Ostwald Ripening: An Approach with Dynamical Systems

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This approach assumes three functions independently acting on a set of microparticles. The first one, w_1, concerns re-distribution of mass to decrease the surface energy. The second one, w_2, concerns re-distribution of mass to increase the entropy of the microparticle set. The third one, w_3, is a further re-distribution of mass that vanishes a microparticle. Once vanished, its mass is distributed among its neighbors. w_1 and w_3 release energy, whereas w_2 absorbs energy. Part of the energy released should be available to sustain w_2. The action frequency of w_1, w_2, and w_3, the amount of mass exchanged in each iteration, the fraction of released energy available to sustain w_2, and the size of a vanishing microparticle can be varied. As the dynamical system formed by w_1, w_2, and w_3 act on an initial microparticle set, it is observed an evolution resembling the Ostwald ripening concerning steady-state size distribution and microparticle growth.

1. Introduction

The decrease surface energy is usually assumed as the driving force for the Ostwald ripening, so that when two microparticles interact with each other by exchanging mass, the larger one grows at the expense of the smaller one. To handle the whole set of microparticles, it is generally assumed that the microparticles are in an average environment, and that there is a critical size, r_c, so that a microparticle larger than r_c will always grow, and one smaller than r_c will always shrink[1]. Although it is recognized that this approach is only "statistically true", and that there are local interactions not following this rule, these mean field approaches neglect these events. Moreover, the collective behavior should also be taken into account through the entropy of the microparticle set. So, in addition to the decrease of the surface energy, its distribution among the microparticles should be considered. To maximize the entropy of the set, this distribution should be uniform, and the microparticles should also be uniformly distributed in space. This is the configuration for the microparticle set with the highest probability if one assumes an intrinsic random re-distribution of mass between the microparticles[2]. Consequently, there is also an intrinsic tendency in the interactions between microparticles to achieve all of them with the same form and size. This tendency should compete with the one to decrease the surface energy[2,3,4].

A microparticle releases mass at a rate depending on its solubility, which is given by the Gibbs-Thomson relation, but it also absorbs mass released by other microparticles at a rate depending on its surface area, the concentration of released mass at its position, and the reactions involved in the absorption process. The energy necessary to increase the surface area as consequence of the absorption is available from the energy released when the surface area of another microparticle is decreased due to the release of mass. The mass release and absorption are treated here separately and as independent of each other.

Some computer simulations are based on interactions between two microparticles. In these approaches the larger microparticle grows at the expense of the smaller one, so that a microparticle can grow when it interacts with one of its neighbors (if it is the larger one), or shrink when it interacts with other neighbor (if it is the smaller one)[5]. These approaches are an improvement in relation to the mean field theory. But the entropy of the microparticle set is also not taken into account. By considering the interactions in this way, there is no tendency for the distribution of the surface energy among the microparticles to become uniform, because the larger microparticles will always grow at the expense of the smaller ones.

The model proposed here assumes that there are three functions acting upon a set of microparticles independently of one another. The first one, w_1, concerns re-distribution

Table 1. The three functions acting upon the set of microparticles.

w_1	w_2	w_3
if $v_1 \geq v_2$ then	if $v_1 \leq v_2$ then	if v_j has "vanishing
$v_1 = v_1 + \Delta v$	$v_1 = v_1 + \Delta v$	size" then
$v_2 = v_2 - \Delta v$	$v_2 = v_2 - \Delta v$	for $i = 0$ to n do
else	else	$v_i = v_i + v_j/n$
$v_1 = v_1 - \Delta v$	$v_1 = v_1 - \Delta v$	$v_j = 0$
$v_2 = v_2 + \Delta v$	$v_2 = v_2 + \Delta v$	else
		do nothing
where v_i ($i = 1, 2$) is the microparticle volume and Δv is the amount of volume transferred.	where the v_i's are neighbors and n their number.	

