Effectiveness Factors in Bidispersed Catalysts under Nonisothermal Conditions

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Introduction

Due to the method of preparation, namely, compaction of porous particles into pellets, many supported catalysts are characterized by bidispersed size distribution, with microparticles lying inside the pellets. Considerable work on diffusion and adsorption in bidispersed catalysts has been reported in the literature (Hashimoto et al., 1976; Uyanik, 1977; Dogu and Smith, 1975; Hashimoto and Smith, 1974), and both the micro- and macroparticle diffusivities can be determined experimentally (Dogu and Smith, 1975; MacDonald and Habgood, 1972; Ma and Lee, 1976; Kumar et al., 1982). Studies on the effectiveness of these catalysts also have been numerous. Thus by the incorporation of pore size distribution (Silveston and Hashimoto, 1971) the micro-macro particle effectiveness factors have been evaluated, while nonisothermal effectiveness factors have been obtained (Mingle and Smith, 1961) by varying several pore distribution functions. In a departure from these conventional studies, an additional parameter, α, the ratio of diffusion times in the macro- and microparticle regions has been defined (Ors and Dogu, 1979) and an analytical equation presented for effectiveness factors for a simple first-order reaction. The analysis has been subsequently extended to include nonlinear rate forms covering power law (Jayaraman et al., 1981, 1983) as well as Langmuir-Hinshelwood kinetics (Namjoshi et al., 1984).

The present study is addressed to the important problem of estimation of effectiveness factors for these types of catalysts in the presence of thermal gradients.

Theoretical Development

Referring to Figure 1, which shows a schematic diagram of the spherical micro-macro particle system, the governing equations for mass and heat conservation can be written in dimensionless form as

Microparticle

$$\nabla_x^2 C_i = \phi^2 \exp\left[\gamma\left(1 - \frac{1}{T_i}\right)\right] C_i,$$

$$C_i(x = 1) = C_a, \quad \left.\frac{dC_i}{dx}\right|_{x=0} = 0 \quad (1)$$

$$\nabla_x^2 T_i = -\phi^2 \beta \exp\left[\gamma\left(1 - \frac{1}{T_i}\right)\right] C_i,$$

$$T_i(x = 1) = T_a, \quad \left.\frac{dT_i}{dx}\right|_{x=0} = 0 \quad (2)$$

Macroparticle

$$\nabla_y^2 C_a = \alpha \left.\frac{dC_i}{dx}\right|_{x=1}, \quad C_a(y = 1) = 1, \quad \left.\frac{dT_a}{dy}\right|_{y=0} = 0 \quad (3)$$

$$\nabla_y^2 T_a = \alpha_T \left.\frac{dT_i}{dx}\right|_{x=1}, \quad T_a(y = 1) = 1, \quad \left.\frac{dT_a}{dy}\right|_{y=0} = 0 \quad (4)$$

Equations 1–4 can be appropriately combined to eliminate T_i and T_a to finally obtain

$$\nabla_x^2 C_i = \phi^2 \exp \cdot \left\{\gamma\left[1 - \frac{1}{1 - \frac{\beta\alpha_T}{\alpha}(C_a - 1) + \beta(C_a - C_i)}\right]\right\} C_i \quad (5)$$

where C_a refers to the dimensionless concentration in the macroparticle whose variations are described by Eq. 3, and the various parameters are defined as

$$\phi = \sqrt{(k/D_i)}\, r_i^2, \quad \beta = \frac{(-\Delta H) D_i C_{as}}{k_i T_s^s}, \quad \alpha = 3(1 - \epsilon)\frac{D_i}{D_a}\frac{R^2}{r_i^2},$$

$$\alpha_T = 3(1 - \epsilon)\frac{k_i}{k_p}\frac{R^2}{r_i^2}, \quad \gamma = E/R_g T_s^s \quad (6)$$

In writing Eqs. 1–5 the concentrations and temperatures in the micro- and macroparticle regions are dimensionalized with respect to the concentration and temperature, respectively, at the surface of the pellet.

