Stochastic Modeling of Particle Coating

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Dry coating of powders, in forming a layer, consists of fine particles of one component onto the surface of coarser particles of another component. In the process, fine particles are transferred among colliding coarse particles (carriers) until a steady-state distribution of fines on the carriers surface is attained. A stochastic model was developed for the kinetics of fines transfer based on a birth-death population balance including theoretically-derived one-step transition probabilities. First, the population balance equation is solved under steady-state conditions leading to the result that, at equilibrium, the number of fines per carrier follows a Bernoulli distribution. Based on the obtained equilibrium distribution, an approximate transient solution proposed agrees fairly well with the numerical solution of the birth-death equation. Model predictions were compared qualitatively with earlier experimental results.

Introduction

When a fine cohesive powder is mixed with a coarser granular material, the structure of the resulting mixture consists of a layer of fines adhered onto the surface of the larger particles. Hersey (1975) coined the term *ordered mixture* to refer to this type of powder mixing system, to distinguish it from the random mixture that results when cohesionless free-flowing powders are mixed. The nature and magnitude of the adhesion forces between the fines and the larger particles (which, hereinafter, will be denoted as "carriers") depend on the particular powder system under consideration. Such forces include, among others, Van der Waals forces, electrostatic forces, moisture bonding, and mechanical interlocking (Staniforth, 1985). In general, the degree of homogeneity attainable in ordered mixtures is far larger than in random mixtures (Lai et al., 1981; Thiel and Stephenson, 1982; Thiel et al., 1983). Coating of powders is also a useful method to avoid component segregation during mixing (Harnby et al., 1985).

Originally, ordered mixtures were used exclusively in the pharmaceutical industry, where a finely-divided active drug ingredient is adsorbed onto the surface of a coarse excipient to prepare a solid drug delivery system. The presense of the drug in a finely-divided nonagglomerated form results in higher dissolution rates, while the coarse carrier particles give the mixture the required flowability and tabletting characteristics (Stephenson and Thiel, 1980).

Ordered mixing offers other attractive possibilities which, however, have remained relatively unexplored until recently. In the last ten years, the powder coating process has gained increasing acceptance as an alternative compounding technique to prepare new materials. Illustrative examples are the preparation of electroconductive networks imbedded in a matrix of plastic particles (Alonso et al., 1991b), the dispersion of ceramic powders into superplastic alloys (Satoh et al., 1992a), the preparation of high-efficiency contact materials of use in the electrical industry (Satoh et al., 1992b), and the manufacture of multicore microcapsules (Mort and Riman, 1992).

In spite of its importance, modeling of the powder coating process has not received enough attention up to the present. The mechanism which leads to the formation of a relatively homogeneous coating layer on the surface of carriers can be summarized as follows: (a) at the very start of mixing, the fine particles (usually in the form of agglomerates) attach to the coarse particles of their neighborhood; (b) carriers having fines adhered on their surface transfer part of them during collisions with other carriers; and (c) the agglomerates of fines, which have been decreasing in size since the start of the operation, complete their dispersion onto the surface of

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carriers provided that the collisions among the latter are sufficiently energetic to overcome the adhesion strength of the aggregates. Actually, the last two stages occur simultaneously.

The theoretical description of any of the above mentioned stages has not been attempted yet, except for two works carried out about ten years ago by the group of the authors. In the first of these two articles (Alonso et al., 1989) the transfer of fines among colliding carriers (stage b above) was modeled on the basis of a discrete population balance relating the distribution of fines within the carriers at a given time to that existing after a small time-interval within which each carrier suffers on the average just one collision. The birth-death population balance equation was solved numerically and some results were shown to be in qualitative agreement with previous experimental findings (Alonso et al., 1988). In the second work (Alonso et al., 1991a) the continuous version of the discrete model was developed, resulting in a Fokker-Planck type equation which could not be solved analytically, but from which we could derive the evolution with time of the moments of the distribution of fines on the carriers.

In the present article the discrete version of the population balance is dealt with again to obtain in a rigorous manner the steady-state distribution of fines among carriers. From this, an approximate transient distribution is derived next and compared with the numerical solution. The connection between the model and some recently published experimental results will also be discussed.

