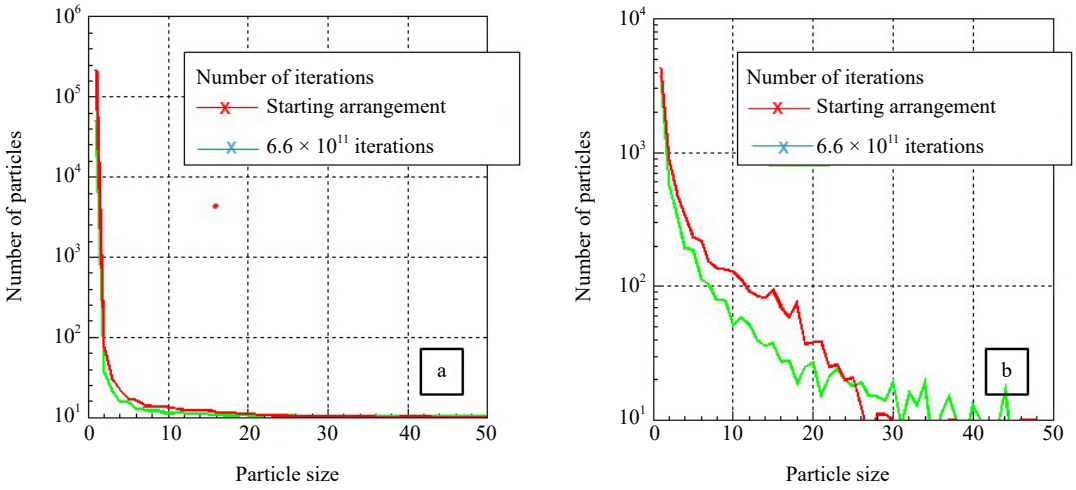

Figure 7. Particle size distribution is displayed with the linear (Plate a) and logarithmic (Plate b) ordinates of an arrangement in the 'soft' mode. These are the size distributions at the beginning (starting arrangement) and after 6.6×10^{11} iterations.

Even when the particle size distributions do not convey a special function, this becomes different after calculating the entropy S^*, according to Equation (3) as a function of the number of iterations. These results are displayed in Figure 8. In this graph, the abscissa is displayed in the logarithmic scale. To demonstrate the small scattering range of the data, in this figure, the results of two different, independent runs are shown. The scattering of the data is so small that, within this graph, differences are not visible. Additionally, a straight line is plotted to demonstrate the exact exponential progress.

Figure 8 displays the entropy as a function of the number of iterations in the 'soft' mode. This figure shows an exponential relationship between the entropy and the number of iterations, leading to a linear relationship between the entropy and the logarithm of the number of iterations.

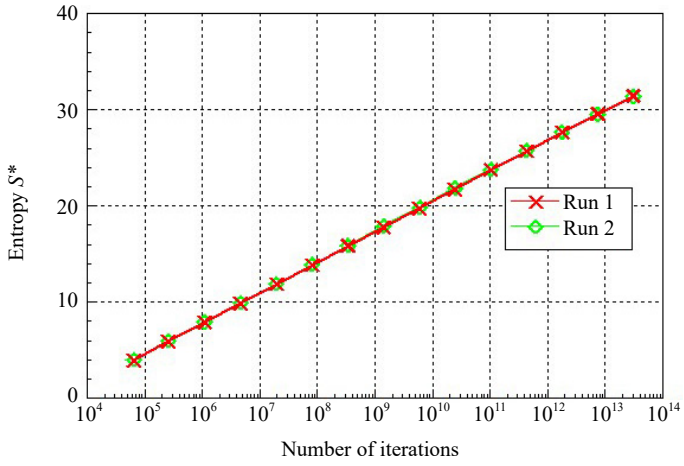

Figure 8. Entropy S^* as a function of the number of iterations for particles that interact in the 'soft' mode. To demonstrate the small scattering ranges of the data. In this graph, the results of two different runs are depicted. The abscissa is displayed on a logarithmic scale.

