The Lattice Monte Carlo Method for Solving Phenomenological Mass and Heat Transport Problems

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Abstract

In this review paper, we introduce the recently developed Lattice Monte Carlo method for addressing and solving phenomenologically-based mass and heat transport problems especially for composite and porous materials. We describe in detail the application of this method to calculate effective mass diffusivities and to determine concentration profiles. Next, we describe in detail the application of this method to the calculation of effective thermal conductivities/thermal diffusivities and the determination of temperature profiles. Where possible, results of the method are compared with exact results or those from application of the Finite Element method. Excellent agreement is demonstrated.

Keywords

Monte Carlo method, mass diffusion, thermal conductivity, composites, porous media

1. Introduction

The Monte Carlo method was first developed at Los Alamos during the WWII Manhattan Project for the purposes of modelling neutron trajectories during fission. Since that time, the Monte Carlo method has undergone numerous developments and has enjoyed applications in virtually every area of science and engineering. Intrinsically a computationally very demanding method, the Monte Carlo method has naturally become far more popular as computers have become faster, less expensive and more accessible. The Monte Carlo method has been a popular method to address both mass and heat transport problems in materials. For mass transport, the Monte Carlo method has been used for many years for addressing *atomistic* problems in crystalline solids (in such problems it is now usually called the Kinetic Monte Carlo (KMC) method; see [1] for an early review and [2] for a typical recent KMC calculation. More recently, a related Monte Carlo method has been used for addressing *phenomenological* problems (where it is has been termed the Lattice Monte Carlo (LMC) method [3,4]). For addressing heat transport, the Monte Carlo method has been used for many years for addressing transient heat conduction

problems in homogeneous materials (where a continuous random walk method has been used [5]). Recently, the LMC method has been adapted to address steady-state and transient heat transport problems in inhomogeneous materials [6,7].

The LMC method, the focus of this contribution, is basically a type of finite-difference method that is embedded in a quasi-simulation of the physical process. It has shown itself to be very useful in addressing and solving complex phenomenological mass and thermal diffusion problems. In this paper, we provide a review at an introductory level of the LMC method, with an emphasis on how the method is actually employed to address and solve phenomenological mass and heat transport problems. In Section 2, we discuss the LMC calculation of the effective mass diffusivity and concentration profiles. In Section 3, we provide the corresponding discussion of the LMC calculation of the effective thermal conductivity, the effective thermal diffusivity and temperature profiles.

2. Effective Mass Diffusivities

The effective mass diffusivity represents the long time limit mass diffusivity of a 'composite material'. Experimentally, this effective diffusivity is probably best known as the diffusivity measured in a tracer diffusion experiment made on a polycrystalline material in the Harrison Type-A kinetics regime. In this regime, the effective diffusivity is some weighted average of the lattice or bulk diffusivity of the diffusant and its grain boundary diffusivity. Other examples are the effective ionic conductivity of a composite solid electrolyte and the effective diffusivity of a diffusant in a two phase material. In Section 2.1, we review the LMC method for determining the effective mass diffusivity and in Section 2.2 we highlight the various published LMC calculations of the effective mass diffusivity. In Section 2.3, we review the LMC method for determining concentration profiles and in Section 2.4 we highlight the various published LMC calculations of concentration profiles.

2.1 The LMC Method for Determining the Effective Mass Diffusivity

Mass diffusion is a random process that can be represented by random walks of particles. The particles can be atoms, molecules or much larger entities such as colloidal particles or even unicellular organisms. The century-old Einstein-Smoluchowski (ES) Equation [8,9] (often referred to simply as the Einstein Equation) describes the self-diffusivity D of randomly walking particles in d dimensions ($d = 1,2,3$):

$$D = \frac{<R^2>}{2dt} \tag{1}$$

(where R is the vector displacement of a *given* particle after some long time t and the brackets $<>$ refer to an average over a very large number (N) of particles).

The ES Equation refers only to a system already at equilibrium. In a mass diffusion context, the ES Equation refers then to the determination of the diffusivity of individual particles that can be followed or traced in a system that is already at chemical equilibrium, i.e. with no concentration gradient acting or external field(s) acting. In other words, each particle needs to be followed for some long time t in order to determine its displacement R. In a real experiment, there are rather few examples where this has been possible to achieve. One well-known example makes use of a field ion microscope to follow or trace individual surface rhodium atoms diffusing on various faces of a f.c.c. rhodium crystal [10]. If the ad-atom fraction is low and the positions of

the ad-atoms are observed frequently, then it is possible in effect to tag the atoms by noting at each observation precisely *which* atom has moved, and how far, since the previous observation. The rhodium surface diffusivity itself can then be formed simply and directly using Eq. 1 after a suitably long diffusion time.

In contrast with its very limited use in experiments, the ES Equation has provided the foundation for much of the theory that describes the diffusion of atoms in the solid state. There, it is commonly assumed that atoms jump from site to site on a lattice with very long residence times on each site between jumps and an assumed zero flight time between sites. (This is often loosely referred to as the 'hopping model'.) The atoms, individually, as well as their collective centre of mass, undergo random walks on a lattice. In a period extending over half a century, a vast literature has been built up that has been especially concerned with describing memories or correlations between individual jumps of the random walk of (mainly) tracer atoms; see, for example, [11]. Since about the early 1970s, a large part of this literature has made use of the Monte Carlo method either for verifying theoretical results or exploring new situations where analytical methods have not yet been developed; see, for example, the review [1].

For random walks (say with correlations) on a simple cubic lattice the diffusivity can be partitioned from Eq. 1 as [11]:

$$D = \frac{\Gamma f r^2}{6}$$ (2)

where Γ is the jump rate, r is the jump distance (the distance between sites) and f is termed the tracer correlation factor. The tracer correlation factor embodies the correlations in the directions of the jumps of the individual atoms on their diffusion paths [11]. The tracer correlation factor has the limits of zero and unity. For a hypothetical walk, where every jump of the individual particles is immediately reversed, then $f = 0$. On the other hand, for a complete random walk, i.e. when each jump in the walk of the particles is completely independent or uncorrelated with all previous ones, then $f = 1$. As an aside, it is worth mentioning that for many solid state diffusion mechanisms such as the vacancy mechanism, there are considerable correlations in the directions of successive jumps of the atoms because of the continued proximity of the vacancy after a tracer or tagged atom jump with the vacancy. For the vacancy diffusion mechanism, the correlation factor is given approximately by:

$$f \approx 1 - \frac{2}{Z}$$ (3)

where Z is the local coordination number; $Z = 4$ and 6 for the square planar and simple cubic lattices respectively.

It is important to recognize that the ES Equation remains valid for long times even when the material has different diffusivities in different regions of the material (for example in a composite), *provided* that the material remains isotropic in its diffusion properties overall. The implication also is that each tracer particle 'explores' a sufficiently large portion of the structure to be representative of the composite structure. The diffusivity represented in the ES equation is then the *effective* diffusivity of the structure.

The process of describing random walk diffusion of particles on a lattice lends itself particularly well to Monte Carlo methods. Directing random walks of particles on lattices with

random numbers was in fact one of the first applications (1951) of the new Monte Carlo method in the post WWII years [12]. Perhaps surprisingly, the ES Equation itself does not seem to have been used until almost twenty years later and then only indirectly. A possible reason for this is the difficulty in dealing with time. In fact, in contrast to the other principal diffusion kinetics simulation method of molecular dynamics, the simulation of real time is not possible in a Monte Carlo kinetics calculation. What one actually does is to use a discrete quantity that is proportional to actual time. This quantity is the number of jump *attempts* per particle. Using the ES Equation with this quantity acting as 'time', one can then calculate a *relative* diffusivity, i.e. a diffusivity that is relative to one of the specified diffusivities (usually the highest) in the system.

We now describe several straightforward LMC calculations, the first to calculate the diffusivity in a homogeneous material, the second to calculate an effective diffusivity in a composite material. In both cases, the particles that explore the lattice are no longer considered to represent the diffusivities of individual entities such as atoms but are virtual particles that represent the macroscopic diffusivities in each region. In contrast with atomistic Monte Carlo calculations, there are no correlation effects here in the diffusion of the particles. Each particle diffuses completely independently of all others. Put another way, multiple occupancy of the lattice sites is permitted.