of mass between two microparticles to decrease the surface energy. This is achieved by taking an amount of volume of the smaller microparticle and adding it to the larger one. The second function, w_2, also concerns re-distribution of mass between two microparticles, but to increase the entropy of the microparticle set. This is achieved by taking an amount of volume of the larger microparticle and adding it to the smaller one. The third function, w_3, is a further re-distribution of mass between microparticles, but at this time one microparticle is vanished. This interaction can only happen if the microparticle has a "vanishing size". Once a microparticle is vanished, its mass is distributed among its neighbors. This interaction decreases the number of microparticles and also the surface energy. Table 1 shows these functions. Conservation of volume (or mass) is assured in w_1, w_2, and w_3. w_1 and w_3 are interactions that release energy, whereas w_2 absorbs energy. Part of the energy released by w_1 and w_3 should be available to sustain w_2, whereas the other part is released to the environment. Before each action of w_2 the stock of released energy that is available should be observed. If there is not enough energy, w_2 cannot act. After each action of w_2, this stock is diminished by the amount of energy absorbed. When w_1, w_2, and w_3 act simultaneously on a set of microparticles they form a dynamical system[6]. The characteristics of the evolution of this system resembles the Ostwald ripening. It is not the purpose of this paper to make an in-depth analysis based on the theory of dynamical systems. The properties of the dynamical system formed by w_1, w_2, and w_3 are only intuitively developed.

2. Implementation

The microparticles are assumed as distributed in a regular three dimensional lattice, as shown in Fig. 1. The microparticle sizes, measured through a linear dimension, were assumed as smaller than the distance between the lattice nodes, so that a microparticle never touches its neighbors. No other assumption concerning the volume fraction of the microparticles is made. A void lattice node means that it is occupied by a microparticle with volume equal to zero. It was taken a lattice with 21 x 21 x 21 = 9261
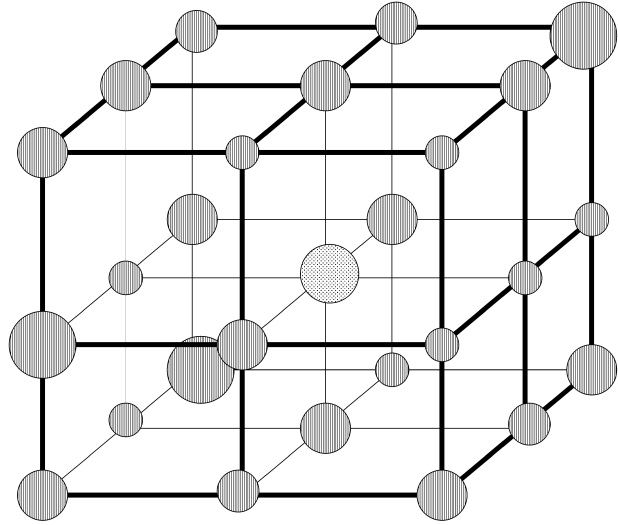
Figure 1. Spatial distribution of the microparticle set assumed in this model.

nodes. An initial set of microparticles with different sizes is distributed among the nodes.

The model works as follows: a) choose at random one of the functions w_1, w_2 or w_3; b) choose at random one node and apply the function chosen in a) to the microparticle located at it. Case the node is empty, do nothing and proceed to the next iteration. In each iteration, the chosen microparticle interacts with all its 26 neighbors. To check the model, some calculations were performed. Δv was taken as

$$\Delta v = 0.01 \left(1 - \frac{v_i}{v_{total}} \right) v_i \qquad (1)$$

where v_{total} is the volume of the microparticles altogether and v_i is the volume of the microparticle that is loosing volume. This equation has no physical meaning and is used only to test the model performance.

3. Results

Figure 2 shows the result of the action of w_1 on an initial microparticle set with the size distribution shown. The diameter is calculated by taking the microparticles as spheres. The mean diameter is calculated from the mean microparticle volume, defined as (volume of all microparticles) / (number of microparticles). If n is the number of microparticles, the final distribution should ideally be one with $n - 1$ microparticles with vanishing size and one microparticle with volume close to v_{tot}. This distribution can be seen as a fixed point of w_1 in the space of size distributions of n microparticles with total volume v_{tot}. Nevertheless, due do the restrictions of the model that allow interactions only with the first neighbors and the spatial correlations developed during the iterations, the final dis-
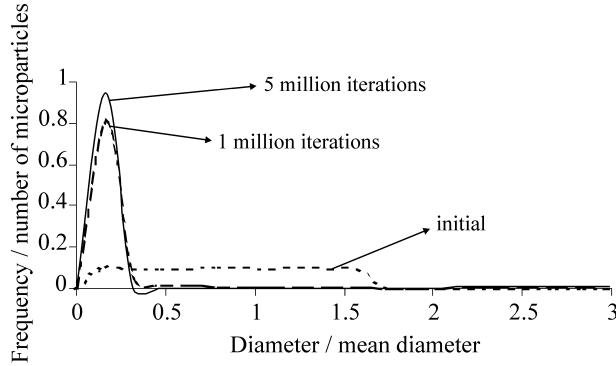
Figure 2. The result of action of w_1.

tribution occurs after 5 millions iterations, with a small population at larger sizes (not shown).

w_2 is not allowed to act alone, because it have to be powered by the energy released by w_1 or w_3. There is one exception to this rule in this implementation for the case where both interacting microparticles have the same volume, but the calculations have shown that this has a negligible effect on the resulted size distributions. If enough energy is given, w_2 also has a fixed point in the space of size distributions above described. It is the distribution with all microparticles with the same size equal to v_{tot}/n.

