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Effective dielectric constant of two phase dielectric systems

Vladimir Petrovsky · Piotr Jasinski · Fatih Dogan

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Abstract Various theoretical approaches are implemented for electrical characterization of two phase material systems. Most of these approaches do not include possibility of percolation of the dispersed material. In this article brick wall model is extended on the systems exhibiting percolation. Transition from brick wall geometry to corresponding equivalent circuits provides final equations for effective dielectric constant. Comparison of theoretical results with experimental data shows that developed equations provide good fitting of effective dielectric constant to experimental values. Dielectric constants of both phases and percolation threshold calculated from the fitting match the corresponding experimental values of the phases.

Keywords Ceramic · Slurry · Impedance spectroscopy · Dielectric constant

1 Introduction

Two phase dielectric systems with high dielectric contrast between the phases are of interest for verity of practical applications. For example, addition of high dielectric constant powders in polymeric materials is a well known efficient method of increasing specific capacitance of dielectric materials [1–6]. Some promising results were also achieved in the area of electrostatic energy storage devices using biphasic systems with nano-powders as loading materials [2]. Mixtures of different dielectric components often used to adjust properties of composite materials [7, 8]. Presence of porosity in ceramics could lead to significant changes in electrical properties and needs to be controlled during ceramic capacitors production [6].

Despite long history of investigations on two phase systems, theoretical background and mathematical description for this type of systems are not fully understood. There are significant differences between theoretically predicted values of effective dielectric constant for two phase systems and experimental data especially for systems with high dielectric contrast [9–12]. The principles for selection of models and mathematical equations that would apply for a particular two phase system are not well understood [13–19]. Although it is relatively straightforward to find an equation which fits particular experimental data, it is challenging to predict behavior of an unknown system or draw conclusions about physical characteristics of two phase systems such as possible agglomeration or sedimentation of powders suspended in liquids.

This paper gives a brief review of theoretical approaches and corresponding equations for analysis of two phase systems. The main objective is to clarify the physical background of two phase systems with respect to their dielectric properties. Mathematical equations describing two phase systems with percolation and experimental verification of these equations will be reported in a follow up article.

2 Theoretical approaches and models

Slurries or suspended particles in liquids are two phase systems in which both components are well intermixed. The same is true for verity of two phase materials such as polymer-ceramic composites and porous ceramic materials. Since an applied electrical field has a complex three dimensional

V. Petrovsky (✉) · F. Dogan
Department of Materials Science and Engineering, Missouri University of Science and Technology,
Rolla, MO 65409, USA
e-mail: vpetrovs@mst.edu

P. Jasinski
Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology,
Gdansk 80-233, Poland

distribution in such systems, any simplified approach (for example equivalent circuit method) cannot guaranty correct calculation of effective dielectric constant of two phase materials. At the same time, equivalent circuit approach can be useful in establishing of boundaries by which effective dielectric constant will be limited.

Typical examples of these boundaries are series and parallel connection between two phases. In the case when two phases of a system are not homogeneously intermixed, they may form columnar or layered structures as shown in Fig. 1(a) and (b). A unit size cube with dimensions (1×1×1cm: 1 cm^3) was used to describe electrical properties of a two phase system where electrical field is distributed uniformly in both phases. Parallel and series equivalent circuit Eqs. (1) and (2), will represent exact dependences of effective dielectric (ε_{eff}) constant from volume fraction of one component (i.e. X_1 for component one) as following:

Parallel connection:

$$\varepsilon_{\mathrm{EFF}} = \varepsilon_1 \mathbf{X}_1 + \varepsilon_2 (1 - \mathbf{X}_1) \tag{1}$$

Where

ε_{eff}	Effective dielectric constant of two phase system
ε_1 and ε_2	Dielectric constants of phases 1 and 2, respectively
X_1	Volume fraction of phase 1.