Carrier Surface Coverage

The number of fine particles of diameter d forming a coating monolayer on the surface of a coarse particle of diameter D is given by (Alonso et al., 1990)

$$n = \frac{2\pi}{\sqrt{3}}\left[\left(1+\frac{D}{d}\right)\frac{1}{\lambda}\right]^2, \tag{1}$$

where λd is the average distance between the centers of contiguous fines in the monolayer. The fines within the monolayer can be arranged orderly as in hexagonal close packing or they can be distributed randomly over the surface of the carrier. The (maximum) number of fines in the monolayer depends on the type of packing, and this dependency is accounted for by the parameter λ. Thus, for hexagonal close packing $\lambda = 1$, that is, each fine is in contact with its six neighbors. In the other extreme, in a completely random structure obtained by random sequential addition of fines onto the carriers, λ takes on the value $4/3$. In a practical situation, λ is likely to attain a value somewhere between 1 and $4/3$ depending on the degree of restructuring of the monolayer during mixing.

When a carrier, at a given time of the process, has a number x of fine particles adhered onto its surface, the degree of surface coverage (sites occupancy) is x/n or, conversely, the fraction of surface sites still available for further accommodation of fines is $1 - x/n$. The degree of surface coverage will be useful to derive the one-step transition probabilities.

Discrete Population Balance

The special case will be considered in which the fine particles are present in the mixture as individual entities, that is, in nonagglomerated form. The number fraction of coarse particles carrying x fines at time t will be denoted as $f(x,t)$. This distribution must satisfy the matter conservation equation

$$\sum_{x=0}^{n} f(x,t) = 1, \tag{2}$$

$$\bar{x} = \sum_{x=0}^{n} x f(x,t) = \text{const}. \tag{3}$$

The last equation gives the average number of fines per carrier, directly related to the overall proportion of the two components in the mixture.

At the start of the mixing operation, the distribution $f(x,0)$ is regarded to be that resulting from the ideal completion of stage (a) described in the Introduction, that is, the system is considered to be initially formed by a few carriers having their surfaces completely coated with fines, with the rest of the coarse particles being free of fines. Furthermore, it is assumed that these initially few coated carriers are randomly distributed within the bulk of the powder or, in other words, that a perfect macromixing of coated and noncoated particles exists at time $t = 0$. This picture is not as idealistic as it might seem, for it is a configuration readily attainable in real experiments (Alonso et al., 1988). The initial distribution can be written thus

$$f(n,0) = \frac{\bar{x}}{n} = 1 - f(0,0);\ \text{and}\ f(x,0) = 0\ \text{for}\ x = 1,2,\ldots,n-1. \tag{4}$$

The distribution $f(x,t)$ changes with time as a result of fines exchange between colliding carriers. A time interval Δt is now chosen in such a manner that during Δt each carrier suffers on the average just one collision. Two further simplifications are introduced: first, that only binary collisions are allowed and, second, that during one collision only one fine at most can be exchanged between the two colliding carriers. Hence, within the time interval Δt, a carrier can either gain one fine, lose one fine, or undergo no fine exchange at all. Denoting by $G_x \Delta t$ and $L_x \Delta t$, the probabilities that an x-carrier (that is, a large particle carrying x fines) gains and loses, respectively, one fine during time Δt, the birth-death population balance equation can be written thus

$$f(x,t+\Delta t) = f(x,t)\left[1-(G_x + L_x)\Delta t\right] + f(x-1,t)G_{x-1}\Delta t + f(x+1,t)L_{x+1}\Delta t. \tag{5}$$

To derive the one-step transition probabilities $G_x \Delta t$ and $L_x \Delta t$, consider the collision between a k-carrier and an x-

