Validity of the Parabolic Profile Assumption in Adsorption Studies

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INTRODUCTION

Modeling of many adsorption processes usually results in coupled partial differential equations involving time and spatial variables. Recently, several authors (Akulov and Ustinov, 1981; Liaw et al., 1979; Rice, 1982; Rice et al., 1983) have simplified the mathematics by assuming that the intraparticle concentration profile has a parabolic shape at all times. Such an assumption is intuitive but, nonetheless, researchers have found that the approximate solutions obtained using the parabolic profile are remarkably simple and agree well with the experimental data except for an initial period.

It is the objective of this short communication to investigate the assumption of an intraparticle parabolic profile by parametrically comparing the approximate solutions and the exact solutions for two physical systems: a single particle response, and batch adsorbent behavior. An extension to a quartic profile is also attempted.

THEORY

Single Particle

Two different models of adsorption will be considered; one is a pore diffusion model, the other is a solid diffusion model. No matter which model one chooses, it can be shown that the following nondimensional equations always rise

$$\frac{\partial A}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2 \frac{\partial A}{\partial x}\right) \tag{1}$$

$$\tau = 0; \quad A = 0, \tag{2a}$$

$$x = 0; \quad \partial A/\partial x = 0, \tag{2b}$$

$$x = 1; \quad \partial A/\partial x = Bi(1 - A), \tag{2c}$$

The nondimensional variables and parameters for the two adsorption models are tabulated in Table 1.

The solution of Eq. 1 is given in Crank (1975). The nondimensional uptake term can be written as:

$$\int_0^\tau \left.\frac{\partial A}{\partial x}\right|_1 d\tau = 2\frac{Bi^2}{(Bi - 1)^2}\sum_{n=1}^{\infty}\frac{\cos^2 \xi_n(1 - e^{-\xi_n^2\tau})}{\xi_n{}^2[1 + \cos^2 \xi_n/(Bi - 1)]}, \tag{3}$$

where ξ_n is determined from the following transcendental equation:

$$\xi_n \cos \xi_n = (1 - Bi) \sin \xi_n. \tag{4}$$

Now we would like to obtain the solution to Eq. 1 by an approximate method. In this method, the intraparticle concentration profile is assumed to have a parabolic shape at any instant of time

$$A = a_1 + a_2x^2. \tag{5}$$

Using Eq. 5, it is not difficult to prove that

$$\left.\frac{\partial A}{\partial x}\right|_1 = \frac{5}{(1 + 5/Bi)}(1 - \bar{A}), \tag{6}$$

in which the boundary condition of Eq. 2c has been used. Here $\bar{A}$ is the volumetric mean concentration. Multiplying Eq. 1 by $3x^2dx$, integrating the result from 0 to 1, and using the relation in Eq. 6, yields the following equation for $\bar{A}$:

$$\frac{d\bar{A}}{d\tau} = \frac{15}{(1 + 5/Bi)}(1 - \bar{A}), \tag{7}$$

which can be solved to yield

$$\bar{A} = 1 - \exp\left[-\frac{15\tau}{(1 + 5/Bi)}\right]. \tag{8}$$

Knowing the mean concentration as a function of time (Eq. 8), the nondimensional flux can be calculated from Eq. 6. The nondimensional uptake term is then obtained as follows:

$$\int_0^\tau \left.\frac{\partial A}{\partial x}\right|_1 d\tau = \frac{1}{3}\left[1 - \exp\left(-\frac{15\tau}{1 + 5/Bi}\right)\right]. \tag{9}$$

To justify the validity of the approximate solution, we define

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Table 1. Definitions of Variables and Parameters for a Single Particle with Two Different Models

Variables and Parameters	Pore Diffusion Model	Solid Diffusion Model
A	C/C_o	q/KC_o
x	r/R	r/R
τ	$D_e t/(\varepsilon + K)R^2$	$D_s t/R^2$
Bi	$k_m R/D_e$	$k_m R/KD_s$

the following ratio

$$R = \frac{\left[\int_0^\tau \left.\frac{\partial A}{\partial x}\right|_1 d\tau\right]_{\text{approx}}}{\left[\int_0^\tau \left.\frac{\partial A}{\partial x}\right|_1 d\tau\right]_{\text{exact}}} \tag{10}$$

