ANALYTICAL STUDY ON THE SHAPE EVOLUTION OF ELLIPSOIDAL PARTICLES UNDER DIFFUSION PROCESSES

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Abstract. *In the treatment of the combustion of solids, or of any physical-chemical processes where solid particles interact with a fluid - such as the evaporation or dissolution of solid particles - it is a common practice to assume, for the sake of simplicity, that particles are spherical. The shape of real particles can be quit different from this simplified approach and, generally, it is not possible to develop simple mathematical models to represent the real particle-fluid interactions. A shape closely related with the sphere is a prolate ellipsoid.*
Diffusion around ellipsoids has already been studied. Pinho and Guedes de Carvalho (1986), for instance, used the ellipsoidal shape to assess the error involved in approximating real particles by spheres. These authors developed an analytical model to represent the shape evolution of a prolate ellipsoid under pure diffusion and used a numerical model in the case of pure kinetic control.
In this work, the shape evolution of a prolate ellipsoid, under pure diffusion or under pure kinetic control, was studied again, but now by means of an entirely analytic solution. As a result, a set of equations and graphs, describing the evolution of the particle being consumed, were obtained in a simpler way.

Keywords: *Ellipsoidal particles, Mass transfer, Diffusion, Kinetic control, Shape evolution*

1. INTRODUCTION

The study of transport phenomena around spheroids is not a new subject. Byerly (1902), Hobson (1931), Lamb (1932) and Bateman (1944), to cite only a few, have worked out the diffusion equation in ellipsoidal geometries. Carslaw and Jaeger (1959) studied steady heat conduction in an infinite medium containing an ellipsoid of different thermal conductivity. Weber (1950) and Smythe (1968) analysed the electromagnetic field generated by a conducting spheroid, held at a constant potential, in a dielectric medium, and obtained an expression for the ratio between the capacitance of the spheroid and the permittivity of the medium. Clift *et al*. (1978) directly applied this result to the case of diffusion from a spheroid into a stagnant external medium. As a result, an equation for the conductance of a prolate spheroid has been obtained

$$\frac{k_G A}{D_G} = \frac{4\pi b(E^2 - 1)^{0.5}}{\ln(E + (E^2 - 1)^{0.5})} \tag{1}$$

where k_G is the overall mass transfer coefficient, A the surface area of the ellipsoid, D_G the diffusion coefficient and E the aspect ratio – a/b – of the spheroid. Figure 1 shows the geometrical notation used.

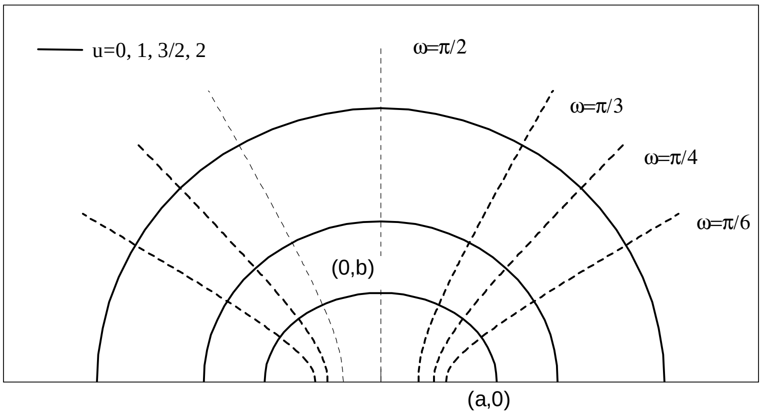

Figure 1- Prolate spheroidal coordinates.

Real complex particles are often modelled as spheres. This fact influences the treatment and interpretation of experimental data as it was shown by Pinho (1984), with regard to the study of fluidised-bed combustion of char particles. Similarly Clift *et al*. (1978) suggested the use of the ellipsoidal geometry in the calculation or measurement of drag on actual particles, since a spheroid can constitute a good approximation to shapes ranging from spheres to needles.

