Generalised Maxwell-Garnett equation: application to electrical and chemical transport†

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In this paper we discuss the implementation of different equilibrium concentrations in each of the phases into the Maxwell-Garnett effective medium formula for diffusion in heterogeneous media. We put the derivation given by Kalnin *et al.*, *J. Phys. Chem. Solids*, 2002, **63**, 449, on safer grounds and extend it to non-dilute carrier concentrations. The relation to Maxwell's mixing rule is also elaborated. It is shown that the formula can not only successfully be applied to conductivity problems but also to describe steady state chemical diffusion in heterogeneous media such as polycrystalline samples. The comparison with the brick layer model corroborates these points but also shows that—in the case of heterogeneous media—one has to be cautious in applying steady state results to transient kinetics.

1. Introduction

Diffusion in heterogeneous media is a very relevant topic in many fields of science and technology ranging from ceramics to biology. Not only multiphase systems are addressed but also polycrystalline materials in which the grain boundary exhibits transport coefficients different from those in the bulk.

In 1904 Maxwell-Garnett (MG)[1] derived a popular mixing rule for optical properties of glasses with metallic inclusions. In essence, MG presented and re-derived an equation that had been, in principle, well known before this date and has been associated with the names of Maxwell, Clausius, Mossotti, Lorentz and Lorenz. The puzzling history of this equation is discussed in a very worthwhile review by Landauer.[2]

These authors concentrated on the isomorphic problems of dielectric permeability (ε) and conductivity (σ) in heterogeneous systems, *i.e.* referred to the dielectric displacement density $\boldsymbol{D} = \varepsilon \boldsymbol{E}$ and the electric current density $\boldsymbol{i} = \sigma \boldsymbol{E}$ (electric field $\boldsymbol{E} = -\sigma \nabla \varphi$; where φ is the electric potential). Later, others used the MG equation for deriving transport coefficients in other linear transport problems, *e.g.* when considering Fickian diffusion and for the derivation of the effective diffusion coefficient defined by $\boldsymbol{j} = -D \nabla c$ (see, *e.g.*, ref. 3–5).

When applied to a heterogeneous medium composed of two phases, 1 and 2, that are structurally invariant up to the phase boundary, which does not exhibit any perceptible interfacial resistance, the MG result reads

$$D_{\text{eff}} = D_2 \left[1 + \frac{d(D_1 - D_2)\Phi_1}{D_1 + (d-1)D_2 - (D_1 - D_2)\Phi_1} \right]. \quad (1)$$

Here $d = 1, 2, 3$ denotes the space dimension, whereas the diffusion coefficients in phase 1 (inclusions) and the host phase 2 (matrix) are D_1 and D_2, respectively. Inclusions are characterised by the fractional volume Φ_1. The derivation refers to the situation shown in Fig. 1, in which the spherical particle 1 is surrounded by the host phase 2, and the whole arrangement is embedded into the effective medium characterised by the effective diffusion coefficient D_{eff}.

The main point addressed in the current work is the fact that in all of these approaches the variation of the equilibrium concentration from phase to phase has been neglected. In other words, a major assumption of the Maxwell-Garnett approach, as applied to the diffusion problem, is that at the contact of phases 1 and 2 (hereafter contact 1/2) the respective concentrations are considered to be equal. However, owing to their different structures, equilibria thermodynamics demands a concentration jump at the plane of contact (from c_1 to c_2). In accordance with the MG derivation we ignore space charge effects and structural inhomogeneities within the phases. Similarly, at the contact to the effective phase (contact 2/eff) equal concentration values were assumed, an assumption which is generally not applicable and also does not take into account the volume of the inclusions (phase 1). In the years since the publication of Maxwell-Garnett's work, numerous attempts were made to generalise this equation (see, *e.g.*, ref. 2–8 and references therein). Recently,[5] two more general boundary conditions for the boundaries 1/2 and 2/eff have been introduced according to

$$c_1 = c_2 \mathit{æ} \quad \text{and} \quad c_{\text{eff}} = c_2 \mathit{æ}'. \quad (2)$$

