Shape Change of Rough Particles

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In the analysis of solid combustion and other fluid-solid noncatalytic reactions, it is customary to treat reacting particles as spherical to simplify the solution of the relevant reaction-transport equations. The analysis of the spherically symmetric problem is generally assumed to set the correct trends on the effect of various parameters, even when the reacting particles are nonspherical. In this work, we analyze reaction and external diffusion for nonspherical, but axially symmetric, particles to determine the change in the shape of a particle due to consumption of the solid material. The shape change can be pronounced over extended conversion even when the initial particle shape is only slightly nonspherical.

The scope of this analysis is limited to the assumption that the reaction is concentrated on the external particle surface and the external mass transfer to be determined by diffusion. These restrictions eliminate consideration of most problems pertinent to heterogeneous catalytic reactions where internal, rather than external, diffusion is rate-limiting. With respect to noncatalytic reactions, the assumption that the reaction is concentrated on or very near the external surface is valid for nonporous or porous particles under conditions of high Thiele modulus.

The most important noncatalytic gas-solid reaction, which often satisfies the above restrictions, is coal or char combustion. However, under conditions of high Thiele modulus, that is, shrinking core combustion, external heat transfer, as well as mass transfer, needs to be considered. In this note, we assume isothermal conditions and consider the external mass-transfer problem only. However, the methodology presented is applicable, with suitable extensions, to simultaneous heat and mass transfer. The latter problem was discussed earlier by Choi and Gavalas (1993) with the focus on coal combustion.

Two techniques are used to treat the problem of reacting nonspherical particles. The first is domain perturbation (DP) (Brenner, 1964; Acrivos and Taylor, 1964), the second is the boundary integral technique (BI) (Brebbia and Walker, 1980; Liggett and Liu, 1972). DP is an analytical technique limited to slightly nonspherical particles. The BI technique is numerical applicable to arbitrary particle shapes. The main advantage of the BI technique over the more customary finite element or difference techniques is the much smaller number of unknowns involved in the problem setup. First, the DP method will be used for a sphere with a slight roughness, and then the BI method will be applied to particles with larger roughness.

Problem Formulation and Discussion

The gas-solid reactions considered here can be denoted by:

$$b_1P(s)+A(g)\rightarrow b_2B(g)$$

where $P(s)$, $A(g)$, and $B(g)$ are the solid reactant, the gaseous reactant, and the gaseous product, respectively, and b_1 and b_2 are stoichiometric coefficients.

Linear diffusion equation

In this section we consider the linear diffusion problem which provides the simplest setup for investigating the effects of particle shape. The problem is approximately linear under the restrictions:

- Mole fraction of A in the free stream or equimolar counterdiffusion is low enough to neglect the Stefan flow term.
- Heat effect is low due to reaction, therefore nearly isothermal system.
- First-order reaction exists in A.

Since the Stefan flow and the temperature were shown to have small effect quantitatively, especially on the shape change of the particle, the analysis will be based on the linear diffusion model. We need to represent the surface roughness by some mathematical formula. Since the Legendre polynomials are complete, they can be used to represent any surface shape. As before, the concentration of A in the gas phase, c_A, satisfies Laplace's equation:

$$\nabla_{\tilde{x}}^2 c_A = 0. \tag{1}$$

The boundary conditions are:

$$c_A \rightarrow c_{Ab} \quad \text{as} \quad |\tilde{\mathbf{x}}| \rightarrow \infty \tag{2a}$$

and

$$D_A \nabla_{\tilde{x}} c_A \cdot \tilde{\nu} = kc_A \text{ on particle surface,} \tag{2b}$$

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where $\tilde{\nu}$ is the outward normal unit vector on the particle surface. After Eqs. 1-2 have been solved, the recession rate of each point on the surface can be calculated from:

$$\frac{1}{|\nabla \tilde{F}|}\frac{\partial \tilde{F}}{\partial t}+\mathbf{v}_s\cdot\tilde{\nu}=0 \tag{3a}$$

where

$$\tilde{F}\equiv\tilde{\rho}-\tilde{R}(\theta,t). \tag{3b}$$

Equation 1 is based on the assumption that the diffusion problem is at quasi-steady state with respect to the slowly changing particle shape. The quasi-steady-state assumption is not strictly valid for a semiinfinite medium, but has been shown by Kirkaldy (1958) to be valid for problems of sublimation and crystal growth and by Bischoff (1963) and Luss (1968) to be valid for gas-solid reactions with moving boundary.