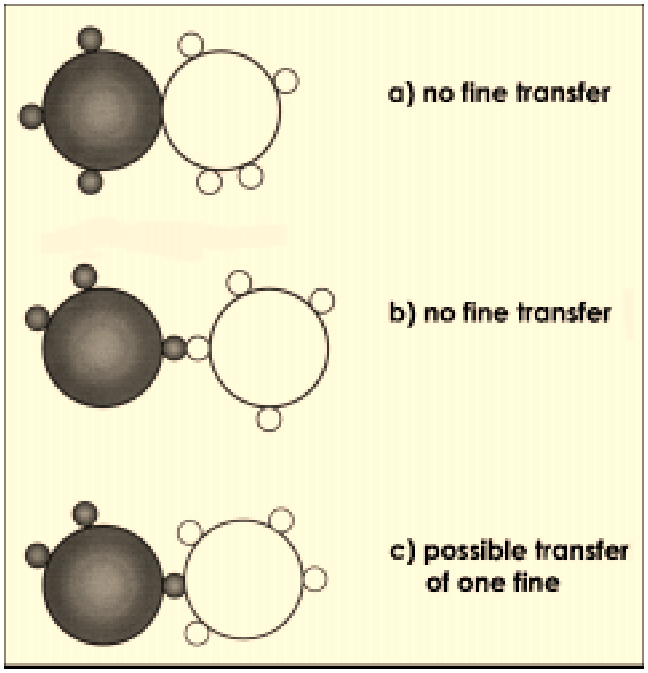

Figure 1. Fine exchange between carriers during collisions.

carrier (Figure 1), and let $P_{kx}\Delta t$ be the probability that a fine of the k-carrier is transferred to the x-carrier during the collision (during the time interval Δt). For the transfer $k \rightarrow x$ to take place, it is first necessary that one fine of the k-carrier contacts the free surface of the x-carrier at the instant of collision. (It is assumed, as depicted in Figure 1, that no fine exchange is possible if in the collision two fines enter into contact, because a fine particle cannot occupy an already occupied site). The probability that one fine of k contacts the free surface of x is $(k/n)(1-x/n)$. Even if this contact takes place, the transfer may or may not occur, depending on the fine-to-carrier adhesion force, impact energy, surface roughness, surface deformability, and so on. Denoting by W_{tr} the probability that the transfer takes place upon contact of the fine with the free surface of the colliding carrier, the transition probability can be expressed as

$$P_{kx}\Delta t = \frac{k}{n}\left(1-\frac{x}{n}\right)W_{tr}. \tag{6}$$

No explicit way of evaluating W_{tr} is proposed. For the sake of simplicity, it will be assumed that W_{tr} is independent of the type of carrier and of time. The probability that the x-carrier, when having a collision, collides specifically with a k-carrier is equal to $f(k,t)$ since perfect macromixing is assumed. Therefore, the probability that the x-carrier gains one fine during the time interval Δt is

$$G_x\Delta t = \sum_{k=0}^{n} f(k,t)P_{kx} = \left(1-\frac{x}{n}\right)W_{tr}\sum_{k=0}^{n}\frac{k}{n}f(k,t)$$

or, recalling Eq. 3

$$G_x\Delta t = \left(1-\frac{x}{n}\right)W_{tr}\frac{\bar{x}}{n}. \tag{7}$$

The probability of gaining one fine is thus proportional to the number fraction of sites available in the carrier, to the average concentration of fines in the system, and to the transfer probability upon contact (W_{tr}). Equation 7 is also consistent with the fact that a completely coated carrier ($x=n$) cannot acquire any more fines because it has no free site available on its surface.

In a similar manner, the probability that the x-carrier loses one fine in the time interval Δt results to be

$$L_x\Delta t = \left(1-\frac{\bar{x}}{n}\right)W_{tr}\frac{x}{n}. \tag{8}$$

As seen, $L_x\Delta t$ is proportional to the number of fines on the surface of the carrier under consideration, to the average availability of free sites in the system, and to the (unknown) transfer probability upon contact. Note also that, according to Eq. 8, an uncoated carrier ($x=0$) cannot lose any fine. The two conditions $G_n=0$ and $L_0=0$ somehow represent the boundary conditions for the birth-death Eq. 5, because they prevent the appearance of carriers with a negative number of fines or with a number of fines larger than the maximum n.

Equations 4, 5, 7 and 8 constitute the proposed stochastic model for the description of the kinetics of fines transfer among carriers in the powder coating process.