In the first case to be considered, we look at a situation where the diffusivity is the same everywhere. Consider then the case of the self-diffusion of isolated particles on a simple cubic lattice having the dimensions, say, of 100 x 100 x 100 i.e. one million lattice sites. There are six jump directions for each jump of a particle, i.e. $Z=6$. We suppose that this lattice has periodic boundaries. This very common type of boundary condition specifies that when a particle reaches an edge or face of the lattice, if the next jump would take it outside of the lattice, then the particle is simply plugged back into the edge or face of the lattice directly on the opposite side of the lattice. In effect, with the imposition of periodic boundaries, the original lattice is now surrounded by periodic images or replicas of itself. The use of periodic boundaries thus enables surface effects to be avoided completely. However, this lattice is still a small system, and, if too small, historical effects may be perpetuated in some diffusion problems as a particle leaves one side and enters on the opposite side into what is, in effect, essentially the same environment that it has just left. In a problem such as diffusion in a thin film, a formal surface(s) is of course necessary and is retained in the calculation.

Monte Carlo methods require of course random numbers: these are nearly always computer generated and, since extremely large numbers of them are required in a calculation, they are produced with highly optimized routines. Random numbers r_i are typically presented *uniformly* on the following interval: $0 \leq r_i < 1$. In our calculation here, a particle is first created at some randomly chosen site in our lattice (random numbers are used to generate the x, y and z coordinates for this site and the direction to jump is also chosen at random (from the six available in this particular case where the simple cubic lattice is used). There are frequently two options available here depending on the problem. We can release all N particles at the same time at randomly chosen sites in the lattice and then start the simulation by choosing them randomly to jump. Provided that we permit multiple occupancy of a given site, the particles would diffuse independently of each other over the lattice for the entire time Nt. The alternative is to release the particles one at a time i.e. we let each particle diffuse for exactly the same time t (the same number of jump attempts) before the next particle is released. At long times, both of these procedures are completely equivalent and would take about the same amount of overall computational time, but the second way is probably slightly easier conceptually and we will assume it in the following for convenience.

After each step of the random walk of a given particle has been directed by the computer-generated random numbers, the corresponding step-by-step contribution to the vector displacement of the particle R from its original position is also accumulated. It has been found that it is probably best to do this by assuming that each particle starts from its own origin (0,0,0). It should be especially noted that when a particle crosses a periodic boundary and is therefore reinserted into the opposite side of the lattice, this process is completely ignored in the calculation of R. In other words, for the purposes of calculating R we think of the original lattice as being surrounded by periodic images of itself. The process of directing the random walk of the particle is allowed to continue for, say, 10 000 jump attempts. The entire process is then repeated with further particles until, say, a total of $N = 10^6$ particles have been released, each one having had 10 000 jump attempts in its walk. In this particular example, every attempt to jump is permitted to be successful (this is equivalent to saying that $\Gamma = 1$ in the units: jump per jump attempt of the particle). The jump distance (see Eq. 2) is $r = 1$ and has the units of 'lattice spacings'. Accordingly, the jump distance can be scaled to any distance. Since $f = 1$ here (the particles diffuse completely independently of each other and there are no correlation effects), Eq. 2 shows immediately that D should equal 1/6 and also carries the units: lattice spacings squared per jump attempt. A calculation of D directly from the LMC procedure using the ES Equation verifies this within statistical uncertainty. The value here of 1/6 taken by D then must of course be scaled to the actual diffusivity in the material.

Now let us consider diffusion in a simple two-component composite material. For the sake of concreteness, we consider the dispersed phase (the inclusions) to be spheres (phase 2) that are embedded in a matrix phase (phase 1) and that the spheres are themselves arranged for convenience here in a simple cubic arrangement. We assume that the diffusivity in the spherical inclusions themselves is D_2 and that the diffusivity in the matrix is D_1. We are then interested in calculating the effective diffusivity D_{eff} of the composite. First of all, as a very rough approximation for the effective diffusivity in such a composite, we can write the effective diffusivity as a simple linear combination of the individual diffusivities:

$$D_{eff} = gD_2 + (1-g)D_1 \tag{4}$$

where g is the volume fraction of the inclusion phase. In the solid state diffusion literature, Eq. 4 is commonly referred to as the Hart Equation [13] and originally referred to the specific situation where the two 'phases' are the bulk (the grains) and the grain boundaries (or dislocation pipes). Eq. 4 is the effective diffusivity measured in the Harrison Type-A kinetics regime where the parallel grain boundary slabs are parallel to the diffusion direction [14]. Eq. 4 is exact only when the two phases or regions are parallel and the diffusivities are measured in that direction.

Now let us consider a LMC method determination of the effective diffusivity in this composite. A fine-grained simple cubic lattice say (100 x 100 x100) is overlaid on this system. A plane of this structure is shown in Fig. 1. The requirement here of course is that the lattice is sufficiently fine grained that it can adequately capture the shape of the spherical inclusions. The volume fraction of inclusions g is simply the number of lattice sites in the inclusion(s) divided by the total number of sites (There is usually a small correction that depends on the choice of the jump frequencies between the two phases and will be discussed below.) The lattice also has periodic boundaries which are implemented exactly as for the homogeneous system described above. Since there are periodic boundaries, it does not actually matter in this particular example if the inclusion is in the centre of the lattice because the arrangement of the spherical inclusions itself is also simple cubic. (Recall that with the employment of periodic boundaries, the lattice is

surrounded by images of itself.) For more complicated arrangements of the inclusions in the lattice, which effectively acts like a unit cell of the structure of the chosen arrangement, the inclusions must be located with care.
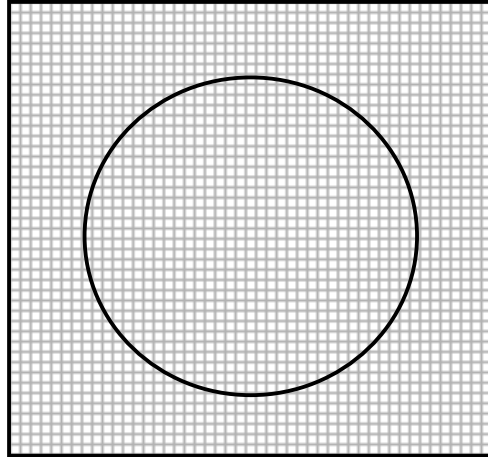

Fig. 1. A plane of a model composite with spherical inclusions in a simple cubic arrangement overlaid by a simple cubic lattice.

As in the earlier example described above, each particle is created and released from a randomly chosen site in the lattice. As before, there are no correlation effects here to be concerned with because the particle is diffusing completely independently of all others. The two diffusivities D_1 and D_2 are now simply individually represented by the two (different) jump probabilities (per unit time) Γ_1 and Γ_2. It is usual to scale the higher Γ to unity for computational efficiency. The jump rate of the particle now varies according to position within the lattice. Thus if the particle is currently on a site known to be in phase 1 (i.e. the spherical inclusion), it has a jump rate Γ_1, whereas if the particle is currently on a site known to be in phase 2, then it has a jump rate of Γ_2. As an example, let us choose $\Gamma_1 = 1$ and $\Gamma_2 = 0.1$ (this means that the ratio of the diffusivities $D_1/D_2 = 10$). Thus when the particle is on a 'phase 2 site', another random number r needs to be generated to determine the outcome of the jump attempt. If r is greater than Γ_2 then this jump attempt is said to have failed and a *jump direction* must again be chosen at random for this particular particle. (Note, if the simulation is being done in such a way that all particles were released at the same time, then, if an attempt to jump is unsuccessful, a particle must again be chosen at random from the cohort.) If r is less than or equal to Γ_2 then the jump attempt is said to have been successful and the particle is permitted to move.

A small difficulty occurs at a boundary between the phases. When a particle is about to cross a boundary, a consistent choice must be made about the jump rate to use. If the jump is between phase 1 and phase 2 and Γ_1 is used, then the reverse jump (from phase 2 to phase 1) must also use Γ_1. Otherwise, the principle of local detailed balance would be violated and there is an implication that there is some kind of segregation of the particles between the two regions. Similarly, if, for argument's sake, the jump between phase 1 and phase 2 used Γ_2 then Γ_2 must also be used for the reverse jump. In practice, the choice made here of Γ has almost no affect on the calculated results for the effective diffusivity. The correction is actually to g – the fraction of

the inclusions. This will arise as a result of this procedure because of the following reason. Obviously, a path of the particle jump with jump rate Γ_i should belong to the phase i. Because of that, we introduce the fraction of sites (exactly $1/Z$, where Z is the coordination number) being taken from one phase and added to the other phase according to the method of handling the jumps at a boundary between the phases that was introduced above. This correction is usually very small and can be shown to be inversely proportional to the number of sites representing an inclusion of a different type.

