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Calculations of the effective diffusion coefficient for inhomogeneous media

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Abstract

We suggest a modification of the well-known Maxwell-Garnett equation for the mobility (effective diffusion coefficient) in two-phase media (a matrix with inclusions) which permits the description of a wide range of experimental situations. The novel approach correctly treats the partial trapping of a diffusing particle by an inclusion as well as consequences of an energy barrier for the particle penetration into an inclusion. Computer simulations show that the presented mean-field theory reproduces surprisingly well results for square inclusions without concentration limitation. For inclusions with other shapes (e.g. spherical) the theory works well up to concentrations at which mobile particles become trapped in ‘pockets’ between inclusions. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Calculation of transport properties of inhomogeneous materials has a long history, starting with the pioneering papers by Maxwell-Garnett [1]. The composite material is usually modeled as a combination of a host phase (matrix) characterized by the diffusion coefficient of a probe particle, D_2 , and spherical inclusions (the second phase) characterized by the particle diffusion coefficient D_1 , radius r_0 and volume fraction Φ . These two diffusion coefficients are expressed through the hop length l and the average waiting time between the two successive hops τ :

$$D_i = \frac{l_i^2}{2d\tau_i}, \quad i = 1, 2, \quad (1)$$

where d denotes the space dimension (1, 2, or 3).

A very similar problem arises in the description of other transport coefficients (electrical and thermal conductivity, dielectric constant, magnetic permeability, elastic moduli, etc.) in two-phase systems [2–10]. Examples of systems for

which it is desired to predict such properties are porous media, polymer blends, foams, and ceramic–metal mixture.

In this paper, we consider cases for which the generally accepted relation for the effective diffusion fails and requires generalization.

2. Standard Maxwell-Garnett approach

Let us reproduce briefly a typical derivation of what is generally known as *the Maxwell-Garnett (MG) formula*. Experimentally the matrix with inclusions is characterized by an *effective diffusion coefficient*, D_{eff} , which is a function of D_1 , D_2 , and Φ . To determine it, one can use the electrostatic analog. We consider a macroscopically homogeneous material with the diffusion coefficient D_{eff} . Following the original derivation of MG equation, we imagine that the particle concentration c has an average gradient \vec{g} (similarly to a homogeneous electric field) along some axis.

Then we insert into the material a spherical inclusion of radius r_0 surrounded by a spherical shell of a host material (matrix) with the radius r_1 and assume that the inclusion does not change the concentration field outside, i.e. at $r \geq r_1$. (The radii r_1 and r_0 are defined in such a way that the inclusion’s volume fraction:

$$\Phi = \frac{r_0^3}{r_1^3}$$

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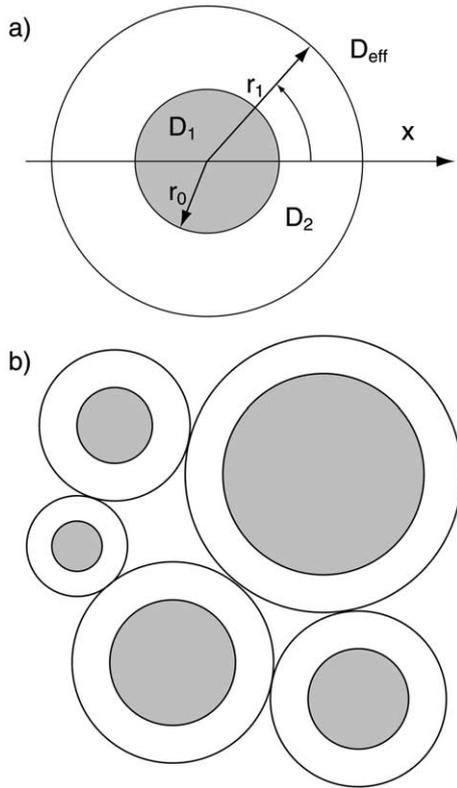


Fig. 1. (a) Schematic presentation of the matrix with inclusions in terms of a core-shell model; (b) the case of different-size inclusions.