The data displayed in Figure 8 leads to the relationship.

$$S^* = a + b\ln(n_{\text{iter}}), \quad a, b \in \mathbb{R} \tag{8}$$

Figure 8 displays the entropy of an ensemble agglomerated in the 'soft' mode as a function of the number of iterations. Furthermore, it is important to realize that the results of two different runs are nearly identical. This proves that the number of particles was sufficiently large to be independent of severe statistical scattering. Fitting the data displayed in Figure 8 leads to the constants $a = -11.279$ and $b = 1.378$ for the starting values of the simulation calculations. The thermodynamic interpretation of the quantities of these constants, a and b is, at the moment, open.

Further interesting data are obtained from a plot that displays the total number of particles as a function of the number of iterations.

$$N_p(t) = \sum_j N(t,i), \qquad N_p \in \mathbb{N} \tag{9}$$

This is displayed in Figure 9. In this graph, the results of two independent runs are displayed. Again, it is obvious, that due to the large number of particles, the statistical scattering is nearly negligible.

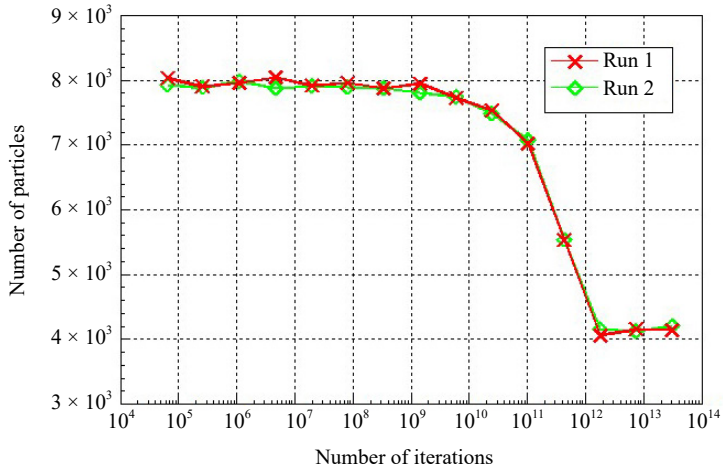

Figure 9. Number of particles $N_p(t)$ according to Equation (9) as a function of the number of iterations. This graph displays the results of two independent runs in the 'soft' mode, demonstrating the statistical significance of these results.

As discussed in the section 'Introduction', besides the interaction leading to 'soft' agglomerates, 'hard' agglomerates, aggregates and aggregates resulting from magnetic interaction need discussion. In the case of magnetic interaction, not only direct neighbors are introduced in the calculations, but also more distant ones. Similarly, for more distant particles, an interaction following the $1/r^2$ law is used. Figure 10 displays the number of particles $N_p(t)$ for the three different cases mentioned above. Each one of the curves shown in this figure is the result of an average of two different runs.

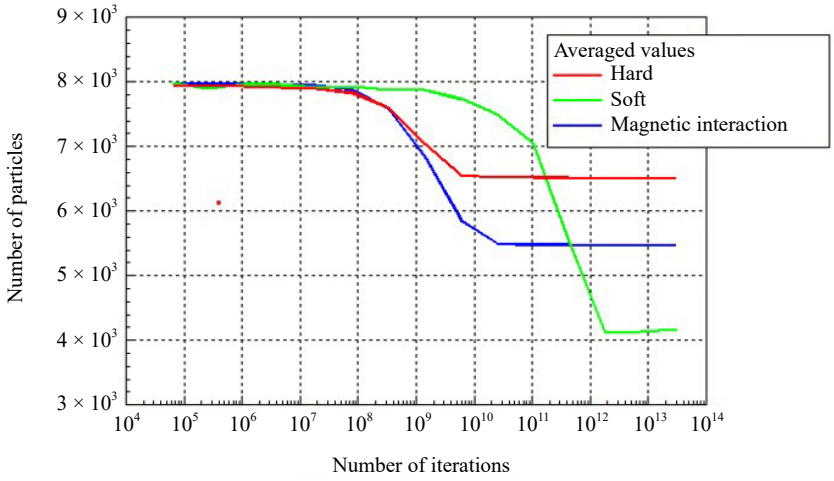

Figure 10. Number of particles $N_p(t)$ for the three different cases: 'soft' agglomerates, 'hard' aggregates, and aggregates resulting from magnetic interaction.

