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## Modified Maxwell-Garnett equation for the effective transport coefficients in inhomogeneous media

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**Abstract.** The well known Maxwell-Garnett equation for the effective diffusion coefficient in two-phase media (a matrix with spherical inclusions) is modified in order to describe a wide range of experimental situations. This novel approach correctly treats the partial trapping of a diffusing particle by an inclusion as well as the consequences of an energy barrier for the particle penetration into an inclusion.

The problem of calculating transport properties of a composite material has a long history, dating back to Maxwell-Garnett [1]. Usually a composite material is assumed to consist 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 diffusion coefficient  $D_1$ , radius  $r_0$  and a fractional volume  $\Phi$ . These two diffusion coefficients are expressed through the hop length  $l$  and the waiting time between the two successive hops  $\tau$  in a very simple form:

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

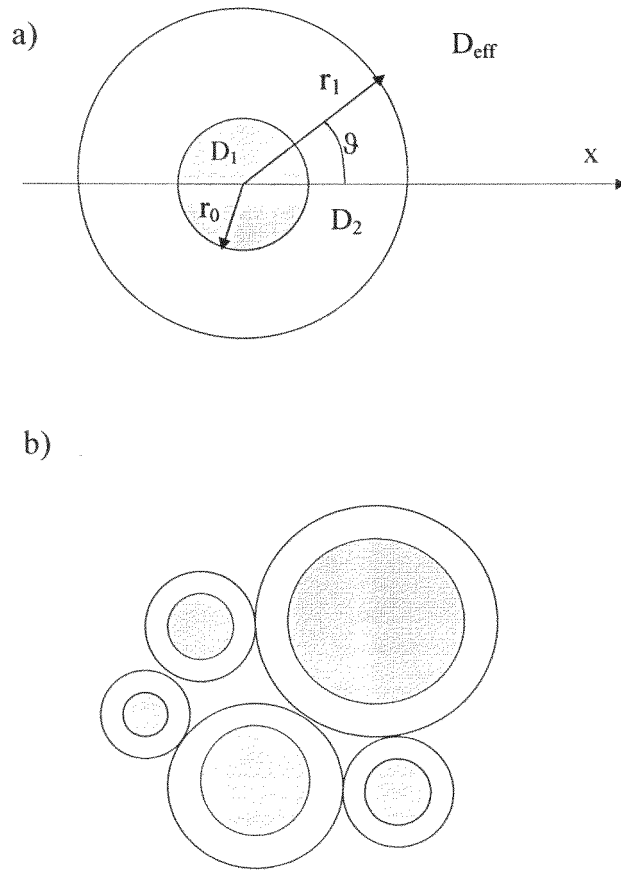
where  $d$  is space dimension (1, 2, or 3).

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 [2–7]. Examples of systems for which it is desirable to predict such properties include porous media, polymer blends, foams, ceramic-metal mixture, etc.

In this paper, we consider cases when the generally accepted relation fails and suggest its generalization. For simplicity, we treat the effective diffusion coefficient. Let us briefly reproduce a typical derivation of what is generally known as *the Maxwell-Garnett formula*. Experimentally, the matrix with inclusions is characterized by the *effective diffusion coefficient*,  $D_{\text{eff}}$ , which is a function of  $D_1$ ,  $D_2$ , and  $\Phi$ . To determine it, one can use the electrostatic analogy. Consider a macroscopically homogeneous material with the diffusion coefficient  $D_{\text{eff}}$ . Imagine that particle concentration  $c$  has a gradient  $g$  (similarly to a homogeneous electric field) along some axis

$$c_{\text{eff}}(\mathbf{r}) = -\mathbf{g} \cdot \mathbf{r}. \quad (2)$$

Then we insert into material a spherical inclusion of radius  $r_0$  surrounded by a spherical shell of a host material (matrix) with 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  $r_0$  define the inclusion's