Note the definitions of parameters α and α_T in Eq. 6: α denotes the ratio of the diffusion time for mass in the macroporous pellet to that in the microporous particle, while α_T refers to

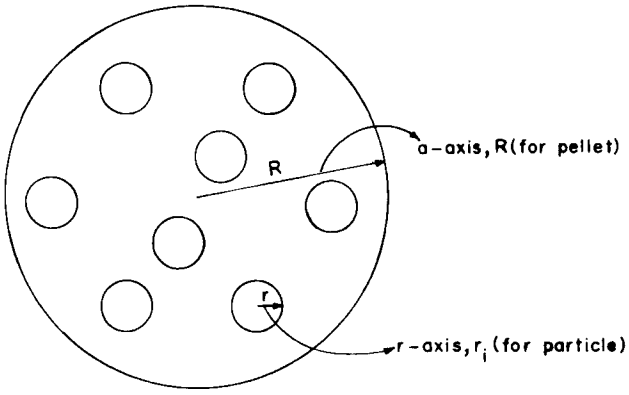

Figure 1. Diagram of micro-macro particles in a pellet.

the ratio of the thermal conductivity times for heat. The ratio D_i/D_a appearing in α is usually less than unity, while the ratio k_i/k_p appearing in α_T is usually far greater than unity. The ratio α_T/α is therefore always greater than unity in practical systems.

The set of Eqs. 3 and 5 has been solved numerically for various values of the parameters ϕ, β, γ, α, and α_T. The results are presented as plots of effectiveness factors. The method employed obtains the solution of Eq. 5 using a second-order polynomial (Galerkin method):

$$C_i = C_a + a_1(1 - u) + a_2u(1 - u), \quad u = x^2 \tag{7}$$

to give $dC_i/dx|_{x=1}$ for several values of C_a for a particular set of other parameter values (β, γ, α_T/α, ϕ). The method involves substituting Eq. 7 in Eq. 5, and we obtain

$$R_N = 6(a_2 - a_1) - 20a_2u - \phi^2 \exp\left\{\gamma\left[1 - \frac{1}{1 - \frac{\beta\alpha_T}{\alpha}(C_a - 1) + \beta(a_1(u-1) + a_2u(u-1))}\right]\right\} \times [C_a + a_1(1 - u) + a_2u(1 - u)] \tag{8}$$

where R_N refers to the remainder. Our interest is now to minimize the residual R_N, and for this purpose R_N is made orthogo-