Figure 10 shows the number of particles as defined by Equation (9). In general, one realizes in all three cases a similar course depending on the number of iterations. It is well understandable that in the case of soft interaction, the reduction of the total number of particles occurs at a higher number of iterations as compared to the other cases. In all three cases, one realizes that for a large number of iterations, the total number of particles approaches an asymptotic value.

As displayed in Figure 11, these differences are also visible in the course of the entropy. Up to the number of 10^9 iterations, the range where, in Figure 10, the progress is nearly identical, and the entropy shows no differences.

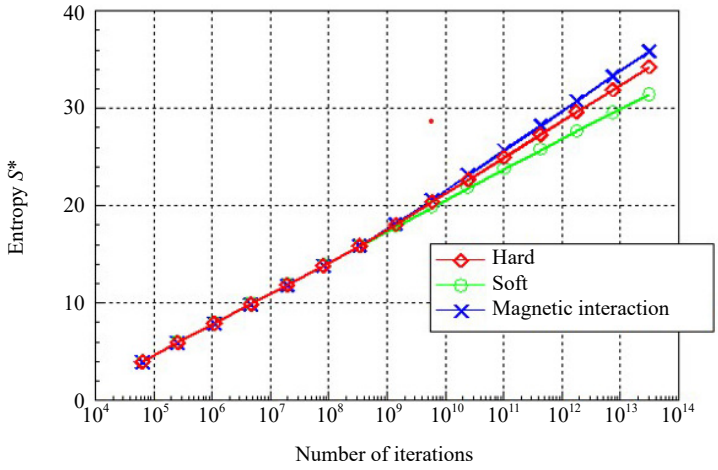

Figure 11. Entropy S^* as a function of the number of iterations for the three types of interaction. It is important to realize that beginning with 10^9 iterations the entropy for 'hard' and magnetic aggregates increases faster than in the case of soft interaction.

This figure shows an exact exponential law for agglomerates from the 'soft' mode. At collision numbers greater than 10^8, wherein Figure 10, the functions for the three different cases start separating, and the entropy values are also separating. It is important to realize that, after the separating point, the course of the entropy is exactly exponential again. This is depicted in Figure 12.

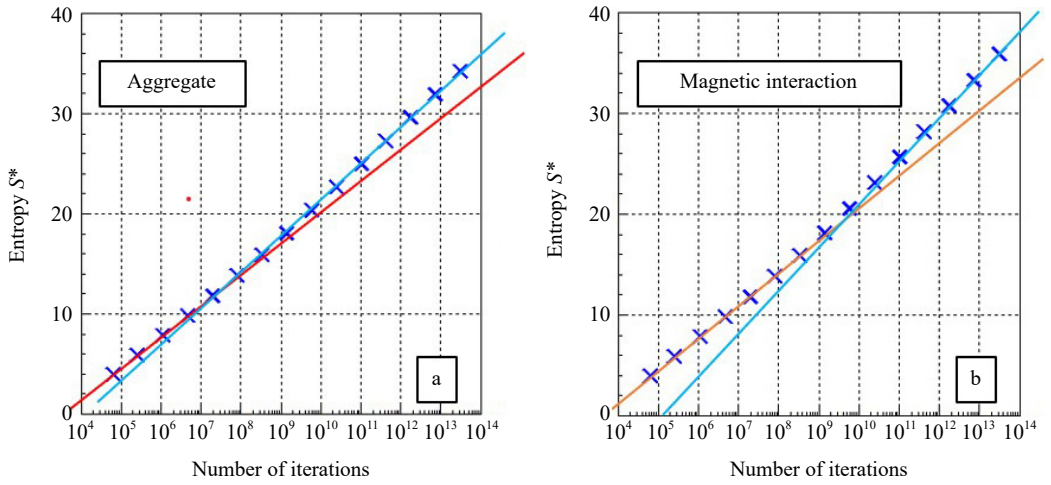

Figure 12. Dependency of the entropy S^* of the number of iterations calculated for the cases 'hard' 'aggregate' (Plate a) and 'magnetic' (Plate b) aggregates. It is important to realize that beyond 108 iterations, the increase of the entropy is larger than in the case of 'soft' agglomerates. In both cases, the green and red straight lines demonstrate the exact exponential relationship in both ranges.

