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A Lattice Monte Carlo analysis on coupled reaction and mass diffusion

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Abstract For the first time, a newly developed Lattice Monte Carlo (LMC) method is used to determine concentration profiles for combined mass diffusion and chemical reaction. Different chemical reaction models are considered: instantaneous reaction, irreversible reaction and reversible reaction. Several simple problems are addressed so that LMC solutions can be compared to exact analytical and numerical reference solutions. Excellent agreement between analytical solutions and numerical results is obtained. In addition, a more complex scenario is considered in order to present the capability of the new method.

Keywords Lattice Monte Carlo, mass diffusion, chemical reaction, coupled analysis.

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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 enormous developments and has enjoyed numerous 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 thermal diffusion problems in materials.

For mass diffusion, 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. Recently, a wholly different type of Monte Carlo method has been developed for addressing multiscale *phenomenological* diffusion problems (where it is called the Lattice Monte Carlo (LMC) method [3,4]). In the LMC method, the phenomenological diffusion problem is mapped onto a simple cubic (usually) lattice which is then explored by virtual particles. Depending on the physics of the problem considered, the virtual particles correspond to fixed amounts of matter (mass diffusion analysis), thermal energy (thermal diffusion analysis) or even elastic deformation energy (elastic analysis) [5]. From another perspective, the LMC method is basically a type of finite-difference method that is embedded in a quasi-simulation of the physical process. The LMC method has shown itself to be very capable for solving complex phenomenological mass and thermal diffusion problems. For example, it has been used to calculate effective mass diffusivities in inhomogeneous materials where the diffusivity may depend on position [6] and to calculate concentration profiles where the diffusivity depends on position [3]. It has also been used to address steady state and transient thermal problems in multi-phase materials. Analogous to effective mass diffusivities, effective thermal conductivities can be obtained for composites [7,8] using LMC steady-state simulation. Furthermore, transient thermal behaviour can be addressed where thermal conductivities are functions of position [9] and temperature [10].

In this paper, and for the first time, a newly developed LMC method is used to address the coupling of mass diffusion and chemical reaction. Such problems are normally addressed with finite element [11] or finite difference methods [12,13]. However, it is shown in the present study that the novel LMC method forms a numerically stable and accurate alternative to these methods and furthermore provides the ability to address highly non-linear problems.

2. Lattice Monte Carlo and chemical reactions

In the Lattice Monte Carlo (LMC) method, mass diffusion is simulated by means of random walks of ‘virtual’ particles that represent quantities of matter. The random walks are directed by jump probabilities p_j which are in fact scaled mass diffusivities D . In the case of a successful jump attempt, matter is transferred from a lattice node to a neighbouring node and the local concentrations c in the volumes represented by the nodes are updated. The arrangement of lattice nodes can be chosen arbitrarily. For reasons of simplicity, a simple cubic arrangement with a constant jump length s is selected for the present analysis. In order to simulate mass diffusion of multiple species, an additional synchronisation algorithm is required.

A flow diagram of the LMC simulation is shown in Fig. 1. Prior to the simulation, initial conditions are fulfilled. In order to initialise the starting concentrations $c_{\text{init}} = c(t = 0)$

‘virtual’ particles are added to particular nodes until the required concentrations are reached. The same procedure applies to constant concentration boundary concentrations.

Fig. 1 LMC flow diagram

Next, the LMC simulation is started. At each jump attempt, a species i is chosen using a simple synchronisation algorithm. To this end, all species are assigned an internal calculation time t_i and the species with the lowest time is selected. In the next step, the position of a random ‘virtual’ particle of this species is determined. Subsequently, a jump direction is randomly obtained. In a simple cubic lattice, a total of six directions is possible. Depending on material properties or concentration at the origin and destination of the jump attempt, the jump probability p_j can now be determined. Jump probabilities are calculated from diffusivities $D_i(x,c)$ that can be functions of location x and/or local concentrations c . The local diffusivities are scaled by the maximum possible diffusivities $\max(D_i)$ and therefore exhibit values between zero and one:

$$p_j = \frac{D_i(x,c)}{\max(D_i)} \quad (1)$$

Next, a uniformly distributed random number $0 \leq r < 1$ is generated and compared to the jump probability. If the condition $p_j > r$ is fulfilled the jump attempt is successful and the concentrations of origin and target nodes are updated. Otherwise, the concentrations remain unchanged before the simulation time t_i is incremented and the next simulation cycle is started. The time increment Δt_i is indirectly proportional to the total number N_i of particles of the species i :