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

volume fraction  $\Phi = \frac{r_0^3}{r_1^3}$ , figure 1(a).) (If we can do it for a single inclusion, in the same manner we can introduce into material any amount of inclusions.) The effective diffusion coefficient  $D_{\text{eff}}$  could be determined from the following steady-state equation

$$\Delta c_{r,\vartheta}(r, \vartheta) = 0 \quad (3)$$

in the coordinates  $r$  and  $\vartheta$ , where  $\vartheta$  is an angle between  $r$  and the external gradient  $g$ . The appropriate solution of equation (3) reads

$$c_1(r, \vartheta) = Ar \cos \vartheta \quad (0 < r \leq r_0) \quad (4)$$

$$c_2(r, \vartheta) = \left( Br + \frac{E}{r^2} \right) \cos \vartheta \quad (r_0 < r \leq r_1) \quad (5)$$

$$c_{\text{eff}}(r, \vartheta) = -gr \cos \vartheta \quad (r_1 < r). \quad (6)$$

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

$$c_1(r_0, \vartheta) = c_2(r_0, \vartheta) \quad (7)$$

$$D_1 \frac{\partial c_1(r, \vartheta)}{\partial r} \Big|_{r=r_0} = D_2 \frac{\partial c_2(r, \vartheta)}{\partial r} \Big|_{r=r_0} \quad (8)$$

$$c_2(r_1, \vartheta) = c_{\text{eff}}(r_1, \vartheta) \tag{9}$$

$$D_2 \frac{\partial c_2(r, \vartheta)}{\partial r} \Big|_{r=r_1} = D_{\text{eff}} \frac{\partial c_{\text{eff}}(r, \vartheta)}{\partial r} \Big|_{r=r_1}. \tag{10}$$

From equations (4)–(10) we obtain a set of equations

$$r_0^3 A - r_0^3 B - E = 0 \tag{11}$$

$$D_1 r_0^3 A - D_2 r_0^3 B + 2D_2 E = 0 \tag{12}$$

$$r_1^3 B + E + r_1^3 g = 0 \tag{13}$$

$$D_2 r_1^3 B + D_{\text{eff}} r_1^3 g - 2D_2 E = 0. \tag{14}$$

Using this set of equations, one gets the Maxwell-Garnett equation sought for

$$D_{\text{eff}} = D_2 \left[ 1 + \frac{3(D_1 - D_2)\Phi}{D_1 + 2D_2 - (D_1 - D_2)\Phi} \right]. \tag{15}$$

In general, for an arbitrary space dimension ( $d = 1, 2$  and  $3$ ) instead of equation (15) one obtains

$$D_{\text{eff}} = D_2 \left[ 1 + \frac{d(D_1 - D_2)\Phi}{D_1 + (d - 1)D_2 - (D_1 - D_2)\Phi} \right]. \tag{16}$$

The same is true for a set of spherical inclusions of different radii  $r_0^i$  if the condition  $\Phi = \frac{(r_0^i)^d}{(r_1^i)^d}$  ( $d$  is space dimension) remains to be fulfilled (figure 1(b)). However, the question, at which volume fractions  $\Phi$  inclusions begin to compete and equation (16) is no longer valid, remains open and could be solved by a comparison with analytical theory incorporating many-particle effects (see, e.g. [7]) and/or by means of direct computer simulations.

We now consider several cases when the generally-accepted Maxwell-Garnett equation (16) gives incorrect results.

(A) Let us begin with a situation when the inclusion core  $r_0$  is totally impenetrable, i.e. a diffusing particle reflects at the  $r_0$ . This could be described by the condition  $\frac{\partial c_2(r, \vartheta)}{\partial r} \Big|_{r=r_0} = 0$  (or considering the limiting case  $\frac{D_1}{D_2} \rightarrow 0$  in equation (8)). In this situation equation (16) gives

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

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

Such relations are well known in the reaction-rate theory [13]. The same result may be obtained from equations (4)–(9), inserting  $c_1(r, \vartheta) = 0$  (as well as  $A = 0$ , see the discussion in [12]).

However, equations (17) and (18) give incorrect  $\Phi$ -dependence (see the discussion in [6].) The correct  $\Phi$ -dependence, as we show below, is

$$D_{\text{eff}} = \frac{D_2}{1 - \Phi} \left[ 1 - \frac{3\Phi}{2 + \Phi} \right] \quad (d = 3) \tag{19}$$

$$D_{\text{eff}} = \frac{D_2}{1 - \Phi} \left[ 1 - \frac{2\Phi}{1 + \Phi} \right] \quad (d = 2). \tag{20}$$

