On the Transient Heat Transfer through the Solid Phase in Aggregates and Deposits

Margaritis Kostoglou and Athanasios G. Konstandopoulos*

Aerosol & Particle Technology Laboratory, Center for Research & Technology Hellas/Chemical Process Engineering Research Institute, P.O. Box 361, Thermi 57001 Thessaloniki, Greece

In this study, explicit criteria are derived for the applicability of the uniform temperature approximation (UTA) to unsteady heat transfer through the solid phase in assemblies of spheres. The sources of unsteadiness studied are temperature variation and contact area variation. It is shown that, for the case of temperature variation, the UTA cannot be used for a certain range of frequency of the fluctuations. For the case of contact area variation, the UTA is shown to be applicable in all cases, provided that the contact radius is smaller than 10% of the particle radius. Following the assessment of its validity, the UTA is employed to illustrate the effect of aggregate and deposit morphology on the aggregate thermal relaxation behavior, considering the limiting case of linear aggregates and simple two-dimensional on-lattice deposits.

Introduction

The problem of unsteady heat transfer through the solid phase between particles in contact is of great importance at all size scales. Unsteady heat conduction behavior can be caused not only by temperature variations, but also by variations in the contact area, between the contacting bodies, as, for example, in the case of particle impact on a surface or on another particle. A relevant example at the nanoscale (10−100 nm) is the heat-transfer characteristics of particle aggregates (e.g., flame-produced inorganic materials as well as soot) that consist of interconnected spherical subunits (primary particles). Of special interest is the thermal response of the aggregate in the case of aggregate-to-surface heat transfer[1] as well as interaggregate heat transfer (e.g., after local heating with laser beams[2,3]). Below a few nanometers, the applicability of the macroscopic Fourier law can come into question, because the length scale associated with the energy carriers becomes comparable to the characteristic length of the structure (i.e., nanoparticle size).[4] At the micrometer scale, the heat-conduction problem is of special interest for the microelectronics industry.[5] Modeling of the thermal response of particulate thin films and deposits can be employed in conjunction with heating experiments under well-controlled conditions (e.g., under vacuum to restrict heat transfer through only the solid phase of the thin film/deposit) to characterize the film microstructure. At the millimeter scale, (i.e., for granular materials) problems related to the effective thermal conductivity of packed beds[6,7] are well-known. Finally, at the macroscopic scale, an obvious application is heat transfer between the components of mechanical equipment (e.g., rotary devices).[8] In this case, gas-phase heat transfer can be omitted because of the magnitude of the thermal conductivity of the (metalic) machinery components with respect to that of air.

The present work is motivated by the need to understand the thermal response characteristics of aggregates of spherical particles, as such aggregates are ubiquitous in many industrial applications as products (e.g., inorganic flame-generated aerosols) or as undesired byproducts of fossil fuel combustion (soot and ash). The transient thermal response during surface impact has been studied only for spherical particles,[1] so there is a need to extend the theory to the case of aggregates and particulate deposits. In the present paper, a mathematical approach that permits this extension is evaluated.

The corresponding steady-state problem has been extensively analyzed with a variety of methods. For dense particle assemblies (homogeneous at the macroscale), it is possible to extend the results of the steady-state analysis simply by solving the unsteady macroscale (homogeneous) heat-transfer equation with an effective thermal conductivity given by the steady-state theory. In practice, particulate deposits often have a loose structure,[9] and aggregate morphology is too complex[10] to be described with a homogeneous model. In these cases, the unsteady heat-transfer problem must be solved at the particle scale. For interparticle contact areas much smaller than the particle surface area, it can be assumed that the temperature in each particle is uniform (uniform temperature approximation, UTA). This approximation has already been established for the steady-state case[11] and provides a great simplification because the resulting network problem is easily solved with numerical linear algebra methods.[12] The corresponding approximation for the transient case leads to a dynamic network problem that also represents a great simplification. The scope of the present work is the investigation of the applicability limits of the UTA to the unsteady heat-transfer problem for simultaneous temperature and contact area variations. The results of this work are also applicable to the contact charge transfer between particles and surfaces.[13]

The structure of the paper is as follows: First, the mathematical problem is formulated for the case of a sphere in contact with a plane. This represents a sufficient unit problem for evaluating the range of validity of UTA and, therefore, its applicability to interparticle contact problems as well. The mathematical analysis is given in the next section. A single integral equation is derived to describe the evolution of the contact point temperature as a function of the particle

* Corresponding author. Fax: + 30 310 498-190. E-mail: agk@cperi.certh.gr.

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surface temperature variation. Although this equation cannot be solved for the complete evolution of the particle temperature, it is exploited in an indirect way. That is, the validity of UTA is stated as a null hypothesis and is employed to compute the mean temperature of the particle. In addition, the mean temperature is computed using the exact integral equation to provide a consistency check. The difference between the two results for the mean temperature determines whether the null hypothesis (i.e., the validity of the UTA) is true or false. Using the above metholodgy, the applicability criteria for the UTA are derived first for the case of temperature variation and then for the case of contact area variation. The UTA can be also used for spheres with multiple contacts between them, provided that the single contact criteria (despite their derivation for a simple geometry) are fulfilled. Finally, two simple applications of the UTA are analyzed to show the influence of aggregate and deposit structure on transient heat-transfer behavior.

Problem Formulation

The unit problem studied involves an almost-spherical particle of radius R having a small but finite contact area A with a perfectly flat surface and exchanging heat through conduction. The contact area A is assumed to remain circular with radius r_c ($A = \pi r_c^2$). The particle has a slightly perturbed spherical shape because of the finite contact area. In this work, the case in which the radius of the contact area is much smaller than the radius of the particle (i.e., $r_c/R < 0.1$) is examined. The problem has two distinct, widely disparate size scales (r_c, R), so its direct numerical solution with some kind of discretization scheme is quite demanding. As an example, we cite the finite-element solution of the steady-state heat-transfer problem for two spheres with a finite contact area presented by Cheng et al.[7] Although in that work care is taken for denser discretization in the contact region, one can see that only two elements are used for the contact radius discretization for the case $r_c/R = 0.1$. The analytical solution of a similar problem for planar surfaces shows that the heat flux at the contact area is a sensitive function of the radius and that the two-element discretization is a quite poor representation of the geometry. For smaller r_c/R values, the direct numerical solution is even more difficult. On the other hand, a general scale separation procedure can greatly simplify the problem. Fortunately this approximation has errors of order $(r_c/R)^2$ because of the unique features of the near-contact region between spheres.