$$\Delta t_i = \frac{s^2}{6 \cdot \max(D_i)} \cdot \frac{1}{N_i} . \quad (2)$$

The symbol s is the distance between two neighbouring nodes (i.e. the length of a jump) and can be scaled to any distance. The accuracy of the LMC simulation is mainly controlled by the size of the time increments Δt_i . In addition, a sufficiently small node distance s must be chosen in order to resolve local concentration gradients and the geometry of the domain. Small time increments are achieved by using large populations N_i of ‘virtual’ particles and/or fine lattice models resulting in a small jump length s . However, the simulation time is then also increased and therefore a compromise between accuracy and computational load must be found.

The simulation of a chemical reaction (cf. Fig 1, grey boxes) in LMC simulations depends on the chosen reaction model. In the case of an instantaneous reaction, local concentrations are corrected after each successful jump attempt to ensure the constant species ratio R (cf. Section 3). In the case of irreversible or reversible rate reactions (cf. Sections 4 and 5) a

different technique is applied. Following a jump attempt of species i , the time t_i is incremented as usual. This time is then compared to the absolute simulation time t which is always the maximum species time $\max(t_j)$ prior to the jump attempt. If $t_i > t$ is valid, the time difference $\Delta t = t_i - t$ is calculated and the simulation time is updated: $t = t_i$. Simultaneously, for each node and species the change in concentration c due to rate reactions is calculated according to $c = c \pm k_j \Delta t$. The k_j are the reaction rates of all relevant (reverse) reactions. Of course, other time increment algorithms along the lines of the n -fold algorithm and others that are commonly used in KMC calculations can also be implemented in the LMC method [14].

3. Instantaneous reaction

First, mass diffusion coupled with an instantaneous chemical reaction is considered. The reactant A diffuses into a stationary solid B and reacts instantaneously ($A + B \rightarrow C$). This type of chemical reaction is governed by the constant ratio R of the concentrations of the diffusing reactants a and immobile products c :

$$R = \frac{c}{a} . \quad (3)$$

The diffusion equation can then be written as [15]:

$$\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - \frac{\partial c}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - R \frac{\partial a}{\partial t} \quad (4)$$

As the name indicates, the reaction occurs instantaneously and a fraction of the mobile reactants is transformed. As a consequence, the diffusion of reactant A is ‘slowed down’ and a corrected diffusion coefficient D' must be used to describe its diffusion behaviour:

$$D' = \frac{D}{R + 1} \quad (5)$$

For a semi-infinite medium with a constant surface concentration a_0 and an initial concentration $a_{\text{init}} = 0$ the concentration profile is then given by the relation [15]:

$$a(x, t) = a_0 \cdot \operatorname{erfc}\left(\frac{x}{2 \cdot \sqrt{D' \cdot t}}\right) \quad (6)$$

Figure 2 shows concentration profiles of the exact analytical solution (6) and LMC data for the cases $R = 2$ and $R = 10$. Full lines correspond to the analytical solutions and LMC results are shown as markers. Excellent agreement between the approaches can be seen.

Fig 2 Concentration profiles for mass diffusion and instantaneous reaction.

4. Irreversible reaction

In this section, irreversible first-order reactions with constant reaction rates k_1 are addressed. For this case, the diffusion equation of species A can be rewritten as [15]:

$$\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - k_1 \cdot a, \quad (7)$$

where a is the concentration of the reactants. Let us again consider a semi-infinite medium with a constant surface concentration a_0 . According to Carslaw and Jaeger [16] the exact solution of the concentration profile is given by:

$$a(x,t) = \frac{a_0}{2} \cdot \left\{ \exp\left(-x \cdot \sqrt{\frac{k}{D}}\right) \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - \sqrt{kt} + \exp\left(-x \cdot \sqrt{\frac{k}{D}}\right) \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) + \sqrt{kt} \right\} \quad (8)$$

Analytical and LMC results are shown in Fig. 3. Again, excellent agreement between the numerical LMC and analytical solutions is obtained. In addition, a dashed line is drawn that corresponds to diffusion without chemical reaction. The comparison with the drawn line of the analytical solution (8) shows that the irreversible rate reaction distinctly alters the concentration profile.

Fig 3 Concentration profiles for mass diffusion and irreversible reaction.

