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A fundamental study of the extent of meaningful application of Maxwell's and Wiener's equations to the permeability of binary composite materials. Part III: Extension of the binary cubes model to 3-phase media

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HIGHLIGHTS

- A new modeling approach to the permeability P of 3-phase composite media is presented.
- It consists of our Part II binary model plus a zone between *cubic* particles and matrix.
- The effect of zone width and permeability on the behavior of P vs composition is studied.
- Coverage of the full composition range is a basic advantage over sphere-based models.
- Previous difficulty to model all types of observed P vs composition behavior is surmounted.

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ABSTRACT

The simple cubic lattice model of cubic particles A dispersed in a continuous (polymeric) matrix B (and occupying a volume fraction $0 \le \nu_A \le 1$ therein), introduced in Parts I and II to establish the meaningful applicability of the Maxwell and Wiener equations to binary composite-medium permeability properties up to $\nu_A \to 1$, is here applied to modeling the practically important case of a three-phase composite medium, where the third phase is considered to take the (idealized) form of zones surrounding particles A which exhibit permeability properties differing substantially from those of the bulk matrix. It is shown, both theoretically and by application to various existing experimental data, that replacing the spherical particles, commonly assumed in such modeling, with cubic ones, leads to remarkable gains in model simplicity and internal consistency, in practical applicability, and ultimately in physical understanding of the observed variety of 3-phase composite-medium permeability behavior.

1. Introduction

In the preceding Parts I (Minelli et al., 2013) and II (Papadokostaki et al., 2015) of this series of papers on binary composite media consisting of (isometric) particles A dispersed in a continuous matrix B (and occupying a volume fraction $0 \le \nu_A \le 1$ of the composite medium), we showed that a model composite medium based on a simple cubic lattice of cubic particles A, provides the requisite theoretical justification for meaningful application of the Maxwell equation throughout the range $0 \le \nu_A \le 1$; in contrast to previous models based on lattices of spherical particles A (Rayleigh, 1892; de Vries, 1952, etc.), which are limited to the low and medium ν_A ranges.

In the present paper, we show that the use of cubic, rather than spherical, particles A is also helpful here, because it leads to a much simpler and internally fully consistent idealized theoretical treatment of three-phase composite polymeric media, where a zone in the polymeric matrix surrounding each particle (B1), exhibiting properties differing materially from those of the bulk matrix (B), may be recognized.

In practice, the interphase B1 (i) may be a third substance introduced deliberately to ensure good adhesion of B to A or (ii) it may represent some modification of the properties of B, notably as a result of the tendency of the polymeric material to harden in the vicinity of A particles (cf., e.g., Berriot et al., 2003). In the latter case, on which attention will be focused in the present paper, routine experimental detection of the interphase is not easy and evaluation of its detailed permeability properties even less so. However, its presence may reasonably be surmised in many cases where

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experimental data are found to deviate markedly from appropriate standard binary composite-medium formulae.

It is thus important to study theoretically the effect of a B1 zone, characterized by permeability P_{B1} and width b_o, as a function of these parameters, on the permeability P of a suitable model 3-phase medium. In this connection, we may note in passing that certain authors (notably Marand and Surapathi, 2012; Singh et al., 2013) are inclined to attribute the aforementioned observed deviations to improper use of the relevant binary formulae as currently applied; thus relegating the invocation of B1 zones to the status of a mere convenient modeling device for introduction into the said standard binary formulae of extra parameters, which can be suitably manipulated to achieve agreement with the relevant data. This view is clearly untenable, because, on one hand, it can be shown beyond doubt (Petropoulos et al., 2014) that current application of standard binary formulae is correct as it stands. On the other hand, the physical reality of B1 zones, as idealizations of measurable polymer hardening effects in the neighborhood of embedded particles, is well established (e.g. Berriot et al., 2003).

In view of our focus here on the polymer hardening effect [case (ii)], our model calculations were parameterized very largely with $P_{B1} < P_B$ values. It is important to bear in mind that the model under consideration is also fully applicable to $P_{\mathbf{B1}} > P_B$ values, such as may be encountered in case (i), depending on the properties of the third substance which serves as adhesive and including also the possibility of the interphase zone appearing simply as a gap, due to poor adhesion of A to B (see, e.g., Mahajan and Koros, 2002a, 2002b) or to failure of the viscous dope fluid (used to cast the loaded polymer in the form of a film) to envelop the dispersed particles fully (Papadokostaki et al., 1998).

It is also worth noting that, in line with our preceding modeling studies of binary composite media (see Parts I and II; Minelli et al., 2013 and Papadokostaki et al., 2015, respectively), the s.c. lattice-of-cubes model presented here may be easily extended for application to 3-phase composite media consisting of similar lattices of non-isometric particles (notably square rods and plates).