is satisfied) (Fig. 1a). The effective diffusion coefficient D_{eff} can be determined from the following steady-state equation:

$$\Delta c_{r,\vartheta}(r, \vartheta) = 0, \quad (2)$$

in the coordinates r and ϑ , where ϑ is an angle between \vec{r} and the external gradient \vec{g} . The appropriate solution of Eq. (2) reads:

$$c_1(r, \vartheta) = \text{Arcos } \vartheta, \quad (0 < r \leq r_0), \quad (3)$$

$$c_2(r, \vartheta) = \left(Br + \frac{E}{r^2} \right) \cos \vartheta, \quad (r_0 < r \leq r_1) \quad (4)$$

$$c_{\text{eff}}(r, \vartheta) = -g r \cos \vartheta, \quad (r_1 < r) \quad (5)$$

where $c_i(r, \vartheta)$ is a local particle concentration in inclusions ($i = 1$) or in a host material ($i = 2$).

Equations for the unknown constants A , B , E and g arise from the boundary conditions for the particle concentrations and fluxes:

$$c_1(r_0, \vartheta) = c_2(r_0, \vartheta) \quad (6)$$

$$D_1 \frac{\partial c_1(r, \vartheta)}{\partial r} \Big|_{r=r_0} = D_2 \frac{\partial c_2(r, \vartheta)}{\partial r} \Big|_{r=r_0} \quad (7)$$

$$c_2(r_1, \vartheta) = c_{\text{eff}}(r_1, \vartheta) \quad (8)$$

$$D_2 \frac{\partial c_2(r, \vartheta)}{\partial r} \Big|_{r=r_1} = D_{\text{eff}} \frac{\partial c_{\text{eff}}(r, \vartheta)}{\partial r} \Big|_{r=r_1} \quad (9)$$

From Eqs. (3)–(9) we obtain a set of equations:

$$r_0^3 A - r_0^3 B - E = 0 \quad (10)$$

$$D_1 r_0^3 A - D_2 r_0^3 B + 2D_2 E = 0 \quad (11)$$

$$r_1^3 B + E + r_1^3 g = 0 \quad (12)$$

$$D_2 r_1^3 B + D_{\text{eff}} r_1^3 g - 2D_2 E = 0 \quad (13)$$

Using this set of equations, one gets the MG equation sought for:

$$D_{\text{eff}} = D_2 \left[1 + \frac{3(D_1 - D_2)\Phi}{D_1 + 2D_2 - (D_1 - D_2)\Phi} \right] \quad (14)$$

In general, for an arbitrary space dimension ($d = 1, 2$ and 3) instead of Eq. (14) one finds:

$$D_{\text{eff}} = D_2 \left[1 + \frac{d(D_1 - D_2)\Phi}{D_1 + (d-1)D_2 - (D_1 - D_2)\Phi} \right] \quad (15)$$

This result holds not only for a periodic set of the same-size spherical inclusions but also for a random inclusion distribution of different r_0^i if the condition:

$$\Phi = \frac{(r_0^i)^d}{(r_1^i)^d}$$

(d is space dimension) remains to be fulfilled (Fig. 1b). However, the question, at which volume fractions Φ inclusions begin to ‘compete’ and Eq. (15) is no longer valid, remains open and could be solved by a comparison with an analytical theory which takes many-particle effects into account [8] and/or by means of direct computer simulations.

3. Disadvantages of MG equation

Consider now several cases when the generally accepted MG Eq. (15) gives incorrect results.

1. Let us begin with a situation when the inclusion is totally impenetrable, i.e. a diffusing particle is reflected at r_0 as could be described by the condition:

$$\frac{\partial c_2(r, \vartheta)}{\partial r} \Big|_{r=r_0} = 0$$

(consider also the limiting case

$$\frac{D_1}{D_2} \rightarrow 0$$

in Eq. (7)). In this situation Eq. (15) gives:

$$D_{\text{eff}} = D_2 \left[1 - \frac{2\Phi}{1 + \Phi} \right], \quad (d = 2) \quad (16)$$

$$D_{\text{eff}} = D_2 \left[1 - \frac{3\Phi}{2 + \Phi} \right]. \quad (d = 3) \quad (17)$$

Such relations are well-known in the reaction-rate theory [12]. The same result may be obtained from Eqs. (3–9), putting there $c_1(r, \vartheta) = 0$ (as well as $A = 0$, see discussion in Ref. [11]).