5. Reversible reaction

Most chemical reactions are in fact reversible reactions. The previously considered irreversible reaction can be extended by introducing a reverse reaction that transforms the products C back into their reactants ($C \rightarrow A$). The reaction rate of this reverse reaction is denoted by k_2 and the diffusion equation for species A must be extended according to [15]:

$$\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - k_1 \cdot a + k_2 \cdot c \quad (9)$$

5.1 Reversible reaction in an infinite sheet

First, a relatively simple problem (cf. Fig. 4a) is considered where an exact analytical solution can be used as a reference for verification. An infinite sheet of thickness $2l_2$ is suspended between two layers of solute (thickness l_1). Reactants are initially dispersed in the solute (concentration a_0) and diffuse into the sheet. As a consequence, the concentration of the reactants in the solute decreases with time. The chemical reaction and its reverse reaction occur in the sheet at rates k_1 and k_2 respectively. The analytical solution for the concentration profile of the reactants is given by [15]:

$$a(x,t) = \frac{l_1 \cdot a_0}{l_1 + \left(\frac{k_2}{k_1} + 1\right) \cdot l_2} + \sum_{n=1}^{\infty} \left[\frac{a_0 \exp(\alpha_n t)}{1 + \left(1 + \frac{k_1 k_2}{(\alpha_n + k_1)^2}\right) \left(\frac{l_2}{2l_1} + \frac{\alpha_n}{2D\beta_n^2} + \frac{\alpha_n^2 l_1 l_2}{2D^2 \beta_n^2}\right)} \cdot \frac{\cos \beta_n x}{\cos \beta_n l_2} \right]. \quad (10)$$

where l_1 and l_2 are geometric dimensions as shown in Fig 4a. The numerical parameters α_n and β_n are the non-zero roots of the following equations:

$$\frac{l_1 \alpha_n}{D_A} = \beta_n \tan \beta_n l_2 \quad (11)$$

$$\beta_n^2 = -\frac{\alpha_n}{D_A} \cdot \frac{\alpha_n + k_1 + k_2}{\alpha_n + k_1} \quad (12)$$

Figure 4b shows normalised concentration profiles a/a_0 for the times $t = 0.01$ s, $t = 0.1$ s and $t = 1$ s. The initial concentration of the reactants a_{init} inside the sheet is zero. At the start of the simulation, reactants of species a diffuse into the sheet. At the time $t = 0.01$ s an error function type concentration profile is obtained. Simultaneous to the mass diffusion, reactants are transformed into products with a reaction rate k_1 and the reverse reaction occurs at a rate k_2 . At the time $t = 1$ s, the reactants are almost homogenously dispersed in the sheet and changes in the concentration profile are mostly due to the chemical reactions. At steady state, the concentration profile is constant $a/a_0 = 0.5$. The comparison between LMC and analytical solution again reveals excellent agreement.

*Fig. 4 Combined diffusion and reversible reaction in a sheet:
a) geometry, b) concentration profile.*

5.2 Reversible reaction in parallel phases

The second considered reversible reaction system consists of two reactants species designated by A and B that are initially separated by an impenetrable barrier (cf. Fig. 5a). The initial concentrations are a_{init} and b_{init} , respectively. The size of the system is assumed to be large enough so that the initial concentrations outside the reaction / diffusion zone remain constant at all times. At time $t = 0$, the barrier is removed and phase A ($D_A > 0$) diffuses and mixes with the immobile species B ($D_B = 0$). The two reactants react with a reaction rate k_1 and form the product species C. The products diffuse with a diffusivity $D_C > 0$ and are transformed back to species A and B via the reverse reaction k_2 . The resulting system of equations can be written as [17]:

$$\frac{\partial a}{\partial t} = D_A \frac{\partial^2 a}{\partial x^2} - k_1 \cdot a b + k_2 \cdot c$$

$$\begin{aligned}\frac{\partial b}{\partial t} &= -k_1 \cdot ab + k_2 \cdot c \\ \frac{\partial c}{\partial t} &= D_c \frac{\partial^2 c}{\partial x^2} + k_1 \cdot ab - k_2 \cdot c\end{aligned}\tag{13}$$

where a , b and c are the concentrations of phases A, B and C, respectively. Due to the increased complexity of the problem, no exact analytical reference solution is available. Instead, LMC solutions are compared to a finite difference solution [17].