Siu and Lee[14] used a method with multiple grids to solve the thermal energy balance for a spherical particle with two contacts and an arbitrary angle between them. The quantity of interest, the heat-transfer resistance of the sphere, is defined as the ratio of the difference between two imposed temperatures at two portions of its external surface to the resulting heat flux. Siu and Lee[14] presented correlations of the above-defined heat-transfer resistance with the contact area (for circular contacts) and the angle defined by the two contacts. According to these correlations for the case of two antidiametric contacts, the error of neglecting intraparticle resistance (or equivalently assuming uniform temperature for the particle) is 12% for $r_c/R = 0.1$ and less than 2% for $r_c/R = 0.01$. This result can be obtained without direct numerical solution by employing the present scale separation procedure.

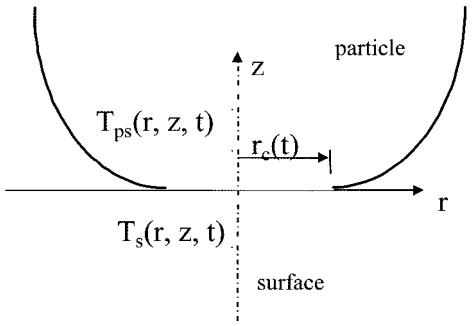

Figure 1. Geometry of the small-scale problem.

The general problem is decomposed into two subproblems, one at the particle scale and the other at the contact scale. The two subproblems are connected through matching of their boundary conditions. A key simplification achieved is that the sphere can be replaced by a second-order surface (paraboloid) in the region of the contact. Ignoring the finite extent of the contact area introduces an error of order $(r_c/R)^2$ because R is the characteristic scale of the problem and the area is proportional to the radius squared. Accordingly at the large scale, the particle can be assumed to be a perfect sphere, and the finite heat-transfer area can be shrunk to a point and treated as a singularity. For the contact-area-scale (small-scale) problem, it can be assumed that the contact is equivalent to that between two infinite planes. Substituting (in the small-scale problem) the sphere−plane contact with a contact between two planes also introduces an error of order $(r_c/R)^2$ because this is the first term of the Taylor expansion of the spherical surface equation around the contact point. Taking into account all of the above considerations, allows the general problem to be decomposed into the small-scale and large-scale subproblems described below with an overall error of order (r_c/R).[2] In the following equations, T_{ps} and T_{pL} are the particle temperatures for the small- and large-scale problems, respectively; T_s is the surface temperature (it enters only into the small-scale problem); a_p, a_s, k_p, and k_s are the thermal diffusivities and conductivities of the particle and surface, respectively; and T_c is an externally imposed temperature.

Small-Scale Problem (in cylindrical coordinates r, z with origin at the center of the contact area, and positive z semiaxis pointing toward the particle; see Figure 1)

$$\frac{\partial T_{ps}}{\partial t} = a_p \nabla_{r,z}^2 T_{ps} \quad z > 0 \tag{1a}$$

$$\frac{\partial T_s}{\partial t} = a_s \nabla_{r,z}^2 T_s \quad z < 0 \tag{1b}$$

Boundary conditions

$$\text{(i) for } z = 0, \quad r < r_c \; k_p \frac{\partial T_{ps}}{\partial z} = k_s \frac{\partial T_s}{\partial z}, \quad T_s = T_{ps} \tag{2a}$$

$$\text{for } z = 0, \quad r > r_c \; \frac{\partial T_{ps}}{\partial z} = \frac{\partial T_s}{\partial z} = 0 \tag{2b}$$

$$\text{(ii) for } z = -\infty, \quad T_s = T_e(t) \tag{2c}$$

$$\text{(iii) for } z = \infty, \quad T_{ps} = T_{pL} \; (r = 1, \theta = 0) \tag{2d}$$

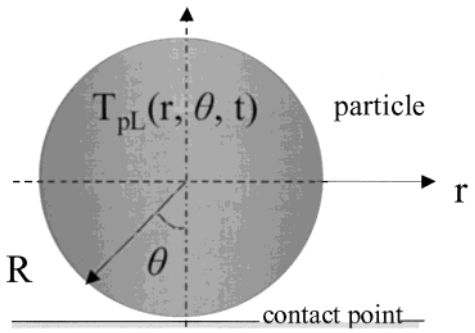

Figure 2. Geometry of the large-scale problem.

Large-Scale Problem (in spherical coordinates r, θ with origin at the center of the particle and angle $\theta = 0$ to denote the contact point; see Figure 2)

$$\frac{\partial T_{pL}}{\partial t} a_p \nabla_{r,\theta}^2 T_{pL} \tag{3}$$

Boundary conditions

(i) for $r = R$,

$$k_p \frac{\partial T_{pL}}{\partial r} = -q_w \delta(\theta) = -\delta(\theta) 2\pi \int_0^{r_c} k_p \left(\frac{\partial T_{ps}}{\partial z}\right)_{z=0} r\,dr \tag{4}$$

where $\delta(\theta)$ is a Dirac delta function in units of (length)$^{-2}$ having the following surface integrals on the sphere $\int_S \delta(\theta)\ d\mathbf{S} = 1$ and $\int_S F(\mathbf{S})\ \delta(\theta)\ d\mathbf{S} = F(\theta{=}0)$ for an arbitrary function F defined on the surface of the particle.

The coupling between the two subproblems is achieved through the boundary conditions in eqs 2d and 4. The boundary condition in eq 2d corresponds to the leading order matching between the inner and outer solutions in singular perturbation problems.[15] It is assumed that, initially ($t = 0$), the particle and the surface are in thermal equilibrium and have a constant temperature T_o. The objective of the present work is to find the response of the particle temperature field to an imposed external temperature disturbance $T_e(t)$.