The reason for this incorrectness lies in the use of relation (9). In fact, concentration of diffusing particles in the matrix (a shell region,  $r_0 < r < r_1$ ) cannot be equal to that in the effective medium because in the latter all particles are ‘smashed’ through a whole system’s

volume and thus their averaged concentration is less by a factor of  $1 - \Phi$ . This indicates that equation (9) should be corrected

$$c_2(r_1, \vartheta) = k_1 c_{\text{eff}}(r, \vartheta) \quad (21)$$

i.e. in reality there is a kink 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 from the expression for *equilibrium* particle concentrations in the three regions: core, shell, and the effective medium:  $c_1$ ,  $c_2$  and  $c_{\text{eff}}$ :

$$c_{\text{eff}} = c_1 \Phi + c_2(1 - \Phi). \quad (22)$$

In the particular case of impenetrable inclusions ( $c_1 = 0$ ) we obtain from equation (22)

$$c_{\text{eff}} = c_2(1 - \Phi) \quad k_1 = \frac{1}{1 - \Phi}. \quad (23)$$

(B) Another restriction of the use of equation (16) arises from Maxwell's boundary condition  $c_1(r_0, \vartheta) = c_2(r_0, \vartheta)$ . In fact it can be shown that equation (16) is valid in the case of different diffusion coefficients in the matrix and inclusion,  $D_1 \neq D_2$ , only if 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 coefficient  $k$  connecting  $c_1$  and  $c_2$ :

$$c_1(r_0, \vartheta) = k c_2(r_0, \vartheta). \quad (24)$$

In order to extend the Maxwell-Garnett equation, we use the analogy with results obtained earlier in the 1D case [10] and equations (21), (24) instead of the original Maxwell's equations (7), (9). In doing so, instead of the standard equation (16) we arrive at

$$D_{\text{eff}} = D_2 k_1 \left[ 1 + \frac{d(D_1 k - D_2)\Phi}{kD_1 + (d-1)D_2 - (kD_1 - D_2)\Phi} \right]. \quad (25)$$

Now let us define the two coefficients  $k$  and  $k_1$  through equilibrium concentrations in inclusions and the matrix:

$$k = \frac{c_1}{c_2} \quad (26)$$

and

$$c_2 = k_1 c_{\text{eff}}. \quad (27)$$

From equation (22) we obtain

$$k_1 = \frac{1}{1 - \Phi + \frac{c_1}{c_2} \Phi}. \quad (28)$$

Using equation (28), one gets instead of equation (25) the following relation:

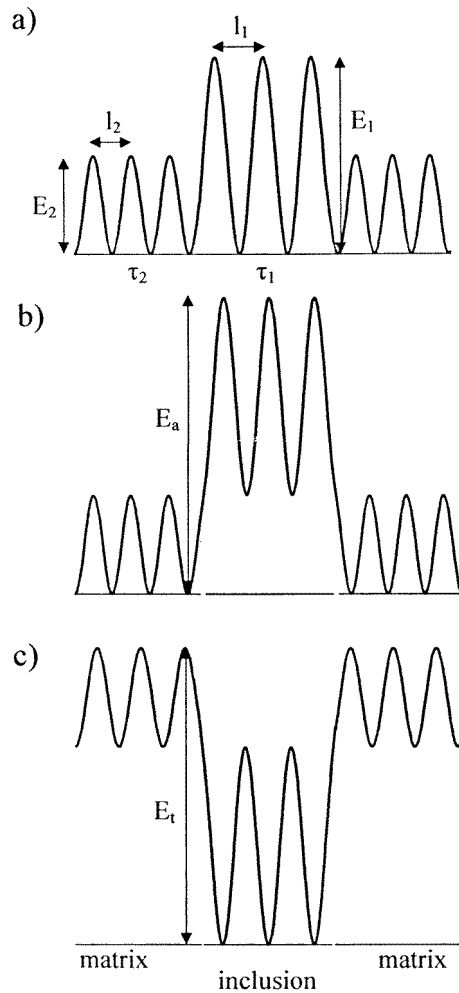
$$D_{\text{eff}} = \frac{D_2}{1 - \Phi + \frac{c_1}{c_2} \Phi} \left[ 1 + \frac{d(D_1 \frac{c_1}{c_2} - D_2)\Phi}{(d-1)D_2 + \frac{c_1}{c_2} D_1 - (\frac{c_1}{c_2} D_1 - D_2)\Phi} \right]. \quad (29)$$

Similarly to the Maxwell-Garnett theory, this equation correctly reproduces both limiting cases, as  $\Phi$  strives for zero and unity. Equation (29) is central to our paper.