Ideally, this ratio is desired to be unity, so that the approximation is nearly exact. The ratio is plotted in Figure 1 vs. nondimensional time τ. It is clear from Figure 1 that the approximate solution is valid when $\tau > 0.05$. To enhance this theoretical finding, we use Rice's (1982) experimental result having $R = 0.0105$ cm, $\mathfrak{D}_s = 1.86 \times 10^{-7}$ cm²/s. The real time domain for validity is

$$t > \frac{R^2(0.05)}{\mathfrak{D}_s} = 30 \text{ s} \tag{11}$$

It is noted that a solid diffusion model was used in Rice's work. Observing Figure 1 of Rice, the approximate solution deviates from the experimental data when $t < 20$ s, which is very close to the domain of validity predicted in Figure 1 of this work.

Batch Adsorber

To generalize the domain of validity for the approximate solution, we now consider the transient response of a batch adsorber. The nondimensional coupled equations for a batch adsorber are:

$$\frac{\partial A}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2 \frac{\partial A}{\partial x}\right) \tag{12a}$$

$$\frac{dA_b}{d\tau} = -N \left.\frac{\partial A}{\partial x}\right|_1, \tag{12b}$$

$$\tau = 0; \quad A = 0,\ A_b = 1, \tag{13a}$$

$$x = 1; \quad \partial A/\partial x = Bi(A_b - A), \tag{13b}$$

Rice et al. (1983) solved a similar system, except that adsorption was not accounted for nor was the finite nature of transfer at the boundary surface included. The nondimensional variables and parameters are defined in Table 2 for two models of adsorption, pore diffusion model and a solid diffusion model.

It is emphasized here that the experimentally observable bulk concentrations obtained for the solid and pore diffusion models are:

$$A_b = A_b^{(s)}(\tau, N^{(s)}, Bi^{(s)}) \tag{14a}$$

and

$$A_b = A_b^{(p)}(\tau, N^{(p)}, Bi^{(p)}), \tag{14b}$$

respectively.

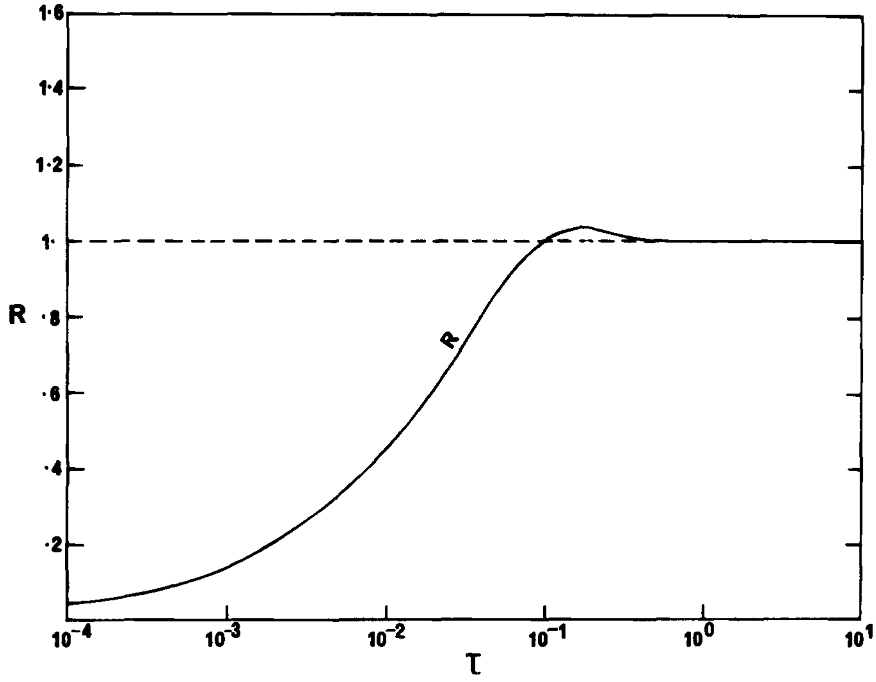

Figure 1. R(Eq. 11) vs. τ for a single particle.