However, Eqs. (16) and (17) give an incorrect concentration dependence (see discussion in Ref. [7]). The correct Φ -dependence, as we show below, is:

$$D_{\text{eff}} = \frac{D_2}{1 - \Phi} \left[1 - \frac{3\Phi}{2 + \Phi} \right], \quad (d = 3) \quad (18)$$

$$D_{\text{eff}} = \frac{D_2}{1 - \Phi} \left[1 - \frac{2\Phi}{1 + \Phi} \right]. \quad (d = 2) \quad (19)$$

The reason for this incorrectness lies in the use of relation (Eq. 8). In fact, the concentration of diffusing particles in the matrix cannot be equal to that in the effective medium because in the latter all particles are stirred over a whole system's volume and thus their averaged concentration should be less by the factor of $1 - \Phi$. This indicates that Eq. (8) should be corrected as:

$$c_2(r_1, \vartheta) = k_1 c_{\text{eff}}(r_1, \vartheta), \quad (20)$$

i.e. in reality there is a jump in concentration on the core (inclusion)-shell (matrix) boundary, $r = r_1$. The question is, how to get the coefficient k_1 ? We propose to obtain it, as a much better approximation, from the expression for the average *equilibrium* particle concentration of the system (total particle number divided by total volume):

$$c_{\text{eff}} = c_1 \Phi + c_2(1 - \Phi). \quad (21)$$

In the particular case of impenetrable inclusions ($c_1 = 0$) we obtain from Eq. (21):

$$c_{\text{eff}} = c_2(1 - \Phi), \quad k_1 = \frac{1}{1 - \Phi}. \quad (22)$$

- Another restriction of the use Eq. (15) arises from the Maxwell's boundary condition $c_1(r_0, \vartheta) = c_2(r_0, \vartheta)$, Eq. (6). In fact it can be shown that Eq. (15) is valid in the case of different diffusion coefficients in the matrix and the inclusion, $D_1 \neq D_2$, *only* if the particle velocities in the matrix and inclusions coincide,

$$\frac{l_1}{\tau_1} = \frac{l_2}{\tau_2}.$$

In a general case it is necessary to introduce the measurable coefficient k connecting c_1 and c_2 :

$$c_1(r_0, \vartheta) = k c_2(r_0, \vartheta). \quad (23)$$

In order to improve the MG equation, in the above-

presented standard derivation of the effective diffusion coefficient, we can use Eqs. (20) and (23) instead of the original Maxwell's Eqs. (6) and (8). When doing so, instead of standard Eq. (15) we arrive at:

$$D_{\text{eff}} = D_2 k_1 \left[1 + \frac{d(D_1 k - D_2)\Phi}{kD_1 + (d - 1)D_2 - (kD_1 - D_2)\Phi} \right] \quad (24)$$

In the 1-D case this equation coincides with the exact solution [13].

The two coefficients k and k_1 are related through the equilibrium concentrations in inclusions and the matrix and volume fraction Φ according to Eqs. (20), (21), (23):

$$k = \frac{c_1}{c_2} \quad (25)$$

and:

$$c_2 = k_1 c_{\text{eff}}. \quad (26)$$

From Eq. (21) we obtain the volume dependence of the coefficient k_1 :

$$k_1 = \frac{1}{1 - \Phi + \frac{c_1}{c_2} \Phi}. \quad (27)$$

Using Eq. (27), one obtains the following relation instead of Eq. (24):

$$D_{\text{eff}} = \frac{D_2}{1 - \Phi + \frac{c_1}{c_2} \Phi} \left[1 + \frac{d \left(D_1 \frac{c_1}{c_2} - D_2 \right) \Phi}{(d - 1)D_2 + \frac{c_1}{c_2} D_1 - \left(\frac{c_1}{c_2} D_1 - D_2 \right) \Phi} \right]. \quad (28)$$

Similarly to the MG theory, this equation reproduces correctly both limiting cases, as Φ strives for zero and unity. Eq. (28) is a basic result of our theory. It should be recalled that c_1 and c_2 are average concentrations of diffusing particles in the two phases—the inclusions and the matrix.