It is important to realize the increase of the entropy at collision numbers beyond 10^9 iterations. Interestingly, also in this range, the course of the entropy follows exactly an exponential law. Table 1 displays the equations for the entropy values found for the case agglomerations as depicted in Figure 12.

Table 1. Entropy a and b, according to Equation (8), found in different cases of neighborhood analysis

	Number of iterations	
	$< 10^9$	**$> 10^9$**
Agglomerates	$S^* = -11.28 + 1.38 \ln (n_{coll})$	
Aggregates	$S^* = -11.28 + 1.38 \ln (n_{coll})$	$S^* = -11.02 + 1.37 \ln (n_{coll})$
Magnetic particles	$S^* = -11.28 + 1.38 \ln (n_{coll})$	$S^* = -19.39 + 1.78 \ln (n_{coll})$

Even when the description of the entropy values given in Table 1 perfectly describes the findings of the simulation analysis, a fundamental theoretical explanation is missing. Certainly, one may think that the strange course of the numbers of particles and the entropy in the cases of 'hard' and magnetic aggregates is a result of inadequate software. However, there is an important argument against this opinion, the course of the entropy in the 'soft' mode as a function of the number of iterations is described by a perfect exponential function. This is certainly not by chance.

4. Conclusion

Monte Carlo simulations based on Markov chains were used to explore agglomeration phenomena. In all cases, the entropy was taken as an indicator of the stability of the newly formed agglomerates. Let us consider the first case, where each primary particle has the possibility of colliding with any other particle. This case describes the formation of particles, e.g., in the case of gas phase synthesis. The analysis of this case led to some interesting phenomena. First of all, one has to take care of different types of agglomerated particles. One has to distinguish 'hard', which means stable aggregates and 'soft' agglomerates. The latter ones are lastly unstable particles, which can break into smaller objects in case of additional iterations. Even when both show a logarithmic dependency of the particle size, their entropy course as a function of the number of iterations is entirely different.

- Hard aggregates show the expected increase of the entropy with the increasing number of iterations.

- In the case of soft agglomerates, entropy shows with the increasing number of iterations a maximum followed by a reduction. This behavior contradicts the second law of thermodynamics.

From the course of the entropy, one has to conclude that completely soft agglomerates are impossible. In reality, one has a mixture of hard and soft properties. It was already shown that the exponential distribution of particle sizes is a consequence of the necessity of maximum entropy. Even when it was possible to derive a clear mathematical description of most of the properties depending on the number of iterations, a theoretical interpretation and justification of these laws are missing.

Even more interesting is the neighborhood analysis. This is the analysis of particles collected in a box or a bag. This problem is technologically most important, however, until now, this problem has nearly not been analyzed. This analysis attempts to describe the agglomeration of particles that touch each other. Also, in this case, we have to differentiate between hard and soft agglomerates. Additionally, one has to take care of further forces, such as magnetic ones, acting via a longer distance. Lastly also in this case one has to assume the formation of hard agglomerates. However, a detailed analysis taught that also in this case, the entropy shows a logarithmic increase with an increasing number of iterations. This relationship is perfect in the case of soft agglomerates; however, in the case of hard or magnetic aggregates, there is a deviation in the case of larger numbers of iterations. Similarly, to the previous case, Monte Carlo simulation leads to clear relationships for the different parameters; however, their theoretical derivation should be a topic of further necessary studies.

Conflict of interest

The author declares no conflict of interest.

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