TABLE 2. DEFINITIONS OF VARIABLES AND PARAMETERS FOR A BATCH ADSORBER WITH TWO DIFFERENT MODELS

Variables and Parameters	Pore Diffusion Model	Solid Diffusion Model
A	C/C_{bo}	q/KC_{bo}
A_b	C_b/C_{bo}	C_b/C_{bo}
x	r/R	r/R
τ	$D_e t/(\varepsilon + K)R^2$	$D_s t/R^2$
N	$\frac{3(m_p/\rho_p)(\varepsilon + K)}{V}$	$\frac{3(m_p/\rho_p)K}{V}$
Bi	$k_m R/D_e$	$k_m R/KD_s$

For most practical adsorption systems, the term ($\varepsilon + K$) shown in Table 2 is approximated by K; therefore the parameter N for the solid diffusion model is the same as that for the pore diffusion model. If these two models are to describe the transient response of the same physical process (i.e., A_b vs. real time), then it is required that

$$\mathfrak{D}_s = \frac{\mathfrak{D}_e}{K}. \tag{15}$$

For example, Rice (1982) used a solid diffusion model to describe his system of adsorption of sodium chloride into bifunctional resin (Bio Rad AG11A8), and it was found that $\mathfrak{D}_s = 1.86 \times 10^{-7}$ cm²/s and $K = 1.13$. Therefore if a pore diffusion model is used to describe his experimental system, the effective diffusivity of sodium chloride in the bifunctional resin is

$$\mathfrak{D}_e = K\mathfrak{D}_s = 1.13 \times 1.86 \times 10^{-7} = 2.10 \times 10^{-7}\ \text{cm}^2/\text{s}$$

The exact solution for A_b (experimentally observable) is obtained by a generalized integral transform and is given by

$$(A_b)_{\text{exact}} = \frac{3}{(3+N)} + \frac{1}{N}\sum_{n=1}^{\infty} e^{-\lambda_n^2\tau} \left[\frac{1}{2}\left(1 - \frac{\lambda_n^2}{N.Bi}\right) + \frac{3}{2N} + \frac{1}{2}\left(1 - \frac{1}{Bi}\right)\frac{\lambda_n^2}{N^2}\right]^{-1} \tag{16}$$

and λ_n is determined from the following transcendental equation

$$\tan\lambda_n = \frac{\lambda_n\left(1 - \frac{1}{N.Bi}\lambda_n^2\right)}{1 + \left(1 - \frac{1}{Bi}\right)\left(\frac{1}{N}\right)\lambda_n^2} \tag{17}$$

Following the same procedure described earlier, an approximate solution for A_b in the batch adsorber is obtained:

$$(A_b)_{\text{approx}} = \frac{3}{(N+3)} + \frac{N}{(N+3)}\exp\left[-\frac{5(3+N)\tau}{(1+5/Bi)}\right]. \tag{18}$$

To justify the validity of the approximate solution, we investigate the bulk composition ratio

$$R = \frac{(A_b)_{\text{approx}}}{(A_b)_{\text{exact}}} \tag{19}$$

It is noted that the two solutions yield the same steady state. The following ranges for N and Bi are expected for most practical systems: $N\varepsilon[0,5]$ and $Bi\ \varepsilon[20,\infty)$. A value of $N = 5$ corresponds to the case of high adsorption capacity. The effect of N and Bi on the ratio R of Eq. 19 is shown in Figures 2 and 3, respectively. It is clear from these figures that if $N < 2$, the

