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On consistency of classical homogenization models for the permittivity of statistically homogeneous mixtures

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Content

Introduction

Major problems

- Finding electrodynamic homogenization type
- Taking into account many-particle reemission and correlation effects
- Modelling a system's microstructure

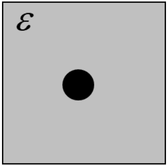
Types of approaches

- Mathematical models (percolation and graph statistical theories)
- Numerical approaches
- Modifications of classical homogenization models

Classical homogenization models

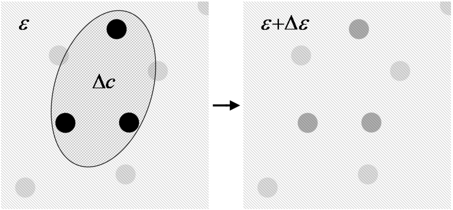
Symmetrical effective-medium approach

In terms of the **symmetrical Bruggeman effective-medium approach** (a.k.a. symmetrical Bruggeman model (**SBM**)) each constituent in the system, including the host medium (matrix), is treated equivalently as a unitary particle embedded in the effective medium, which is formed by all the other constituents.



For macroscopically homogeneous and isotropic dielectric systems of spherical balls:

$$(1-c)\frac{\varepsilon_0-\varepsilon}{2\varepsilon+\varepsilon_0}+c\frac{\varepsilon_1-\varepsilon}{2\varepsilon+\varepsilon_1}=0. \tag{1}$$



(a) (b)

Asymmetrical (differential) Bruggeman model (ABM) assumes, that addition of a small portion of new particles with concentration $\Delta c/(1-c)$ in the particle-void region to the current effective medium with permittivity ε (the lighter area in fig. (a)) leads to the formation of a new effective medium with permittivity $\varepsilon + \Delta\varepsilon$, which serves as the matrix for the next portions of inclusions (fig. (b)); ε changes according to the Maxwell-Garnett mixing rule.

$$\frac{dc}{1-c} = \frac{d\varepsilon}{3\varepsilon}\,\frac{(2\varepsilon+\varepsilon_1)}{\varepsilon_1-\varepsilon} \quad \Rightarrow \quad (1-c) = \frac{\varepsilon-\varepsilon_1}{\varepsilon_0-\varepsilon_1}\left(\frac{\varepsilon_0}{\varepsilon}\right)^{1/3}. \qquad (2)$$

[M.Ya. Sushko, *Zh. Eksp. Teor. Fiz.* **132** (2007) 478; *J. Phys. D: Appl. Phys.* **42** (2009) 155410; *Phys. Rev. E* **96** (2017) 062121]

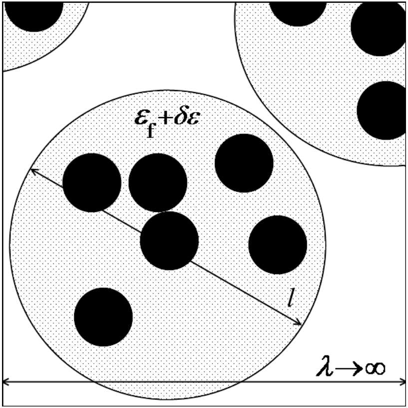
Physical interpretation of the CGA:

◦ The system is viewed as a set of macroscopic regions (**compact groups**), having linear sizes *d* much smaller than the wavelength in the system: $l \ll \lambda$.

◦ These groups are embedded in an auxiliary medium with permittivity ε_f.