Although it will not be used in this article, for the sake of completeness, it is appropriate to point out that the above discrete model is equivalent to the Fokker-Planck type equation (see Alonso et al., 1991a for details)

$$\frac{\partial f(x,\tau)}{\partial \tau} = -\frac{\partial}{\partial x}[(\bar{x}-x)f(x,\tau)] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left\{\left[\bar{x}+\left(1-\frac{2\bar{x}}{n}\right)x\right]f(x,\tau)\right\}, \tag{9}$$

where

$$\tau = \frac{W_{tr}t}{n\Delta t} \tag{10}$$

is a dimensionless time (note that $1/\Delta t$, according to what has been mentioned above, can be regarded as the average number of collisions that a carrier suffers per unit time).

Figure 2 shows a typical example of the time evolution of the distribution of fines within carriers, computed with the discrete birth-death Eq. 5. At the initial stages, there are two partial distributions, one corresponding to highly coated carriers (values of x/n closer to 1), and the other consisting of carriers coated to a lesser extent (values of x/n closer to 0).

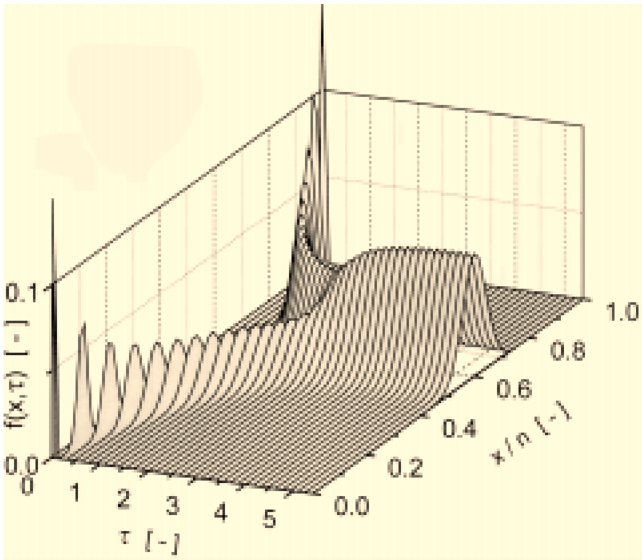

Figure 2. Typical example of the evolution of the distribution of fines within carriers.

$f(x,\tau)$ is the number fraction of carriers coated with x fines at dimensionless time τ, and n is the maximum number of fines in a coating monolayer. In this example: carrier-to-fine size ratio $D/d = 5$; dimensionless average distance between centers of neighboring fines in the monolayer $\lambda = 1$; transfer probability upon contact $W_{tr} = 1$; and average number of fines per carrier $\bar{x}/n = 0.6$. (The peaks appearing at time $\tau = 0$ are actually higher than shown).

The two partial distributions gradually approach each other as a consequence of the ''overall'' transfer of fines from the population of highly coated carriers to that of less coated ones.

Steady-State Distribution

Taking the limit of Eq. 5 as $\Delta t \to 0$ leads to

$$\frac{\partial f_x}{\partial t} = (L_{x+1} f_{x+1} - G_x f_x) - (L_x f_x - G_{x-1} f_{x-1}) \quad (11)$$

where, to simplify the nomenclature, f_x has been written instead of $f(x,t)$. At the steady-state, Eq. 11 becomes

$$L_{x+1} f^*_{x+1} - G_x f^*_x = L_x f^*_x - G_{x-1} f^*_{x-1} \quad (12)$$

Here, f^*_x denotes the steady-state number fraction of x-carriers. For $x=0$, Eq. 12 becomes $L_1 f^*_1 - G_0 f^*_0 = 0$. For $x=1$, $L_2 f^*_2 - G_1 f^*_1 = L_1 f^*_1 - G_0 f^*_0 = 0$. Proceeding in this manner, one sees that in general $L_{x+1} f^*_{x+1} - G_x f^*_x = 0$, or

$$f^*_{x+1} = \frac{G_x}{L_{x+1}} f^*_x \quad (13)$$

and, consequently

$$f^*_x = \frac{G_0 \cdots G_{x-1}}{L_1 \cdots L_x} f^*_0 \ \text{for}\ 0 < x \le n. \quad (14)$$

