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Letter to the Editor

The effective diffusion coefficient in a one-dimensional discrete lattice with the inclusions

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ABSTRACT

The expression for the effective diffusion coefficient in one-dimensional discrete lattice model of random walks in matrix with inclusions and unequal hopping lengths is derived. This allowed us to suggest a physical interpretation to the concentration jump – *ad hoc* parameter commonly used in extended effective medium theory for accounting particle partial reflection on the boundary matrix–inclusion. The analytical results obtained are in excellent agreement with computer simulations.

1. Introduction

Transport properties (in particular, the effective diffusion coefficients) of heterogeneous materials, including composites, ceramics with grain boundaries, polycrystalline materials etc. is of fundamental importance for a numerous problems in materials science, physics, chemistry, biology (e.g. Ref. [1]). One of the goals of the extended effective medium (EEM) theory [2,3] is to calculate the effective diffusion coefficient D_{eff} as a function of the particle diffusion coefficients in the matrix D_1, in the inclusions, D_2 and inclusion volume fraction f. In recent studies, the particle concentration jump on the boundary matrix–inclusion was introduced as a phenomenological *ad hoc* parameter. The derived effective diffusion coefficient [2,3].

$$D_{eff} = \frac{D_1}{(1-f+kf)\left(1-f+\frac{D_1}{D_2 k}f\right)} \tag{1}$$

contains the parameter $k = \frac{\bar{c}_2}{\bar{c}_1}$ which is a ratio of the average particle concentrations in the inclusion $\bar{c}_2$ and matrix $\bar{c}_1$ (or ratio of corresponding equilibrium concentrations). The continuous diffusion approximation gives no other interpretation to the parameter k. In this short paper we present a general one-dimensional theory, based on the random walk (RW) arguments where the boundary conditions appear in the natural way. The concentration jump will be expressed through the RW parameters—hopping lengths and waiting times. Model is extended also to the case where the reflection or trapping of particles by the inclusions are allowed. The analytical results are compared with the computer simulations of diffusion on discrete lattice with inclusions.

2. Effective diffusion coefficient in the simple RW model

Let us derive an expression for the effective diffusion coefficient in the simple RW model. Consider a discrete lattice consisting of periodically repeated regions of length L (representative element) consisting of matrix region and inclusion characterized by the hopping lengths and waiting times l_1, τ_1 and l_2, τ_2, respectively, (Fig. 1). The number of lattice sites in matrix and inclusions we denote by N_1 and N_2.

The residence time τ_L of the particle on the representative element L is related to the effective diffusion coefficient D_{eff} sought for

$$\tau_L = \frac{L^2}{2D_{eff}} \tag{2}$$

In order to derive the formula for the effective diffusion coefficient in this general case when, hopping lengths and waiting times in the matrix and inclusion are different, we first reduce the problem to the case of equal hopping lengths l_1 both in matrix and inclusion (but different waiting times).

Equal hopping lengths in a matrix and inclusion may be achieved by stretching inclusion by a factor l_1/l_2 (if $l_1 > l_2$). The hopping lengths over a whole new representative element L' now will be equal to l_1. In this particular case the effective diffusion coefficient could be easily obtained as

$$D^{\tau}_{eff} = \frac{Nl_1^2}{2\tau_{L'}} = \frac{Nl_1^2}{2(N_1\tau_1 + N_2\tau_2)} = \frac{l_1^2}{2[(1-\Phi)\tau_1 + \Phi\tau_2]} \tag{3}$$

where N_1 and N_2 are the numbers of particle hops in the matrix and inclusion, respectively, $N = N_1 + N_2$ is the total number of hops with the length l_1 on L', and Φ the volume (length) fraction of the inclusion in the stretched representative element. It is easily seen, that

$$\Phi = \frac{fl_1/l_2}{1-f+fl_1/l_2} \tag{4}$$

and the length of stretched representative element is related with L by $L' = L(1-f+fl_1/l_2)$. After the stretching of L to L' one gets Fig. 2 instead of Fig. 1.