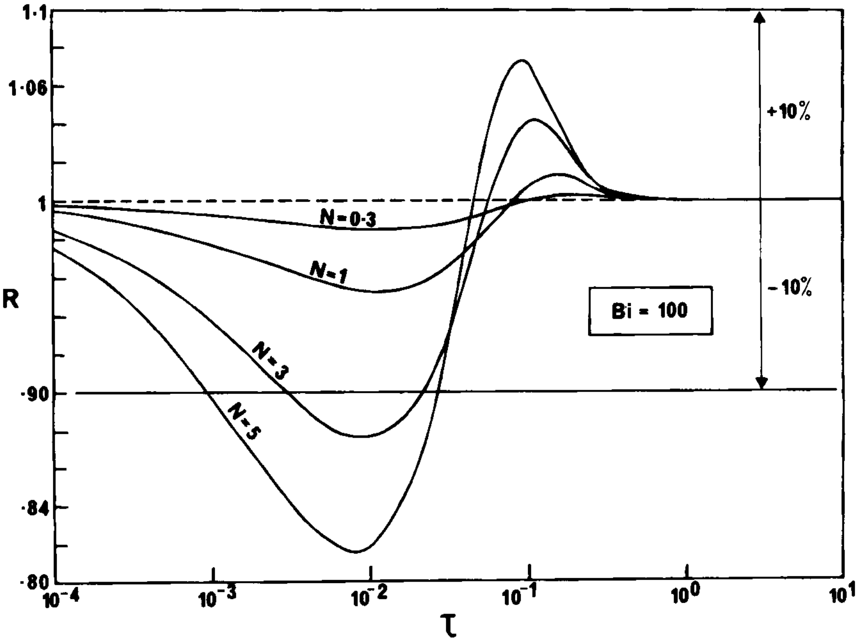

Figure 2. R(Eq. 20) vs. τ for a batch adsorber with N as the varying parameter.

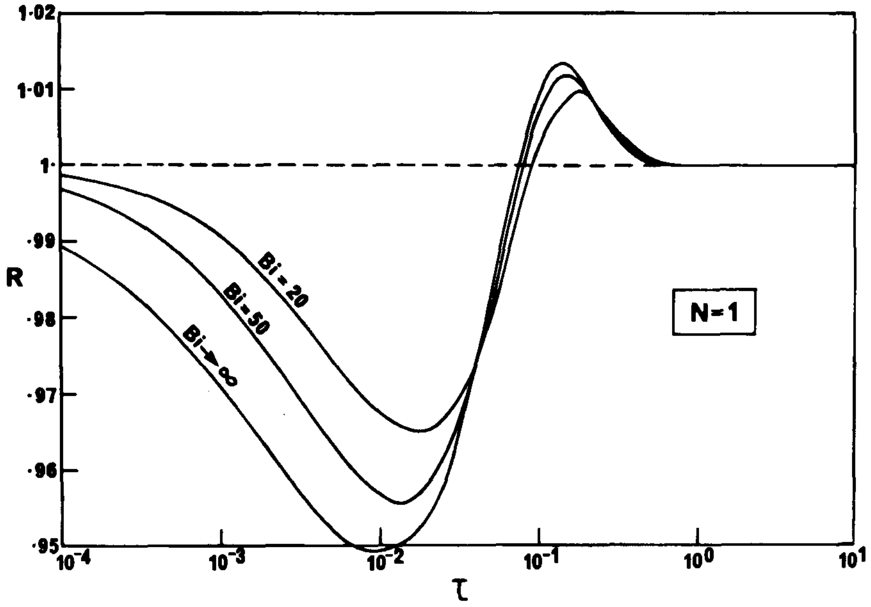

Figure 3. *R* (Eq. 20) vs. *τ* for a batch adsorber with *Bi* as the varying parameter.

approximate solutions are valid throughout the time domain if a deviation of ±10% is acceptable. However, if $N > 2$, the time domain of validity of the approximate solution is

$$\tau > \tau_0 = 0.03. \tag{20}$$

Therefore, if we apply this result to Rice's system of batch adsorber having $R = 0.0105$ cm, $\mathfrak{D}_s = 1.86 \times 10^{-7}$ cm²/s, the time domain of validity is

$$t = \frac{R^2(0.03)}{\mathfrak{D}_s} = 18 \text{ s} \tag{21}$$

So the approximate solution is valid only when t is greater than 18 s. This is very consistent with Rice's result that the experimental data deviate from the approximate solution when $t <$ 20 s.

Combining the result of this section and that of the single particle gives the time domain of validity of the approximate solutions using a parabolic profile

$$\tau > \tau_o = 0.05. \tag{22}$$

In dimensional terms, the time must be greater than t_o, where

$$t_o = 0.05 \frac{\varepsilon R^2}{\mathfrak{D}_e} \tag{23}$$

If the effective diffusivity is written in terms of pore fluid diffusivity $\mathfrak{D}$ and the particle tortuosity (i.e. $\mathfrak{D}_e = \varepsilon\mathfrak{D}/\tau$) Eq. 23 then becomes:

$$t_o = \frac{0.05\, R^2\, \tau}{\mathfrak{D}}. \tag{24}$$

This equation reveals that smaller particles develop parabolic profiles very quickly and, with particles of a given size, the profiles take longer to develop as tortuosity increases.