In many materials, one can expect that the diffusant can undergo segregation among the various phases that are present. For two phases, this is conveniently expressed through a segregation factor s which is defined in the usual Henry's Law way as:

$$s = \frac{c_2}{c_1} \left(= \exp\left(-\frac{E_s}{kT} \right) \right) \tag{5}$$

where, for convenience, $c_1 < c_2$ where c_i is the (equilibrium) concentration of the diffusant in phase i. In Eq. 5, E_s is the segregation energy of the diffusant between the two phases, k is the Boltzmann constant and T is the absolute temperature. In the implementation of segregation in the LMC method, the jump probability Γ_{12} for a jump from phase 1 to phase 2 and the jump probability Γ_{21} for a jump from phase 2 to phase 1 are related to the segregation factor at equilibrium by:

$$\Gamma_{12} / \Gamma_{21} = s \tag{6}$$

When segregation is present, the initial release of the particles must also be adjusted. This is simply achieved by weighting the regions according to Eq. 5 and their relative fractions.

As in the earlier example above, after a large number of particles have been released, say $N = 10^6$, then the effective diffusivity for the composite can be formed directly from the ES Equation. The effective diffusivity of the composite is automatically scaled relative to the highest diffusivity (in this particular case, to that of the matrix D_1). It is clear that it is very easy to introduce other inclusions having different diffusivities into the matrix. It is also straightforward to allow position-dependent diffusivities even within the inclusions or the matrix by simply mapping such dependencies onto the corresponding jump frequencies Γ_i. This method of calculating the effective diffusivity is basically a finite-difference method for the solution of the corresponding inverse Diffusion Equation (see, for example, Manning's [15] derivation of the ES Equation with the Diffusion Equation (Fick's Second Law) as a starting point).

The principal difficulty in the LMC method determination of the effective diffusivity is ensuring that the number of jump attempts is sufficiently large to ensure that the long-time effective diffusivity of the composite is correctly determined. At very short diffusion times for each particle (one or two jumps), as might be expected, the effective diffusivity is simply given by the approximate Eq. 4 because this would also be the *instantaneous* effective diffusivity. At very long diffusion times, after each particle has adequately 'explored' the structure, the correct long-time limit effective diffusivity of the composite is obtained. As a good estimate for what would be a sufficiently long time for a given calculation, it is best to first form the effective diffusivity according to the approximate Eq. 4 and then use this via a calculation of the 'diffusion length', $(6D_{\text{eff}} t)^{1/2}$ to determine the number of jump attempts (t) appropriate for the problem. As

a reasonable guide, the diffusion length should be at least half the length of the lattice, or unit cell of the ordered arrangement of the inclusions.

In some applications, one may wish to introduce some degree of randomness to the arrangement of the inclusions or to their size, or possibly their shape. This poses no major problems. For the purposes of changing the arrangement of the inclusions, at one extreme, one may start from an ordered arrangement of the inclusions which is then randomized to some extent by making appropriate random shifts of the inclusions within the lattice but without allowing the inclusions to overlap. At the other extreme, one might first prepare a gas-phase like distribution or even a dense random packing distribution [16] of the inclusions in a separate calculation. This distribution is then mapped onto a fine-grained lattice. In both cases, the effective diffusivity is still determined simply as described above from the ES Equation. Of course, in such cases, it will also be necessary to average over a number of random starting distributions of the inclusions in order to obtain a reliable estimate of the effective diffusivity of the composite model being addressed. Dealing with a distribution of sizes of the inclusions is straightforward and needs no explanation. Inclusions that take the standard geometrical shapes of spheres, cubes, ellipses etc are, of course, straightforward to implement. In principle, actual experimental inclusion shapes could be mapped onto the Monte Carlo lattice making use of image analysis of micrographs from a confocal microscope, but this has not been attempted.

As noted above, the highest jump rate (diffusivity) is scaled to unity for efficiency. When one of the diffusivities is very small, the Monte Carlo method with the basic algorithm described above frequently tends to run into difficulties arising from rather large computational inefficiency (most attempts to jump are rejected in that region) and a slight non-randomness in the random number generation and the subsequent inhomogeneity of the random numbers generated over the range zero to unity. This will be magnified for diffusion in the slow diffusivity region. These difficulties can be avoided or at least minimized by making use of straightforward residence time algorithms; see, for example, [17-19]. Such algorithms can be very useful when the diffusivities vary by many orders of magnitude. A popular choice makes use of an algorithm that guarantees a jump on every attempt [19] wherein the particle's site residence time (the reciprocal of the jump rate) is simply added to the elapsed time at each move. In principle, this can lead to overshooting of the specified time though this is unlikely to be a serious problem at very long diffusion times. There is, of course, a significant computational overhead with such algorithms that may offset some of the efficiency gains.

As an alternative to the ES Equation for the calculation of the effective diffusivity, it is also possible to make use of Fick's First Law [6]:

$$J = -D\frac{\partial C}{\partial x} \tag{7}$$

where J is the particle flux and $\partial C/\partial x$ is its concentration gradient. In a LMC calculation Eq. 7 is most conveniently used under steady-state conditions by introducing a source plane, at which particles can be created at a random position and released one at a time, and a sink plane, at which the particles are annihilated as soon as they arrive. This of course gives an apparent particle concentration of $1/n$ for the source plane (where n is the number of sites on that plane) and zero for the sink plane. This, along with the length of the lattice between the source plane and the sink plane, provides a uniform concentration gradient $\partial C/\partial x$. This gradient can also be adjusted by changing the length of the lattice or by adjusting the probability for the particle being annihilated at the sink plane. For example, if a particle arrives at the sink plane and is annihilated

with a probability of P_i (appropriately evaluated on the spot using a new random number), the effective concentration of particles on that plane is then simply given by $(1-P_i)/n$ and the concentration gradient in the problem is thus reduced. In a lattice of dimensions 100 x 100 x 100 the source and sink planes are separated by 50 planes in the $+x$ direction and by the same number of planes via the periodic boundary in the $-x$ direction. A particle is released from the source plane and is permitted to diffuse to the sink, thereby providing, in effect, a well-defined uniform concentration gradient. The mass flux J is simply calculated as the *net* number of particles that have crossed between two neighboring planes in the x-direction as calculated over a long time t during which time some 10^5 particles are released from the source and annihilated at the sink. Inclusions are introduced in exactly the same way as the ES Equation method described above and diffusion is simulated in the same way. However, it should be noted a particle may 'see' in effect only one isolated inclusion in its lifetime in going from source to sink and give an incorrect result for the effective diffusivity. For this reason, periodic arrangements of inclusions would require at least two inclusions between the source plane and the sink plane of particles.

Results of calculations of the effective mass diffusivity (also the effective thermal conductivity see below) in simple 2D composites via the ES Equation and Fick's First Law have been described as being in very good agreement [6]. In general, however, it must be mentioned that for calculating the effective diffusivity, the ES Equation method is considerably easier to use than the Fick's First Law method and, furthermore, is rather more flexible in its application. The authors seriously doubt if the Fick's First Law method in general has any particular advantages for the calculation of the effective diffusivity: it is likely that the method will remain largely of pedagogical interest.

2.2 LMC Calculations of the Effective Mass Diffusivity
2.2.1 Effective Mass Diffusion in Two Phase Materials

Most of the LMC calculations for the effective mass diffusivity have been on two phase materials. In many cases, the second 'phase' has been the grain boundary region.

The first LMC calculation of the effective mass diffusivity was concerned with determining the effective diffusivity of the void space of a simple model of porous media that was constructed from spheres [16]. Various ordered (f.c.c., b.c.c. and s.c.) and random packing arrangements of impermeable spheres were examined in that first LMC study. Random distributions of touching spherical particles were generated in the following way. First, spheres were introduced randomly into a volume (non-periodic) without overlap. In order to generate dense random packing of the spheres there are quite a number of possible algorithms available; see, for example, [20]. However, it is generally accepted that the dense random packing of spheres always depends slightly on the actual algorithm used and that there may in fact be no perfect algorithm for generating dense random packing [20]. In the LMC study [16], a dense random packing of spheres was first obtained by starting with a very simple Lennard-Jones pair-potential between particles that was tailored to have a very dominant repulsive part of the potential (this was intended to closely approximate hard spheres) and an extremely weak attractive part of the potential. The potential energy function for the system of spheres was then minimized by taking very small fixed spatial steps of the spheres in random directions. This minimization procedure tends to avoid collapsing to the most stable f.c.c. arrangements which is a frequent difficulty when standard numerical minimization techniques with pair-wise interactions are employed with spheres of equal size. Arrangements of 'spheres' at densities higher than dense random packing were generated in the study by the simple artifice of simply enlarging the spheres further after minimization, thereby in effect overlapping the spheres. In addition, the case of equal

concentrations of spheres of two different sizes was also examined in dense random packing arrangements.

Once the densely randomly packed arrangement of spheres had been prepared it was overlaid with a fine-grained grid with a mesh size of typically 100-spacings per sphere diameter as described in general terms in above. The effective diffusivity of the void space between the spheres was obtained according to the ES Equation as described above. The diffusivity within the spheres was assumed to be zero. In the study, the results for both ordered and random arrangements of spheres were compared with a number of analytical expressions for the effective diffusivity.