The two constants $\mathit{æ}$ and $\mathit{æ}'$ are not independent, and the relation between $\mathit{æ}$ and $\mathit{æ}'$ is found through the ansatz

$$c_{\text{eff}} = (1 - \Phi_2)c_1 + \Phi_2 c_2, \quad (3)$$

where $\Phi_2 = 1 - \Phi_1$ and Φ_1 are the volume fractions of phase 2 (matrix) and phase 1 (inclusion). Eqn (3) is exact for the equilibrium concentrations (as long as density variations can
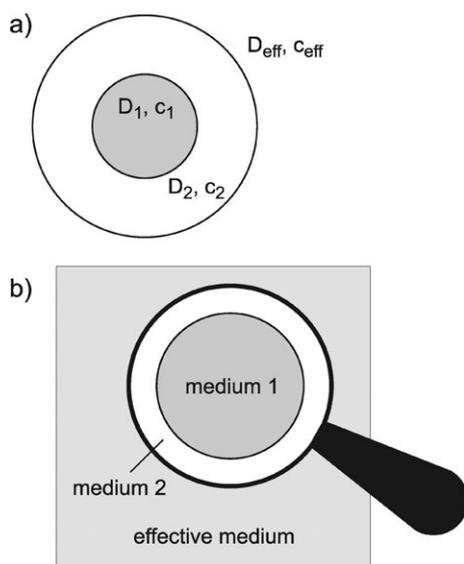
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Fig. 1 (a) Matrix with inclusions in the effective medium model, and related materials parameters; (b) schematic illustration of the effective medium model.

be ignored) and leads to

$$\alpha' = 1/[(1 - \Phi_2) + \Phi_2\alpha]. \qquad (4)$$

(Note that from $\alpha = 1$ the identity $\alpha' = 1$ follows immediately.)

This results in the following generalised relation (see ref. 5)

$$D_{\text{eff}} = \frac{D_2}{1 - \Phi_1 + \alpha\Phi_1}\left[1 + \frac{d(D_1\alpha - D_2)\Phi_1}{(d-1)D_2 + \alpha D_1 - (\alpha D_1 - D_2)\Phi_1}\right]. \qquad (5)$$

For simplicity let us now concentrate on the case $d = 3$ in the following. Then we can rewrite eqn (5) as

$$D_{\text{eff}}c_{\text{eff}} = D_2 c_2\left[1 + \frac{3(D_1 c_1 - D_2 c_2)\Phi_1}{D_1 c_1 + 2D_2 c_2 - (D_1 c_1 - D_2 c_2)\Phi_1}\right]. \qquad (6)$$

Application of the Nernst–Einstein relation (also applied to the effective medium!) gives

$$\sigma_{\text{eff}} = \sigma_2\left[1 + \frac{3(\sigma_1 - \sigma_2)\Phi_1}{\sigma_1 + 2\sigma_2 - (\sigma_1 - \sigma_2)\Phi_1}\right], \qquad (7)$$

an equation that was derived even earlier than eqn (1) by J. C. Maxwell.[9] At first glance, not very much seems to be gained by this procedure. It is however noteworthy that in the original derivation eqn (7) has been obtained by neglecting concentration variations from one phase to another. Erroneously $\Delta\varphi = 0$ was used on the boundaries, even though every boundary gives rise to an electrical potential jump (as we ignore boundary resistance, this has no influence on the terms of eqn (7)).

Considering conductivities right from the beginning, the derivation of eqn (7) for the general conditions ($\Delta\varphi \neq \Delta c \neq 0$) is however very straightforward (and also shows the accuracy of eqn (5)) if we use $i = -\sigma\nabla\tilde{\mu}$, i.e. the electrochemical potential gradient $\nabla\tilde{\mu} = \nabla\mu + zF\nabla\varphi$ instead of $\nabla\varphi$ ($z =$ charge number, $F =$ Faraday's constant, $\varphi =$ electric poten-

tial). Now the boundary condition $\Delta\tilde{\mu} = 0$ is correct, expressing the fact that the electrochemical potential is the decisive thermodynamic potential to be used. Owing to the isomorphicity of the problem, eqn (7) also follows directly for cases of varying equilibrium concentrations, showing that the Nernst–Einstein equation is correct for the effective medium.

In order to generalise the mixing formula with respect to higher concentrations, let us refer to the D-representation and its derivation. Application of linear irreversible thermodynamics will allow us not only to demonstrate the correctness of the above boundary conditions for small signals but also to show that α in eqn (5) is an equilibrium material constant determined by chemical capacitance. The latter point emphasises the accuracy of eqn (5) that was questioned in ref. 4.