Figure 3 shows cases where both w_1 and w_2 act. Although it is possible to vary the probabilities of action of w_1 and w_2, it was considered only the case where these probabilities are equal, because the system doesn't "prefer" any of these functions. According to the theory of dynamical systems, w_1 and w_2 form an iterated function system (IFS) that converges to a size distribution for the microparticle set (called attractor), which can be obtained by increasing the number of iterations. This figure suggests that this is the case for the dynamical system formed by w_1 and w_2, and that the final size distribution is very similar to the one resulted from the action of w_1. The effect of w_2 is to slow down the action of w_1 (the IFS needs a greater number of iterations to achieve a size distribution). The increase of the fraction of released surface energy available to power w_2 enhances this effect. There should be a situation where the action of w_1 could be virtually stopped by w_2.

Concerning the action of w_3, the vanishing size, defined as the critical size for the collapse of a microparticle, was arbitrarily established as any size with diameter smaller than 16% of the initial mean diameter. It can only vanish the smaller microparticles until they are exhausted, what was already observed for 0.5 millions iterations. The IFS formed by w_2 and w_3 shows a very similar result. w_2 can only act while w_3 delivers energy released by the vanishing of the smaller microparticles. Once they are exhausted, both w_2 and w_3 are no more allowed to act.

Figure 4 shows the case of action of both w_1 and w_3. The attractor of this IFS was achieved for 12 millions iterations.
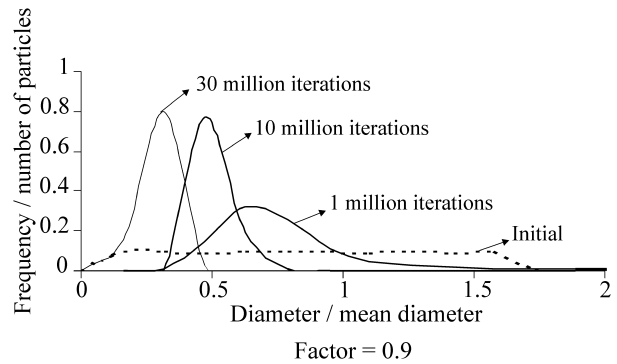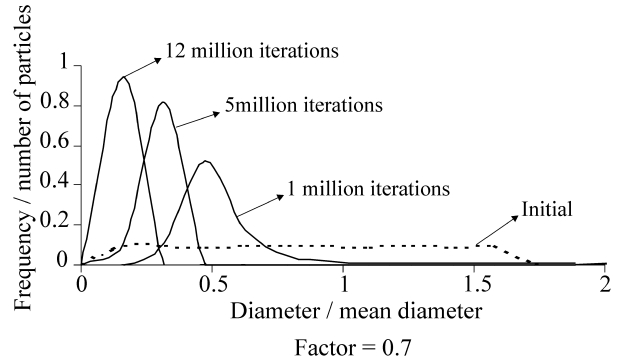

Factor = 0.7

Factor = 0.9

Figure 3. The action of w_1 and w_2 for two fractions (factor) of the released surface energy available to power w_2.

This figure also shows the increase of the mean volume of the microparticles as a function of the number of iterations. Initially, it was observed a linear growth law. At about 4.5 millions iterations this behavior was disturbed probably due to spatial correlations developed because of the implementation of the model. The growth stopped at 12 millions iterations, when the attractor was achieved.

Figure 5 shows cases for the IFS formed by w_1, w_2, and w_3. The fraction of released energy available to power w_2 was considered as in Fig. 3. The attractor was not achieved in these cases because the required number of iterations is prohibitively large. The linear growth law was observed for the mean volume after an "incubation" period. Both the linear growth law and the incubation period are strongly influenced by the fraction of released energy available to power w_2. Compared to Fig. 4, the effect of w_2 is to slow down the action of the IFS formed by w_1 and w_3 and to decrease the scattering of the size distributions. If Δv is doubled, the evolution of the size distribution becomes more rapid, the increase of the mean volume is also more rapid, and the incubation period decreases. The growth stopped at 45 millions iterations.