Another pioneering LMC study explored the effective mass diffusivity in 2D models of a composite composed of circular and square inclusions for the condition where the concentration of diffusant in the inclusions was equal to zero [21]. The next LMC study [22] was put into the context of the effective mass diffusivity in nanomaterials where diffusion occurs via both the grains (nanocrystals) and the interface regions (grain boundaries). Two very simple 2D square grain configurations were examined. The particular situation that is of course relevant to this context is where the grain boundary diffusivity is considerably larger than the diffusivity within the grains. The effective diffusivity was calculated according to the ES Equation and the results for the effective diffusivity were compared to several derived expressions.

A closely related LMC study to the above examined the effective diffusivity for a model of cubic grains in a simple cubic arrangement [23]. Again the relevant case where the diffusivity in the grain boundaries is much greater than that in the grains was examined. Importantly, over the entire grain boundary fraction range it was shown that an excellent equation to describe the effective mass diffusivity is the (mass diffusion version) of the Maxwell-Garnett Equation [24,25]:

$$\frac{D_{eff}}{D_1} = \frac{2(1-g)D_1 + (1+2g)sD_2}{(1-g+sg)((2+g)D_1 + (1-g)sD_2)} \tag{8}$$

A later and quite comprehensive LMC study of the effective diffusivity in two component composites examined the effective diffusivity for a simple model of dispersed *spherical* inclusions in f.c.c., b.c.c. and s.c. arrangements [26]. In that study, two cases of the relative diffusivities were examined: 1) the diffusivity of the inclusions was less than the matrix phase, and 2) the diffusivity of the inclusions is greater than the diffusivity of the matrix phase. It was again found that the Maxwell-Garnett Equation does very well in describing the effective diffusivity up to the percolation threshold where the spheres touch.

The problem of determining and analyzing the effective diffusivity in a material that has contributions from grain and grain boundary diffusion was reviewed [27] and some further LMC data were included in that review. Special emphasis was put on the limits of usefulness of the Hart and Maxwell-Garnett Equations. Comparison of the LMC data of the effective diffusivity of cubic and spherical grain models (the diffusivity was always assumed to be greater in the grain boundaries) showed that the Maxwell-Garnett Equation consistently provides a superior description of the effective diffusivity than the Hart Equation unless the diffusion time is sufficiently small that the problem can be conceived as diffusion only along parallel paths extending in from the surface.

A very detailed comparison of LMC and Finite Element calculations of the effective diffusivity (expressed in that paper as the effective conductivity) of circular and square inclusions

both in square planar arrangements was undertaken in [28] for the case where the diffusivities of the matrix and inclusions differ by up to an order of magnitude. Both cases of the inclusions having a higher and lower diffusivity than the matrix were examined. Excellent agreement for the effective diffusivity was found between these quite different methods. It was also shown in that study that the results are in excellent agreement with the Maxwell-Garnett Equation except in the case of the circular inclusion fractions above the percolation threshold (i.e. where the circular inclusions already touch).

Finally in this section, we mention a detailed study of the effective diffusivity for the case of 2D square inclusions arranged in square planar and brickwork patterns where the inclusions have a diffusivity three orders of magnitude less than that of the matrix phase [29]. It was shown that the Maxwell-Garnett Equation describes this rather extreme situation roughly but for an accurate representation of the effective diffusivity it is necessary to take into account the actual arrangement of the dispersed phase.

2.2.2 Effective Mass Diffusion in Three Phase Materials

The problem of determining the effective diffusivity in three phase material has also been addressed with the LMC method. The first LMC calculation [29] was couched in terms of determining the effective diffusivity in a material containing two alternating (in all directions) stable cubic phases (phases A and B with diffusivities D_A and D_B and volume fractions g_A and g_B respectively) that are separated by interphase boundaries ('phase' C) having a high diffusivity D_C. A general expression for the thermal conductivity in a model of a three-phase material was derived many years ago by Brailsford and Major [30]. Brailsford and Major's expression was derived in a more general way in [29] and was extended to include possible differing segregation of the diffusant in the three phases. The extended Brailsford and Major expression for the effective mass diffusivity in three phase material is, from [29]:

$$\frac{D_{eff}}{D_C} = \frac{1 - 2g_A \dfrac{D_C - s_A D_A}{2D_C + s_A D_A} - 2g_B \dfrac{D_C - s_B D_B}{2D_C + s_B D_B}}{\left(1 + (s_A - 1)g_A + (s_B - 1)g_B\right)\left(1 + g_A \dfrac{D_C - s_A D_A}{2D_C + s_A D_A} + g_B \dfrac{D_C - s_B D_B}{2D_C + s_B D_B}\right)} \tag{9}$$

where s_A and s_B are the segregation factors for phases A and B: $s_A = c_A/c_C$, $s_B = c_B/c_C$. Two other equations for the effective diffusivity were also derived in [29] using Maxwell-type arguments in succession. The LMC results for the effective diffusivity show that the effective diffusivity in the composite is certainly described roughly by Eq. 9. However, the detailed pattern of behaviour of the effective diffusivity is rather complicated in this model: the other expressions give better agreement but in different ranges of the individual diffusivities and fractions of inclusions. At the present time, it is not possible to guide, at least in general terms, the choice for the best overall expression for the effective mass diffusivity.

The electrical (ionic) conductivity in three phase composites in which an insulating phase (phase B) is embedded in an ionically conducting matrix (phase C) has recently been of great interest for enhancing the overall ionic conductivity of the material [31,32]. Such materials are frequently called 'composite electrolytes'. Because of space charge effects, a 'phase' having a much higher electrical conductivity ('phase A') is present immediately around the insulating phase. There are two percolation thresholds in this problem: one where the highly conducting

regions overlap and, later at high inclusion fractions, a second one where the insulating regions start to overlap. The problem is then to determine the effective ionic conductivity σ_{eff} of this three 'phase' composite. Provided the same type of ions carry the current in all three phases one can make use of the Nernst-Einstein relation for each phase:

$$\sigma_i = c_i q^2 D_i / kT \tag{10}$$

where q is the charge on the ion. The problem has been modelled by the LMC method using a similar procedure to that described above [33]. An approximate expression for the effective ionic conductivity was also derived using Maxwell-type arguments and was found to be in better agreement with the LMC results than expressions derived in previous treatments. The expression, in effective mass diffusivity form, is:

$$\frac{D_{eff}}{D_C} = \frac{1 - 2(g_A + g_B)\dfrac{D_C - D_{AB}s_{AB}}{2D_C + D_{AB}s_{AB}}}{\left(1 + (s_A - 1)g_A + (s_B - 1)g_B\right)\left(1 + (g_A + g_B)\dfrac{D_C - D_{AB}s_{AB}}{2D_C + D_{AB}s_{AB}}\right)} \tag{11}$$

where

$$s_{AB} = \frac{s_A g_A + s_B g_B}{g_A + g_B}$$

and

$$\frac{D_{AB}}{D_A} = \frac{g_A + g_B - 2g_B\dfrac{D_A s_A - D_B s_B}{2D_A s_A + D_B s_B}}{\left(g_A + s_A^{-1}s_B g_B\right)\left(g_A + g_B + g_B\dfrac{D_A s_A - D_B s_B}{2D_A s_A + D_B s_B}\right)}$$

2.3 The LMC Method for Determining Concentration Profiles

Obtaining the concentration profile using the LMC method is equivalent to solving the Diffusion Equation (Fick's Second Law) for a problem once initial and boundary conditions have been designated. In order to demonstrate the procedure, we will focus first on two simple cases where the diffusivity is the same everywhere in the material. (Both cases have very well known analytical solutions for the case when the solid is semi-infinite and the mass diffusivity does not depend on position.) Case 1 refers to a situation where a very thin layer of tracer (the diffusant) is deposited at the surface at time $t = 0$. (This is sometimes referred to as the thin-film or instantaneous source condition.) The tracer is then permitted to diffuse into the material for some diffusion anneal time t. Case 2 refers to a situation where the concentration of the diffusant is held constant at the surface throughout the diffusion time.