Introducing the dimensionless variables and parameters defined by:

$$\mathbf{x}=\frac{\tilde{\mathbf{x}}}{\tilde{R}_s(t)},\ u_A=\frac{c_A}{c_{Ab}},\ R(\theta,t)=\frac{\tilde{R}(\theta,t)}{\tilde{R}_s(t)} \tag{4a}$$

and

$$Q[\tilde{R}_s(t)]=\frac{k\tilde{R}_s(t)}{D_A},\ \tau=\frac{b_1k^2c_{Ab}}{\rho_sD_A}t, \tag{4b}$$

where $\tilde{R}_s(t)$ is the radius of a sphere having the same volume as the particle, yields the following dimensionless governing equation and boundary conditions:

$$\nabla_x^2u_A=0. \tag{5a}$$

$$R^2\frac{\partial u_A}{\partial \rho}-\frac{\partial R}{\partial \theta}\frac{\partial u_A}{\partial \theta}=QR^2\sqrt{1+\left(\frac{1}{R}\frac{\partial R}{\partial \theta}\right)^2}\,u_A\quad \text{at } \rho=R(\theta,\tau). \tag{5b}$$

$$u_A\rightarrow 1\quad \text{as}\quad \rho\rightarrow\infty. \tag{5c}$$

$$-\left(\frac{dQ(\tau)}{d\tau}R+Q(\tau)\frac{\partial R}{\partial \tau}\right)=\sqrt{1+\left(\frac{1}{R}\frac{\partial R}{\partial \theta}\right)^2}\,u_A\quad \text{at } \rho=R(\theta,\tau). \tag{5d}$$

$$\frac{dQ}{d\tau}=-\frac{1}{2}\int_{-1}^{1}R^2\sqrt{1+\left(\frac{1}{R}\frac{\partial R}{\partial \theta}\right)^2}\,u_Ad\eta \tag{5e}$$

Auxiliary relations

Before proceeding with the solution of systems 5, we would like to list for later use certain constraints satisfied by $R(\theta,\tau)$, as well as a general relation for the rate of change of particle shape. The dimensionless variable $R(\theta,\tau)$ describing the particle surface (Eq. 4a) must satisfy two constraints. The first is volume conservation which gives:

$$\int_{-1}^{1}R^3(\theta,\tau)d\eta=2, \tag{6a}$$

where

$$\eta=\cos\theta. \tag{6b}$$

The second constraint is that the center of mass of the particle remains at the origin, which is expressed as:

$$\int_{-1}^{1}R^4(\theta,\tau)\eta d\eta=0. \tag{7}$$

Slightly deformed sphere

This section is pertinent to the limiting case of a particle which differs only slightly from spherical. $R(\theta,\tau)$ and $u_A(\rho,\theta,\tau)$ can then be expanded in the series:

$$R(\theta,\tau)=R_0(\theta,\tau)+\epsilon R_1(\theta,\tau)+\epsilon^2R_2(\theta,\tau)+\cdots \tag{8a}$$

$$u_A(\rho,\theta,\tau)=u_0(\rho,\theta,\tau)+\epsilon u_1(\rho,\theta,\tau)+\epsilon^2u_2(\rho,\theta,\tau)+\cdots, \tag{8b}$$

where $\epsilon<<1$ is a small dimensionless parameter and R_i's are of $O(1)$ with respect to the parameter ϵ. The parameter ϵ is introduced as usual to indicate the order of approximation of the results finally obtained. For a slightly deformed sphere, the method of domain perturbation can be used to obtain an analytical solution and thus gain a qualitative understanding about the change of the surface shape. We just give a few important results without details of derivation:

$$Q=-1+\sqrt{[1+Q_0]^2-2\tau}+O(\epsilon^2), \tag{9a}$$

$$R=1+\epsilon\sum_{n=2}^{\infty}\beta_nP_n(\cos\theta)+O(\epsilon^2), \tag{9b}$$

$$u_A=\frac{1}{Q+1}\frac{1}{\rho}+\epsilon\sum_{n=2}^{\infty}\frac{Q(Q+2)}{(Q+1)(Q+n+1)}\beta_n(\tau)P_n(\cos\theta)\rho^{-(n+1)}+O(\epsilon^2). \tag{9c}$$