◦ They create local deviations of permittivity:

$$\varepsilon(\mathbf{r}) = \varepsilon_\mathrm{f} + \delta\varepsilon(\mathbf{r}).$$



Compact group approach (CGA)
Mathematical basis

The effective permittivity ε is determined as a proportionality coefficient in the relation

$$\langle \mathbf{D}(\mathbf{r})\rangle = \langle \varepsilon(\mathbf{r})\mathbf{E}(\mathbf{r})\rangle = \varepsilon\langle \mathbf{E}(\mathbf{r})\rangle. \tag{3}$$

The average fields are found in the following steps:

1) Presenting the wave propogation equation in the system

$$\Delta\mathbf{E} - \mathrm{grad}\,\mathrm{div}\,\mathbf{E} + k_0^2\varepsilon_{\mathrm{f}}\,\mathbf{E} = -k_0^2\delta\varepsilon\,\mathbf{E}$$

in the equivalent integral form:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) - k_0^2\int_V d\mathbf{r}'\,\hat{\mathrm{T}}(|\mathbf{r}-\mathbf{r}'|)\delta\varepsilon(\mathbf{r}')\,\mathbf{E}(\mathbf{r}'). \tag{4}$$

2) Associating the propogator $\hat{\mathrm{T}}$ with the tensor $\widetilde{\mathrm{T}}$ such that for "sufficiently good" scalar function ψ holds

$$\int_V d\mathbf{r}\hat{\mathrm{T}}(\mathbf{r})\psi(\mathbf{r}) = \int_V d\mathbf{r}\widetilde{\mathrm{T}}(\mathbf{r})\psi(\mathbf{r}),$$

and proceeding to the limit $k_0 \to 0$:

$$\lim_{k_0\to 0} k_0^2 \widetilde{T}_{\alpha\beta}(\mathbf{r}) = \widetilde{T}^{(1)}_{\alpha\beta} + \widetilde{T}^{(2)}_{\alpha\beta} = \frac{1}{3\varepsilon_{\mathrm{f}}}\delta(\mathbf{r})\delta_{\alpha\beta} + \frac{1}{4\pi\varepsilon_{\mathrm{f}} r^3}\left(\delta_{\alpha\beta} - 3\frac{r_\alpha r_\beta}{r^2}\right). \quad (5)$$

[W. Weiglhofer, *Am. J. Phys.* **57** (1989) 455]

3) Substituting (5) into (4), making elementary algebraic manipulations, and averaging statistically, we obtain the relation

$$\langle \mathbf{E}(\mathbf{r})\rangle = \left\langle \frac{3\varepsilon_{\mathrm{f}}}{3\varepsilon_{\mathrm{f}} + \delta\varepsilon(\mathbf{r})}\right\rangle \mathbf{E}_0 - 3\varepsilon_{\mathrm{f}} \int_V d\mathbf{r}' \widetilde{\mathrm{T}}^{(2)}(|\mathbf{r}-\mathbf{r}'|)\left\langle \frac{\delta\varepsilon(\mathbf{r}')}{3\varepsilon_{\mathrm{f}} + \delta\varepsilon(\mathbf{r})}\mathbf{E}(\mathbf{r}')\right\rangle. \quad (6)$$

4) For macroscopically homogeneous and isotropic mixtures

$$\langle \mathbf{E}(\mathbf{r}) \rangle = (1-\eta)\mathbf{E}_0, \quad \langle \mathbf{D}(\mathbf{r}) \rangle = \varepsilon_\mathrm{f}(1+2\eta)\mathbf{E}_0, \quad \eta = \left\langle \frac{\delta\varepsilon(\mathbf{r})}{3\varepsilon_\mathrm{f} + \delta\varepsilon(\mathbf{r})} \right\rangle. \quad (7)$$

5) Together with the boundary conditions for the normal components of the electric fields: $\varepsilon_\mathrm{f}(\mathbf{E}_0)_n = \varepsilon\langle \mathbf{E} \rangle_n$, we get:

$$\eta = \frac{\varepsilon - \varepsilon_\mathrm{f}}{2\varepsilon_\mathrm{f} + \varepsilon} = \frac{\varepsilon - \varepsilon_\mathrm{f}}{\varepsilon} \quad \Rightarrow \quad \begin{matrix} \varepsilon_\mathrm{f} = \varepsilon \\ \eta = 0 \end{matrix}$$

The resulting equation on the effective permittivity of statistically homogeneous and isotropic mixtures:

$$\boxed{\left\langle \frac{\delta\varepsilon(\mathbf{r})}{3\varepsilon + \delta\varepsilon(\mathbf{r})} \right\rangle = 0.} \quad (8)$$

[A. K. Semenov, *J. Phys. Commun.* **2** (2018) 035045]

The same result can be obtained using the Hashin-Shtrikman variational theorem [M. Ya. Sushko, *Phys. Rev. E* **96** (2017) 062121].