It is convenient to express the ratio c_1/c_2 entering Eq. (28) through the kinetic parameters of inclusions and the matrix. In equilibrium, the steady-state situation fluxes of particles to and from inclusions are equal:

$$c_1 \frac{l_1}{\tau_1} = c_2 \frac{l_2}{\tau_2}. \quad (29)$$

Remember that the diffusion coefficients D_1 and D_2 are defined by Eq. (1).

Fig. 2 shows several important situations for the potential energy profiles of the diffusing particle, modeling its partial trapping by an inclusion (potential energy well) and the (partial) reflection from it due to the energy barrier, respectively. To describe these situations, let us introduce the *penetration probabilities* p_1 from the inclusion to the matrix and p_2 from the matrix to inclusions, respectively. Thus, in the general case one gets:

$$\frac{c_1}{c_2} = \frac{l_2 p_2 \tau_1}{l_1 p_1 \tau_2}. \quad (30)$$

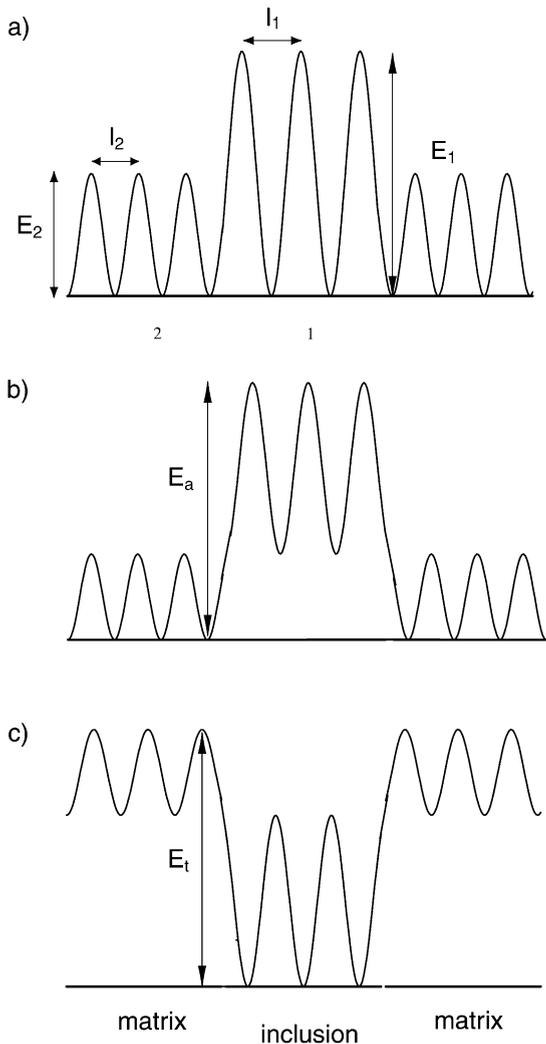


Fig. 2. Different cases of energy barriers between the matrix and inclusions, l_i , E_i are a hop length and an activation energy for diffusion in the two phases, $i = 1, 2$: (a) an inclusion with the diffusion coefficient in the inclusions smaller than in the matrix; there is no energy barrier between them; (b) an energy barrier E_a for the penetration into inclusion, $p_2 \leq 1$; (c) partial trapping of particles inside inclusions, $p_1 \leq 1$. The detrapping energy is E_t .

In the case of a potential barrier the penetration probability (per unit time) is defined entirely by the activation energy E_{12} [14]:

$$p_2 = \tau_2 \cdot \exp\left(\frac{-E_{12}}{kT}\right). \quad (31)$$

The same is true for the particle hop from the inclusion with the probability p_1 . Eqs. (28) and (30) allow one to describe many diffusion-controlled processes in composite media with trapping and release of mobile particles.