The zeroth and the first modes in R vanish by virtue of the condition of volume conservation. The nth mode β_n is governed by the differential equation:

$$\frac{d\beta_n}{d\tau}=\frac{(n+1)+(2-n)Q}{Q(Q+1)(Q+n+1)}\beta_n. \tag{10}$$

Integration of Eq. 10 using Eq. 9a yields:

$$\beta_n(\tau)=\beta_n(0)\frac{Q_0}{Q}\left(\frac{Q+n+1}{Q_0+n+1}\right)^{n-1}. \tag{11}$$

Since the sign $(d\beta n)/(d\tau)$ is determined by the values of n

and Q in Eq. 10, the second mode increases monotonically while the third and higher modes can increase or decrease depending on the Damköhler number, Q. For the third and higher modes, there is a critical Q below which the mode increases and above which it decreases. The critical value of the nth mode is given by:

$$Q_{cr} = \frac{n+1}{n-2}. \tag{12}$$

As the mode order n increases, the critical value tends to one. According to this analysis, all shapes, including the spherical, are unstable to small irregularities.

As an example, consider the evolution of a particle whose initial second mode is zero and for which the initial value of Q is large. Then, all the modes decrease until Q drops below four when the third mode will start growing. As Q declines further progressively, higher modes will start growing.

Particles with larger irregularities

In the previous section, the DP technique was applied to treat a slightly deformed sphere. Now, by using the BI technique we shall treat the same problem for a surface with larger irregularities which is beyond the scope of domain perturbation. With the use of the boundary condition,

$$u_A \to 1 \quad \text{as} \quad |\mathbf{x}| \to \infty,$$

Green's second identity (Stakgold, 1972) for Laplace's equation reduces to

$$4\pi - 2\pi u_{Ai} = \int_{\Omega_1} \left[-u_A \frac{\partial g}{\partial \nu} + g \frac{\partial u_A}{\partial \nu} \right] dS. \tag{13}$$

Here, Ω_1 is the smooth surface of the particle, and g is Green's function for three-dimensional Laplace equation. Applying the reaction boundary condition on the particle surface:

$$\frac{\partial u_A}{\partial \nu} = Q u_A, \tag{14}$$

we finally obtain

$$4\pi - 2\pi u_{Ai} = \int_{\Gamma_1} u_A \left(-\frac{\partial G}{\partial \nu} + QG \right) d\Gamma, \tag{15}$$

where

$$G = \int_0^{2\pi} g \, d\phi \tag{16}$$

and Γ_1 is the boundary line of axisymmetric particle.

Among various ways to represent the surface roughness, using the Legendre polynomials is the most convenient because of their completeness property. Using Legendre polynomials also provides convenient comparison with the results of the DP technique. We consider two modes of roughness represented by:

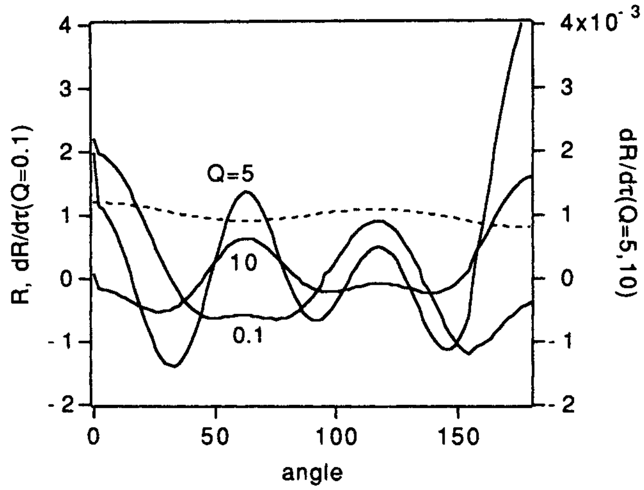

Figure 1. Surface distance from the origin (---), $R = 0.994 + (0.2)P_3$, and moving rate of surface (—), $(\partial R)/(\partial \tau)$, for $Q = 0.1, 5, 10$ vs. angle over surface.