Denoting the effective diffusion coefficient on the stretched representative element by D^{τ}_{eff} we have for the residence time on L'

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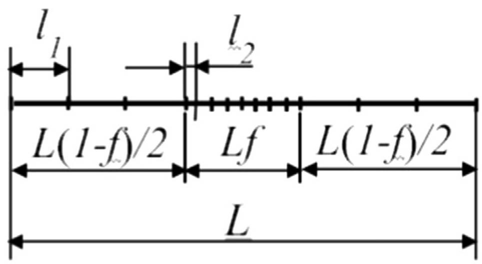

Fig. 1. The representative element of the length L (hopping lengths $l_1 = 4l_2$).

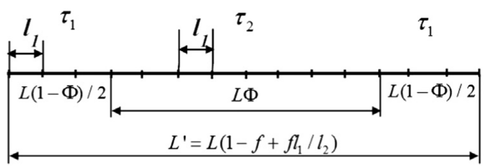

Fig. 2. The stretched representative element.

$$\tau_{L'} = \frac{L'^2}{2D^{\tau}_{eff}} = \frac{L^2(1-f+fl_1/l_2)^2}{2D^{\tau}_{eff}}. \tag{5}$$

Since the number of lattice sites on L' remain the same as on L, both residence times τ_L and $\tau_{L'}$ are equal. Thus using Eqs. (2), (4) and (5), we get

$$D_{eff} = \frac{l_1^2}{2\tau_1\left(1-f+\frac{\tau_2 l_1}{\tau_1 l_2}f\right)\left(1-f+\frac{l_1}{l_2}f\right)} \tag{6}$$

Using the definitions $D_1 = \frac{l_1^2}{2\tau_1}$, $D_2 = \frac{l_2^2}{2\tau_2}$, we arrive at Eq. (1) with the parameter

$$k = \frac{l_1\tau_2}{l_2\tau_1} \tag{7}$$

Remembering that $k = c_2/c_1$, we get from Eq. (7)

$$c_1u_1 = c_2u_2 \tag{8}$$

where u_1 and u_2 are particle "velocities" ($u = c/\tau$) in the matrix and inclusion, respectively.

Eqs. (7) and (8) give the RW interpretation to the origin of concentration jump: the particle fluxes into the inclusion and from it should be equal. Eq. (8) allows us a natural generalization for the case when the inclusions reflect or trap particles. Instead of Eq. (8) we then get

$$p_1c_1u_1 = p_2c_2u_2 \tag{9}$$

The generalized one-dimensional effective diffusion coefficient reads now

$$D_{eff} = \frac{D_1}{\left(1-f+\frac{p_1\tau_2 l_1}{p_2\tau_1 l_2}f\right)\left(1-f+\frac{p_2}{p_1}\frac{l_1}{l_2}f\right)} \tag{10}$$

In the case of $l_1 = l_2$ Eq. (10) reads

$$D_{eff} = \frac{D_1}{\left(1-f+\frac{p_1\tau_2}{p_2\tau_1}f\right)\left(1-f+\frac{p_2}{p_1}f\right)} \tag{11}$$

The derived Eq. (10) was tested for the wide range of parameter values for l_1, l_2, τ_1, τ_2 and p_1/p_2, performing discrete lattice computer simulations. The agreement of the simulation results with the theoretical results were within the precision 2–3%. For example, in the case $l_1 = l_2 = 0.025$, $L = 10$, $f = 0.2$ and $p_1/p_2 = 0.01$ (Fig. 1) for $N = 10^7$ and the number of repeated histories $5\cdot10^4$ we obtained $D_{sim}/D_{eff} = 1.021$ (D_{sim} is the result of simulations). More details will be published elsewhere.

3. Effective diffusion coefficient in the generalized transition rate model

We can establish a connection between our effective diffusion coefficient, Eq. (10), received in a discrete model for arbitrary diffusion parameters, and the discrete rate model of heterogeneous periodic medium developed in Refs. [4,5]. Let us consider the one-dimensional model with N sites on the length of periodicity L'. The rate constants for the transition left–right in the matrix we denote by α_1 and for right–left by β_1 (in inclusion by α_2, β_2, respectively) (Fig. 3).