The simulation results are shown in Fig. 5b. Concentration profiles are plotted for all species at the time $t = 5000$ s. The concentration of the reactants A decreases locally in the region where the initial divider was located ($x/l = 0.5$). Inside this reaction zone, product C is formed and diffuses in both directions. Concentration profiles of reactants B are shown for several times t . It is seen that the reaction front propagates to the right as reactants B are consumed. An interesting phenomenon already described in [17] can be observed: the concentration of reactants B can locally exceed the initial concentration b_{init} . The explanation is the high diffusivity D_c of the product. The product is formed inside the reaction zone and diffuses out. The reverse reaction then increases the concentration of the immobile reactants B in the proximity of the reaction zone. In addition to the LMC results, a concentration profile obtained by a finite difference method is plotted. The finite difference solution is only valid for sufficient long times t where a local equilibrium between the diffusion and reaction terms in equation system (13) is reached. The convergence of the LMC profiles towards this long time solution is noted.

Fig.5 Reversible reaction of two initially separated reactant : a) geometry, b) concentration profiles (finite difference profile taken from [17, Fig. 1]).

6. Non-linear mass diffusion and reversible reaction

Up to this point, only relatively simple reaction-diffusion problems were considered in order to verify LMC results with analytical or numerical reference solutions. However, the LMC method allows addressing systems with a complexity far beyond the previous examples. In order to illustrate the potential of this novel technique, a reversible reaction system with non-linear mass diffusion is considered. Let us assume a diffusion system where the concentration-dependent diffusivities are given by the following relations:

$$\begin{aligned}D_A(a) &= C_1 \cdot a + C_2 \\ D_B(b) &= C_3 \cdot b + C_4\end{aligned}$$

$$D_c(c) = C_5 / (c + C_6) \quad (14)$$

Phase A diffuses through one surface (constant surface concentration $a_0 = 0.1 \text{ } b_{\text{init}}$) into a cube of side length $l = 0.1 \text{ m}$ with initial concentration b_{init} (cf. Fig. 6a). The reaction (reaction rate $k_1 = 1 \text{ s}^{-1}$) produces a component C. The reverse reaction is governed by the reaction rate $k_2 = 0.01 \text{ s}^{-1}$.

Figures 6b and 6c show the evolution of the concentrations profiles over time. At small times (i.e. $t = 0.1 \text{ s}$), the concentration profile of reactants B is similar to the initial condition $b(x) = b_{\text{init}}$. Due to the concentration dependence of the diffusivity $D_A(a)$ and the high concentration gradient da/dx the initial diffusion of the reactant A is strongly non-linear. Since, the chemical reaction is proportional to the product $k_1 \cdot a \cdot b$ and the starting concentrations a are very low, products C are only slowly formed. With increasing time, the concentration a increases throughout the cube. Simultaneously, the chemical reaction gains ‘momentum’ and the concentration of the products c is increased. At the time $t = 10 \text{ s}$, a significant fraction of reactants B has been consumed and the local product concentrations c already exceed the concentrations a of the reactants A.

Fig. 6 Non linear diffusion reaction: a) geometry and boundary conditions, b) concentration profiles of reactants, c) concentration profiles of products.

6 Conclusions and future research

This paper has introduced the use of a novel LMC method in addressing problems of coupled mass diffusion and chemical reaction. Three different reaction types, namely instantaneous, irreversible and reversible reactions were considered. First, relatively simple problems were addressed so that the LMC results could be verified with exact solutions. For all considered cases an excellent agreement between numerical results and reference solutions was found. In the last section, a more complex system with concentration-dependent mass diffusivities was addressed. A reversible reaction was simulated and concentration profiles were obtained for reactants and products. Thus, it was demonstrated that the LMC method can also be used for addressing highly non-linear problems. In our future research, the LMC method will be further extended to include coupled heat transfer. Chemical reactions release or require thermal energy that may change local temperatures which in turn affect temperature-dependent mass diffusivities and reaction rates. In order to obtain accurate temperature and concentration distributions, thermal diffusion must be accounted for.

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Fig 2 Concentration profiles for mass diffusion and instantaneous reaction.

Fig 3 Concentration profiles for mass diffusion and irreversible reaction.

Fig. 4 Combined diffusion and reversible reaction in a sheet:

a) geometry, b) concentration profile.

Fig.5 Reversible reaction of two initially separated reactants : a) geometry, b) concentration profiles (finite difference profile taken from [17, Fig. 1]).

Fig. 6 Non linear diffusion reaction: a) geometry and boundary conditions, b) concentration profiles of reactants, c) concentration profiles of products.

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