$$R = a_3 + b_3 P_3(\eta) \quad \text{and} \quad R = a_4 + b_4 P_4(\eta).$$

These shapes must satisfy volume conservation,

$$\int_0^{\pi} R^3 \sin\theta \, d\theta = 2, \tag{17}$$

which imposes one relation between a_i's and b_i's.

After u_A is obtained using the BI technique, the dimensionless recession rate $(\partial R)/(\partial \tau)$ can be calculated from Eqs. 5d and 5e. Figure 1 shows the rate $(\partial R)/(\partial \tau)$ vs. position along the surface for the initial shape $R = 0.994 + (0.2)P_3$ and for three different Damköhler numbers $Q = 0.1, 5, 10$. It is recalled that for $n = 3$ the critical Q was equal to four. The graph for $Q = 0.1$ in Figure 1 shows that $(\partial R)/(\partial \tau)$ is positive for R larger

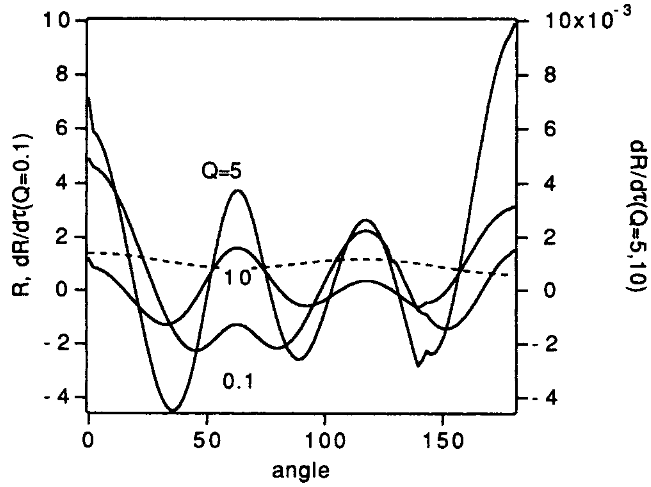

Figure 2. Surface distance from the origin (---), $R = 0.977 + (0.4)P_3$, and moving rate of surface (—), $(\partial R)/(\partial \tau)$, for $Q = 0.1, 5, 10$ vs. angle over surface.

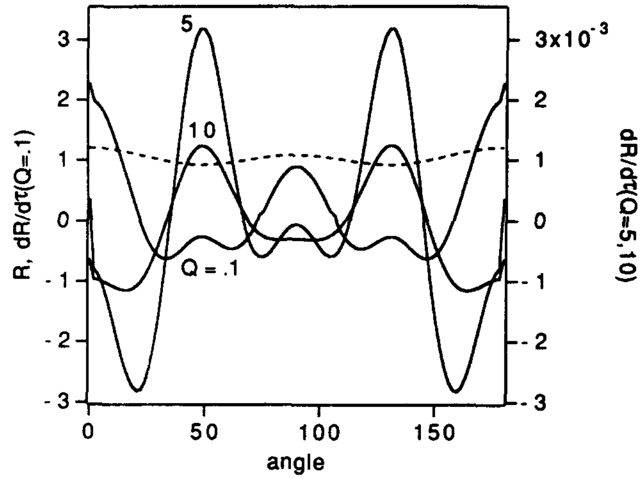

Figure 3. Surface distance from the origin (---), $R = 0.997 + (0.2)P_4$, and moving rate of surface (—), $(\partial R)/(\partial \tau)$, for $Q = 0.1, 5, 10$ vs. angle over surface.