Equation 14 gives the steady-state number fraction of x-carriers as a function of the steady-state number fraction f^*_0 of noncoated coarse particles. Taking Eqs. 2 and 14 into account, one can write

$$1 = f^*_0 + \sum_{x=1}^{n} f^*_x = f^*_0 \left(1 + \sum_{x=1}^{n} \frac{G_0 \cdots G_{x-1}}{L_1 \cdots L_x}\right)$$

and, therefore

$$f^*_0 = \frac{1}{1 + \sum_{k=1}^{n} \frac{G_o \cdots G_{k-1}}{L_1 \cdots L_k}}, \quad (15a)$$

$$f^*_x = \frac{\frac{G_0 \cdots G_{x-1}}{L_1 \cdots L_x}}{1 + \sum_{k=1}^{n} \frac{G_0 \cdots G_{k-1}}{L_1 \cdots L_k}} \quad \text{for} \quad 0 < x \le n. \quad (15b)$$

Inserting the one-step transition probabilities, given by Eqs. 7 and 8, one finds after some algebraic manipulations

$$\frac{G_0 \cdots G_{x-1}}{L_1 \cdots L_x} = \frac{n!}{x!(n-x)!} \left(\frac{\bar{x}/n}{1 - \bar{x}/n}\right)^x$$

and

$$1 + \sum_{k=1}^{n} \frac{G_0 \cdots G_{k-1}}{L_1 \cdots L_k} = \left(1 - \frac{\bar{x}}{n}\right)^{-n},$$

so that finally

$$f^*_x = \frac{n!}{x!(n-x)!} \left(\frac{\bar{x}}{n}\right)^x \left(1 - \frac{\bar{x}}{n}\right)^{n-x}, \quad (16)$$

an expression which is also valid for $x = 0$. It has thus been found that the steady-state distribution of fines onto the carriers is a Bernoulli distribution with mean $\bar{x}$ and variance

$$\sigma^{*2} = \bar{x}\left(1 - \frac{\bar{x}}{n}\right). \quad (17)$$

In practical situations, $\bar{x}$ and n are both very large and the Bernoulli distribution can be approximated by the Gaussian distribution

$$f^*_x = \frac{1}{\sqrt{2\pi\sigma^{*2}}} \exp\left[-\frac{(x-\bar{x})^2}{2\sigma^{*2}}\right]. \quad (18)$$

Figure 3 shows some examples of steady-state distributions obtained by numerical solution of the discrete birth-death Eq. 5 along with the analytical expressions (Eqs. 16 and 18).

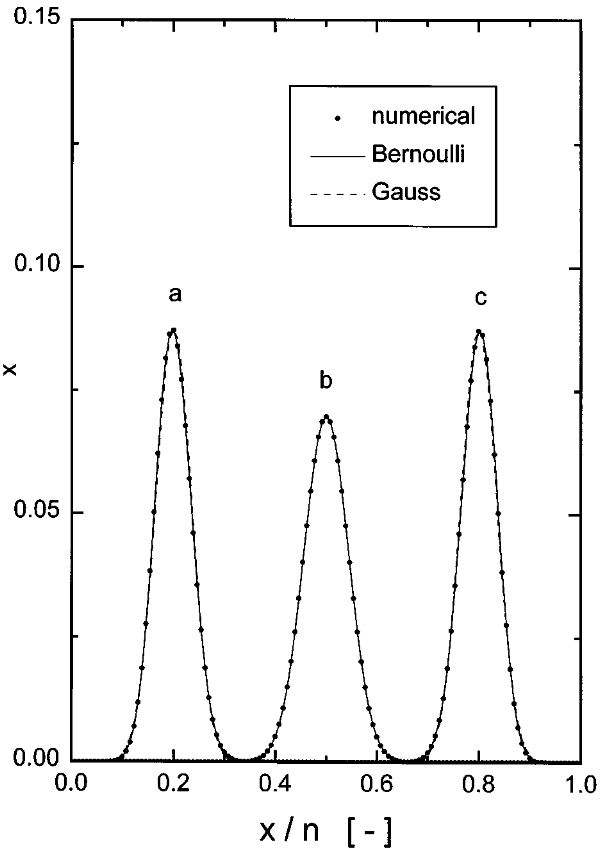

Figure 3. Steady-state distribution of fines on carriers surface.