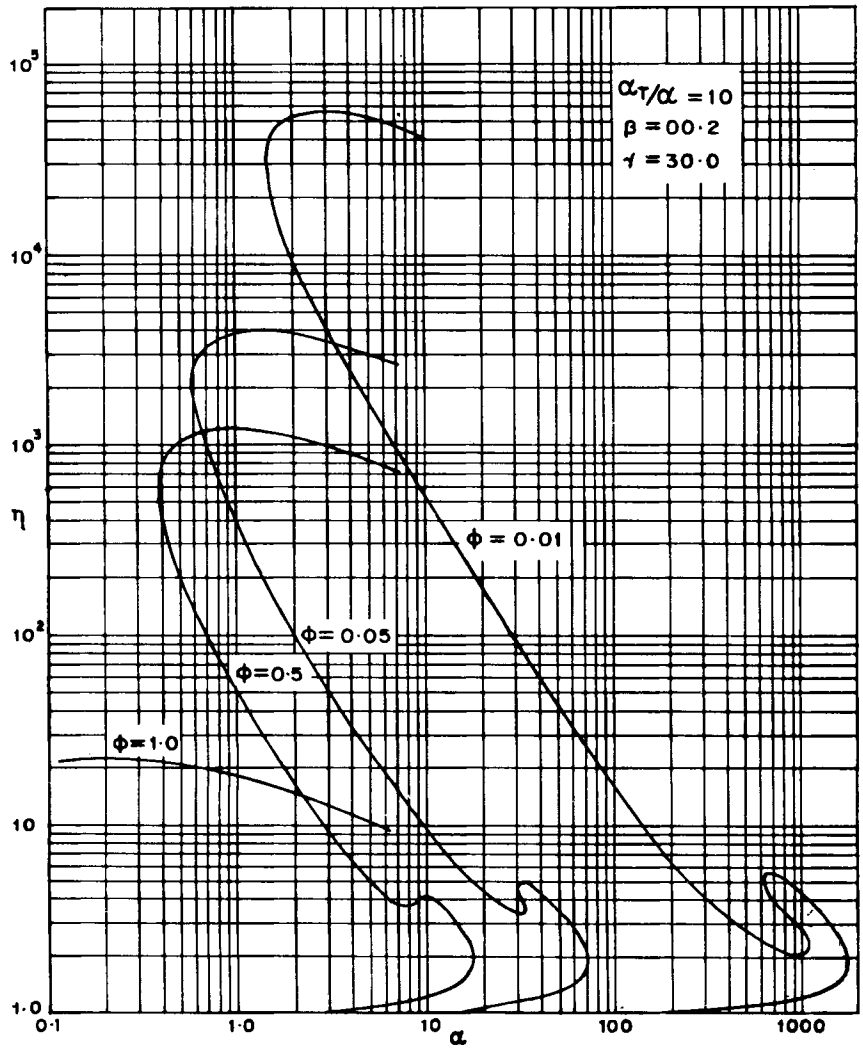

Figure 2. Effectiveness factors for nonisothermal micro-macro particle system: $\eta - \alpha$ variations with respect to ϕ.

nal on $\partial C_i/\partial a_k$, $k = 1, 2, \ldots, N$ over the volume of the spherical pellet. For $N = 2$, the resulting equations can be written as

$$\int_0^1 R_N(a, u)(1 - u)^{1/2}\, du = 0 \quad k = 1 \tag{9}$$

$$\int_0^1 R_N(a, u)(1 - u)u^{3/2}\, du = 0 \quad k = 2 \tag{10}$$

Integrals in these equations cannot always be evaluated analytically and may have to be solved numerically using quadratures.

Equations 9 and 10 can thus be written as

$$\int_0^1 F_j(u)(1 - u)u^{1/2}\, du = \sum_{k=1}^{M} W_k F_j(u_k) = 0 \tag{11}$$

where $F_j(u) = R_N(a, u)u^{j-1}$, $j = 1, 2, \ldots, N$. M may have any value $\geq N$. The u_k's are chosen to be the roots of the Jacobi polynomial $p^{(1,1/2)}$ (Villadsen and Michelsen, 1978). Equation 11 is solved using Gaussian quadratures to obtain a_1 and a_2, which are subsequently used in the calculation of the flux. In general, a large number of data points were generated and the results interpolated to obtain a value for $dC_i/dx|_{x=1}$ for any value of C_a. The spline interpolation scheme was used for this purpose. The information was subsequently employed in Eq. 3, which was solved using the method of Weisz and Hicks (1962). The effectiveness factor was finally obtained as

$$\eta = \frac{9 \left.\dfrac{dC_a}{dy}\right|_{y=1}}{\alpha\phi^2} \tag{12}$$

Results and Discussion

The effectiveness factors calculated thus are presented as $\eta - \alpha$ plots showing the influence of variations in ϕ, β, γ, and α_T/α. Figure 2 indicates the influence of ϕ on the $\eta - \alpha$ plot. The figure indicates the existence of a five-steady-states region which extends with decrease in ϕ. Thus for $\phi = 0.01$ the five-steady-states region covers the α-parameter space from $\alpha = 600$ to 1,100, while for $\phi = 0.05$, it covers a narrower α-range, 30–34. For $\phi = 0.1$ the five-steady-states region has completely disappeared but multiplicity (three states) still persists. For $\phi = 1$ multiplicity has disappeared altogether. Also, as evident from