The basic LMC procedure to generate concentration profiles has a great many similarities to that described already in Section 2.1 above. We first illustrate the procedure with Case 1. A source plane of particles is established in the centre of a large periodic simple cubic lattice in order to avoid edge effects in the calculation. Particles are generated at random positions on this source plane and released from the plane either sequentially or all at once. Assuming the latter for convenience here, we allow the particles to diffuse independently of one another for the entire

time Nt, at which time the final position of each particle is recorded. The final positions of all of the particles are then simply assembled from the individual final positions to form a concentration penetration profile. If the lattice is large in the diffusion direction, at relatively short times, the profile is the familiar Gaussian profile as appropriate for diffusion into a 'semi-infinite' solid, see Fig. 2.
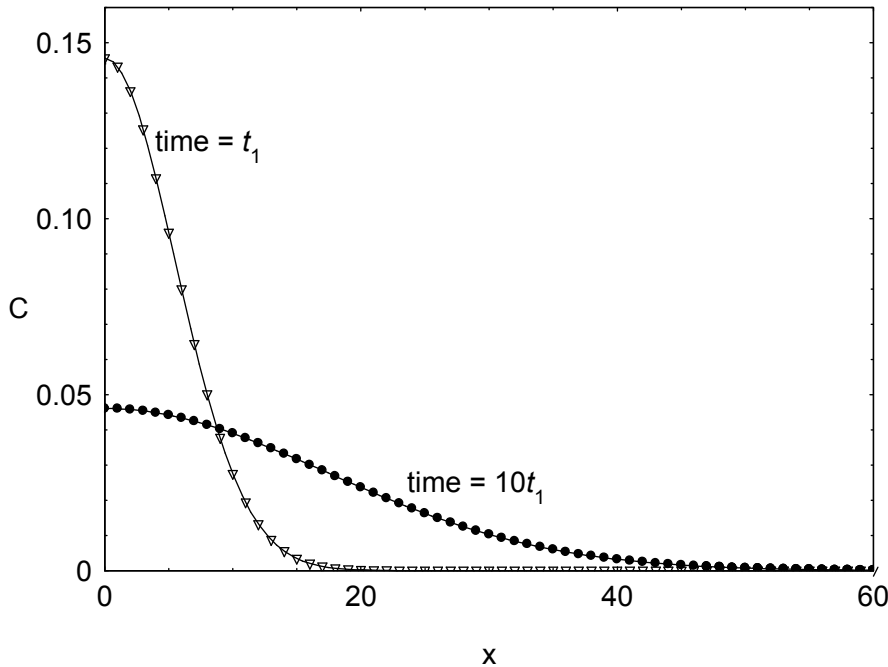

Fig. 2. Typical Gaussian concentration profiles for tracer diffusion from an instantaneous source at x=0 for two different times (symbols represent LMC results).

Case 2 requires a constant source of particles to be maintained at the 'surface' for all diffusion times and is obtained in the following way. The basic idea is simply to keep the total number of particles at the source plane constant at all diffusion times. This is achieved in the following way. All particles are released at the same time. As each particle makes a jump from the source plane it is immediately replaced by a new one, which is again generated at a random position on this plane in order to maintain the number designated. On the other hand, whenever a particle returns to the source plane, thereby exceeding the number designated for the source, then that particle is permanently removed from the system. Over a period of time, the number of particles within the system naturally increases as more particles diffuse away from the source than return to it. Accordingly, the diffusion time t must be constantly re-scaled since the time is required to be proportional to the number of attempts *per particle*. At longer times, the two profiles emanating from each side of the source start of course to meet up via the periodic boundary. However, if the particle source is then conceived as two 'separated' surfaces, then the profile represents diffusion from two surfaces into a material of a finite width.

In principle, it is possible to determine the effective mass diffusivity of a model material by analyzing the simulated concentration profiles. This would assume that there has been averaging of the profile over all possible locations of the second phase in the matrix phase. The profile would then be processed to give the effective mass diffusivity in much the same way as an experimental diffusant concentration depth profile by using the appropriate solution to the

Diffusion Equation. In practice, it is much easier to calculate the effective diffusivity of the model material in a separate calculation using the ES Equation along the lines of what has been described above in Section 2.1.

2.4 LMC Calculations of Concentration Profiles

In the first LMC calculation to produce concentration profiles, tracer concentration depth profiles were determined for diffusion from a thin-film tracer source in the presence of dislocation 'pipes' that are normal to the source at the surface [34]. Typical profiles for this situation (obtained later in [42]) are shown in Fig. 3.
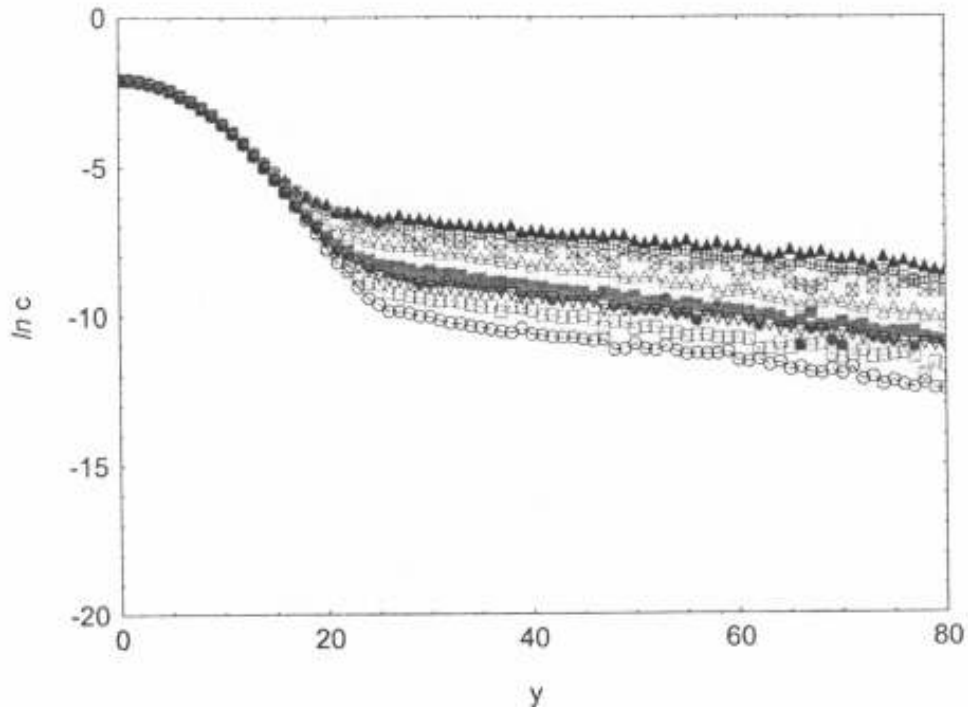
Fig. 3. Representative LMC concentration depth profiles for various distances between isolated dislocation pipes (spaced along a line) for the case of diffusion from an instantaneous source (at y = 0) [39].

In another LMC calculation, impurity concentration depth profiles were determined for diffusion from a thin film source into an array of finite sized grains arranged in a brick-wall configuration. In this calculation, segregation of the impurity to the grain boundaries was specifically allowed for, with the result that secondary peaks were found at locations where the grain boundaries are parallel to the surface [17,18,35]. In another study, the behaviour of the tracer concentration depth profiles was examined for diffusion from a thin-film source in the presence of overlapping diffusion fields from equally spaced grain boundary slabs [36]. This study was greatly extended much later [37] by two of the present authors in an in-depth Lattice Monte Carlo study to determine the transition from Harrison Type-A kinetics to Type-B kinetics. The latter study also allowed surface diffusion within the source to have a comparable rate to grain boundary diffusion. Surface diffusion at the source had also been explored in an earlier study where it was

shown that fast surface diffusion can expedite the 'pumping away' of tracers via the grain boundaries [38]. A recent study examined the Harrison Type-A to Type-B transition point for several cubic grain and square to explore the effect of shape and dimensionality on the transition point [39]. In another study, the concentration depth profiles were examined to explore the size and characteristics of an intermediate A-B transition region [40]. LMC calculations have been made on concentration depth profiles for diffusion from a thin-film source where the grains are randomly oriented with the goal of fitting the depth profiles with an empirical equation [41]. We make mention of a calculation of the contour angle made by iso-concentration lines for the case of an isolated grain boundary with diffusion from a thin-film source [43]. Finally, recent LMC calculations have been made of oxygen concentration depth profiles from a constant oxygen source at the surface into a *Ag/MgO* cermet where allowance is made for segregation (of oxygen at the interfaces between *Ag* and *MgO* [44,45]. An example is shown in Fig. 4.
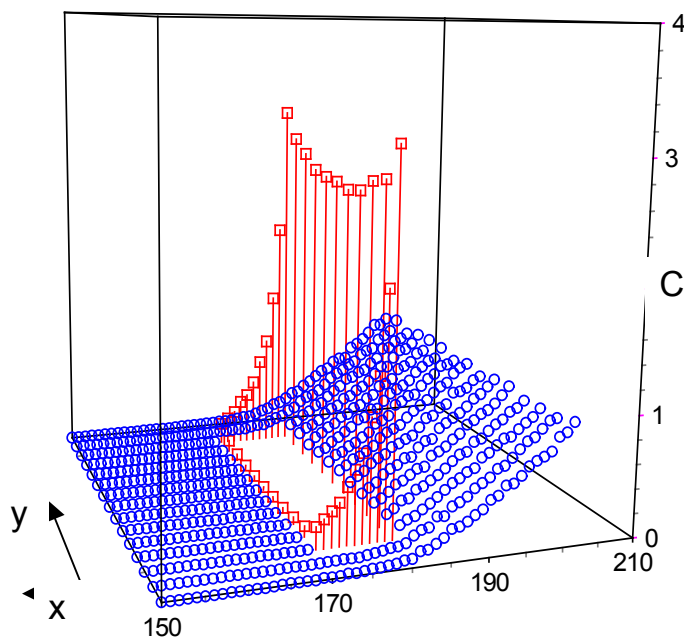

Fig. 4. A typical distribution map of oxygen in a model *Ag/MgO* cermet with a square inclusion of *MgO* with allowance made for segregation of oxygen at the metal-ceramic interface. The (constant) source of oxygen is at plane x=205.