Series connection:

$$\frac{1}{\varepsilon_{\mathrm{EFF}}} = \frac{\mathbf{X}_1}{\varepsilon_1} + \frac{1 - \mathbf{X}_1}{\varepsilon_2} \tag{2}$$

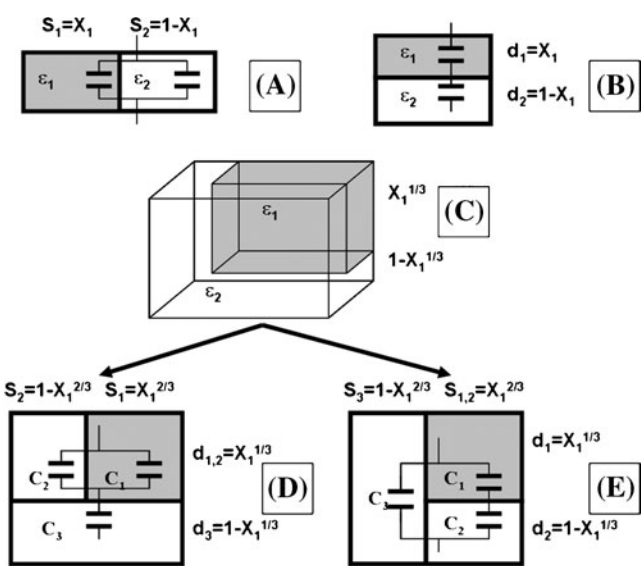

Fig. 1 Equivalent circuits for analysis of two phase systems. (**a**) Parallel connection (column structure); (**b**) Series connection (layered structure). (**c**) Brick wall model (unit cube as elementary cell containing single particle); (**d**) Transition to equivalent circuit (Model1); (**e**) Transition to equivalent circuit (Model2)

Figure 2 shows dependence between ε_{eff} and volume fraction of component 1 (X_1) for three different theoretical models describing two phase systems, namely equivalent circuit models, effective media and phenomenological approaches,. Equations (1) and (2) are shown in all three pictures of Fig. 2 as black dashed lines that define limitation of the area for effective dielectric constant (ε_{eff}) of any two phase system. However, the corresponding area is very broad so that little information can be obtained by comparing of experimental results with these theoretical limitations.

Experimental data from [6] were used as an example of two phase systems with high dielectric contrast between the components (as shown in Fig. 2). These experimental data were obtained from measurements of barium titanate slurries (upwards triangles). In addition, porous bulk samples of barium titanate (downwards triangles) were also prepared by sintering of powder compacts with different amount of fugitive pore provider, so that combination of slurries and

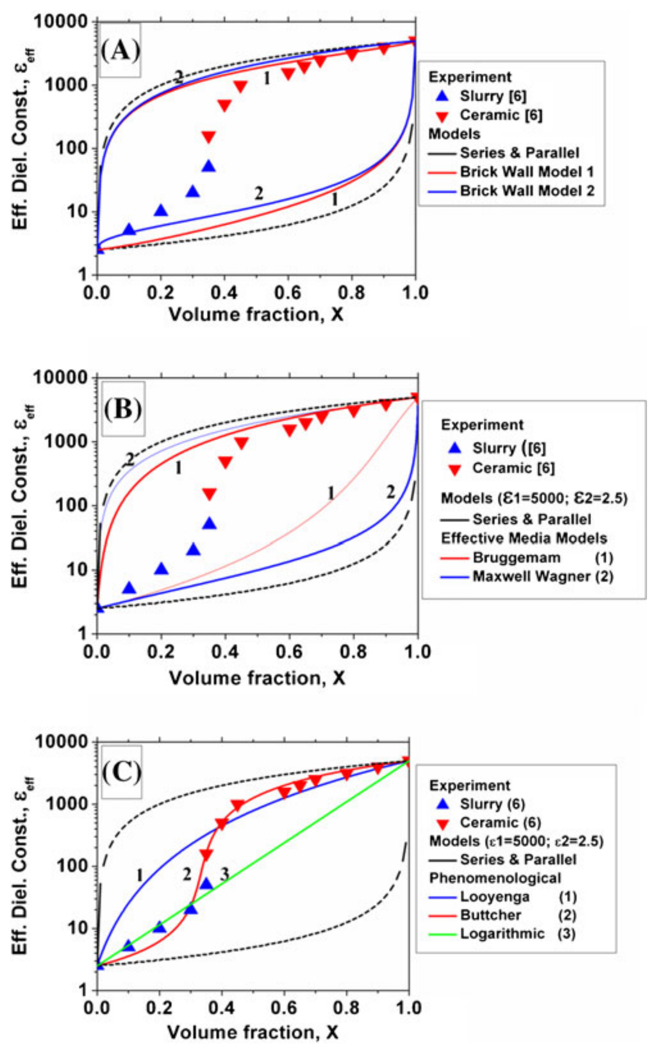

Fig. 2 Three different methods for ε_{eff} modeling. (**a**) Equivalent circuit; (**b**) Effective media; (**c**) Phenomenological