Now let us compare our results with previous theories. In

the 1-D case Eq. (28) reproduces the exact result derived for a periodical inclusion distribution in the Kronig-Penny model with particle reflections (Eq. (4) in Ref. [13]) which reads in our notations as:

$$D_{\text{eff}} = \left[\frac{\Phi}{D_1 k} + \frac{1 - \Phi}{D_2} \right]^{-1} \cdot \frac{1}{1 - \Phi + \Phi k}. \quad (32)$$

where $k = c_1/c_2$.

In turn, in the 3-D case our Eq. (28) for D_{eff} coincides with that obtained in Ref. [7] for a particular case of periodic distribution of inclusions using mathematically very complicated formalism of irreversible thermodynamics with chemical potentials. The analytical results presented in Ref. [15] also demonstrate the presence of a distinctive co-factor:

$$\left(1 - \Phi + \frac{c_1}{c_2} \Phi\right)^{-1}$$

entering the D_{eff} .

In the case of a complete particle reflection from the inclusions; $D_1 = 0$, $\frac{c_1}{c_2} = 0$, Eq. (28) transforms into Eqs. (18) and (19) as quoted above. For a small volume fraction of the inclusions, $\Phi \ll 1$, one arrives at:

$$D_{\text{eff}} = D_2 \left[1 - \frac{\Phi}{2}\right], \quad (d = 3) \quad (33)$$

$$D_{\text{eff}} = D_2 [1 - \Phi]. \quad (d = 2). \quad (34)$$

Eq. (33) was received earlier in Ref. [16] whereas Eq. (34) was derived in Ref. [11] using the effective medium approximation. The expression (Eq. 33) was also derived calculating the effective self-diffusion constant of the mobile species in solution [17].

Let us consider now several limiting cases for D_{eff} . In the case of impenetrable inclusions (complete reflection of particles, $c_1/c_2 \rightarrow 0$), Eq. (28) is simplified:

$$D_{\text{eff}} = \frac{D_2(d-1)}{d-1+\Phi}. \quad (35)$$

As $\Phi \rightarrow 1$, one gets in 2-D and 3-D cases $D_{\text{eff}} = D_2/2$ and $2D_2/3$, respectively, while the MG equation yields a zero effective diffusion coefficient. This result means that in these limiting cases the particle diffusion becomes in fact one- or two-dimensional as shown in Fig. 3 for square and cubic inclusions.

To stress the role of a potential barrier in D_{eff} , let us consider the limiting case of a strong trapping, $c_2/c_1 \rightarrow 0$. From Eq. (28) one obtains:

$$D_{\text{eff}} = \frac{D_2}{k\Phi} \cdot \frac{1+d-\Phi}{1-\Phi}, \quad (36)$$

which demonstrates that D_{eff} is independent of the diffusion in inclusions. The same results in the limiting case $D_2/D_1 \rightarrow 0$.