A QUARTIC PROFILE APPROXIMATION

In the previous section we justified the parabolic profile approximation assumption and concluded that when the nondimensional time scaled with respect to the diffusion time is greater than 0.05, the approximate solutions may be used confidently for prediction or design purposes. In this section we attempt to make a logical extension of that assumption: The intraparticle concentration profile is assumed to have a quartic profile at any instant of time.

$$A = a_1 + a_2x^2 + a_3x^4. \tag{25}$$

From Eq. 25 it is not difficult to prove that

$$\left.\frac{\partial A}{\partial x}\right|_1 = \frac{1}{3}(27A_1 + 8A_o - 35\bar{A}), \tag{26}$$

where $\bar{A}$ is the volumetric mean concentration, A_1 is the concentration at $x = 1$, and A_o is the concentration at $x = 0$.

To test the validity of the quartic profile assumption, we consider a single particle analysis. The nondimensional governing equations are given in Eq. 1. Multiplying Eq. 1 by $3x^2\,dx$, integrating the result from 0 to 1, and making use of Eqs. 26 and 2c to eliminate A_1, we obtain

$$\frac{d\bar{A}}{d\tau} = \frac{1}{(1 + 9/Bi)}(27 + 8A_o - 35\bar{A}), \tag{27}$$

and

$$\left.\frac{\partial A}{\partial x}\right|_1 = \frac{1}{3\left(1 + \dfrac{9}{Bi}\right)}(27 + 8A_o - 35\,\bar{A}). \tag{28}$$

It is noted that Eq. 27 now involves the centerline concentration A_o. Therefore, before Eq. 27 can be solved, an equation for A_o must be found.

Evaluating Eq. 1 at the center of the particle yields

$$\frac{\partial A_o}{\partial \tau} = \nabla^2 A|_o. \tag{29}$$

Using the quartic approximation (Eq. 25), it is not difficult to show that

$$\nabla^2 A|_o = (35\bar{A} - 15A_1 - 20A_o). \tag{30}$$

Next, combining Eqs. 30 and 2c to eliminate A_1 gives:

$$\nabla^2 A|_o = \frac{1}{(1 + 9/Bi)} \left[35\left(1 + \frac{4}{Bi}\right)\bar{A} - 20\left(1 + \frac{7}{Bi}\right)A_o - 15 \right]. \qquad (31)$$

Finally, substituting $\nabla^2 A|_o$ of Eq. 31 into Eq. 29 yields an ordinary differential equation for A_o:

$$\frac{dA_o}{d\tau} = \frac{1}{\left(1 + \frac{9}{Bi}\right)} \left[35\left(1 + \frac{4}{Bi}\right)\bar{A} - 20\left(1 + \frac{7}{Bi}\right)A_o - 15 \right]. \qquad (32)$$

Equations 27 and 32 are coupled first-order differential equations in terms of A_o and $\bar{A}$. Their solutions are

$$\bar{A} = 1 + C_1 e^{r_1 \alpha \tau} + C_2 e^{r_2 \alpha \tau}, \qquad (33)$$

$$A_o = 1 + \frac{C_1}{8}(r_1 + 35)e^{r_1 \alpha \tau} + \frac{C_2}{8}(r_2 + 35)e^{r_2 \alpha \tau}. \qquad (34)$$

where

$$C_1 = \frac{27 + r_2}{r_1 - r_2}, \qquad C_2 = \frac{27 + r_1}{r_2 - r_1}, \qquad (35)$$

$$r_{1,2} = \frac{-(35 + 20\gamma) \pm \sqrt{\Delta}}{2}, \qquad \Delta = (35 - 20\gamma)^2 + 1{,}120\beta \qquad (36)$$

$$\alpha = \frac{1}{(1 + 9/Bi)}, \qquad \beta = 1 + \frac{4}{Bi}, \; \gamma = 1 + \frac{7}{Bi} \qquad (37)$$

Knowing the mean and centerline concentrations given in Eqs. 33 and 34, the nondimensional flux is given in Eq. 28. Then the nondimensional uptake term is

$$\int_0^\tau \frac{\partial A}{\partial x}\bigg|_1 d\tau = \frac{1}{3}\left[C_1(e^{r_1 \alpha \tau} - 1) + C_2(e^{r_2 \alpha \tau} - 1)\right]. \qquad (38)$$