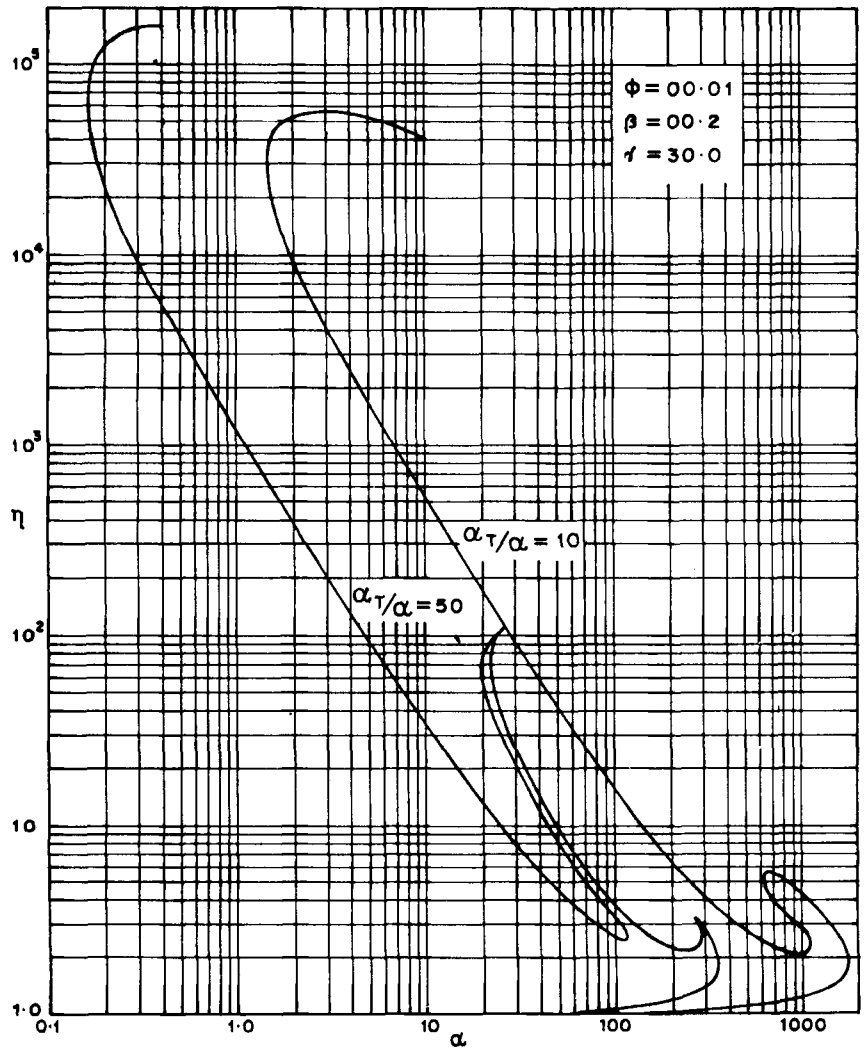

Figure 3. Effectiveness factors for nonisothermal micro-macro particle system: $\eta - \alpha$ variations with respect to α_T/α.

the figure, higher values of η are realized for lower values of α, especially when ϕ is also smaller.

Two points may be noted at this stage. First, the values of η as calculated are higher than those reported for monopore systems. A direct comparison with the monopore case, however, is not possible due to the presence of α and α_T in the present case. Second, the region where five steady states exist appears to shift to higher values of α when ϕ becomes smaller. The existence of five steady states in monoporous systems is known, especially when external transport limitations are present (Pereira and Varma, 1978). The present case reveals that the biporous nature of the catalyst can also induce five steady states in certain regions of the parameter space.

Figure 3 shows the influence of the ratio α_T/α on the $\eta - \alpha$ plot. The figure again reveals the existence of five steady states. The curve for $\alpha_T/\alpha = 50$ is especially interesting in that it reveals two different regions in the parameter space where five steady states can prevail. On increasing α, the figure reveals the multiplicity pattern 1-3-5-3-5-3-1. Such a pattern is rather unusual and provides perhaps the first instance of its occurrence. This figure also shows that higher values of η are realized when α_T/α is larger. The five-steady-states region occurs at lower values of α for higher values of α_T/α and the region in general is narrower than at lower values of the α_T/α. The intermediate states also lie closer to each other for higher values of (α_T/α).

Figure 4 shows the influence of β on the $\eta - \alpha$ plot. As expected, for a reaction of higher nonisothermicity the $\eta - \alpha$ plot shifts to the left. The five-steady-states region occurs at lower values of α, the intermediate states move closer to each other, and higher values of η can be realized at lower values of α. Figure 5 shows the influence of γ. Increasing γ has the same effect as increasing β, and the results indicated in Figures 4 and 5 are qualitatively in accord with those known for a monoporous system.