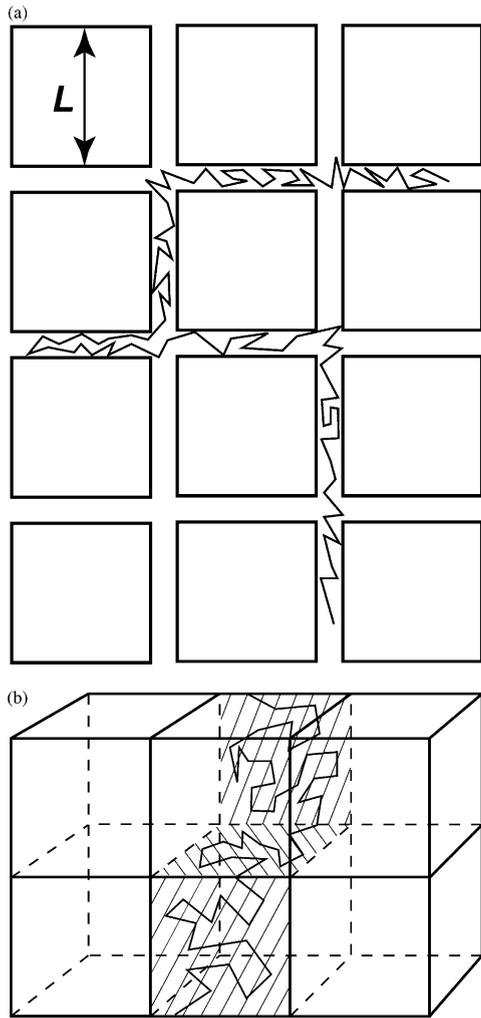


Fig. 3. Transformation of the 2-D (3-D) diffusion into 1-D and 2-D diffusion as square (cubic) inclusion fractional volume approaches unit ((a) and (b), respectively).

4. Random walk simulations

In order to compare Eq. (28) with computer simulations, we have modeled periodical arrays of spherical and square inclusions of the same size in 2-D varying the kinetic parameters l_1 , τ_1 , and l_2 , τ_2 for particle diffusion in the matrix and inclusions in a very wide range of magnitudes thus simulating very different situations mentioned above. For a periodical distribution of inclusions in the matrix we monitored a particle diffusion and calculated D_{eff} by the standard formula:

$$D_{\text{eff}} = \frac{\langle r^2 \rangle}{2dt}, \quad (37)$$

where t is diffusion time and the mean-square particle displacement during its random walks on the lattice:

$$\langle r^2 \rangle = \frac{\sum_{i=1}^N r_i^2}{N} \quad (38)$$

was averaged over more than (typically) $N = 10^5 - 10^6$ runs. The waiting time τ was chosen to be sufficient to satisfy the standard condition: $\langle r^2 \rangle$ is much larger than the squared distance between adjacent inclusions L^2 . For this purpose we used the first-passage algorithm [8]. We modeled cases of both impenetrable and penetrable inclusions. The hop length l was always chosen to be much smaller than both the shortest distance between boundaries of the two nearest inclusions and inclusion radius. Results of computer simulations are discussed below.

5. Simple exactly solvable model

There is one particular case in which D_{eff} could be determined exactly for the two-phase inhomogeneous media in all dimensions: $l_1 = l_2$, $\tau_1 \neq \tau_2$, $D_1 \neq D_2$. That is, the waiting times in the matrix and inclusions differ but hopping lengths are equal (Fig. 2a). In this case after N walks we get from Eq. (37):

$$D_{\text{eff}} = \frac{\langle r^2 \rangle}{2d(N_1 \tau_1 + N_2 \tau_2)} \quad (39)$$

Here N_1 and N_2 are numbers of particle walks in the phases 1 and 2, respectively. For sufficiently large N (diffusing particle visits inclusions many times) one obtains, obviously:

$$N_1 = \Phi N, \quad N_2 = (1 - \Phi)N \quad (40)$$

Substituting Eq. (40) and $\langle r^2 \rangle = 2dNl^2$ into Eq. (39), we receive results well-known for conductivity in inhomogeneous media [5,6]:

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D_1} \Phi + \frac{1}{D_2} (1 - \Phi) \quad (41)$$

Note that this equation is often considered to be valid only for 1-D but as we have demonstrated, in fact it could be used in any space dimension. (Compare this equation with Eq. (32) where energy barriers for particle penetration to/from inclusions are incorporated.)

The same result also follows immediately from our general Eq. (28), taking into account that at $l_1 = l_2$:

$$\frac{c_1}{c_2} = \frac{\tau_1}{\tau_2} \quad (42)$$

which leads to

$$D_{\text{eff}} = \frac{D_2}{1 - \Phi + \frac{\tau_1}{\tau_2} \Phi}. \quad (43)$$