Analysis and Results

The characteristic times of the two subproblems are $t_L = 1/(a_p R^2)$ and $t_s = 1/(a_s r_c^2)$. Obviously the ratio t_s/t_L is of order $(r_c/R)^2$. This means that changes in the surface temperature with characteristic times of order t_s cannot be sensed by the particle, which has a much larger characteristic thermal response time. For this reason, only surface temperature changes with characteristic times larger than t_s need to be studied. In this case, the small-scale problem can be considered as a series of steady states (quasi-steady state) and can be solved analytically to give the appropriate boundary conditions for the large-scale problem in closed form. This analytical solution is given by Batchelor and O'Brien[11] as

$$q_w = 4 r_c \frac{k_s k_p}{k_s + k_p} [T_{pL}(R,0,t) - T_c(t)] \tag{5}$$

The approach to the steady state given above has been studied by Greenwood[16] using asymptotic methods.

To simplify the analysis, the following dimensionless quantities are introduced

$$T = \frac{T_{pL} - T_o}{T_o}, \quad \bar{T}_e = \frac{T_e - T_o}{T_o}, \quad \bar{r} = \frac{r}{R}, \quad \tau = \frac{t a_p}{R^2} \tag{6}$$

and the problem that must be solved takes the form

$$\frac{\partial T}{\partial t} = \nabla_{\bar{r},\theta}^2 T \tag{7}$$

with boundary condition at $\bar{r} = 1$

$$\frac{\partial T}{\partial \bar{r}} = B[4\pi R^2 \delta(\theta)][\bar{T}_e(\tau) - T] \tag{8a}$$

where

$$B = 4\left(\frac{r_c}{R}\right)\frac{k_s}{k_p + k_s} \tag{8b}$$

and initial condition $T = 0$. The above problem is a transient two-dimensional problem with a singular boundary condition. The direct numerical solution requires a dense nonuniform grid to capture accurately the boundary singularity. Checking the accuracy of the solution in such a problem is difficult, and an error estimation cannot be derived easily. On the other hand, the linearity of the problem can be exploited. The transformation to an integral equation is ideally suited to the particular problem because the boundary singularity renders it one-dimensional.

In general, the transformation of eq 7 into an integral equation can be done in two ways, by the integral transform method[17] and by the Green's function method.[18] The second method is preferable because it has a clearer physical meaning. The boundary condition in eq 8 is of the mixed Neumann−Robin type, so the conventional approach, formulated for nonmixed boundary conditions, cannot be used. On the other hand, the alternative approach formulated by Arce et al.[19] for one-dimensional problems can easily be extended to the present two-dimensional problem. According to this method, the temperature of any point of the sphere is given by a superposition of Green's functions as

$$T(\bar{r},\theta,\tau) = \int_S \int_0^\tau \left(\frac{\partial T}{\partial \bar{r}}\right)_{\bar{r}=1} G(\bar{r},\theta,\tau;\bar{r}',\theta',\tau')\ d\tau'\ d\mathbf{S} \tag{9}$$

where the function G is the transient axisymmetric Neumann−Green function of the Laplacian operator for the spherical geometry. Substituting the boundary condition into the above equation results in the relationship

$$T(\bar{r},\theta,\tau) = B\int_0^\tau [\bar{T}_e(\tau') - T(1,0,\tau')] G(\bar{r},\theta,\tau;1,0,\tau')\ d\tau' \tag{10}$$

Equation 10 gives the temperature everywhere in the particle in terms of the temperature evolution at the particular point of contact ($\bar{r} = 1$, $\theta = 0$). In this way, the problem is reduced to finding the temperature history of this point. Using the simplified notation $\bar{T}(\tau) = T(1,0,\tau)$, eq 10 can be written as

$$\bar{T}(\tau) = B\int_0^t [T_e(\tau') - \bar{T}(\tau')] K(\tau;\tau')\ d\tau' \tag{11}$$

where the kernel $K(x,y)$ is connected to the Green's function through the relation $K(x,y) = G(1,0,x;1,0,y)$. This equation is a scalar, singular, linear Volterra equation. It is quite remarkable that the transient two-dimensional problem is thus transformed into a scalar integral equation.

To proceed to the solution of the problem, the appropriate Green's function must be found. The Green's function for the particular case is the solution of eq 7 with the term $\delta(r - r')\,\delta(\theta - \theta')$ added to the right-hand side, subject to a Neumann boundary condition. There are several methods for the derivation of the Green's function of a parabolic partial differential equation. For example, Carslaw and Jaeger[20] employed the Laplace transform; Arce et al.[19] used the properties of the associated Sturm−Liouville problem; and Kostoglou[21] followed a very simple approach, expanding the Dirac function directly in terms of the eigenfunctions of the differential equation. For the particular problem at hand, the Green's function for an arbitrary source at $\bar{r}'$, θ' is found to be

$$G(\bar{r},\theta,\tau;\bar{r}',\theta',\tau') = \frac{1}{2\pi\sqrt{\bar{r}\bar{r}'}}\sum_{n=0}^{\infty}(2n+1)P_n[\cos(\theta)]\,P_n[\cos(\theta')]\times \sum_{m=1}^{\infty}\frac{{\lambda_{nm}}^2 J_{n+1/2}(\lambda_{nm}\bar{r})J_{n+1/2}(\lambda_{nm}\bar{r}')}{[{}^1/_4 + {\lambda_{nm}}^2 - (n+{}^1/_2)^2]{J_{n+1/2}}^2(\lambda_{nm})}\,e^{-\lambda_{nm}^2(\tau-\tau')} + \frac{3}{4\pi} \quad (12)$$

where the eigenvalue λ_{nm} is the mth zero of the derivative of the nth-order spherical Bessel function (that is, $d\lambda^{-1/2}J_{n+1/2}(\lambda)/d\lambda = 0$).