It should be recalled that  $c_1$  and  $c_2$  are equilibrium *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 equation (29) through the kinetic parameters of inclusions and the matrix. In the equilibrium, steady-state situation fluxes of particles to and from inclusions are equal:

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



**Figure 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  $E_t$ .

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

Figure 2 shows several important situations for the potential energy profiles of diffusing particle modelling; 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 obtains

$$\frac{c_1}{c_2} = \frac{l_2 p_2 \tau_1}{l_1 p_1 \tau_2}. \quad (31)$$

In the case of a potential barrier the penetration probability is defined entirely by the

activation energy  $E_a$

$$p_2 = \text{constant} \cdot \exp\left(\frac{-E_a}{kT}\right). \quad (32)$$

A similar relation is true for the particle hop from the inclusion with the probability  $p_1$ . Equations (29), (31) allow us 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 1D case equation (29) reproduces the exact result derived for a periodical inclusion distribution in the Kronig–Penny model with particle reflections (equation (4) in [10]) which reads in our notations as

$$D_{\text{eff}} = \left[ \frac{\Phi}{D_1 k} + \frac{1 - \Phi}{D_2} \right]^{-1} \cdot \frac{1}{1 - \Phi + \Phi k} \quad (33)$$

where  $k = c_1/c_2$ .

In its turn, in the 3D case equation (29) with  $D_{\text{eff}}$  has been obtained in [6] for a regular (periodic) distribution of inclusions and using irreversible thermodynamics. (The main result is given in terms of  $c_1$  and  $c_2$  without the coefficient  $k$  interpretation.) Analytical results presented in [8] also demonstrate the presence of a distinctive cofactor  $(1 - \Phi + \frac{c_1}{c_2}\Phi)^{-1}$  entering the  $D_{\text{eff}}$ .

In the case of a complete particle reflection from the inclusions ( $D_1 = 0$ ,  $\frac{c_1}{c_2} = 0$ ) equation (29) transforms into equations (19) and (20) quoted above. For a small inclusion volume fractions,  $\Phi \ll 1$ , one arrives at

$$D_{\text{eff}} = D_2 \left[ 1 - \frac{\Phi}{2} \right] \quad (d = 3) \quad (34)$$

$$D_{\text{eff}} = D_2 [1 - \Phi] \quad (d = 2). \quad (35)$$

Equation (34) was received earlier in [9] whereas equation (35) in [14] uses the effective medium approximation. The expression (34) was also derived calculating the effective self-diffusion constant of mobile species in solution [11].

In order to compare equation (29) with computer simulations, we have modelled mono-dispersive periodic spherical inclusions of the same radius  $r_0$  in 1D and 2D varying the kinetic parameters  $d_1, l_1, \tau_1$ , and  $d_2, l_2, \tau_2$  for particle diffusion in the matrix and inclusions in a very wide range of magnitudes thus simulating very different situations mentioned above [14]. For a periodical distribution of inclusions in the matrix we monitored a particle diffusion and calculated  $D_{\text{eff}}$  by the standard formula

$$D_{\text{eff}} = \frac{\langle r^2 \rangle}{2dt} \quad (36)$$

where  $t$  is diffusion time and the mean-square particle displacement

$$\langle r^2 \rangle = \frac{\sum_{i=1}^N r_i^2}{N} \quad (37)$$

was averaged over more than  $N = 10^5$  runs. The waiting time  $\tau$  was chosen to be sufficient to satisfy the condition  $\langle r^2 \rangle > L$ , where  $L$  is the distance between adjacent inclusions. We have used the first-passage algorithm [7].