- Symmetric Bruggeman approach

$$\delta\varepsilon_{\mathrm{CGA}}(\mathbf{r}) = (\varepsilon_0 - \varepsilon)(1 - \tilde{\chi}_1(\mathbf{r})) + (\varepsilon_1 - \varepsilon)\tilde{\chi}_1(\mathbf{r}) \tag{9}$$

$$(1-c)\frac{\varepsilon_0 - \varepsilon}{2\varepsilon + \varepsilon_0} + c\frac{\varepsilon_1 - \varepsilon}{2\varepsilon_{\mathrm{eff}} + \varepsilon_1} = 0. \tag{10}$$

- Asymmetric Bruggeman approach
  Low-concentrations limit:

$$\begin{aligned} \delta\varepsilon^{(I)}_{\mathrm{ABM}}(\mathbf{r}) &= (\varepsilon - (\varepsilon + \Delta\varepsilon))[1 - \tilde{\chi}_1(\mathbf{r}) - \Delta\tilde{\chi}_1(\mathbf{r})] \\ &\quad + (\varepsilon_1 - (\varepsilon + \Delta\varepsilon))\Delta\tilde{\chi}_1(\mathbf{r}) \\ &\approx -\Delta\varepsilon[1 - \tilde{\chi}_1(\mathbf{r})] + (\varepsilon_1 - \varepsilon)\Delta\tilde{\chi}_1(\mathbf{r}), \end{aligned} \tag{11}$$

$$-(1-c)\frac{\Delta\varepsilon}{3\varepsilon} + \Delta c\frac{\varepsilon_1 - \varepsilon}{2\varepsilon + \varepsilon_1} = 0 \quad \Rightarrow \quad 1-c = \frac{\varepsilon - \varepsilon_1}{\varepsilon_0 - \varepsilon_1}\left(\frac{\varepsilon_0}{\varepsilon}\right)^{1/3}. \tag{12}$$

- Asymmetric Bruggeman approach
  High concentrations limit:

$$\begin{aligned}\delta\varepsilon^{(h)}_{\mathrm{ABM}}(\mathbf{r}) &\approx -[1-\tilde{\chi}_0(\mathbf{r})]\Delta\varepsilon + (\varepsilon_0-\varepsilon)\Delta\tilde{\chi}_0(\mathbf{r}) \\ &= -\tilde{\chi}_1(\mathbf{r})\Delta\varepsilon - (\varepsilon_0-\varepsilon)\Delta\tilde{\chi}_1(\mathbf{r}). \end{aligned} \tag{13}$$

$$c = \frac{\varepsilon-\varepsilon_0}{\varepsilon_1-\varepsilon_0}\left(\frac{\varepsilon_1}{\varepsilon}\right)^{1/3}. \tag{14}$$

- The Looyenga and Lichtenecker rules

$$\delta\varepsilon_{\mathrm{LL}}(\mathbf{r}) = (f(\varepsilon_0)-f(\varepsilon))(1-\tilde{\chi}_1(\mathbf{r})) + (f(\varepsilon_1)-f(\varepsilon))\tilde{\chi}_1(\mathbf{r}) \tag{15}$$

$$\begin{aligned} f(x) = x^{1/3} \quad &\Rightarrow \quad \varepsilon^{1/3} = (1-c)\varepsilon_0^{1/3} + c\varepsilon_1^{1/3}, \\ f(x) = \log x \quad &\Rightarrow \quad \log\varepsilon = (1-c)\log\varepsilon_0 + c\log\varepsilon_1 \end{aligned}$$