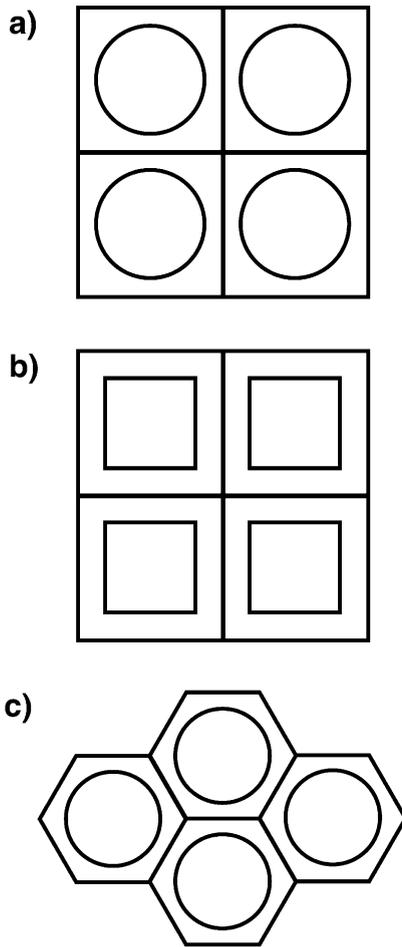


Fig. 4. Different types of lattices and inclusions: spherical and square shape inclusions in the square lattice (a, b), spherical inclusions in the hexagonal lattice (c).

Eq. (43) coincides with Eq. (41), we just have to replace: τ_1/τ_2 by D_2/D_1 .

The effective diffusion coefficient could be easily related to the fractions of time which mobile particle spends in matrix (t_1) and inclusions (t_2):

$$D_{\text{eff}} = D_1 \frac{t_1}{t_1 + t_2} + D_2 \frac{t_2}{t_1 + t_2} \quad (44)$$

From Eqs. (28) and (44) one obtains:

$$\begin{aligned} \frac{t_2}{t_1} &= 1 - \frac{1}{A}, \quad A \\ &= \frac{k(1-d-\Phi)}{(1-\Phi+k\Phi) \left[k \frac{D_1}{D_2} (1-\Phi) + d - 1 + \Phi \right]} \end{aligned} \quad (45)$$

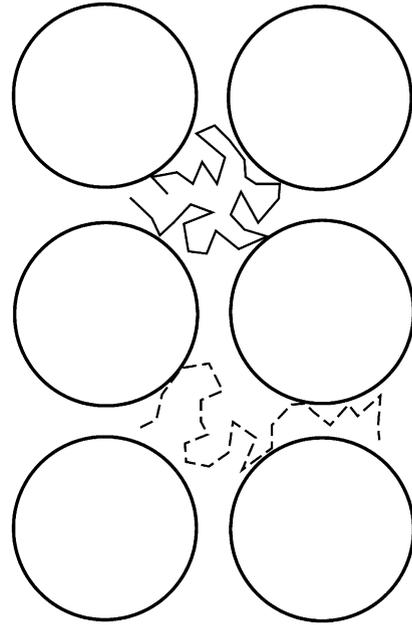


Fig. 5. A pocket effect when particles become trapped between inclusions which results in zero effective diffusion coefficient.

6. Results of computer simulations

It should be mentioned that at high concentrations of the inclusions their *shape* becomes important (Fig. 4)—the effect never discussed earlier in the literature. If inclusions are circular or spherical and touch each other at one point, $D_{\text{eff}} \rightarrow 0$ as $\Phi \rightarrow \Phi_{\text{lim}}$ (which could be easily calculated as $\Phi_{\text{lim}} = \pi/4$ and $3/\pi$ for circular inclusions in the square lattice and hexagonal lattice, respectively). The reason is that a particle spends most of its time in a ‘pocket’ formed by nearest inclusions (Fig. 5).

Let us discuss here results of modeling inclusions of different shapes as shown in Fig. 4. (Very preliminary results were presented in Ref. [18]). First of all, our computer simulations clearly demonstrated the correctness of our theory in the case of large concentrations of the square inclusions (Fig. 6) in a whole range of concentrations and failure of the MG theory. Our simulations agree within 1% with exact but complicated result [19]. This figure presents also the results of calculations for the effective diffusion coefficient at completely reflecting *circular* inclusions in the 2-D square and hexagonal lattices (Fig. 4a,c), $D_1/D_2 = 0$.