2. Thermodynamic basis of the boundary conditions

For simplicity let us restrict this discussion to aspects of pure diffusion (i.e., $\tilde{\mu} = \mu$). A result of general validity close to equilibrium is the proportionality of flux density (j) and driving force, which for pure diffusion is the gradient of the chemical potential μ (as this disappears in equilibrium and not ∇c). Applying this to the contact 1/2, one gets

$$j^\perp R^\perp \propto \Delta_\perp\mu, \qquad (8)$$

where $j^\perp$ is the flux across the contact, $R^\perp$ the diffusional contact resistance, and $\Delta_\perp\mu$ the difference $\mu_2 - \mu_1$ at the contact. As we assume that $R^\perp$ vanishes, $\Delta_\perp\mu$ also vanishes. Assuming the absence of interfacial hindrances, one obtains for the contacts 1/2 and 2/eff

$$\mu_1 = \mu_2 \qquad (9)$$

and

$$\mu_2 = \mu_{\text{eff}} \qquad (10)$$

For each homogeneous phase the chemical potential can be written as

$$\mu_{1,2} = \mu_{1,2}^0 + RT \ln c_{1,2} + RT \ln \gamma_{1,2}(c_{1,2}), \qquad (11)$$

where μ^0 is a constant in the given phase, and γ (the activity coefficient) expresses the deviation from Boltzmann behaviour. For small concentrations (i.e., $\gamma = 1$) eqn (2) is trivially valid for the equilibrium case; α then represents the distribution mass action constant. Eqn (3) is also fulfilled, as it expresses mass conservation. (As the effective medium is not a proper phase with a given μ^0, eqn (4) is only formal and the formal mass action constant is a function of Φ_1).

For $\gamma = 1$ and as long as eqn (9)–(11) are valid, eqn (2) holds for any deviation from equilibrium. If $\gamma = \text{const.} \neq 1$ (which in fact is only rarely the case), eqn (1) would still be fulfilled with α now not just being the mass action constant but also including the γ ratio. However, eqn (2) fails for strong interactions as in this case μ is far from being a linear function of $\ln c$.

Let us investigate the situation by assuming small signals for which $\mu(c)$ can be linearised around the equilibrium value $\hat{c}$ (δc expresses the deviation from $\hat{c}$). Then it can be readily shown

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that eqn (1) and (2) are fulfilled. Taylor expansion of $\mu(c)$ while retaining the linear term leads to

$$\mu(c) = \hat{\mu}(c) + \delta c/\hat{C}, \quad (12)$$

where $\hat{C}\left(\frac{\delta c}{\delta \mu}\right)$ is the chemical capacitance, which, under equilibrium conditions, is a pure material constant. (According to eqn (11), $\partial\mu/\partial c$ can also be expressed as $[1 + \partial\ln\gamma/\partial\ln c]/c$, with the term in brackets representing the thermodynamic factor.) It can again be seen that for $\gamma = $ const. (in particular for the realistic case of $\gamma = 1$), eqn (1) is obtained.

More specifically, at the contact 1/2,

$$\frac{\delta c_1}{\delta c_2} = \frac{\hat{C}_2}{\hat{C}_1} = \text{\ae}, \quad (13)$$

and hence also

$$\frac{c_1}{c_2} = \frac{\hat{c}_1}{\hat{c}_2} = \text{\ae}. \quad (14)$$

Similarly, at the contact 2/eff we get $\mu_2 = \mu_{\text{eff}}$, which yields

$$\text{\ae}' = \frac{\delta c_2}{\delta c_{\text{eff}}} = \frac{\hat{C}_{\text{eff}}}{\hat{C}_2} = \frac{c_2}{c_{\text{eff}}} = \frac{\hat{c}_2}{\hat{c}_{\text{eff}}}. \quad (15)$$

Obviously $\text{\ae}$ and $\text{\ae}'$ are defined by the equilibrium concentrations and we can use eqn (2) to derive eqn (5). As $\text{\ae}$ and $\text{\ae}'$ can also be expressed by δc instead of $\hat{c}$, the mixing formula, eqn (3), written for c, also applies to δc as well as to chemical capacitance since $\delta\mu$ is invariant, i.e.

$$\hat{C}_{\text{eff}} = \Phi_1 \hat{C}_1 + \Phi_2 \hat{C}_2. \quad (16)$$

For strong deviations from equilibrium and from the dilute situation, eqn (2) and (3) can not be generally valid. In order to generalise the situation for both diffusional and electrical effects we write the local flux[10,11] as

$$j = -\frac{\sigma}{z^2 F^2}\nabla\tilde{\mu} = -\frac{\sigma}{zF}\nabla\varphi - \frac{\sigma}{z^2 F^2}\nabla\mu$$
$$= -\frac{\sigma}{zF}\nabla\varphi - \frac{\sigma RT}{z^2 F^2 C}\nabla c. \quad (17)$$