In the application of the diffusion equation (Crank, 1975) to electromagnetism, heat conduction or fluid flow, there is no need to consider particle consumption. Obviously this does not happen in the case of mass transfer where the application of Eq. (1), for example, is restricted to static conditions. And hence the need of studying the shape evolution of particles under diffusion conditions.

In the referred work, Pinho and later Pinho and Guedes de Carvalho (1986), in order to assess the error involved in approximating real particles by spheres, studied diffusion around spheroidal particles. An analytical model was developed for the case of pure diffusion and a numerical one for the case of pure kinetic control. As a result, a set of graphs, allowing the comparison between the behaviour of spheres and ellipsoids, under diffusion conditions, were obtained.

In this work the results of Pinho (1984) are reworked through an exclusively analytical approach, mainly in the case of pure kinetics. In the treatment of diffusion a stagnant external phase was considered, the chemical species concentration, near the particle surface, is considered constant and no allowance is made for convective terms; in the case of pure kinetic control, first-order kinetics was assumed.

2. PURE DIFFUSION AROUND A PROLATE ELLIPSOID

Pinho and Guedes de Carvalho (1986) used prolate spheroidal coordinates to study diffusion around ellipsoids. This coordinate system is obtained by rotating the confocal ellipses and hyperboles of Fig. 1 about the z axis, defining coordinate surfaces u and ω; the third set of coordinate surfaces – θ – is defined by planes passing through de z axis. The conversion relations (Spiegel, 1968) between prolate spheroidal and rectangular coordinates are

$$x = c\sinh(u)\sin(\omega)\cos(\theta) \tag{2a}$$
$$y = c\sinh(u)\sin(\omega)\sin(\theta) \tag{2b}$$
$$z = c\cosh(u)\cos(\omega) \tag{2c}$$

c being the focal distance.

Considering fluid at rest, absence of chemical reaction, steady state and uniform concentration (C) of the diffusing species on the particle surface, denoted by the subscript s, the continuity equation in prolate spheroidal coordinates takes the following one-dimensional form

$$\frac{d}{du}\left(\sinh(u)\frac{dC}{du}\right) = 0 \tag{3}$$

Applying the appropriate boundary conditions, specifying the concentration near the surface, C_s, and far from the particle, C_∞, the concentration profile in the surrounding fluid is given by

$$\frac{C - C_\infty}{C_s - C_\infty} = \frac{\ln(\tanh(u/2))}{\ln(\tanh(u_s/2))} \tag{4}$$

and the total molar flow rate from the particle, W_{el}, can be obtained from

$$W_{el} = -\frac{4\pi c D_g (C_s - C_\infty)}{\ln(\tanh(u_s/2))} \tag{5}$$

where the subscript specifies that we are dealing with an ellipsoidal geometry. Considering the case of a sphere with equal volume and equivalent diameter d_{eq}, the following equation would be obtained for the molar flow rate, W_{sp}

$$W_{sp} = 4\pi c D_g (C_s - C_\infty)(\sinh^2(u_s)\cosh(u_s))^{1/3} \tag{6}$$

and the ratio between the total molar flow rates, for both particles, can be written as

$$\frac{W_{sp}}{W_{el}} = -\ln(\tanh(u_s/2))(\sinh^2(u_s)\cosh(u_s))^{1/3} \tag{7}$$

Pinho and Guedes de Carvalho (1986) carried out the above-described development. In addition, studying the shape evolution of a prolate spheroid under pure diffusion, Pinho

(1984) arrived to the conclusion that, while being consumed, it evolves as a sequence of ellipsoids with constant eccentricity –eccentricity =1–*e*=1–*b/a*– and decreasing focal length. Furthermore, the same author proved that the relative error, made by considering that the particle evolution follows a family of confocal ellipses, may be calculated through

$$\Delta\varepsilon=\left(\sqrt{\left(\frac{\sin\omega\cos\omega}{\sinh u\cosh u}\right)^{2}+1}-1\right) \tag{8}$$