Using the above Green's function, the kernel of the integral in eq 11 can be written as

$$K(\tau;\tau') = \frac{1}{2\pi}\sum_{n=0}^{\infty}\sum_{m=1}^{\infty}\frac{(2n+1){\lambda_{nm}}^2}{{}^1/_4 + {\lambda_{nm}}^2 - (n+{}^1/_2)^2}\,e^{-\lambda_{nm}^2(\tau-\tau')} + \frac{3}{4\pi} \quad (13)$$

The transfer function of the integral in eq 11 can be derived in closed form, but in any attempt to obtain explicit results (for example, frequency analysis through the transfer function or discretization of the integral equation for numerical solution), terms with double infinite sums that are similar to those in eq 13 but without the exponential term and the eigenvalue term in the numerator appear. The inner sum with respect to m for a given n converges similarly to the sum in the relevant one-dimensional problems.[19] Using asymptotic formulas for the eigenvalues,[22] it can be shown that the sum over n for a given m diverges. More precisely, for large m and $m \gg n$, the eingenvalue λ_{nm} is proportional to πm. This means that the above-mentioned terms decrease in proportion to m^{-2} as m increases for any constant n. This series converges. On the other hand, for large n, the leading-order approximation of the $m = 1$ eigenvalue is $\lambda_{n1} = (n + {}^1/_2) + 0.808(n + {}^1/_2)^{1/3}$. Using this result, it can be shown that the above-mentioned terms decrease in proportion to $n^{-1/3}$ as n increases for $m = 1$, and therefore, this series does not converge. The poor performance of the Legendre polynomial expansion in representing Dirac function is responsible for this lack of convergence. The nonconvergence does not imply that the Green's function in eq 12 is not valid, only that it cannot be employed directly for computations of temperature in the particular application. Fortunately, an indirect methodology can employed for the examination of the limits of validity for the uniform temperature approximation. To overcome the limitations of the Legendre polynomial expansion, use is made of the mean outer-shell temperature defined as $\bar{T}_m(\tau) = ({}^1/_4\pi R^2)\int_S \bar{T}\,d\mathbf{S}$. Taking the mean surface value of both sides of eq 10 leads to the relation

$$\bar{T}_m(\tau) = \bar{B}\int_0^t [T_e(\tau') - \bar{T}(\tau')]K_m(\tau;\tau')\,d\tau' \quad (14)$$

where

$$\bar{B} = \frac{3}{4\pi}B$$

$$K_m(\tau,\tau') = \frac{1}{3R^2}\int_S G(\bar{r},\theta,\tau;1,0,\tau')\,d\mathbf{S} = \frac{2}{3}\sum_{i=1}^{\infty}e^{-\lambda_i^2(\tau-\tau')}$$

and λ_i is the ith zero of the derivative of the zero-order spherical Bessel function.

According to the uniform temperature approximation (UTA), the (uniform) temperature of the particle is given by

$$\frac{d\bar{T}_u}{d\tau} = \bar{B}(\bar{T}_e - \bar{T}_u) \quad (15)$$

Let us assume as a null hypothesis that the UTA is valid. Then, $\bar{T} = \bar{T}_u$ can be used in eq 14, and $\bar{T}_m$ can be computed exactly. If the assumption about the validity of the UTA is correct, then $\bar{T}_m$ must be equal to, or at least close to, $\bar{T}_u$. Thus, the limits of validity of the UTA can be assessed from the difference between $\bar{T}_u$ and $\bar{T}_m$. After some algebra the equations for $\bar{T}_u$ and $\bar{T}_m$ take the form

$$\bar{T}_u = \bar{B}\int_0^\tau e^{-\bar{B}(\tau-\tau')}\bar{T}_e(\tau')\,d\tau \quad (16)$$

$$\bar{T}_m = \bar{T}_u + \frac{2}{3}\bar{B}\int_0^\tau [T_e(\tau') - \bar{T}_u(\tau')]\sum_{i=1}^{\infty}e^{-\lambda_i^2(\tau-\tau')}\,d\tau' \quad (17)$$

In general, the parameters of the problem are the heat-transfer coefficient $\bar{B}$ and the shape of the external disturbance $\bar{T}_e(\tau)$. To obtain explicit results, a frequency response analysis of the problem is made by imposing a periodic external disturbance $\bar{T}_e(\tau) = \sin(\omega\tau)$.[23] Frequency response analysis is typically used to study transient heat-transfer processes.[24] Substituting into eqs 16 and 17, performing the integrations, and dropping the transient terms, the following long-time asymptotic behavior is derived

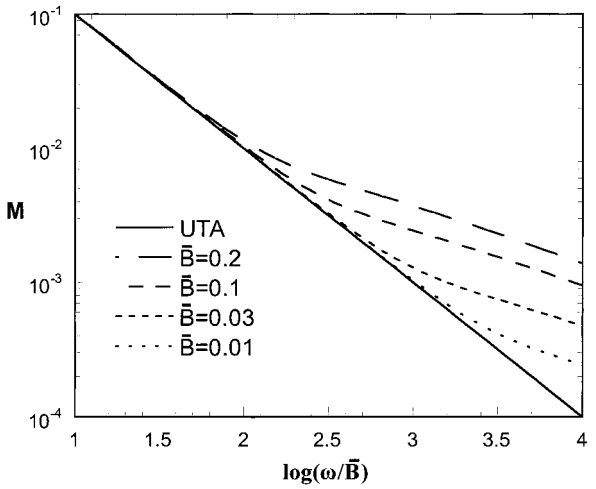

Figure 3. Modulus M of the periodic oscillations of $\bar{T}_u$ (UTA) and $\bar{T}_m$ (mean shell temperature) versus logarithm of the normalized external disturbance frequency.