To summarize, the present work reports effectiveness factors for a micro-macro particle system in the presence of an exothermic first-order reaction. The results indicate that in general higher values of η can be realized for such systems in comparison with those for monoporous systems, especially at lower values of α. The system can possess five stationary states in a certain parameter region even in the absence of external transport limitations. The influence of parameters such as ϕ, β, γ, and α_T/α has been investigated and the results suggest that increase in the value of any of these parameters would shift the $\eta - \alpha$ plot to the

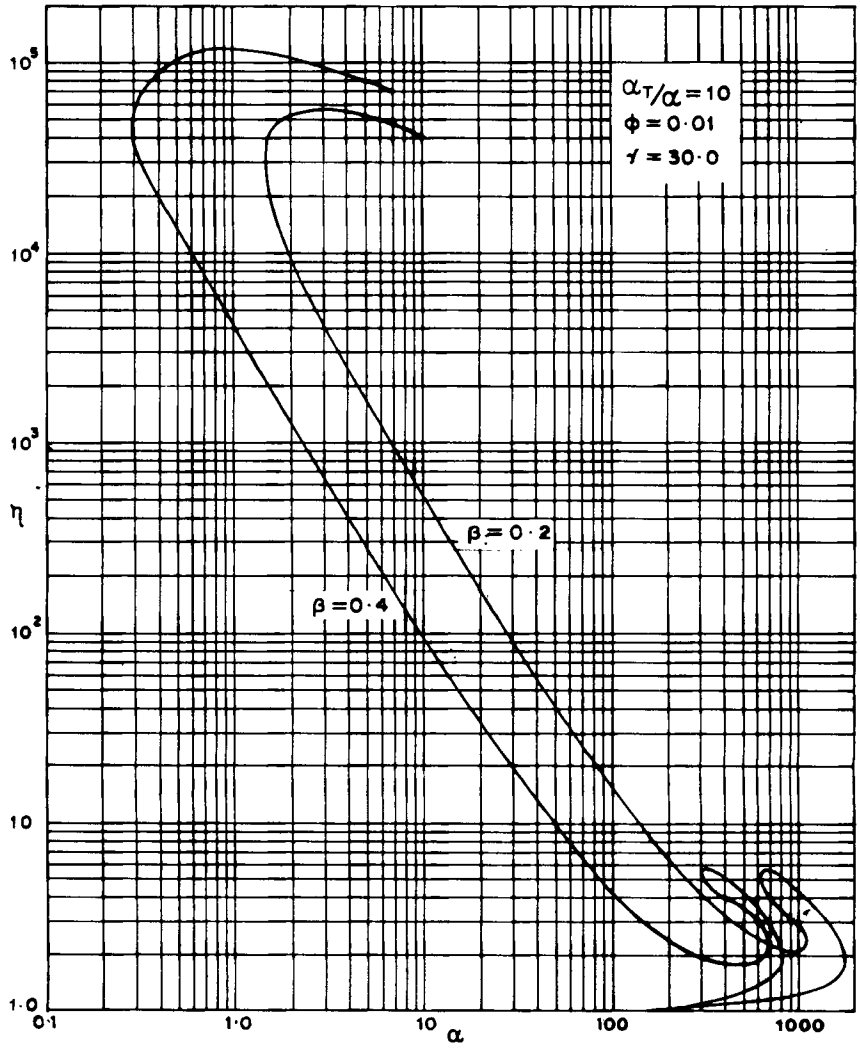

Figure 4. Effectiveness factors for nonisothermal micro-macro particle system: $\eta - \alpha$ variations with respect to β.