On the interface site the transition rates are α and β. As it was shown in [5], eq. (19), the Derrida's [4] equation for one-dimension hopping model may be rewritten in the following form

$$D_{eff} = \frac{\alpha_1 N^2 l^2}{\left(1+\sum_{n=2}^{N}\prod_{j=2}^{n}\frac{\alpha_{j-1}}{\beta_j}\right)\left(1+\sum_{n=2}^{N}\prod_{j=2}^{n}\frac{\beta_j}{\alpha_j}\right)} \tag{12}$$

Eq. (12) assumes explicitly a single hopping length (distance between nodes) l, so that $L' = Nl$. A direct calculation of Eq. (12) for the discrete model by eliminating separately matrix and inclusions gives for the effective diffusion coefficient

$$D_{eff} = \frac{l^2\alpha_1}{\left(\frac{N_1}{N}+\frac{N_2}{N}\frac{\alpha\beta_1}{\beta\alpha_2}\right)\left(\frac{N_1}{N}+\frac{N_2}{N}\frac{\beta}{\alpha}\right)} \tag{13}$$

where N_1 and N_2 are the numbers of sites in the matrix and inclusion, respectively. When deriving Eq. (13), we assumed that N_1, $N_2 \gg 1$. Denoting the volume (length) fraction occupied by the inclusion by Φ and taking into account that $\alpha_1 = \beta_1$, $\alpha_2 = \beta_2$ for the symmetrical diffusion, one gets instead of Eq. (13)

$$D_{eff} = \frac{D_1}{\left(1-\Phi+\frac{\alpha\alpha_1}{\beta\alpha_2}\Phi\right)\left(1-\Phi+\frac{\beta}{\alpha}\Phi\right)} \tag{14}$$

where $D_1 = l^2\alpha_1 = \frac{l^2(\alpha_1+\beta_1)}{2} = \frac{l^2}{2\tau_1}$ and $\Phi = N_2/N$.

Eq. (14) has the form of Eq. (11) above and thus confirms our result, Eq. (9), where the parameters $p_1 = \frac{\alpha}{\alpha+\beta}$, $p_2 = \frac{\beta}{\alpha+\beta}$ are random walk probabilities from the matrix into the inclusion and vice versa, respectively. Eq. (14) suggests the interpretation of parameters used in the extended effective medium model [6].

Lastly, we can generalize the discrete model, Eq. (14), for the case of different hopping lengths l_1 and l_2 in the matrix (sites with α_1, β_1) and in the inclusion (sites with α_2, β_2), respectively. Taking into account Eq. (6) and $L' = L(1-f+fl_1/l_2)$ one gets

$$D_{eff} = \frac{D_1}{\left(1-f+\frac{\alpha\alpha_1 l_1}{\beta\alpha_2 l_2}f\right)\left(1-f+\frac{\beta l_1}{\alpha l_2}f\right)} \tag{15}$$

A comparison of Eq. (15) with Eq. (1) demonstrates that the particle concentration jump k could be expressed through the combination of transition rates in matrix, inclusion and the

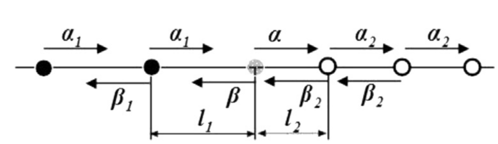

Fig. 3. One-dimensional lattice rate model. Solid circles are matrix sites, empty circles inclusions, gray the boundary site.

boundary site

$$k = \frac{\alpha\alpha_1 l_1}{\beta\alpha_2 l_2} \tag{16}$$

4. Conclusions

Using the discrete lattice model of random walks, we derived in a simple way expression for the effective diffusion coefficient in one-dimensional case. The proposed method permits us to generalize discrete transition rate model to the case of unequal hopping lengths in the matrix and inclusion, to obtain corresponding effective diffusion coefficient and interpret parameters of EEM, introduced *ad hoc*. Despite the fact that the transition rate model is derived in the one-dimensional case, we believe that suggested interpretation of EEM parameters remains valid also in two and three dimensions. The two-dimensional EEM theory and computer simulation results will be presented elsewhere.

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