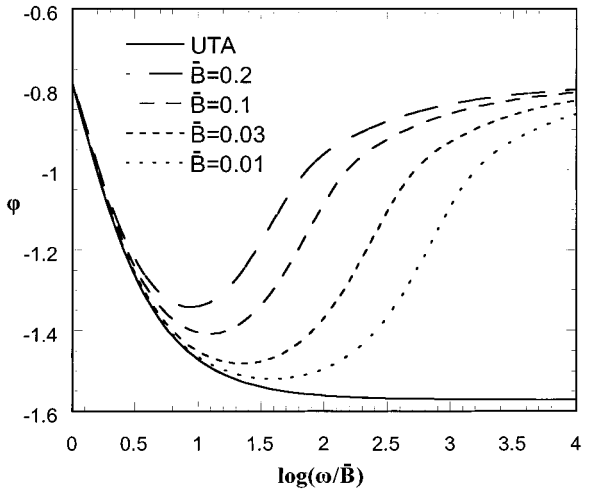

Figure 4. Phase φ of the periodic oscillations of $\bar{T}_u$ (UTA) and $\bar{T}_m$ (mean shell temperature) versus logarithm of the normalized external disturbance frequency.

$$\bar{T}_u = \frac{1}{1+(\omega/\bar{B})^2}\sin(\omega\tau) - \frac{\omega/\bar{B}}{1+(\omega/\bar{B})^2}\cos(\omega\tau) \quad (18)$$

$$\bar{T}_m = \bar{T}_u + \frac{2\bar{B}}{3}\frac{1}{1+(\omega/\bar{B})^2}\times \left[(\omega/\bar{B})^2\sum_{i=1}^{\infty}\frac{\lambda_i^2}{\lambda_i^4+\omega^2} + (\omega/\bar{B})\sum_{i=1}^{\infty}\frac{1}{\lambda_i^4+\omega^2}\right] \sin(\omega\tau) + \frac{2\bar{B}}{3}\frac{1}{1+(\omega/\bar{B})^2}\times \left[(\omega/\bar{B})\sum_{i=1}^{\infty}\frac{\lambda_i^2}{\lambda_i^4+\omega^2} - \omega(\omega/\bar{B})^2\sum_{i=1}^{\infty}\frac{1}{\lambda_i^4+\omega^2}\right]\cos(\omega\tau) \quad (19)$$

The eigenvalues λ_i are computed with a Newton−Raphson method with initial values taken from the relevant McMahon expansion.[22] In all cases, one iteration is enough for five-digit accuracy. The first 500 terms are added explicitly, whereas, for the rest, asymptotic formulas permit the transformation of the sum into an integral that can be integrated analytically. The above periodic temperatures can be written in the form $M\sin(\omega\tau+\varphi)$, where M is the modulus and φ is the phase.

An important observation is that, in eqs 18 and 19, the frequency is scaled with the coefficient $\bar{B}$, that is, the external heat-transfer rate (and not the internal rate, which has already been employed to make the variables dimensionless) defines the characteristic time scale of the problem. In Figures 3 and 4, respectively, the modulus and phase are plotted versus the scaled frequency $\omega/\bar{B}$ for the UTA and for several $\bar{B}$ values. The result of the UTA does not explicitly depend on $\bar{B}$ (except through the scaled frequency) and corresponds to $\bar{B}=0$, i.e., it is the limit of the extremely slow process. The restriction $r_c/R < 0.1$, imposed to enable the overall problem separation into particle- and contact-scale problems that are amenable to perturbation analysis, also means that $\bar{B} < 0.1$. The conclusions from Figures 3 and 4 can be summarized as follows: For values of $\bar{B}$ smaller than 0.01, the UTA can be used safely for all types of temperature perturbations because the UTA loses its accuracy only for very large values of $\omega/\bar{B}$ where the perturbations are too fast to influence the heat-transfer problem considerably, as is obvious from the small modulus in Figure 1. For $\bar{B}$ greater than 0.01, the UTA should be avoided for frequencies corresponding to the range $0.5 < \log(\omega/\bar{B}) < 2$. For smaller frequencies, the UTA is accurate, whereas larger frequencies cannot influence the process because, as shown in Figure 1, the modulus M is negligible.

For the study of the problem of transient contact area, frequency response analysis is not appropriate because no steady state exists. A change of the form $r_c\sin(\omega\tau)$ for $0 < \tau < \pi/\omega$ is assumed for the radius of the contact area (e.g., representing an initially increasing and subsequently receding contact area during particle impact and rebound), and the temperature of the surface is assumed to be constant. In this case, the term in brackets in eq 17 must be replaced by $\sin(\omega\tau)(1-T)$. An analysis similar to that above for the temperature perturbations gives

$$\bar{T}_u = 1 - e^{\bar{B}[\cos(\omega\tau)-1]/\omega} \quad \text{for } \tau < \pi/\omega$$

and

$$\bar{T}_u = 1 - e^{-2\bar{B}/\omega}\,e^{-\bar{B}\tau} \quad \text{for } \tau > \pi/\omega \quad (20)$$

$$\bar{T}_m = \bar{T}_u + \frac{2}{3}\bar{B}\int_0^{\tau}\bar{T}_u(\tau')\sum_{i=1}^{\infty}e^{-\lambda_i^2(\tau-\tau')}\,d\tau' \quad (21)$$

To assess the accuracy of the UTA, the two temperatures $\bar{T}_u$ and $\bar{T}_m$ are compared at the moment $\tau=\pi/\omega$. To avoid numerical integration of weakly singular terms and taking into account the susceptibility of the large $\omega/\bar{B}$ case to deviations from the UTA, it is assumed that $\omega/\bar{B}$ is large enough to permit linearization of the exponential terms. After some analytical integrations, the following result is obtained

$$\bar{T}_{uo} = 2\frac{\bar{B}}{\omega} \quad (22)$$

$$\bar{T}_{mo} = T_{uo} + \frac{4\pi}{3}\left(\frac{\bar{B}}{\omega}\right)^2 \sum_{i=1}^{\infty} \frac{\omega}{\pi\lambda_i^2}(1 - e^{-\pi\lambda_i^2/\omega}) + \frac{\pi\lambda_i^2/\omega}{(\pi\lambda_i^2/\omega)^2 + \pi^2}(1 + e^{-\pi\lambda_i^2/\omega}) \quad (23)$$

The above series is computed in a manner similar to the series in eq 19. The computation shows that the series has two asymptotes with respect to ω. Using this fact, the series can be fitted extremely well by a simple function employing the Churchill interpolation method.[25] The final result is

$$\frac{\bar{T}_{mo}}{T_{uo}} = 1 + \frac{2\pi}{3}\frac{\bar{B}}{\omega}[(0.0634\omega)^{-2.5} + (0.544\omega^{0.5})^{-2.5}]^{-0.4} \quad (24)$$

For $\bar{B} < 0.1$, the error is less than 1% irrespective of the frequency. This means that the UTA can be used in every case of transient contact area provided that $r_c/R < 0.1$.