3. Effective Thermal Diffusivities/Conductivities

In heat transport problems, the long time limit effective heat transport quantity that is best known is probably the effective thermal conductivity of a composite material. In Section 3.1, we review the LMC method for calculating the effective thermal diffusivity and effective thermal conductivity and in Section 3.2 we highlight the various published LMC calculations of the effective thermal diffusivity and thermal conductivity. In Section 3.3, we review the LMC method for determining temperature profiles and in Section 3.4 we highlight several LMC calculations of temperature profiles, shown here for the first time.

3.1 The LMC Method for Determining the Effective Thermal Diffusivity and Thermal Conductivity

The diffusion of heat, like mass, is a random process that can be represented by random walks of particles that can be considered as virtual 'heat particles'. The ES Equation also describes the thermal diffusivity K in d dimensions ($d = 1,2,3$):

$$K = \frac{<R^2>}{2dt} \tag{12}$$

It should be noted that the thermal conductivity λ_i in a phase i is directly related to the thermal diffusivity K_i in that phase by the well-known expression $K_i = \lambda_i / \rho_i C_{p,i}$ where ρ_i is the density of phase i and $C_{p,i}$ is its specific heat. In a model composite, by simply requiring that the densities and the specific heats take values equal to unity everywhere in the calculation, the effective thermal conductivity λ_{eff} then simply equals the effective thermal diffusivity K_{eff}. To the authors' knowledge, in a diffusion of heat context the ES Equation has no physical meaning in the sense that it can be made use of experimentally. It purely provides a useful means for calculating in models the effective thermal diffusivity (and thermal conductivity) from random walks of virtual heat particles using the LMC method.

3.2 LMC Calculations of the Effective Thermal Diffusivity and Thermal Conductivity

The methods in Section 2.1 above (without the inclusion of segregation) for the calculation of the effective mass diffusivity apply equally to the calculation of the effective thermal conductivity. Accordingly, all of the corresponding results for the various models that have been obtained for the effective mass diffusivity apply equally to the effective thermal conductivity. Several calculations have been specifically directed to the LMC calculation of the effective thermal conductivity [6,46-48]. These include calculations of the effective thermal conductivity of models of syntactic metallic hollow sphere structures, usually known as MHSS materials [47] and compact heat sinks based on cellular metals [48]. An example of the results of a LMC calculation of the effective thermal conductivity is shown in Fig. 5 for the case of circular inclusions in a matrix [6]. In the same figure are also the results for the effective thermal conductivity using finite element analysis. The agreement is seen to be excellent.

There have been no *direct* LMC calculations of the effective thermal diffusivity. However, this quantity can be readily formed from the effective thermal conductivity calculated by LMC using the following equation:

$$K_{eff} = \frac{\lambda_{eff}}{(\rho C_p)_{eff}} \tag{13}$$

where

$$(\rho C_p)_{eff} = \sum_{\text{all phases } i} \rho_i C_{p,i} g_i$$

Exactly analogous to the method for using Fick's First Law (Section 2.1) under steady-state conditions to obtain the effective mass diffusivity, the Fourier Equation can also be used to determine the effective thermal conductivity. But, as with the Fick's First Law method, this does not provide any obvious advantages over the method using the ES Equation.
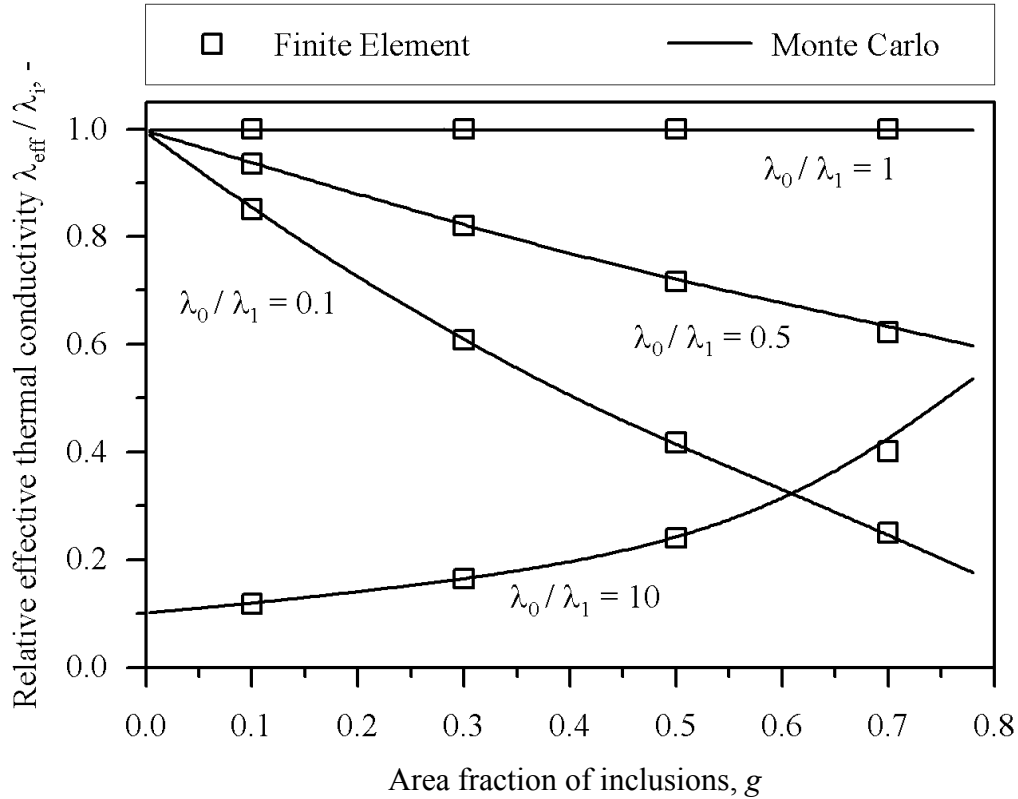
Fig. 5. Comparison of results from LMC and Finite Element Method calculations of the relative effective thermal conductivity of a composite with circular inclusions (0) in a matrix (1) in a square planar arrangement as a function of area fraction of inclusions for several values of the matrix and dispersed phase thermal conductivities.

3.3 The LMC Method for Determining Temperature Profiles

Because of the role of the density and specific heat in *transient* heat transport problems, the determination of temperature profiles requires a different procedure from that described for concentration profiles given above in Section 2.4. As an example frequently found experimentally, we will focus on the situation where the temperature at the surface or source is held constant at T_c. The number of virtual heat particles in the source plane is N_n. The amount of thermal energy E_p corresponding to a *virtual thermal energy particle* is given by the relation:

$$E_p = T_c \cdot r^3 \cdot \rho \cdot C_p \cdot \frac{1}{N_n}, \qquad (14)$$

where r is the distance between two neighbouring lattice sites.