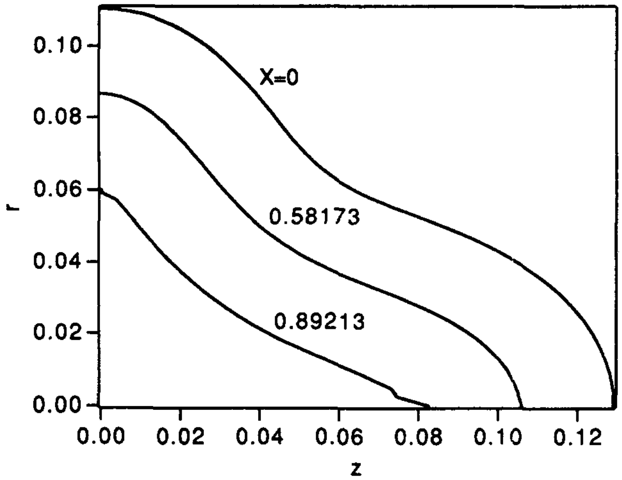

Figure 5. Typical example showing how the surface moves with conversion starting with $Q(0) = 0.1$ and $R = 0.990 + (0.3)P_4$.

than unity and vice versa. Thus, the particle becomes more and more nonspherical. For $Q = 10$ in the same figure $(\partial R)/(\partial \tau)$ is negative for R larger than unity and vice versa. Then, the shapes reduce to spherical, as was predicted by the DP technique. The curve for $Q = 5$ shows that the particle surface goes neither away from nor toward spherical with time, giving a mixed behavior, converse to a slightly nonspherical particle which goes toward spherical. Although the analysis using the domain perturbation does not show oscillation of shape for a deformed sphere, it happens to highly irregular shapes. The graphs for $R = 0.977 + (0.4)P_3$ in Figure 2 lead to the same discussions as done for $R = 0.994 + (0.2)P_3$.

Figures 3 and 4 displaying the curves of $(\partial R)/(\partial \tau)$ obtained for $R = 0.997 + (0.2)P_4$ and $R = 0.983 + (0.4)P_4$, respectively, lead to the discussions similar to those done above except the graphs of $(\partial R)/(\partial \tau)$ for $R = a_4 + b_4 P_4$ are symmetric just as R. The graphs for $Q = 0.1$ in Figures 3 and 4 show that $(\partial R)/(\partial \tau)$ is positive for R larger than unity and vice versa, and consequently imply the particle shapes become more and more nonspherical. Oppositely it is shown that for $Q = 10$ the particle shapes go toward spherical. At $Q = 5$, which is close to $Q_{cr} = 2.5$ obtained by the DP technique, the behavior seems transient (the shape shows a mixed behavior).

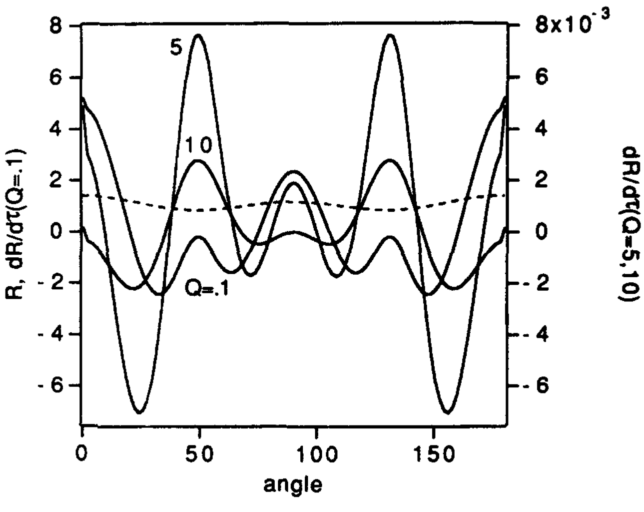

Figure 4. Surface distance from the origin (---), $R = 0.983 + (0.4)P_4$, and moving rate of surface (—), $(\partial R)/(\partial \tau)$, for $Q = 0.1, 5, 10$ vs. angle over surface.