When the eccentricity is less than 0.5, this equation shows that the assumption that particles evolve as a series of confocal ellipsoids it is not acceptable, and all these developments are not applicable. However, with this in mind, the model can be used to describe the shape evolution, under pure diffusion, of ellipsoidal particles with eccentricity ratios closer to unity. And, since the eccentricity ratio remains constant, simple mathematical manipulations lead to the following equations, which describe the particle evolution

$$\frac{a}{c_i}=\frac{1}{\sqrt{1-e^2}}\sqrt[3]{1-\Delta V/V_i} \tag{9}$$

$$\frac{b}{c_i}=\frac{e}{\sqrt{1-e^2}}\sqrt[3]{1-\Delta V/V_i} \tag{10}$$

$$\frac{d_{eq}}{2c_i}=\frac{\sqrt[3]{e^2}}{\sqrt{1-e^2}}\sqrt[3]{1-\frac{\Delta V}{V_i}} \tag{11}$$

$$\frac{(V/A)_{sp}}{c_i}=\frac{1}{3}\frac{\sqrt[3]{e^2}}{\sqrt{1-e^2}}\sqrt[3]{1-\frac{\Delta V}{V_i}} \tag{12}$$

$$\frac{(V/A)_{el}}{c_i}=\frac{2}{3}\frac{e^2}{e^2\sqrt{1-e^2}+e\arcsin\sqrt{1-e^2}}\sqrt[3]{1-\frac{\Delta V}{V_i}} \tag{13}$$

In these equations the subscript *i* refers to the initial conditions, $(V/A)_{el}$ is the ratio volume-area for the ellipsoid and $(V/A)_{sp}$ is the ratio volume-area for the sphere with the same volume; ΔV is the volume variation of the spheroid when compared with its initial value.

3. SHAPE EVOLUTION OF A PROLATE ELLIPSOID UNDER KINETIC CONTROL

Under kinetic control, the reaction rate is constant over the particle surface. The particle is uniformly consumed, and its eccentricity becomes more pronounced. So, considering a sequence of ellipsoids with decreasing size, if they satisfy the prolate spheroidal coordinate system, their focal length remains constant and the eccentricity increases. On the other hand, if they are obtained by a diffusion process, their eccentricity is maintained and the focal length diminishes. Under kinetic control, their eccentricity increases and their focal length decreases.

In the following development the initial particle eccentricity is designated by e_i. Assuming first order kinetics and a process kinetically controlled, at any point of the particle surface the consumption rate may be related with the concentration of the gaseous phase far away from the particle, $C_s = C_\infty$ through the kinetic reaction rate constant, k_c

$$\frac{ds_u}{dt} = -k_c C_\infty \tag{14}$$

When this equation is applied to the spheroid minor and major axes, and integrated between instants 0 and t, the obtained results are

$$a = a_i - k_c C_\infty\, t \tag{15a}$$
$$b = b_i - k_c C_\infty\, t \tag{15b}$$

or

$$a_i - a = b_i - b \tag{16}$$

The geometric parameters at initial conditions may be related through

$$a_i = \frac{c_i}{\sqrt{1-e_i^2}} \tag{17a}$$
$$b_i = \frac{e_i\, c_i}{\sqrt{1-e_i^2}} \tag{17b}$$

and the change in the ellipsoid volume when it is being consumed can be calculated through

$$\frac{\Delta V}{V_i} = 1 - \frac{c^3 \sinh^2(u)\cosh(u)}{c_i^3 \sinh^2(u_i)\cosh(u_i)} = 1 - \frac{ab^2}{a_i b_i{}^2} \tag{18}$$

The preceding equations may be combined to obtain relations between the volume variation of the ellipsoid and its characteristics geometrical parameters, as previously done in the case of diffusional control (Eqs. (9)-(13)). However, the obtained equations, though explicit relatively to the volume change, when considered from the point of view of the geometrical parameters are implicit ones. Eqs. (19)-(23) present the achieved results.