We organize the random walks of the particles in such a way that they are now directed by two parameters: the jump probability p_j (scaled thermal conductivity) and the selection probability p_s (scaled inverse product $\rho_i \cdot C_{p,i}$). We treat the selection probability as an 'amount of inertia' assigned to a virtual thermal particle in the particular phase: i.e. the higher the specific heat in the phase the slower the virtual thermal particle. Both jump and selection probabilities depend on the material parameters of the phase i. The jump and selection probabilities p_j and p_s are defined to have values between zero (the event never occurs) and unity (the event always

occurs). Then the jump probability in a phase must be scaled with respect to the highest thermal conductivity so that:

$$p_{j,i} = \lambda_i / \lambda_{max} \tag{15}$$

And the selection probability $p_{s,i}$ is scaled with respect to the lowest value of the product $\rho_i \cdot C_{p,i}$:

$$p_{s,i} = \frac{(\rho_j C_{p,j})_{min}}{\rho_i C_{p,i}} . \tag{16}$$

According to Eq. 16, materials with a high specific heat and density possess a low selection probability. Different selection probabilities between sites from different material regions results in the modified (Eq. 14) definition of the energy E_p corresponding now to a *virtual heat particle*:

$$E_p = T_c \cdot r^3 \cdot (\rho \cdot C_p)_{min} \cdot \frac{1}{N_n} \tag{17}$$

Let us assume that phase 1 has a lower selection probability than phase 2 i.e.: $p_1 < p_2$. The overall probability of a jump of a probing heat particle in phase 1 is then equal to $p_{s,1} \cdot p_{j,1}$ and similarly for a particle in phase 2. (This value is, in fact, a scaled thermal diffusivity.) The increased number of unsuccessful jump attempts in phase 1 simulates an accumulation of virtual heat particles in that phase. It should be mentioned here that the selection of p_s and jump probabilities p_j of virtual heat particles inside the source plane ($x = 0$) are equal to unity.

At the beginning of each time-step, a particle is randomly selected. Next, a random number between 0 and 1 is generated and compared to the selection probability corresponding to the phase at that lattice site. If this random number is higher than the selection probability, the attempt is unsuccessful; the LMC time is increased and another particle is randomly chosen. Otherwise, a jump direction for the particle is randomly chosen and, depending on the phase(s) of the starting and target lattice sites, the jump probability p_j is now determined. In the case that the jump attempt is successful, the coordinates of the particle are updated before the LMC time is increased and a new particle is selected. The incremental increase to the Monte Carlo time t_{MC} depends on the total number N_{ges} of virtual heat particles in the system. At the end of the specified time t_{MC} the final positions of all of the particles are recorded.

The results of the LMC analyses are virtual heat particle distributions that correspond to particular Monte Carlo times t_{MC}. In order to obtain temperature profiles, the heat particles are translated into site temperatures T according to:

$$T = \frac{n \cdot E_p}{r^3 \cdot (\rho_i \cdot C_{p,i})_{min}} , \tag{18}$$

where n is the number of virtual heat particles currently located at the site.

Next, the Monte Carlo time t_{MC} needs to be converted into real time t. To do this, we will use a standard parametric analysis approach. Consider the Heat Equation in its dimensionless form:

$$\frac{dT}{dt'} = \frac{Kt*}{(x*)^2} div(\nabla T) \tag{19}$$

where $x*$ is a characteristic length for which we will use the jump distance r: $x* = r$, $t*$ is characteristic time that is most naturally a jump attempt per virtual heat particle and $t*$ should be determined in real time units; t' and x' are the dimensionless time and space coordinates. $Kt*/(x*)^2$ is the dimensionless parameter of the heat diffusion processes. It is obvious that the value of this parameter used in LMC simulations should be equal to its value in real units.

For the case of multiphase material, it is clear that we need to consider this correspondence only in one phase, provided that the other phases are modelled correctly. Let us choose phase i where the thermal conductivity is the highest λ_{max}. Then the LMC value of the heat diffusion parameter is:

$$\left(\frac{Kt*}{(x*)^2}\right)^{MC} = \frac{1}{6}\frac{(\rho C_p)_{min}}{\rho_i C_{p,i}}\frac{1}{1^2} \tag{20}$$

Equating this value to the heat diffusion parameter in real units we have that:

$$\frac{\lambda_{max}t*}{\rho_i C_{p,i}r^2} = \frac{Kt*}{(x*)^2} = \left(\frac{Kt*}{(x*)^2}\right)^{MC} = \frac{1}{6}\frac{(\rho C_p)_{min}}{\rho_i C_{p,i}} \tag{21}$$

Solving the equation between the leftmost term and the rightmost term we soon arrive at:

$$t* = \frac{1}{6}\cdot\frac{s^2(\rho C_p)_{min}}{\lambda_{max}} \tag{22}$$

Therefore, for the total time in real units we have the following connection to the LMC simulation time as follows:

$$t = t* t^{MC} = \frac{t^{MC}}{6}\cdot\frac{s^2(\rho C_p)_{min}}{\lambda_{max}} \tag{23}$$

In much the same way as for mass diffusivity, it would be possible in principle to determine the effective thermal diffusivity of a model composite by analyzing simulated temperature profiles. This would assume that there has been averaging of the temperature profile over all possible locations of the second phase. The temperature profile could then be processed to give the effective diffusivity in much the same way as an experimental temperature profile by using the appropriate solution to the Heat Equation. In practice, as with the mass diffusion case, it is much easier to calculate the effective thermal diffusivity of the model composite in a separate calculation using the ES Equation along the lines of what has been described above in Sections 3.1 and 3.2.

3.4 LMC Calculations of Temperature Profiles

Fig. 6 shows three example temperature profiles in aluminium calculated by the LMC method described above for the condition of a constant surface temperature. In the same figure, we include the exact analytical error function solution (dashed lines) and also a determination of the temperature profiles using Finite Element analysis (solid lines).
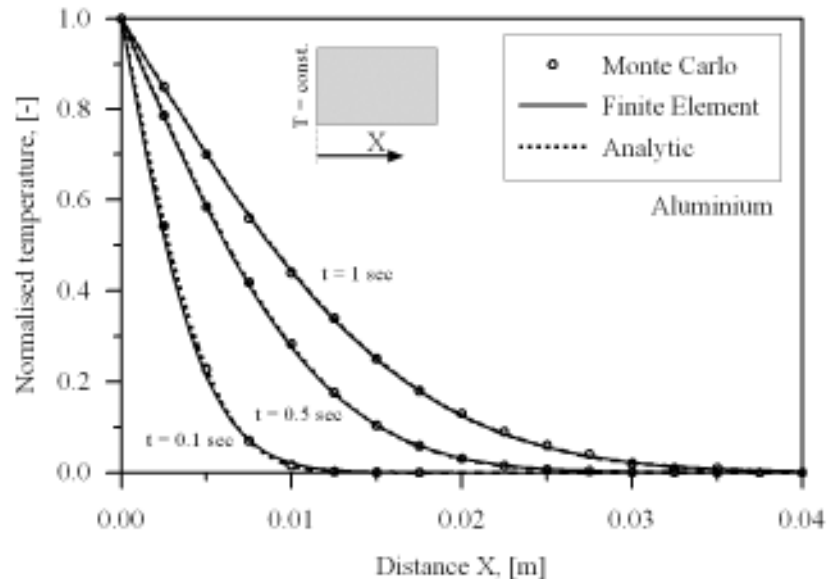

Fig. 6   Simulated temperature profiles in homogeneous aluminium.

It can be seen that there is excellent agreement between all three results.

Fig. 7 shows an example temperature profile obtained by the LMC method in a layered composite of aluminium and paraffin with the layers arranged normal to the heat flow. Here, the thermal parameters of the two phases are of course very different. In the same figure are the results of a determination of the temperature profile using Finite Element analysis. It can be seen that there is excellent agreement between the two methods.
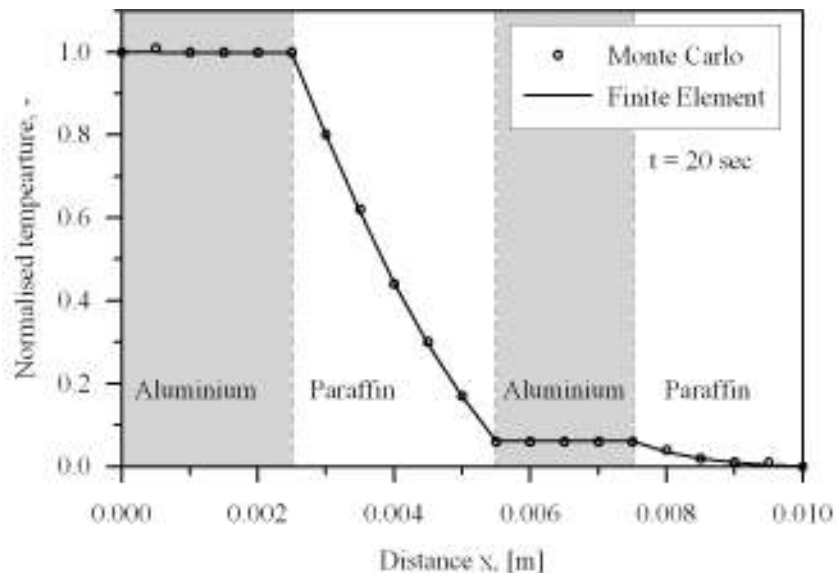

Fig. 7   Simulated temperature profile in a layered two phase aluminium – paraffin composite.