There is one particular case when  $D_{\text{eff}}$  may 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 the hopping lengths are equal (figure 2(a)). In this case after  $N$  walks we get from equation (36)

$$D_{\text{eff}} = \frac{\langle r^2 \rangle}{2d(N_1 \tau_1 + N_2 \tau_2)}. \tag{38}$$

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

$$N_1 = \Phi N \quad N_2 = (1 - \Phi)N. \tag{39}$$

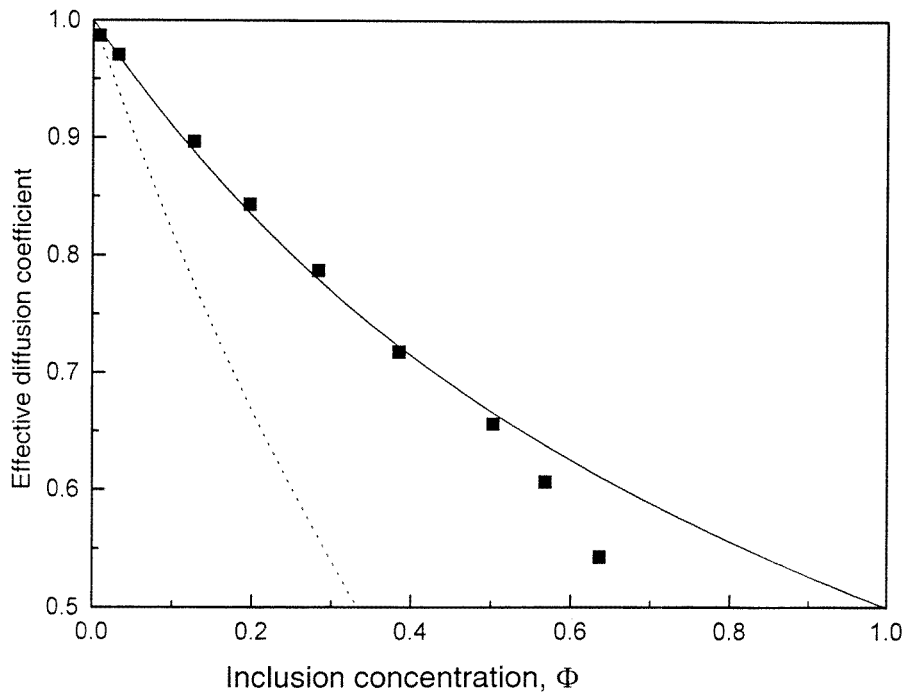
Substituting equation (39) and  $\langle r^2 \rangle = 2dNl^2$  into equation (38), we receive results well known for conductivity in inhomogeneous media [5]

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D_1} \Phi + \frac{1}{D_2} (1 - \Phi). \tag{40}$$

Note that this equation is often considered to be valid only for 1D but as we have demonstrated, it could in fact be used in any space dimension if  $l_1 = l_2$ . (Compare this equation with equation (33) where energy barriers for particle penetration to/from inclusions are incorporated.)

The same result also follows immediately from our general theory, equation (29), taking into account that at  $l_1 = l_2$

$$\frac{c_1}{c_2} = \frac{\tau_1}{\tau_2} \tag{41}$$



**Figure 3.** Comparison of Maxwell-Garnett theory (dotted curve, equation (15)) and our equation (29) (full curve) with computer simulations (squares) for reflecting inclusions versus their dimensionless concentration.



which leads to

$$D_{\text{eff}} = \frac{D_2}{1 - \Phi + \frac{\tau_1}{\tau_2} \Phi}. \quad (42)$$

Equation (42) coincides with equation (40) just by replacing  $\frac{\tau_1}{\tau_2}$  by  $\frac{D_2}{D_1}$ .

We will present results of detailed analysis of these computer simulations in a separate paper [14]. To give here an idea of the accuracy of our approach, figure 3 illustrates the calculations for the effective diffusion coefficient at completely reflecting inclusions at the 2D square lattice ( $\frac{D_1}{D_2} = 0$ ). The conclusion could be drawn that computer simulations coincide with our theory, equation (29), with the precision of 1% up to inclusion volumes as large as  $\Phi = 0.5$ . A further discrepancy is due to an approximation in the theory which simulates inclusions as spheres surrounded by the matrix shells. What should be stressed here is that the Maxwell-Garnett equation (15) (dotted curve) gives incorrect  $\Phi$  dependence even at small  $\Phi$  since it neglects differences in particle concentrations in inclusions and in the matrix.

It should be stressed in conclusion that the modified Maxwell-Garnett equation (29) is derived in the framework of mean-field theory. A suggested expression for the effective diffusion coefficient (also valid for other transport coefficients in inhomogeneous two-phase media) permits treatment of inhomogeneous systems with very different properties of spherical inclusions and the host matrix, including a partial reflection of diffusing particles from inclusions and their trapping inside inclusions.

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