Identifying $\frac{\sigma RT}{z^2 F^2 C}$ with the diffusion constant D, i.e. applying the generalised Nernst–Einstein equation for non-dilute situations as well as for the effective medium, one again ends up with eqn (7). The reason for this is as follows: if pure diffusion ($\propto \nabla c$) or pure conduction ($\propto \nabla\varphi$) is assumed, the initially described derivation is in principle not applicable as $\nabla c = 0$ or $\nabla\varphi = 0$ fails at realistic two phase contacts. If, however, the generalised flux force relation $j \propto \sigma\nabla\tilde{\mu}$ is used, $\nabla\tilde{\mu} = 0$ is valid at the boundaries. An analogous derivation yields eqn (7) again because σ is the relevant transport coefficient in all cases. In short, eqn (7) is generally valid, even though initially derived for a simplified situation.

3. Electrical conductivity

It is very instructive to compare the equation for σ_{eff} (eqn (7)) with the solution for the brick layer model for polycrystals (primitive arrangement of cubic grains of size L, in contact via grain boundaries of thickness d) in which σ_1 refers to the bulk (inclusions) and σ_2 refers to the boundaries. In order to apply

the above model, we will consider isotropic boundary conductivities (i.e. $\sigma_2^{\perp} = \sigma_2^{\parallel}$). (A more elaborate treatment of the brick layer model is given in ref. 12). The volume fraction of the boundaries is $\Phi_2 = 1 - \Phi_1$. Let us first refer to $\Phi_2 \ll \Phi_1$, i.e. $\Phi_1 \approx 3d/L$. Unsurprisingly, the correct solutions of the equivalent circuit model follow. For a highly conducting bulk (i.e. $\sigma_1 \gg \sigma_2$), eqn (7) simplifies to $\sigma_2 L/d$ (which obviously corresponds to the resistance being dominated by the perpendicular grain boundaries), and for highly conducting grain boundaries ($\sigma_1 \ll \sigma_2$) to $2\sigma_2 d/L$ corresponding to the fact that now the parallel boundaries short-circuit and dominate the conductance. The factor of two in the second expression arises from the fact that there are 6 halves, i.e. three boundaries per grain, two of them being parallel. These limiting cases refer to very thin boundaries ($1 - \Phi_2 \simeq 1$).

It is more instructive to consider significant Φ_2 values, for instance by referring to nanocrystalline arrangements. Then there are—already in 2D—two simple but different equivalent circuit models (see Fig. 2). In the first (Fig. 2a) the bulk and perpendicular boundary (corner area not included) are connected in series to which the parallel boundary (including corner area) is connected in parallel; in the second (Fig. 2b) the bulk and parallel boundary (without corner area) are connected in parallel, with this combination being in series with the perpendicular boundary (including edge area). The results differ if Φ_2 is non-negligible (note that we assume isotropic boundary conductivities). This is best seen for insulating bulk: in the first case the perpendicular boundary without corner area does not contribute at all, while in the second case it fully contributes as if it were penetrated by parallel current lines. As shown in Fig. 2c, σ_{eff} is
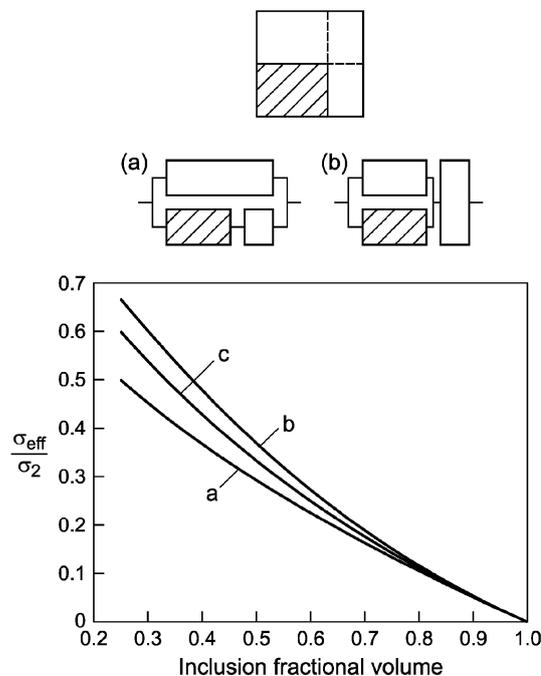

Fig. 2 A comparison of the results from eqn (7) (curve c) with those obtained from the brick layer model (curves a and b: see models above). The shaded areas refer to the bulk, the unshaded ones to the boundaries.

underestimated in case 1 while it is overestimated in case 2. In reality the current lines are only approximately parallel in the parallel boundary and partly penetrate into the region which is not reflected at all in case 1. Obviously, the intermediate situation is better represented by the effective medium model (see Fig. 2c). The accuracy of the effective medium solution was demonstrated in ref. 7 through numerical calculations.