An application in which variations in contact area are important is during the initial stages of sintering in particle assemblies and aggregates, where the temperature and contact area evolve simultaneously in a highly coupled manner.

Application to Linear Aggregates

An interesting question concerns the effect of structure (single-particle or aggregate) on the characteristic time for thermal equilibration between a particle assembly and a surface. In the present work, the extreme case of a linear-chain aggregate, which provides analytical insight into the problem of thermal relaxation, is considered. The particular choice of linear aggregates (except for their simplicity) is because they include the two extremes of long-chain aggregates (large number of primary particles N, very open structure, fractal dimension equal to 1) and solid spheres ($N = 1$, fractal dimension equal to 3). Thus, the heat-transfer characteristics at these two morphological extremes can be studied simply by changing the number of primary particles N.

The first step is to explore the validity of the UTA for the case of a step change of the surface temperature, i.e., $\bar{T}_e = 0$ for $\tau < 0$ and $\bar{T}_e = 1$ for $\tau > 0$. This is equivalent to the establishment of contact between a particle and a surface at the moment $\tau = 0$. Using the same procedure as for the case of the sinusoidal temperature variation leads to the results

$$\bar{T}_u = 1 - e^{-\bar{B}\tau} \quad (25)$$

$$\bar{T}_m = \bar{T}_u + \frac{2}{3}\bar{B}\sum_{i=1}^{\infty}\frac{e^{-\lambda_i^2\tau} - e^{-\bar{B}\tau}}{\lambda_i 2 - \bar{B}} \quad (26)$$

Numerical computation of the above temperatures shows that their relative difference is a decreasing function of τ with a slight dependence on $\bar{B}$. This difference reaches 5% for $\tau \approx 1.5$ for all $\bar{B}$ values. If the $\bar{B}$ value is small, the initial temperature rise is $\bar{T}_m = \bar{B}_t$, which means that the amount of heat transferred during the initial period when the UTA is not applicable is negligible. In practice, for $\bar{B} < 0.01$, the UTA is quite accurate.

To study the influence of the particle structure on the dynamics of the thermal relaxation process, a linear aggregate of volume V consisting of N spherical particles is considered. The contact radius between the particles is r_{cpp}, whereas the contact radius at the unique particle−surface contact is r_{cps}. The temperature of the ith particle is T_i, where the particles are numbered from the surface outward. In the following, the surface temperature is T_e, and the initial aggregate temperature is T_o. Assuming that the contact radii are small enough for the UTA to be valid, the temperature evolution can be described by the following system of ODEs

$$\frac{V}{N}\frac{dT_1}{dt} = 4r_{cps}\frac{a_p k_s}{k_p + k_s}(T_e - T_1) + 2r_{cpp}a_p(T_2 - T_1) \quad (27a)$$

$$\frac{V}{N}\frac{dT_i}{dt} = 2r_{cpp}a_p(T_{i+1} - 2T_i + T_{i-1}) \quad (27b)$$

$$\frac{V}{N}\frac{dT_N}{dt} = 2r_{cpp}a_p(T_{N-1} - T_N) \quad (27c)$$

The following dimensionless variables are introduced

$$\bar{t} = \frac{2r_{cpp}a_p t}{V}, \quad Bi = \frac{2r_{cps}}{r_{cpp}}\frac{k_s}{(k_p + k_s)}, \quad \bar{T}_i = \frac{T - T_e}{T_o - T_e} \quad (28)$$

where Bi is a generalized Biot number, which denotes the ratio of the external (aggregate-to-surface) heat transfer to the intra-aggregate heat transfer. Using the new variables, the above system (eqs 27) is transformed into

$$\frac{d\bar{T}_1}{d\bar{t}} = -NBi\bar{T}_1 + N(\bar{T}_2 - \bar{T}_1) \quad (29a)$$

$$\frac{d\bar{T}_i}{d\bar{t}} = N(\bar{T}_{i+1} - 2\bar{T}_i + \bar{T}_{i-1}) \quad (29b)$$

$$\frac{d\bar{T}_N}{d\bar{t}} = N(\bar{T}_{N-1} - \bar{T}_N) \quad (29c)$$

For large N, the discrete variable i can be approximated by a continuous one, denoted by x, which represents the length along the aggregate. In this way, the center of the particle i is mapped onto the coordinate $x = (2i + 1)$. The discrete temperature distribution along the aggregate is also approximated by a continuous distribution, $\bar{T}(x)$, using the mapping $\bar{T}_i = \bar{T}[(2i + 1)R]$. Derivatives of the continuous temperature distribution are related to the discrete particle temperatures via a Taylor series expansion

$$\bar{T}_{i+1} = \bar{T}_i + \sum_{j=1}^{\infty}\frac{1}{j!}\left(\frac{\partial^j\bar{T}}{\partial x^j}\right)_{x=(2i+1)R}(2R)^j \quad (30)$$

Keeping the first three terms of the above series and following a procedure similar to that used for the derivation of the well-known Fokker−Plank equation[26] results in the following partial differential equation

$$\frac{\partial \bar{T}}{\partial \bar{t}} = \frac{1}{N}\frac{\partial^2 \bar{T}}{\partial \bar{x}^2} \tag{31}$$

with the boundary conditions

$$\frac{\partial \bar{T}}{\partial \bar{x}} = -NBi\bar{T} \quad \bar{x} = 0 \tag{32}$$

$$\frac{\partial \bar{T}}{\partial \bar{x}} = 0 \quad \bar{x} = 1 \tag{33}$$

where $\bar{x} = x/L$ and L is the total length of the aggregate given by

$$L = 2NR = \left(\frac{6V}{\pi}\right)^{1/3} N^{2/3} \tag{34}$$

The characteristic time of the thermal relaxation process is estimated by the evolution of the average temperature of the aggregate, which is defined as

$$\bar{T}_{\text{ave}} = \frac{1}{N}\sum_{i=1}^{N} \bar{T}_i \tag{35}$$

For the continuous (large-N) approximation, the average temperature is defined as

$$\bar{T}_{\text{ave}} = \int_0^1 \bar{T}(\bar{x})\, \mathrm{d}x \tag{36}$$

The continuous problem can be solved with the method of separation of variables to give the result

$$\bar{T}_{\text{ave}} = 4\sum_{i=1}^{\infty} \frac{\sin^2(b_i)}{2b_i^2 + b_i \sin(2b_i)} \mathrm{e}^{-b_i^2 \bar{t}/N} \tag{37}$$

where b_i represents the roots of the transcedental equation

$$b_i \tan(b_i) = NBi \tag{38}$$

It can be shown that the behavior of T_{ave} is dominated by the first term of the series except for small times, so the characteristic time for thermal relaxation can be approximated by $\bar{t}_c = (N/b_1^2)$.