The analysis is repeated for an inverted arrangement of the aluminium and paraffin phases. Again, an excellent agreement between the LMC and Finite Element solutions can be found (see Fig. 8).
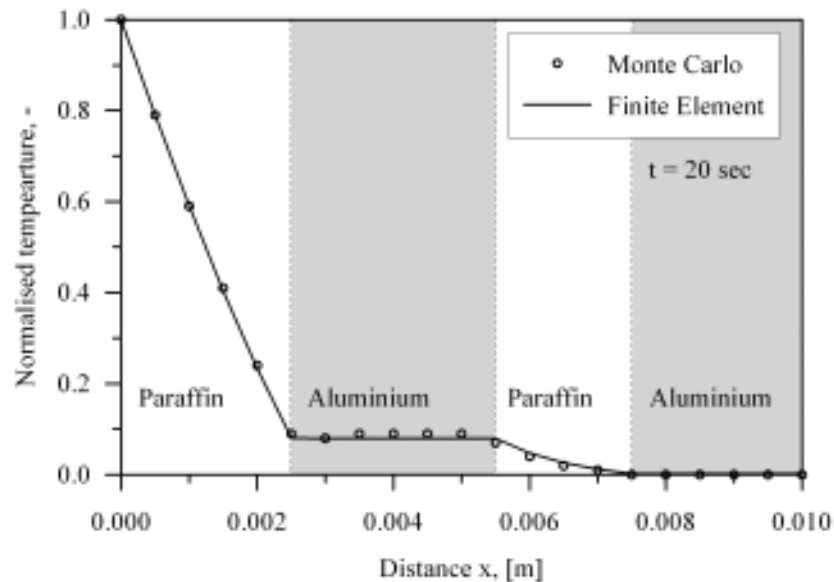

Fig. 8   Simulated temperature profile in a layered two phase paraffin - aluminium composite.

4. Concluding remarks

In this review paper, we introduced the recently developed LMC method for addressing and solving phenomenologically-based mass and heat transport problems especially for composite and porous materials. We described in detail the application of this method to calculate effective mass diffusivities and to determine concentration profiles. Next, we described in detail the application of the LMC method to the calculation of effective thermal conductivities, thermal diffusivities and the determination of temperature profiles. Where possible, in both cases, results of the method were compared with results of exact or Finite Element methods. Excellent agreement was shown. These applications have demonstrated the power, flexibility and reliability of the LMC method for addressing phenomenological mass and heat transport problems. Compared with the Finite Element method, the LMC method is of course much slower. For the same level of accuracy computation times with the LMC method can be expected to be many thousands of times greater than with the Finite Element method. This must be considered a disadvantage of the LMC method. Moreover, there are many commercial Finite Element software packages available but there are none for the LMC method at this time: a new program must be written for each problem. The principal advantage of the LMC method is being able to address readily mass and heat transport problems that are almost impossible to mesh with the Finite Element method.

References

[1] G.E. Murch, in G.E. Murch and A.S. Nowick (Eds.) Diffusion in Crystalline Solids, Academic Press, Orlando, 1984, p.379.

[2] Y. Mishin, I.V. Belova and G.E. Murch, Def. Diffus. Forum, **237-**240 (2005)271.

[3] I.V. Belova and G.E. Murch, Sol. St. Phen., 129 (2007) 1.

[4] I.V. Belova, G.E. Murch, N. Muthubandara and A. Öchsner, Sol. St. Phen., 129 (2007) 111.

[5] A. Haji-Sheikh and E.M. Sparrow, J. Heat Transfer, (Trans ASME), 89 (1967) 121.

[6] T. Fiedler , A. Öchsner, N. Muthubandara, I.V. Belova and G.E. Murch, Mat. Sc. Forum, 553 (2007) 51.

[7] I.V. Belova and G.E. Murch, in A. Öchsner, G. E. Murch and J. S. de Lemos (Eds.) Cellular and Porous Materials. Thermal Properties, Simulation and Prediction, Wiley – VCH, Weinheim, in press.

[8] A. Einstein, Ann. Phys. (Leipzig) 17 (1905) 549.

[9] M. v. Smoluchowski, Ann Phys. (Leipzig) 21 (1906) 756.

[10] G. Ayrault and G. Ehrlich, J. Chem. Phys. 60 (1974) 281.

[11] A.D. Le Claire, in: H. Eyring, D. Henderson and W. Jost (Eds.) Physical Chemistry: An Advanced Treatise, Vol. 10, Academic Press, New York, 1970, p. 261.

[12] G.W. King, Indust. Eng. Chem., 43 (1951) 2475.

[13] E.W. Hart, Acta Met., 5 (1957) 597.

[14] I. Kaur, Y. Mishin and W. Gust, Fundamentals of Grain and Interphase Boundary Diffusion, Wiley, Chichester, 1995.

[15] J.R. Manning, Diffusion Kinetics for Atoms in Crystals, Van Nostrand, Princeton, 1968.

[16] D.P. Riley, I.V. Belova and G.E. Murch, Proc. Mat. Res. Soc. Symp., 677 (2001) AA7.11.1 (e-published).

[17] J.P. Lavine and D.L. Losee, J. Appl. Phys. 59 (1984) 924.

[18] J.P. Lavine, in K. Board and D.R.J. Owen (Eds.) Simulation of Semiconductor Devices and Processes, Pineridge Press, 1984.

[19] P. Metsch, F.H.M. Spit and H. Bakker, Phys. Stat. Sol. (a), 93 (1986) 543.

[20] S. Torquato, Random Heterogeneous Materials, Springer-Verlag, New York 2002.

[21] J.R. Kalnin, E.A. Kotomin and J. Maier, J. Phys. Chem. Solids, 63 (2002) 449.

[22] I.V. Belova and G.E. Murch, J. Phys. Chem. Solids, 64 (2003) 873.

[23] I.V. Belova and G.E. Murch, in P. Vincenzini and V. Buscaglia (Eds.) Mass and Charge Transport in Inorganic Materials, Techna, Faenza, Italy, 2002, p. 225.

[24] J.C. Maxwell, A Treatise on Elasticity and Magnetism, Third Edition, Clarendon Press, 1892, p. 435.

[25] J.C. Maxwell-Garnett, Phil. Trans. Royal Soc., 203 (1904) 386.

[26] I.V. Belova and G.E. Murch, Def. Diffus. Forum, 218/220 (2003) 79.

[27] I.V. Belova and G.E. Murch, J. Meta. Nanocryst. Mat., 19 (2004) 23.

[28] I.V. Belova and G.E. Murch, Def. Diffus. Forum, 261/262 (2007) 103.

[29] I.V. Belova and G.E. Murch, Phil. Mag., 84 (2004) 17.

[30] A.D. Brailsford and K.G. Major, Br. J. Appl. Phys., 15 (1964) 313.

[31] P. Knauth, J. Electroceramics, 5 (2000) 111.

[32] P. Heitjans and S. Indris, J. Phys. Condens. Matter, 15 (2003), R1257.

[33] I.V. Belova and G.E. Murch, J. Phys. Chem. Solids, 66 (2005) 722.

[34] G.E. Murch, Diffus. Def. Data, 32 (1983) 1.

[35] J.P. Lavine and D.L. Losee, J. Appl. Phys. 59 (1984) 924.

[36] G.E. Murch and S.J. Rothman, Diffus. Def. Data, 42 (1985) 17.

[37] I.V. Belova and G.E. Murch, Phil. Mag. A, 81 (2001) 2447.

[38] P. Metsch, F.H.M. Spit and H. Bakker, Phys. Stat. Sol. (a), 93 (1986) 543.

[39] I.V. Belova and G.E. Murch, Def. Diffus. Forum, in press.

[40] S.V. Divinski, F. Hisker, Y.-S. Kang, J.-S. Lee and Chr. Herzig, Z. Metallk. 93 (2002) 256.

[41] J.D. Hodge, J. Am. Ceram. Soc. 74 (1991) 823.

[42] I.V. Belova and G.E. Murch Proc. Mat. Res. Soc. 677 (2001) AA7.7 (e-published)

[43] I.V. Belova and G.E. Murch, Proc. Mat. Res. Soc., 677 (2001) AA7.20 (e-published).

[44] I.V. Belova, N. Muthubandara, G.E. Murch, M. Stasiek and A. Öchsner, Sol. St. Phen., 129 (2007) 111.

[45] I.V. Belova, A. Öchsner, N. Muthubandara, and G.E. Murch, Def. Diffus. Forum, 266 (2007) 29.

[46] I.V. Belova and G.E. Murch, J. Mat. Proc. Tech., 153/154 (2004) 741.

[47] T. Fiedler, A. Öchsner, I.V. Belova and G.E. Murch, Adv. Engg. Mat., in press.

[48] T. Fiedler, A. Öchsner, I.V. Belova and G.E. Murch, Adv. Engg. Mat., in press.