4. Discussion

In this implementation, the number of iterations can be associated with time according to a linear relationship.
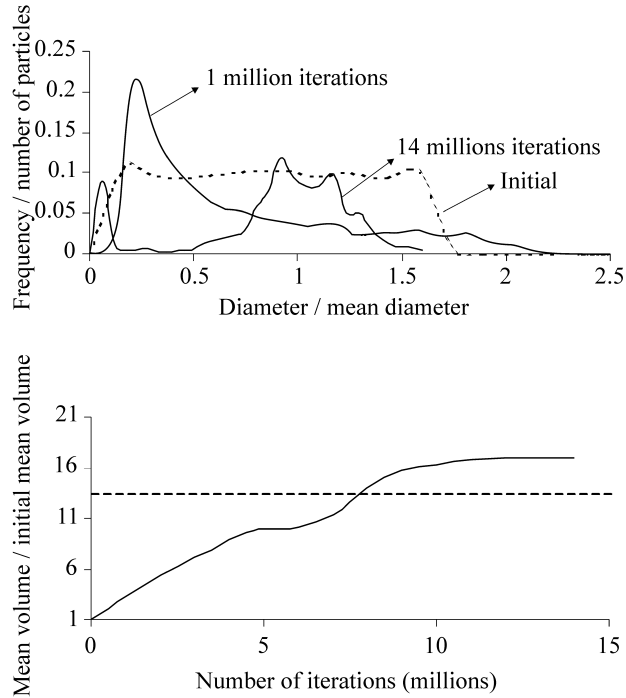
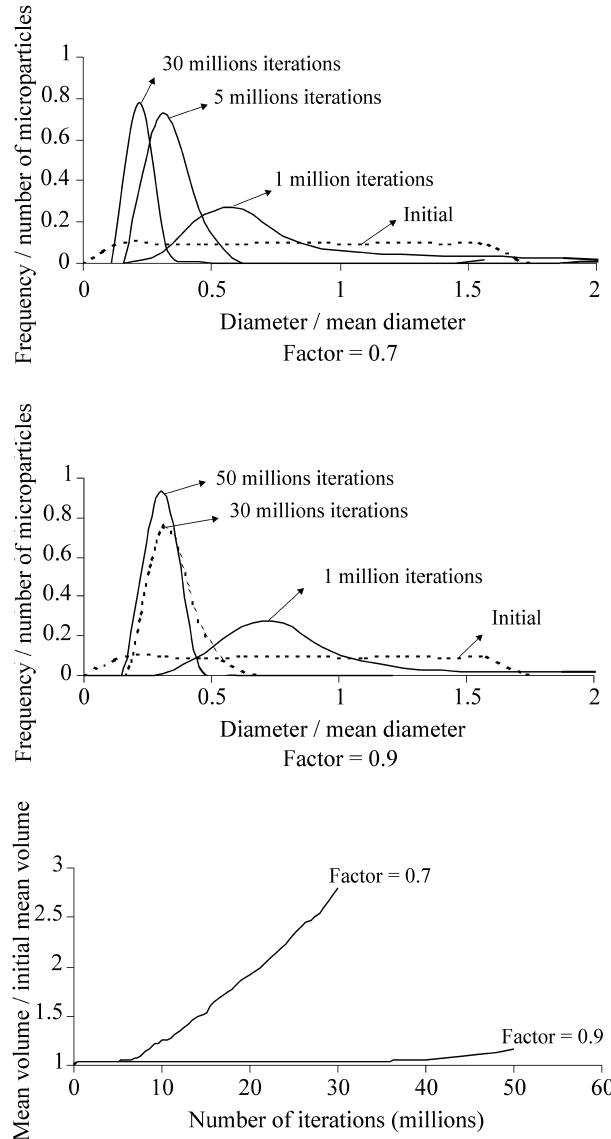**Figure 4.** The result of action of w_1 and w_2.

The fraction of released surface energy available to power w_2 should depend on the size and geometry of the sample, as well as on the material properties and temperature. Because of its strong influence on the evolution, it is advisable to avoid a simple fit of this fraction to experimental data. It should be derived based on physical backgrounds.

The amount of mass transferred in the interactions between microparticles and the vanishing size should also be appropriately modeled. Different models can be introduced in this implementation.