The first root b_i of eq 38 can be approximated by the following asymptotic solutions at the limits of small and large NBi, respectively

$$b_1 = (NBi)^{1/2}\left[1 - \frac{1}{6}NBi + \frac{11}{360}(NBi)^2\right] \tag{39}$$

$$b_1 = \frac{\pi}{2}\left[1 - \frac{1}{NBi} + \frac{1}{(NBi)^2}\right] \tag{40}$$

In Figure 5, the characteristic time t_c is shown as a function of NBi. The approximations that arise using the perturbation solutions for b_1 are also shown. For small NBi, all of the heat-transfer resistance is at the particle−surface contact, so the time t_c is independent of the internal structure of the aggregate (number N in the present case). In the other limit of large NBi, the heat-transfer resistance is inside the aggregate, and it is proportional to the number of particle-to-article contacts, so t_c is proportional to N. Figure 5 shows the crossover between these two limiting behaviors.

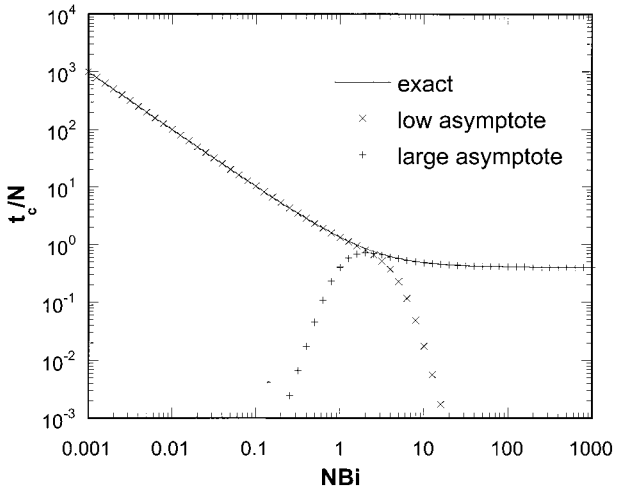

Figure 5. Thermal relaxation characteristic time t_c versus NBi for a large linear aggregate. Comparison of t_c computed using eq 38 with the result of the asymptotic eqs 39 and 40.

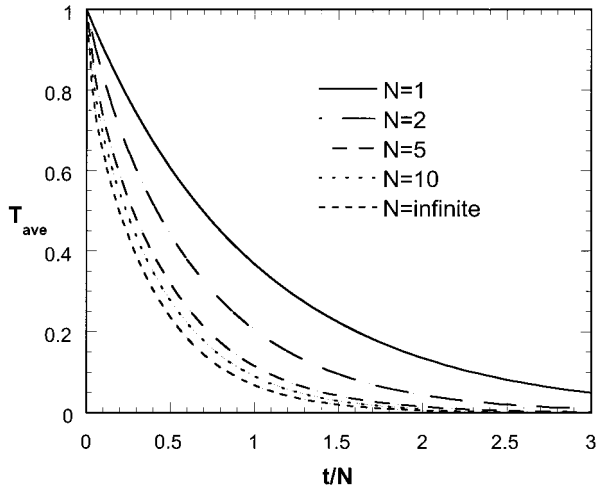

Figure 6. Evolution of the average temperature of a linear aggregate with N monomers during the thermal relazation process ($Bi = 1$).

To show the effect of the discrete nature of the problem on its transient heat-transfer behavior, the system of ODEs (eqs 29) is solved numerically using a Runge−Kutta integrator with self-adjusting step.[27] In Figure 6, the temperature T_{ave} is shown versus time scaled by the number of particles N for several values of N and $Bi = 1$. For small N, the thermal relaxation behavior is a weak function of N, but as N increases, the T_{ave} curve tends to the continuous one ($N = \infty$) for which t_c is proportional to N.

Application to Two-Dimensional Deposits

To assess the effect of the deposit morphology on its thermal relaxation behavior, some results for the temperature evolution of simple deposits will be shown. Simple two-dimensional deposits are constructed using the on-lattice deposition technique developed by Tassopoulos et al.[28] This technique is a combination between the DLA (diffusion-limited aggregation) and ballistic models for deposition.[10,29] The relative weight between the two models is expressed with the aid of the mass transfer Peclet number Pe. In general, for large Pe, the deposit is compact and becomes more open as Pe decreases. In the following, it is assumed that the

Table 1. Structural Features of the Created Deposits for $Pe = 1$

run no.	1	2	3	4	5
solid fraction	0.626	0.609	0.605	0.655	0.610
mean coordination number	2.03	2.057	2.085	2.15	2
particles in contact with substrate	47	45	48	43	52

Table 2. Structural Features of the Created Deposits for $Pe = 0.1$

run no.	1	2	3	4	5
solid fraction	0.460	0.452	0.436	0.421	0.427
mean coordination number	1.932	1.947	2.005	1.967	2.03
particles in contact with substrate	32	34	27	28	26