4. Chemical diffusion and validity for storage phenomena

We now turn to the kinetics of chemical changes (*e.g.* change of the oxygen stoichiometry of an oxide *via* chemical diffusion). For clarity we use the label δ for the transport coefficient under consideration. As we have seen (see eqn (12)) the concentration, c has, if we depart from dilute solutions, to be replaced by the chemical capacitance C and hence eqn (6) has to be replaced by (for simplicity we drop the hat)

$$D_{\text{eff}}C_{\text{eff}} = D_2 C_2 \left[1 + \frac{3(D_1 C_1 - D_2 C_2)\Phi_1}{D_1 C_1 + 2D_2 C_2 - (D_1 C_1 - D_2 C_2)\Phi_1} \right]. \tag{18}$$

This result could be directly exploited for the calculation of the effective diffusion coefficient D^δ under steady state conditions; there the product $D^\delta C^\delta$ is directly proportional to the effective so-called ambipolar conductivity σ^δ describing the flux of a neutral component caused by a chemical potential of the neutral component, whereby the neutral flux is constituted by the motion of two charge carriers (see *e.g.* ref. 11 and 13). If we consider, *e.g.* oxides and refer to chemical diffusion of oxygen (O), we involve both oxygen ions (oxygen defects) and electrons (electronic defects) and the effective conductivity σ^δ (which eventually replaces σ in eqn (7)) can be written as

$$\sigma_O^\delta = \frac{\sigma_{\text{ion}}\sigma_{\text{eon}}}{\sigma_{\text{ion}} + \sigma_{\text{eon}}}. \tag{19}$$

The chemical capacitance refers to the storage of the neutral component (*e.g.* $C^\delta = \partial c_O / \partial \mu_O$) and is thus far from unity.

Let us rewrite eqn (18) as

$$D_{\text{eff}}^\delta = \frac{\sigma_{\text{eff}}^\delta}{4F^2[C_1^\delta \Phi_1 + C_2(1 - \Phi_1)]}$$
$$= \frac{\sigma_2^\delta}{4F^2 C_{\text{eff}}} \left[1 + \frac{3(\sigma_1^\delta - \sigma_2^\delta)\Phi_1}{\sigma_1^\delta + 2\sigma_2^\delta - (\sigma_1^\delta - \sigma_2^\delta)\Phi_1} \right] \tag{20}$$

and again simplify the obtained result for the brick layer microstructure with (i) resistive and (ii) highly conductive grain boundaries.

For $d \ll L$, *i.e.* $\Phi_1 \approx 1 - 3d/L$

$$D_{\text{eff}}^\delta \approx \frac{\sigma_2^\delta}{4F^2 C_1^\delta} \frac{L}{d} \tag{21}$$

is obtained for resistive boundaries, while in the opposite limit of highly conductive grain boundaries

$$D_{\text{eff}}^\delta \approx \frac{\sigma_2^\delta}{4F^2 C_1^\delta} \frac{3d}{L} \tag{22}$$

is obtained.

An interesting point can be set out here. In homogeneous media the diffusion coefficient derived from the steady state behaviour can also be used for describing the non-stationary behaviour, *e.g. via*

$$D^\delta \propto 1/\tau^\delta, \tag{23}$$

where τ^δ typically represents the relaxation time of the diffusion. This is not as straightforward here, as can be seen from comparison with the results of the brick layer model derived from the relaxation times in the limits of hardly permeable bulk and hardly permeable boundaries (denoted as D_τ^δ).[2] In the first case the evaluation of the transient approximately yields for the brick layer model

$$D_\tau^\delta = (3a^2/L^2)\sigma_1^\delta/(C_1^\delta 4F^2), \tag{24}$$

where a is sample size, whilst in the second case

$$D_\tau^\delta = (L/d)\sigma_2^\delta/(C_1^\delta 4F^2) \tag{25}$$

is obtained. As in the first case it is the chemical resistance of the bulk ($\propto 1/\sigma_1^\delta$) that is relevant for the time constant, in the second the chemical resistance of the boundary ($\propto 1/\sigma_2^\delta$) is relevant for the time behaviour. In both cases the decisive capacitance is the chemical capacitance of the bulk (as long as the boundary is so thin that most of the storage occurs in the bulk). Obviously only the latter result is compatible with the MG solution. Note that the conception of the multiphase arrangement as an effective medium requires the identification of τ_{eff}^δ with the rate determining relaxation time (*i.e.* the relaxation time of the long term process in the first case).