porous bulk samples cover the entire range of barium titanate volume fractions X_1 (from 0 to 1). Figure 2 reveals that experimental data are within the area of theoretical curves for parallel and series connection. Although the location of the experimental data can be roughly predicted, for an accurate prediction the data are far away from the curves obtained using parallel and series models. Further details in these models need to be included to improve fitting of the data.

Brick wall model is based on two assumptions with respect to distribution of two phases in the system [13]; namely, cubic particles are oriented and uniformly distributed within the second phase as shown in Fig. 1(c). This model is more suitable for real systems and should provide better fitting of experimental data. Unfortunately, direct transition from this model to equivalent circuit is not possible because of non-uniformity in electrical field distribution. Elementary cube in Fig. 1(c) can be divided on several regions such that electrical field is suggested to be uniform in each region allowing transition to equivalent circuit. Two logical approaches for this division are shown in Fig. 1(d) (model 1) and Fig. 1(e) (model 2). It is obvious that exact solution for brick wall model should be within the area surrounded by models 1 and 2 which is a significantly narrower area in comparison with that produced by parallel and series connection models. Detailed discussion of this transition from brick wall model to equivalent circuits (models1 and 2) can be found in our previous article [13]. Corresponding formulas for effective dielectric constant are presented in Eqs. 3 and 4.

Model1:

$$\frac{\varepsilon_{\mathrm{EFF}}}{\varepsilon_2} = \frac{1}{1 - \mathbf{X}_1^{1/3} + \frac{\mathbf{X}_1^{1/3}}{1 - \mathbf{X}_1^{2/3}\left(1 - \frac{\varepsilon_1}{\varepsilon_2}\right)}} \tag{3}$$

Model2:

$$\frac{\varepsilon_{\mathrm{EFF}}}{\varepsilon_2} = 1 - \mathbf{X}_1^{2/3} + \frac{\mathbf{X}_1^{2/3}}{1 - \mathbf{X}_1^{1/3}\left(1 - \frac{\varepsilon_2}{\varepsilon_1}\right)} \tag{4}$$

Brick wall model suggests that one phase in the system is interconnected (phase 2 in Eqs. 3 and 4) and another phase is disconnected (phase 1) in all ranges of X_1, so that each model generates a set of two curves depending on which phase is considered as disconnected as shown in Fig. 2(a). Lower pare of red and blue curves (marked as 1 and 2 in the picture for models 1 and 2 correspondingly) correspond to slurries with interconnected liquid and disconnected suspended powder. Upper pare of red and blue curves (also marked as 1 and 2 in the picture for models 1 and 2) correspond to sintered barium titanate cubes with varying porosity. Figure 2 reveals that brick wall based models show much better fitting with the experimental data than series and parallel models, but at intermediate values of X_1 differences are significant. More importantly, experimental data are positioned out of the area defined by models 1 and 2, i.e. experimental systems are physically different from the brick wall model.

Another approach for evaluation of $\varepsilon_{\mathrm{eff}}$ is implemented by effective media models. These models consider suspended particles as electrical dipoles influencing electrical field in the host phase that leads to changes in effective dielectric constant of a two phase system. Mathematical representation of this approach is Maxwell Wagner Eq. (5). Several modifications of this equation were developed for multi-component systems by considering polarization of particles of a particular composition suspended with other particles of different composition (effective media approaches). Bruggeman Eq. (6) represents an example of this type of approaches.