Comparison between numerical results obtained from solution of the population balance, Eq. 5 (points), Bernoulli distribution (solid line), and normal distribution (dashed line). f_x^* is the steady-state number fraction of carriers coated with x fines, and n is the maximum number of fines in a coating monolayer. All the conditions, as in the example of Figure 2, except the average number of fines per carrier $\bar{x}/n$ which is (a) 0.2, (b) 0.5, and (c) 0.8.

Transient Distribution

We have not been able to find a rigorous solution to the transient birth-death Eq. 5. An approximate analytical expression for $f(x,\tau)$ can be found as follows. First, from the plot presented in Figure 2, it seems apparent that the transient solution must be the sum of two partial distributions: a distribution $f_1(x,\tau)$ accounting for the carriers which originally at time $t=0$ were uncoated and are becoming progressively coated, and a second distribution $f_2(x,\tau)$ involving the carriers which at time $t=0$ were completely coated and are progressively losing part of their fines during collisions. The mean values of these two distributions $\overline{x_1}$ and $\overline{x_2}$ evolve with time according to

$$\overline{x_k}(t+\Delta t) = \overline{x_k}(t) + \left(G_{\overline{x_k}} - L_{\overline{x_k}}\right)\Delta t, \quad k=1,2.$$

In the last expression, $G_{\overline{x_k}}$ and $L_{\overline{x_k}}$ are the transition probabilities per unit time for a carrier coated with $\overline{x_k}$ fines. Taking the limit as $\Delta t \to 0$, inserting the corresponding one-step transition probabilities (Eqs. 7 and 8), and introducing the dimensionless time defined by Eq. 10, one finds

$$\frac{d\overline{x_k}}{d\tau} = \bar{x} - \overline{x_k}, \quad k=1,2. \tag{19}$$

Integration of Eq. 19 with initial conditions $\overline{x_1}=0$ and $\overline{x_2}=n$ at time $\tau=0$ leads to

$$\overline{x_1} = \bar{x}(1-e^{-\tau}), \tag{20}$$

$$\overline{x_2} = \bar{x} + (n-\bar{x})e^{-\tau}. \tag{21}$$

To arrive at the approximate analytical expression for the transient distribution $f(x,\tau)$, it is now assumed that each of the two partial distributions $f_k(x,\tau)$ $(k=1,2)$ is itself a Bernoulli distribution with mean $\overline{x_k}$, weighted by the initial number fraction of noncoated particles or of completely coated particles depending on where the partial distribution in consideration evolves from. That is

$$f(x,\tau) = \frac{n!}{x!(n-x)!}\left[f(0,0)\left(\frac{\overline{x_1}}{n}\right)^{x}\left(1-\frac{\overline{x_1}}{n}\right)^{n-x} + f(n,0)\left(\frac{\overline{x_2}}{n}\right)^{x}\left(1-\frac{\overline{x_2}}{n}\right)^{n-x}\right] \tag{22}$$

where the initial number fractions of noncoated, $f(0,0)$, and completely coated, $f(n,0)$, carriers are given by Eq. 4. Figure 4 shows a comparison between the rigorous distribution $f(x,\tau)$ computed with the birth-death Eq. 5 and the approximate solution (Eq. 22) for a typical case. As seen, except at the early stages of the process, the approximate analytical expression 22 reproduces fairly well the rigorous numerical solution.

Experimental Evidence Supporting the Model

As a conclusion to this article, a few experimental results which agree qualitatively with this stochastic model will be reported. The agreement must be, at most, qualitative in nature because the model contains some parameters whose experimental determination is quite difficult to carry out in practice, in particular, the transfer probability upon contact W_{tr} and the average number of collisions per unit time $1/\Delta t$. In spite of this difficulty, there are at least three points of agreement between the present model and experiments. First, it was demonstrated in a previous publication (Alonso et al., 1989) dealing with the numerical solution of Eq. 5 that the model is coherent with the viewing of the coating process as formally analogous to a second-order autocatalytic chemical reaction, an analogy which was successfully put to experimental test in a work of the present author (Alonso et al., 1988). Second, Shinohara et al., (1996, 1998) conducted experiments of powder coating by high-speed gas impact blending and found a reasonable agreement between their experimental results and the time evolution of the two partial distributions given by Eqs. 19 to 21. Finally, a more recent experimental work of powder coating in a fluidized bed (Abe et al., 1998)