The immediate conclusion can be drawn that the computer simulations also coincide, with a precision of 1%, with our theory, Eqs. (28) and (35), for the case of spherical inclusions, up to inclusion volume fractions as large as $\Phi = 0.6$ and 0.8 , for square and hexagonal lattices, respectively. The discrepancy at larger volume fraction is due to

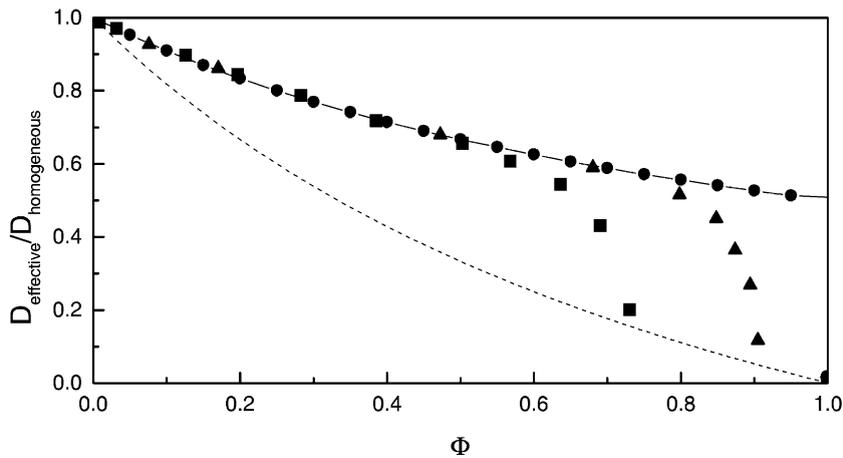


Fig. 6. Comparison of generally accepted Maxwell-Garnett theory (dotted line, Eq. (14)), and our Eq. (28) (solid line) with 2-D computer simulations for periodically distributed reflecting inclusions versus their dimensionless concentration; square symbols are for the spherical inclusions on a square lattice; triangles for the spherical inclusions on a hexagonal lattice; and full circles are for square inclusions on a square lattice.

the just explained ‘pocket’ effect (Fig. 5) neglected in the analytical theory. What should be stressed here is that the MG Eq. (14) (dotted line) gives a rather incorrect Φ -dependence even at small Φ since it neglects differences in the particle concentrations in inclusions and in matrix. This becomes very transparent in the case of impenetrable inclusions.

7. Discussion and conclusions

In this paper a modified Maxwell-Garnett Eq. (28) was derived which gives surprisingly good description of the mobility in the 2-D heterogeneous media with square inclusions. (We believe that this is also true for 3-D case.) The main advantage of our mean-field theory is its simplicity, transparency and validity for any space dimension—in contrast to previous mathematically very complicated approaches based on irreversible thermodynamics with chemical potentials [7], cluster expansion [15], etc. Validity of our universal relation for the effective diffusion coefficient is proved by computer simulations. These latter demonstrated for the first time the effect of inclusion shape at high inclusion concentrations.

Note that the concentration jump on the inclusion boundary, Eq. (25), commonly known as *partition coefficient*, is not new and was observed in all previous theories [15,20,21]. The more so, this partition coefficient was found also experimentally, e.g. for metallic alloys Al-Cu, Al-Ge, Al-In, Al-Sn [20]. The concentration jump is not surprising which becomes obvious in the limiting case of impenetrable inclusions ($c_2 > 0$, $c_1 = 0$).

The expression suggested for the effective diffusion coefficient permits treatment of solid-state inhomogeneous systems (composites, ceramics) with very different properties

of inclusions and the host matrix, including a partial reflection of diffusing particles from inclusions and a trapping inside inclusions. The more so, it could be useful in quite different fields like mathematical modeling of the release of antimicrobial agent from packaging material to a food product [21], transport through membranes, or self-diffusion of small molecules in colloidal systems containing polymers, proteins, micells, etc. [7].

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