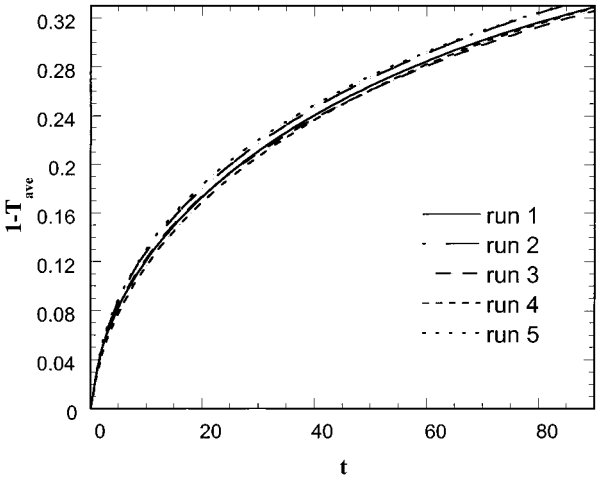

Figure 7. Evolution of the average deposit temperature for the five deposits with structural features given in Table 1 ($Pe = 1$).

deposit and the substrate are initially at the same temperature T_o and suddenly the substrate temperature becomes T_e. The particles are assumed to be spherical, and the heat is transferred solely by solid-phase conduction. By employing the UTA, a differential equation for each particle in the deposit can be written in a manner similar to that of the linear aggregate. The resulting system of equations is usually very large, so a simple method must be used for its integration. Here, the second-order explicit Nystrom method is used.[30] Its advantage is that, although it has the same computational effort as the Euler method, it has a higher order of accuracy. Five deposits with $Pe = 1$ and five deposits with $Pe = 0.1$ consisting of 400 particles are constructed using different sets of random numbers with the Tassopoulos et al.[28] algorithm. The length of the substrate is $160R$. The stuctural characteristics of these deposits are shown in Tables 1 and 2. The solid fraction is defined with respect to the mean deposit height.[28] The mean coordination number is the mean number of particle−particle contacts per particle. The number of particles in contact with the deposit is crucial, because it determines the surface-to-deposit heat-transfer rate, whereas the mean coordination number determines the intradeposit heat transfer. The evolution of the average deposit temperature T_{ave} for the deposits of Tables 1 and 2 in the case where the heat-transfer resistance of the particle−surface contact is negligible with respect to that of the particle−particle contact (i.e., $r_{cps} \gg r_{cpp}$) is shown in Figures 7 (for $Pe = 1$) and 8 (for $Pe = 0.1$). The dimensionless nature of the temperature and time is similar to that for the case of aggregates (eq 28), but

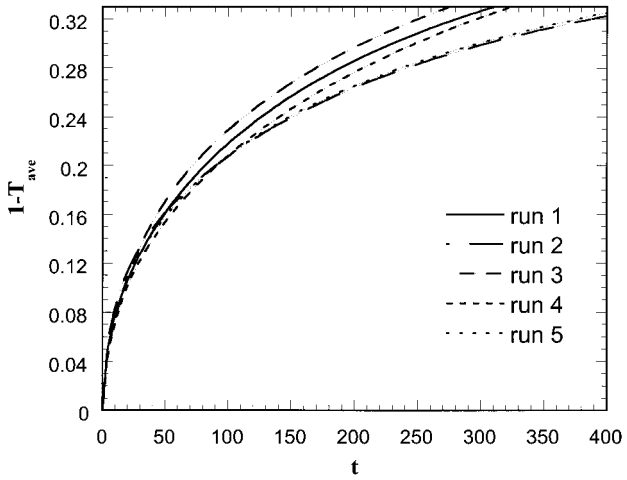

Figure 8. Evolution of the average deposit temperature for the five deposits with structural features given in Table 2 ($Pe = 0.1$).

now V is taken to be the particle, rather than the aggregate, volume. The scatter of the temperature evolution between the several deposits is much larger for $Pe = 0.1$ than for $Pe = 1$, and it cannot be attributed to the scatter between the deposit features (see Tables 1 and 2), which is about the same for the two cases. The explanation is that, for relatively compact deposits, low-order descriptors (e.g., solid fraction) are sufficient to describe the thermal relaxation behavior, so for deposits with similar solid fractions, similar temperature evolutions are expected.

On the other hand, for open (highly porous) deposits higher-order descriptors (incorporating more microstructural details) are required to describe the thermal relaxation behavior. Hence, for the same solid fraction, differences in microstructure lead to different thermal relaxation behavior. It is precisely for this case where a macroscopic approach (based on an effective thermal conductivity derived using the volume averaging method[31]) does not seem advantageous and the heat-transfer problem must be solved at the scale of the particle by employing the UTA.

The above view is confirmed by the very recent analysis of Vargas and McCarthy[32] for transient heat conduction through the solid phase in granular materials. In this case, the nonuniformity of the stress in the bed of particles and the corresponding nonuniformity of the contact areas between the particles make the UTA (which is embedded in the so-called thermal particle dynamics method by the above authors) preferable over the effective-medium approximation. The mathematical model employing the UTA is validated against experimental temperature distributions in the granular bed obtained by liquid crystal thermography[32] and thus substantiates the utility of the present analysis.

The present analysis represents a first step toward the study of the transient heat-transfer properties of particulate aggregates and deposits. In practice, aggregates and deposits usually have complex structures (sometimes fractal), and the UTA is expected to be indispensable for the numerical computation of their transient heat-transfer behavior. One can see in the literature[33] that there is a significant effort to evaluate the transport properties of fractal aggregates and to correlate them with the fractal dimension. A relevant effort concerning transient heat-transfer characteristics suggested by the present work is underway.

Conclusions

In the present work, explicit criteria are derived for the applicability of the uniform temperature approximation to the problem of unsteady heat transfer through the solid phase in spherical assemblies. For the case of temperature variations, the UTA cannot be used for a certain range of the frequency of the fluctuations, but for the case of contact area variations, the UTA is applicable in all cases, provided that the contact radius is smaller than 10% of the particle radius. The UTA provides a great simplification for the solution of the unsteady heat-transfer problem in particle deposits and aggregates, because an ordinary differential equation substitutes for the three-dimensional partial differential equations for each particle. In this way, the heat-transfer problem is transformed into a dynamic network one. In the second part of the present work, the UTA is used to show the effect of the aggregate and deposit morphology on its thermal relaxation behavior, considering the limiting case of linear aggregates and two-dimensional deposits. This effect is significant, and further work is needed to relate thermal relaxation times to the morphological characteristics of realistic aggregates and deposits.

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