Maxwell Wagner Equation [11, 13]:

$$\frac{\varepsilon_{\mathrm{EFF}} - \varepsilon_2}{\varepsilon_{\mathrm{EFF}} + 2\varepsilon_2} = \mathbf{X}_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \tag{5}$$

Bruggemann [14]:

$$\mathbf{X}_1 = 1 - \frac{\varepsilon_1 - \varepsilon_{\mathrm{eff}}}{\varepsilon_1 - \varepsilon_2}\left(\frac{\varepsilon_2}{\varepsilon_{\mathrm{eff}}}\right)^{1/3} \tag{6}$$

Similar to equivalent circuit models, both Maxwell Wagner and Bruggeman equations generate two different $\varepsilon_{\mathrm{eff}}$ (X_1) curves depending on whether each phase is a host or suspended in a multi-component system as shown in Fig. 2(b). It is revealed that Eqs. (5) and (6) provide better fitting for experimental data (especially Bruggeman equation), but at intermediate values of X_1 differences are still significant.

Various empiric or quasi empiric equations were suggested to insure better fitting of experimental data [14]. Examples of such approaches are logarithmic mixed rules (7); Bottcher (8); and Looyenga (9) equations (Fig. 2(c)).

Logarithmic mixed rules:

$$\varepsilon_{\mathrm{EFF}} = \varepsilon_1^{\mathrm{x}_1}\varepsilon_2^{(1-\mathrm{x}_1)} \tag{7}$$

Bottcher (1952):

$$\mathbf{X}_1 = \frac{(\varepsilon_{\mathrm{eff}} - \varepsilon_2)(2\varepsilon_{\mathrm{eff}} + \varepsilon_1)}{3\varepsilon_{\mathrm{eff}}(\varepsilon_1 - \varepsilon_2)} \tag{8}$$

Looyenga (1965):

$$\mathbf{X}_1 = \frac{\left(\varepsilon_{\mathrm{eff}}^{1/3} - \varepsilon_2^{1/3}\right)}{\left(\varepsilon_1^{1/3} - \varepsilon_2^{1/3}\right)} \tag{9}$$

Empirical approaches do not consider distribution of a particular phase in the mixture and generate only one curve to reveal ε_{eff} (X_1) dependence in Fig. 2(c). It is shown that empiric formulas provide better fitting to experimental data. These formulas (especially the mixed rule equation) were extensively used to calculate the value of ε_{eff} for various two phase systems.

However, application of empiric equations is limited and requires modifications for a given system. For example Eqs. (7) and (9) are applicable only for two phase systems with low dielectric contrast (high dielectric contrast, $\varepsilon_1/\varepsilon_2\rightarrow\infty$, results in unlimited values of ε_{eff} for all X_1), so that empiric equations cannot be considered as universal.

It is obvious that any equation providing universal description of two phase systems should at least fulfill the following boundary or extreme conditions for such systems:

(a) Single second phase	$\mathbf{X_1 = 0}$	should give	$\varepsilon_{eff} = \varepsilon_2$;
(b) Single first phase	$\mathbf{X_1 = 1}$	should give	$\varepsilon_{eff} = \varepsilon_1$;
(c) Low dielectric contrast	$\varepsilon_2 \sim \varepsilon_1$	should give	$\varepsilon_{eff} \sim \varepsilon_1$ for all $\mathbf{X_1}$;
(d) High contrast	$\varepsilon_1/\varepsilon_2 \rightarrow \infty$	should give	ε_{eff} $(\varepsilon_2,\mathbf{X_1}) \neq \mathbf{f}(\varepsilon_1)$;

Equations (1, 2, 3, 4, 5 and 6) do not contradict these boundary or extreme conditions but neither of the equations are close to real experimental data. It is obvious that differences between equations and experimental data are due to differences of phase distribution in two phase systems. A specific parameter (or parameters) should be introduced into the equations to address this issue.