$$\frac{\Delta V}{V_i} = 1 - \frac{\sqrt{(1-e_i^2)^3}}{e_i^2}\left(\frac{a}{c_i}\right)^3 + \frac{2(1-e_i)(1-e_i^2)}{e_i^2}\left(\frac{a}{c_i}\right)^2 - \frac{(1-e_i)^2\sqrt{1-e_i^2}}{e_i^2}\left(\frac{a}{c_i}\right) \tag{19}$$

$$\frac{\Delta V}{V_i} = 1 - \frac{\sqrt{(1-e_i^2)^3}}{e_i^2}\left(\frac{b}{c_i}\right)^3 - \frac{(1-e_i)(1-e_i^2)}{e_i^2}\left(\frac{b}{c_i}\right)^2 \tag{20}$$

$$\frac{\Delta V}{V_i} = 1 - \frac{(1+e_i)^3}{8e_i^2}\left(\frac{c}{c_i}\right)^6 + \frac{(1-e_i^2)^2}{8\,e_i^2(1-e_i)}\left(\frac{c}{c_i}\right)^4 - \frac{(1-e_i)(1-e_i^2)}{8e_i^2}\left(\frac{c}{c_i}\right)^2 - \frac{(1-e_i)^3}{8e_i^2} \tag{21}$$

$$\frac{d_{eq}}{2c_i} = \frac{\sqrt[3]{e_i^2}}{\sqrt{1-e_i^2}} \sqrt[3]{\left(1 - \frac{\Delta V}{V_i}\right)} \tag{22}$$

$$\frac{(V/A)_{sp}}{c_i} = \frac{1}{3} \frac{\sqrt[3]{e_i^2}}{\sqrt{1-e_i^2}} \sqrt[3]{1 - \frac{\Delta V}{V_i}} \tag{23}$$

A relation between the ratio volume-area of the ellipsoid and the its volume variation, although implicit through the ratios a/c_i and b/c_i, is

$$\frac{(V/A)_{el}}{c_i} = \frac{2}{3} \frac{\frac{b}{c_i}\sqrt{1-\left(\frac{b/c_i}{a/c_i}\right)^2}}{\frac{b/c_i}{a/c_i}\sqrt{1-\left(\frac{b/c_i}{a/c_i}\right)^2} + \arcsin\left(\sqrt{1-\left(\frac{b/c_i}{a/c_i}\right)^2}\right)} \tag{24}$$

3. GRAPHICAL PRESENTATION OF THE RESULTS

The analysis of the obtained results is easier if conveniently plotted. The following graphs, have been adapted from Pinho (1984), with kinetic values obtained through the present analytical procedure.

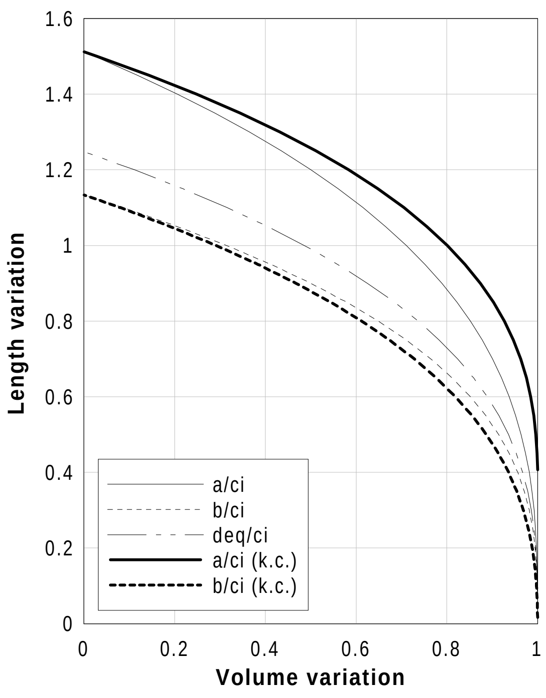

Figure 2- Particle shape evolution under diffusion or kinetics when $e_i = 0.75$.