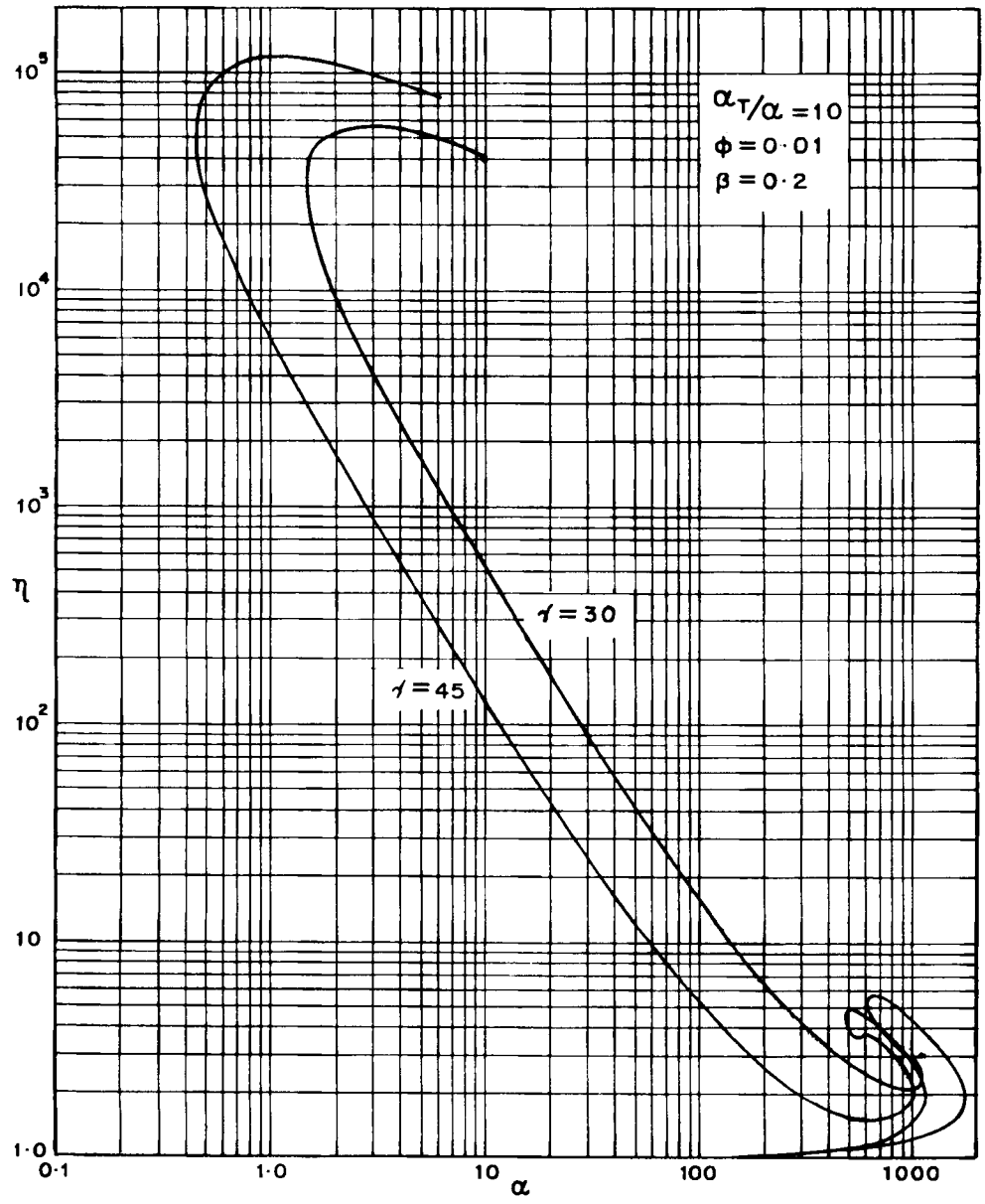

Figure 5. Effectiveness factors for nonisothermal micro-macro particle system: $\eta - \alpha$ variations with respect to γ.

left. The ratio α_T/α has an especially important influence in that two separate regions of five steady states can be identified. The influence of β and γ is similar to that for the monoporous system and has been quantified.

Notation

a_1, a_2 = polynomial constants
C_i = dimensionless concentration in microparticle
C_a = dimensionless concentration in macroparticle
C_{as} = concentration of species at the surface of the catalyst pellet
D_i = effective diffisivity in microparticle
D_a = effective diffusivity in macroparticle
k_i = thermal conductivity in microparticle
k_p = thermal conductivity in macroparticle
r_i = radius of the microparticle
R = radius of the macroparticle
T_a = dimensionless temperature in macroparticle
T_i = dimensionless temperature in microparticle
T_s^s = temperature at the surface of the catalyst pellet
u = parameter defined as x^2
x = dimensionless distance variable used in microparticle
y = dimensionless distance variable used in macroparticle

Greek letters

α = parameter defined as $3(1-\epsilon)(D_i/D_a)(R^2/r^2)$
α_T = parameter defined as $3(1-\epsilon)(k_i/k_p)(R^2/r_i^2)$
β = exothermicity factor defined as $(-\Delta H)D_iC_{as}/k_iT_s^s$
γ = defined as $E/R_gT_s^s$
η = effectiveness factor
ϕ = Thiele modulus
ϵ = void fraction of the pellet

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