The growth of the microparticle mean volume shows three features: a) an incubation period, that depends on the fraction of released surface energy available to power w_2 and on the amount of mass transferred in each interaction between two microparticles. It may even not be observed in some situations, as in Fig. 4; b) a linear growth law after the incubation period, which can be described by

$$\frac{1}{N} = \left(\frac{1}{N_0} \right) [\ 1 + \alpha(t - t_0)\ ] \tag{2}$$

where N is the number of microparticles at instant t; t_0, and N_0 are the initial instant and number of microparticles, respectively, and α is a constant. This is similar to the grain growth law proposed by Rhines and Craig (7) for the steady-state. Because of this similarity the growth is called "steady-state" when Eq. (2) is observed; c) a perturbation on the growth law of Eq. (2) is observed for larger mean sizes, followed by the full stop of the growth. These events

Figure 5. The result of action w_1, w_2 and w_3.

are related to spatial correlations developed because of this implementation.

After the onset of the linear growth law (steady-state), the size distributions developed for the IFS formed by w_1 and w_2, and w_1, w_2, and w_3 can be described by

$$n_i = n_0\ e^{[\ \lambda\ (\ d_0 - d_i\ )\ d_i^{\ 2}\ ]} \tag{3}$$

where n_i is the number of microparticles in the i-th size class with size d_i, and n_0 is the number of vanishing microparticles. λ and d_0 are parameters related to the scattering and position of the distribution in the d_i-axis, respectively. This distribution is derived elsewhere (2). A small population of microparticles at larger sizes was developed. Although this population has slowly decreased as the iterations proceeded, it persisted up to the full stop

of growth. It cannot be described by Eq. (3). I also explain this population as consequence of the spatial correlations. The steady-state size distributions for the IFS formed by w_1 and w_3 cannot be described by Eq. (3). These are more close to the lognormal distribution (see Fig. 4, 1 million iterations).

This implementation works while the microparticles don't touch each other. The volume fractions admitted by this restriction depends on the size and position of the larger microparticles: a) if they are adjacent, the maximum volume fraction admitted can be calculated as *maximum volume fraction = (6/π) * v_{total} / (largest microparticle diameter)^3 * (number of lattice nodes)*. For the case of Fig. 4, this volume fraction is 1.2%; b) if they are not adjacent, larger volumetric fractions can be admitted. It is possible to implement a monitoring routine to check if "collisions" between microparticles take place. While these collisions don't happen, larger volume fractions can be admitted.

5. Summary

The iterated function system formed by three functions acting independently of each other on a set of microparticles of different sizes randomly distributed into a three dimensional lattice shows characteristics that resemble the Ostwald ripening. These functions concern the re-distribution of mass during the interactions between microparticles. The first one, w_1, promotes interactions to decrease the surface energy of the microparticle set. The second one, w_2, promotes interactions to increase the entropy of the microparticle set. The third one, w_3, eliminates microparticles of vanishing sizes and distributes their mass among neighbors. w_1 and w_2 are interactions that release energy, whereas w_2 absorbs energy. Part of the energy released by w_1 and w_3 should be available to sustain w_2.

This system was implemented by arbitrarily defining the amount of mass transferred in each interaction, the fraction of released energy available to sustain w_2, and the vanishing size. Different models can be introduced in place of these arbitrary definitions. The Rhines and Craig's growth law for steady-state was observed after an incubation period with no growth. At later stages this linear growth law is disturbed followed by a full stop of the growth, which are events associated with spatial correlations developed during the iterations. After the onset of the linear growth, the size distributions can be described by Eq. (3) for the iterated function systems formed by w_1 and w_2, and w_1, w_2, and w_3. For the system formed by w_1 and w_3 the distributions are more close to the lognormal one.

References

1. Vengrenovitch, R.D. *Acta Metall.*, v. 30, p. 1079-1086, 1982.

2. Lameiras, F.S. *Scripta Metall.*, v. 28, p. 1435-1440, 1993.

3. Rivier, N.; Lissowski, A. *J. Phys. A: Math. Gen.*, n. 15, p. L143-L148, 1982.

4. Rivier, N. *Phil. Mag. B*, n. 52, p. 795, 1985.

5. Hunderi, O.; Ryum, N. *Acta Metall.*, v. 29, p. 1737-1745, 1981.

6. Barnsley, M. *Fractals Everywhere*, Academic Press, Inc., San Diego, Ca-USA, 1988.

7. Rhines, F.N.; K.R. Craig. *Metallurgical Trans.*, v. 5, p. 413-425, 1974.