To justify the validity of the approximate solution using the quartic profile approximation, we plot the following ratio as before:

$$R = \frac{\left[\int_0^\tau \frac{\partial A}{\partial x}\Big|_1 d\tau\right]_{\text{approx}}}{\left[\int_0^\tau \frac{\partial A}{\partial x}\Big|_1 d\tau\right]_{\text{exact}}} = \frac{\frac{1}{3}\left[C_1(e^{r_1 \alpha \tau} - 1) + C_2(e^{r_2 \alpha \tau} - 1)\right]}{\sum_{n=1}^{\infty} \frac{\langle 1, K_n \rangle^2 (1 - e^{-\xi_n^2 \tau})}{\langle K_n, K_n \rangle}} \qquad (39)$$

vs. nondimensional time τ, Figure 4. The same ratio for the parabolic profile approximation is also plotted in Figure 4. It is seen in this figure that the quartic profile approximation is only slightly superior to the parabolic profile approximation. The quartic profile approximate solution is valid when the nondimensional time τ is greater than 0.015, compared to 0.05 for the parabolic profile approximate solution. However, the complexity involved in the quartic analysis does not justify the use of this approximation in the preliminary study of adsorption processes.

CONCLUSION

The simple parabolic profile model for intraparticle composition was tested for two physical systems. It was shown that early time experiments using the approximate models would be in error by around 10%, but for larger times $\tau > 0.05$ the parabolic model is quite satisfactory and leads to significant simplications in model building. When a quartic profile assumption is made, the approximate solution is found to be valid when $\tau > 0.015$ but the advantage of simplicity is lost.

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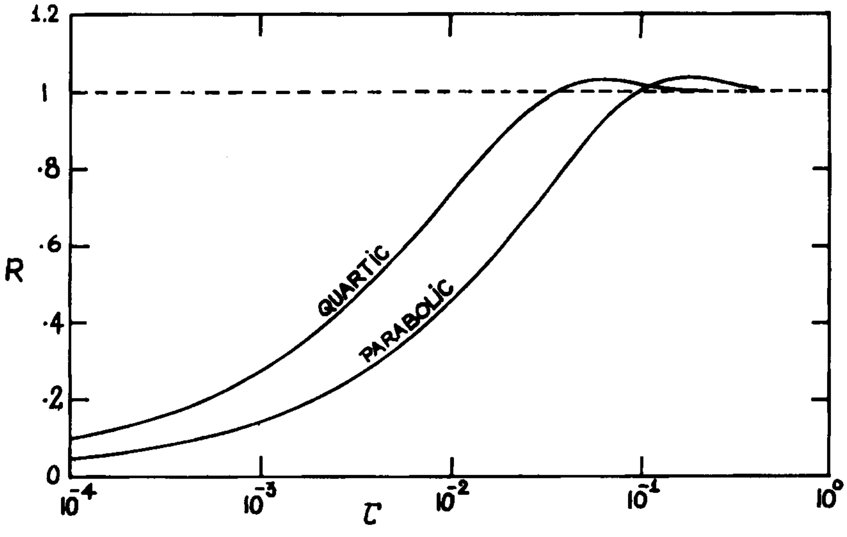

Figure 4. R (Eq. 41) vs. τ for quartic and parabolic approximations.

NOTATION

A = nondimensional concentration, defined in Table 1
$\bar{A}$ = volumetric mean concentration
A_b = nondimensional bulk concentration, defined in Table 2
Bi = Biot number for mass transfer, defined in Table 1
C_n = coefficient, defined in Eq. 17
$\mathfrak{D}_e$ = effective pore diffusivity
$\mathfrak{D}_s$ = solid diffusivity
k_m = mass transfer coefficient
K = linear equilibrium adsorption constant
m_p = mass
N = parameter, defined in Table 2
R = ratio, defined in Eqs. 11 and 20
t = real time
V = volume
x = nondimensional spatial variable
ε = particle voidage
λ = eigenvalue, defined in Eq. 18
ξ_n = eigenvalue, defined in Eq. 5
τ = nondimensional time, defined in Table 1
∇^2 = Laplacian operators defined in Eq. 2

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