2. Formulation of simple 3-phase composite medium modeling

2.1. The general approach

The basic idea underlying the formulation of current simple 3-phase composite medium modeling, first enunciated clearly by Mahajan and Koros (2002a), is to consider particles A, with their surrounding zones B1, as pseudo-particles (A+B1) of effective permeability P_E dispersed in the bulk matrix (B); and then proceed to (i) determine P_E by identifying it with that calculated by a chosen standard formula for a similar binary medium consisting of A particles dispersed in a matrix of B1, and (ii) apply the same (or some other) binary formula to the virtual binary composite material (A+B1, B), the permeability of which (P) should be identical with that of the 3-phase medium.

This approach of double binary formula application has been applied extensively by the aforementioned authors and by others (e.g. Vu et al., 2003; Moore et al., 2004; Moore and Koros, 2005; Pal, 2008; Shimekit et al., 2011; Hashemifard et al., 2010) to a variety of gas permeability data. Various binary formulae have been used for this purpose, wherein Maxwell's original adoption of congruent spherical particles is maintained, with the exception of Hashemifard et al. (2010)'s choice to represent particles A as congruent short cylinders.

In this respect, preliminary examination of the main binary formulae currently used for the above purpose is useful.

2.2. Discussion of pertinent binary formulae for particles A dispersed in a matrix B

The advantage of choosing highly symmetrical hard spherical particles for Maxwell's original rigorous derivation of his equation (shown as Eq. (1)), intended for application at the limit of infinite dilution ($v_A \to 0$), is obvious.

$$\frac{P}{P_B} = 1 + \frac{3v_A}{(\alpha+2)/(\alpha-1) - v_A} \tag{1}$$

where $\alpha = P_A/P_B$.

However, for practical purposes, it is important to determine how far the Maxwell (spheres) equation itself or suitable extensions/modifications thereof:

(1) may be usefully employed at higher $v_A \le 1$, in principle, and
(2) may prove useful for the interpretation of permeability behavior in practice.

At the present stage, we focus attention on point (1). In this respect, we proceed to review briefly the main post-Maxwell analytical modeling developments of interest here, which include:

(a) Extension of the Maxwell equation to higher v_A by accounting for interactions between spheres, on the basis of idealized geometrical models consisting of simple regular cubic lattices of congruent spheres (Rayleigh, 1892) or of similar b.c.c. or f.c.c. lattices (de Vries, 1952; see also Petropoulos, 1985), represented by Eq. (2) below (as formulated by de Vries)

$$\frac{P}{P_B} = 1 + 3v_A \left(\frac{\alpha+2}{\alpha-1} - v_A - \frac{K_1\,(\alpha-1)\,v_A^{10/3}}{(\alpha+4/3)} + \cdots \right)^{-1} \tag{2}$$

where $K_1 = 1.31$ (s.c.), 0.129 (b.c.c.) or 0.0752 (f.c.c.).
The range of applicability of such models is necessarily limited to $0 \le v_A \le v_{A,max}$, where $v_{A,max} = 0.524$ (s.c.), 0.60 (b.c.c.) or 0.72 (f.c.c.) represents the highest possible degree of packing congruent spheres in each of these regular configurations. It is noteworthy that the last configuration can justify use of the simple Maxwell (spheres) equation with error $<1\%$ up to quite high v_A values (for examples, see Part II; Papadokostaki et al., 2015). The above limits can be exceeded, if variability of the size of the spheres is allowed (cf. the experimental demonstration of this point quoted by Petropoulos, 1985), but this can be done only at the expense of undue complication of the model and ensuing loss of its analytical tractability.

(b) The above $v_{A,max}$ limits are also rendered ineffective by the Bruggeman (1935) approach, which leads to the implicit analytical expression

$$\left(\alpha - \frac{P}{P_B}\right)\left(\frac{P_B}{P}\right)^{1/3} = (1 - v_A)(\alpha - 1) \tag{3}$$

This approach restricts modeling of the spatial arrangement of the dispersed congruent spheres to that present under the condition of $v_A \to 0$ originally envisaged by Maxwell; which (failing any other pertinent structural postulate) can only be conceived as a *disordered* arrangement. In fact, Bruggeman proceeds to build up his model composite medium gradually, by starting at $v_A = 0$, adding only a few spheres at each step and (at the same time) consigning those added previously to "dissolution" in a (uniform and continuous) AB "effective medium" (of composition given by the current value of v_A), which constitutes the environment of the newly added spheres. Thus, as v_A rises, the newly added spheres (too dilute to interact among themselves) are exposed to interaction with *all* previously