The discrepancy between D_{eff}^δ (derived from the steady state behaviour) and D_τ^δ (derived from the transient) in the case of hardly permeable bulk refers to the fact that the bulk diffusion coefficient determines the transient behaviour (Fig. 3) but it is the boundary diffusion that determines the steady state behaviour (Fig. 4), thus leading to two different effective diffusion coefficients in the case of a two phase media even close to the equilibrium.

In more general terms, the relative role of the two media (and hence the "structure of the effective medium") changes
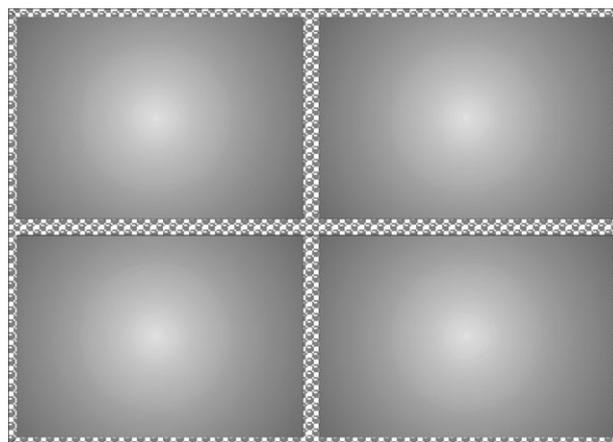

Fig. 3 Schematics of oxygen diffusion into a four-grain crystal in the transient case (for fast interfacial diffusion, with a response to sudden change of the outer homogeneous oxygen partial pressure, top and bottom sealed). See also ref. 14.
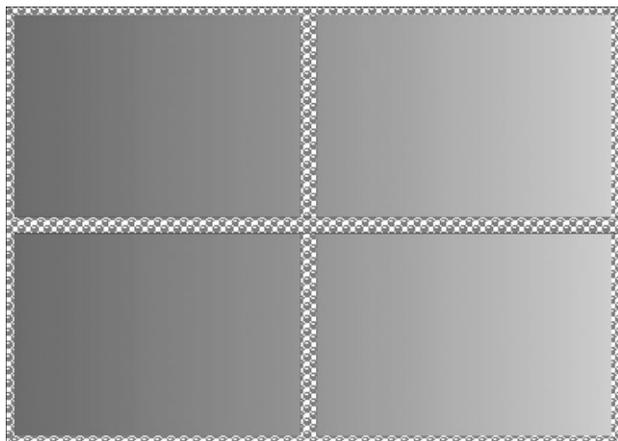
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Fig. 4 Schematics of oxygen diffusion into a four-grain-crystal in the steady-state case (for interfacial diffusion sample exposed to a steady-state partial pressure gradient from the left to the right, top and bottom sealed). See also ref. 14.

with time. As the second Fick's law arises by coupling the flux force equation with the continuity equation and while this is unproblematic in the homogeneous case, it is more subtle in the heterogeneous case.

5. Conclusions

The Maxwell-Garnett equation, generalised to the case of different equilibrium concentrations in the two phases, is shown to be exact within the MG constraints, and in fact can be directly derived by a MG procedure with σ as transport coefficient and the gradient of the electrochemical potential. The mixing formula for D (eqn (1)) has to be generalised to eqn (6), while the mixing formula for σ (eqn (7)) maintains its form even for the non-zero chemical gradients which were neglected in the derivation. This is due to the Nernst–Einstein equation which does not lose its validity when applied to the effective medium.

Here we extended the relation to non-dilute carrier concentrations. As long as proximity to equilibrium is guaranteed for small signals, one just has to exchange the equilibrium concentration with the equilibrium chemical capacitance. This is equivalent to applying to the effective medium a Nernst–Einstein equation which is generalised to high concentrations. This result can be directly used to describe chemical diffusion in the steady state. The comparison with the brick layer model shows the accuracy of the approach even for nanocrystalline samples. The comparison with the transport brick layer solutions indicates that in heterogeneous media diffusion coefficients derived from the transients are generally different from those derived from the steady state flux as the two phases contribute differently in transient and steady states.

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