Figure 2 shows that the ratio a/c_i diminishes in a slower way in the case of kinetic control; the ratio b/c_i behaves in the opposite way. The volume-area ratio of the particle, as it is being consumed, is represented in Figure 3. Figure 4 allows comparison between diffusion control and kinetic control.

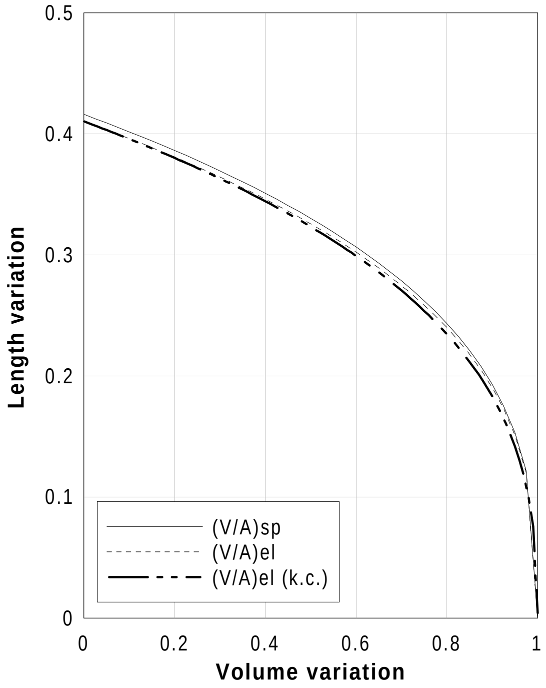

Figure 3- Volume-area ratio under diffusion or kinetics control for e_i = 0.75.

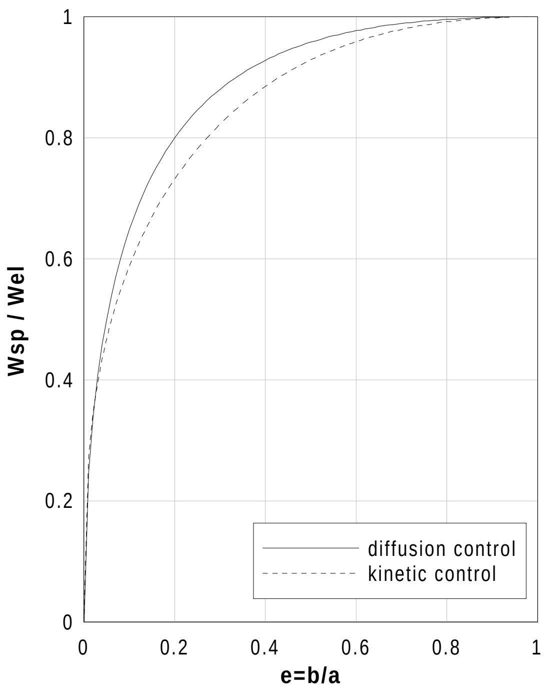

Figure 4-Dependence of the ratio W_{sp}/W_{el} upon particle eccentricity for the extreme conditions of diffusion control and kinetic control.

3. CONCLUSION

The assumption that particles are spherical can lead to errors in the interpretation of experimental data. If particles can be well modelled using the ellipsoidal shape, this error may be estimated easily in the cases of pure diffusion or pure kinetic control. This may happen at high enough temperatures, when combustion is diffusion controlled, or at low temperatures, when the combustion rate is low and kinetics dominates. Figure 4, adapted from Pinho and Guedes de Carvalho (1984) may be used, under these conditions, to access the error made.

The aim of this work was to re-work previous models using an exclusively analytic approach for the kinetically controlled situation. In the future the obtained results can be used to extend the model, in order to link the limiting referred cases of pure diffusion and pure kinetic control, in the study of kinetic versus diffusion competing phenomena.

Acknowledgements

The first author acknowledges the support of PRODEP II, Programa de Desenvolvimento Educativo para Portugal.

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