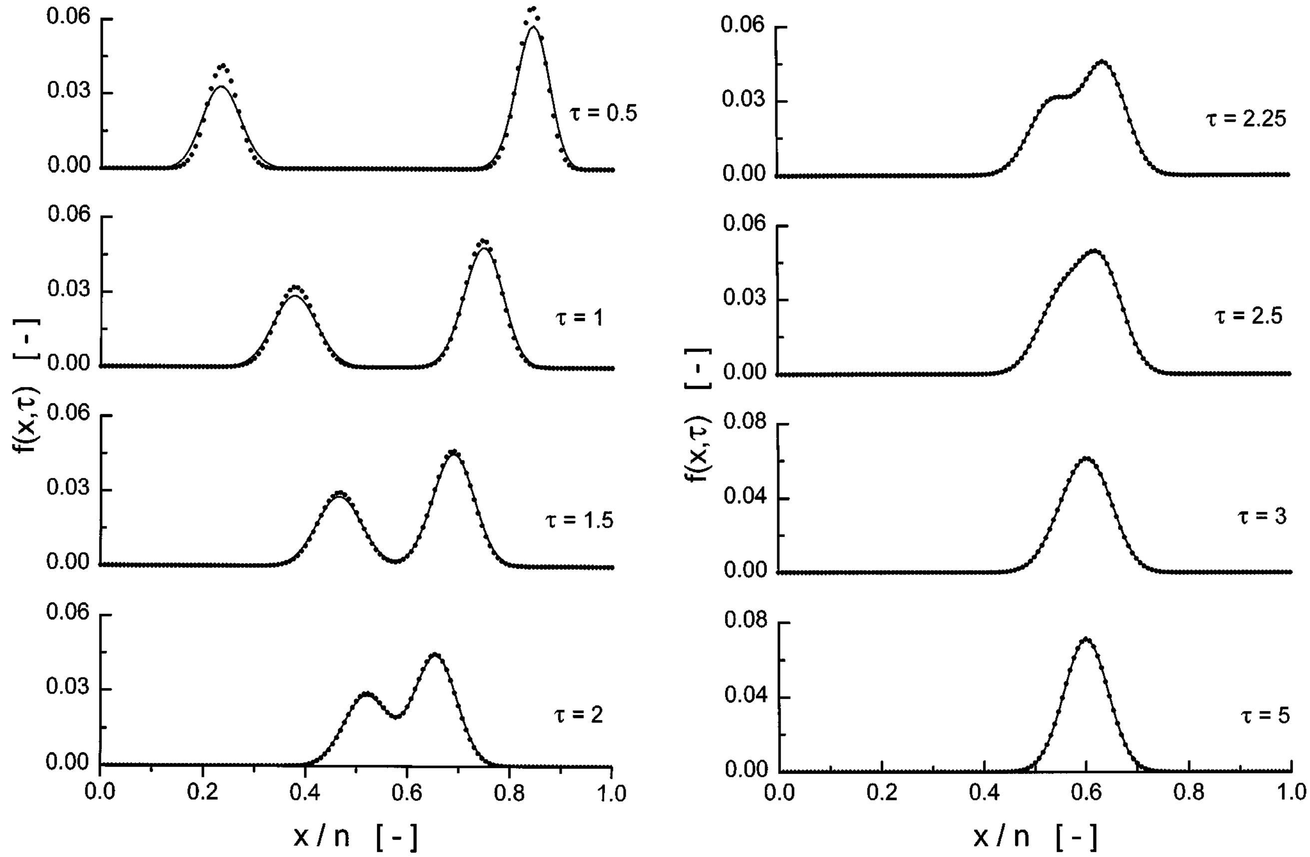

Figure 4. Transient distribution of fines on carriers surface.

Comparison between the numerical solution of the population balance, Eq. 5 (points), and the approximate analytical solution given by Eq. 22 (solid lines). $f(x,\tau)$ is the number fraction of carriers coated with x fines at dimensionless time τ, and n is the maximum number of fines in a coating monolayer. All the conditions as in the example of Figure 2.

has shown that the number of fines onto the surface of the coarse particles follows a normal distribution, in agreement with the results of the present model.

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