Figure 5 shows an example of shape change with conversion. The initial particle shape is $R = 0.990 + (0.3)P_4$ and the initial Damköhler number, $Q(0) = 0.1$. The curves represent the particle shapes at three consecutive conversions, $X = 0$, 0.582, 0.892. Since the particle is symmetric rotationally and with respect to y axis, quarters of the particle are drawn. All the surface points are shown to shrink by equal amount. However, since the whole volume reduces, the surface roughness increases relatively. At 58.2% conversion, the overall particle shape is very close to the initial shape, but quite different from the initial shape at 89.2% conversion.

Since the Legendre functions are complete, any particle shape can be represented by their infinite series. Although only the effects of P_3 and P_4 modes were treated, one could attack any shape of particle in a similar way. A very irregular surface, having many modes, is expected to show an irregular surface evolution with time.

Particles lacking rotational symmetry

For particles without rotational symmetry, the terms related to the azimuthal ϕ-variation and which have been neglected so far must be retained. It turns out that to first order in ϵ, all the differential equations and boundary conditions remain the same as in the axisymmetric case. If the reduced particle radius R is expressed in terms of spherical harmonics,

$$R = 1 + \epsilon \sum_{m,n} \beta_{mn} Y_n^m(\theta,\phi), \tag{11}$$

then by following the same procedure as in the axisymmetric case, we obtain:

$$\frac{d\beta_{mn}}{d\tau}=\frac{(n+1)-(n-2)Q}{Q(Q+1)(Q+n+1)}\beta_{mn}. \tag{12}$$

Since the coefficient of β_{mn} at the right side does not contain m, the initial shape variations in the azimuthal direction are preserved as reaction progresses.

Conclusions

From the method of domain perturbation, the mode of $n=2$ increases with time but the higher modes increase or decrease depending on Q. The nth mode decreases if $Q>Q_{cr}=(n+1)/(n-2)$ and vice versa.

The boundary integral method applied to the particle shapes $a_3+b_3P_3$ and $a_4+b_4P_4$ with small ratios of b_i/a_i shows that the particle becomes more and more nonspherical for $Q=0.1$ and that the particle shape goes toward spherical for $Q=10$. The particle shows the transient behavior for $Q=5$. Highly irregular particles do not have sharp critical values of Q, but show mixed behaviors in a certain range around Q_{cr}.

Notation

$A(g)$ = gaseous reactant
$B(g)$ = gaseous product
b_1, b_2 = stoichiometric coefficients
c_A = concentration of A in gas
D_{AB} = binary diffusion coefficient
$\tilde{F}$ = function defining particle shape
g = Green's function for 3-D Laplace's equation
G = Green's function integrated in azimuthal angle (Eq. 16)
k = reaction constant
$P(s)$ = solid reactant
Q = Damköhler number (Eq. 4b)
$R(\theta,\tau)$ = dimensionless radial distance from particle center, $[\tilde{R}(\theta,\tau)]/[R_s(\tau)]$
$\tilde{R}(\theta,\tau)$ = dimensional radius of a surface point
$\tilde{R}_s(\tau)$ = dimensional radius of the fictitious sphere of equal volume
t = time
u_A = dimensionless concentration of A, c_A/c_{Ab}
$\mathbf{x}$ = dimensionless position vector, $\tilde{\mathbf{x}}/[R_s(\tau)]$
$\tilde{\mathbf{x}}$ = dimensional position vector
Y_n^m = spherical harmonics

Greek letters

β_n = coefficients used in expanding $R(\theta,\tau)$
Γ_1 = line boundary of axisymmetric domain
ϵ = small perturbation parameter
η = $\cos\theta$
θ = spherical angle
ν = outward normal unit vector on the particle surface
ρ = radial variable
ρ_s = molar density of solid
τ = dimensionless time variable defined by Eq. 4b
ϕ = azimuthal angle
Ω_1 = surface boundary of domain

Subscripts

A = gaseous reactant A
b = bulk position at ∞
i = singular point
0 = initial value
t = total rate all over particle surface

Superscripts

v = sphere of equal volume
s = sphere of equal surface area

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