3 Phase distribution and percolation

Physical modeling is a prospective method to correlate mathematical models and real physical objects [13]. The brick wall model based on oriented cubic particles that are distributed periodically in the host phase, allow exact physical modeling as described in reference [13]. Experimental data and fitting curves of ε_{eff} (X_1) from reference [13] are shown in Fig. 3. Barium titanate cubes (ε_1=3850) periodically distributed in butoxyethanol (ε_2=10) and propylene carbonate (ε_2=67) were used for physical modeling. Figure 3 reveals that the brick wall model (Eq. (3)–green curves and Eq. (4)–red curves) completely surround experimental data and provide good fitting with physical modeling. Maxwell Wagner model (Eq. (5)–black curves) also situated between curves (3) and (4) and provides nearly ideal fitting with experimental data. It is reasonable to conclude that Eqs. (3, 4 and 5) are physically correct and can be implemented in a universal model of two phase systems. The question is how to extend these models on real systems with particles of different shape and distribution. Figure 2(a) and (b) show that the models do not provide good fittings due to non-uniformity of material distribution in real

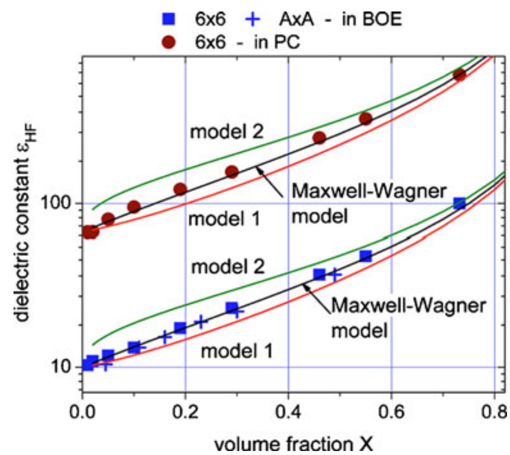

Fig. 3 Physical modeling using barium titanate cubes submerged in different liquids shows that the brick-wall models and Maxwell-Wagner equation give best fitting for two phase systems without percolation [13]

systems. It is clear that additional parameters need to be included in the models.

Brick wall model describes an ideal case of material distribution in a two phase system. Suspended phase particles are disconnected in all range of X_1 until this phase fills the whole volume (X_1 = 1), so that such two phase systems are without percolation (percolation threshold X_P = 1). Real systems, however, percolate earlier (X_P < 1) since particle shape and distribution are different from that used in brick wall model. Additional parameters need to be introduced in models to address these differences.

Physical nature of Maxwell Wagner model or other effective media models do not consider any contact or percolation between suspended particles independent on the shape of particles. Percolation parameters can be introduced in these models only empirically.

Since brick wall model considers physical contacts between particles, percolation can be introduced in this model simply by changing the shape of suspended particles (introduction elongation parameter α) (see Fig. 4). Suspended cubes can be elongated (α>1) or suppressed (α<1) in direction of electrical field which will lead to columnar or layered type of percolation, respectively. First type of percolation will dominate in the case when suspended particles have higher dielectric constant than host material whereas volume fraction of particles at percolation threshold (X_P) will be equal to the square of reverse percolation parameter ($X_P = 1/\alpha^2$). Second type of percolation will dominate when suspended particles have lower dielectric constant than host material. Volume fraction of particles at percolation threshold (X_P) will be equal to percolation parameter ($X_P = \alpha$) ([19]).

Transition to equivalent circuit approach can be accomplished by the same way as considered for cubic particles. It will generate two models surrounding exact solution (see Fig. 4(a) and (b)). Corresponding equations are:

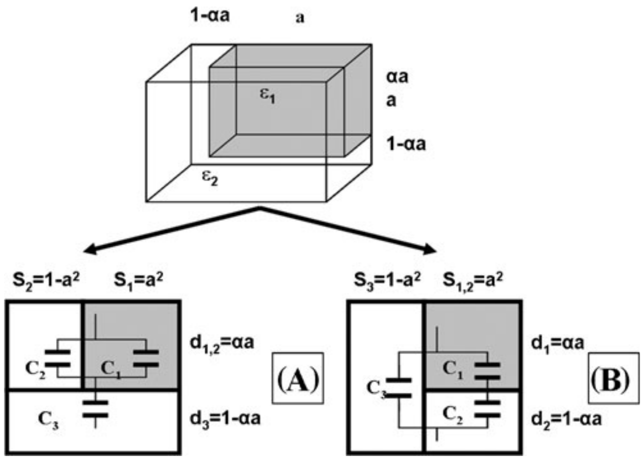

Fig. 4 Brick-wall model of two phase systems with elongated bricks causing percolation (unit cube as elementary cell containing single particle). Two possible transitions to equivalent circuit: model-1* (**a**) and model-2* (**b**)

Model1*:

$$\frac{\varepsilon_{\mathrm{EFF}}}{\varepsilon_2} = \frac{1}{1-(\mathrm{X}_1\alpha^2)^{1/3} + \frac{(\mathrm{X}_1\alpha^2)^{1/3}}{1-\left(\frac{\mathrm{X}_1}{\alpha}\right)^{2/3}\left(1-\frac{\varepsilon_1}{\varepsilon_2}\right)}} \tag{10}$$

Model2*:

$$\frac{\varepsilon_{\mathrm{EFF}}}{\varepsilon_2} = 1-\left(\frac{\mathrm{X}_1}{\alpha}\right)^{2/3} + \frac{\left(\frac{\mathrm{X}_1}{\alpha}\right)^{2/3}}{1-(\mathrm{X}_1\alpha^2)^{1/3}\left(1-\frac{\varepsilon_2}{\varepsilon_1}\right)} \tag{11}$$

It is reasonable to suggest that averaging of Eqs. (10) and (11) will provide good fitting for real two phase systems with percolation as following:

$$\overline{\varepsilon}_{\mathrm{EFF}} = (\varepsilon_{\mathrm{EFF}}(\mathrm{Mod.1}) * \varepsilon_{\mathrm{EFF}}(\mathrm{Mod.2}))^{1/2} \tag{12}$$

These modified models (Eqs. 10, 11 and 12) were compared with experimental results from reference [6] as shown in (Fig. 5). It reveals that modified brick wall model provides good fitting to experimental data for dispersed powder (red curves) as well as for porous ceramic (blue curves). Models1* and 2* are surrounding experimental points over the entire range of X_1 (thin curves). The averaging Eq. (12) exactly follows experimental points. It was mentioned earlier that two types of percolation are possible in the system depending on which phase has a higher dielectric constant. Corresponding formulas should be used to calculate percolation threshold from the percolation parameter α. The values of percolation threshold calculated by this method (X_{1P} = 0.4 for slurries and X_{1P} = 0.33 or X_{2P} = 0.67 for porous ceramics) are quite reasonable and within the range of percolation for spherical particles.

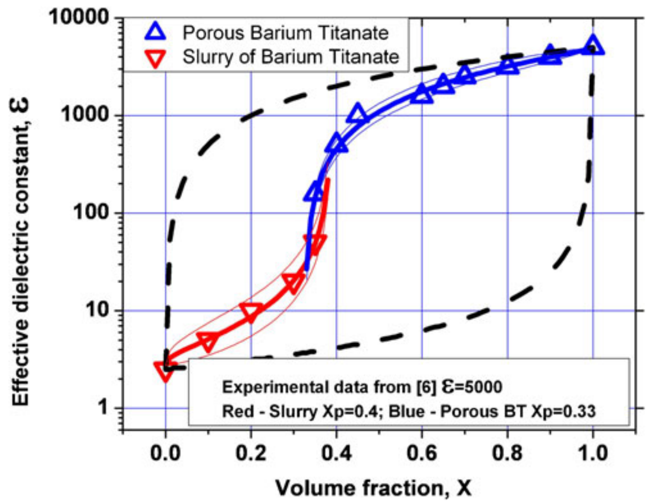

Fig. 5 Introduction of percolation in brick wall models allows extending this method to real (non ideal) two phase system. *Dashed black lines* are for parallel and series connections; *Down triangles* and *red lines* are for slurries; *Up triangles* and *blue lines* are for porous ceramics; *Thin lines* are for Models-1* and-2* and *thick lines* for their averaging

The modified brick wall model (Eqs. 10, 11 and 12) can be implemented as a universal model for two phase systems within a reasonable range of percolation thresholds. This model has clear physical background, and insures a good fitting to experimental data.

4 Summary

Various physical approaches and corresponding equations were used to analyze two phase dielectric systems. Brick wall model has several advantages in comparison with other models. It is physically transparent, allows logical transition to equivalent electrical circuit and can be extended on the systems with percolation. Method based on brick wall model (Eqs. 10, 11 and 12) shows good fitting to experimental data obtained from analysis of dielectric slurries and porous ceramics.

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