Suppose that an infinitesimal addition of inclusions to the system causes the filler concentration and the effective permittivity to change by small Δc and $\Delta\varepsilon$, respectively. In view of the $\delta\varepsilon_{\mathrm{CGA}}$ form (9), the new permittivity distribution in the system becomes

$$\widetilde{\delta\varepsilon}_{\mathrm{CGA}}(\mathbf{r}) = \delta\varepsilon^{(l)}_{\mathrm{ABM}}(\mathbf{r}) + \delta\varepsilon^{(h)}_{\mathrm{ABM}}(\mathbf{r}) + \delta\varepsilon_{\mathrm{CGA}}(\mathbf{r}), \quad (16)$$

which is brings us to the differential equation

$$\left[\frac{\varepsilon_1 - \varepsilon}{2\varepsilon + \varepsilon_1} dc - (1 - c)\,\frac{3\varepsilon_0}{(2\varepsilon + \varepsilon_0)^2} d\varepsilon\right] + \left[-\frac{\varepsilon_0 - \varepsilon}{2\varepsilon + \varepsilon_0} dc - c\,\frac{3\varepsilon_1}{(2\varepsilon + \varepsilon_1)^2} d\varepsilon\right] = 0. \quad (17)$$

Low concentration limit

$$\widetilde{\delta\varepsilon}_{\mathrm{CGA}}^{(l)} \approx \delta\varepsilon_{\mathrm{ABM}}^{(l)} + \delta\varepsilon_{\mathrm{CGA}}, \tag{18}$$

$$\frac{dc}{1-c} = d\varepsilon \frac{3\varepsilon_0(2\varepsilon+\varepsilon_1)}{(\varepsilon_1-\varepsilon)(2\varepsilon+\varepsilon_0)^2}, \tag{19}$$

High concentration limit

$$\widetilde{\delta\varepsilon}_{\mathrm{CGA}}^{(h)} \approx \delta\varepsilon_{\mathrm{ABM}}^{(h)} + \delta\varepsilon_{\mathrm{CGA}}, \tag{20}$$

$$\frac{dc}{c} = -d\varepsilon \frac{3\varepsilon_1(2\varepsilon+\varepsilon_0)}{(\varepsilon_0-\varepsilon)(2\varepsilon+\varepsilon_1)^2}. \tag{21}$$

$\delta\varepsilon_{\mathrm{CGA}}$ can be neglected if (1) $\varepsilon_0 \approx \varepsilon$ and $\varepsilon_1 \approx \varepsilon$, respectively; (2) the concentration of the constituent being added is small; (3) $|\varepsilon_1 - \varepsilon_0|$ is small as well.

Differential scheme within the CGA

Improved ABM mixing rules

The integration of the obtained equations results in the following mixing rules:

Low concentration limit

$$\ln(1-c) = \frac{9\varepsilon_0\varepsilon_1}{(2\varepsilon_1+\varepsilon_0)^2}\ln\left[\frac{3\varepsilon_0(\varepsilon-\varepsilon_1)}{(\varepsilon_0-\varepsilon_1)(2\varepsilon+\varepsilon_0)}\right] - \frac{2(\varepsilon_0-\varepsilon_1)(\varepsilon_0-\varepsilon)}{(2\varepsilon_1+\varepsilon_0)(2\varepsilon+\varepsilon_0)}; \quad (22)$$

High concentration limit

$$\ln c = \frac{9\varepsilon_0\varepsilon_1}{(2\varepsilon_0+\varepsilon_1)^2}\ln\left[\frac{3\varepsilon_1(\varepsilon-\varepsilon_0)}{(\varepsilon_1-\varepsilon_0)(2\varepsilon+\varepsilon_1)}\right] - \frac{2(\varepsilon_1-\varepsilon_0)(\varepsilon_1-\varepsilon)}{(2\varepsilon_0+\varepsilon_1)(2\varepsilon+\varepsilon_1)}. \quad (23)$$

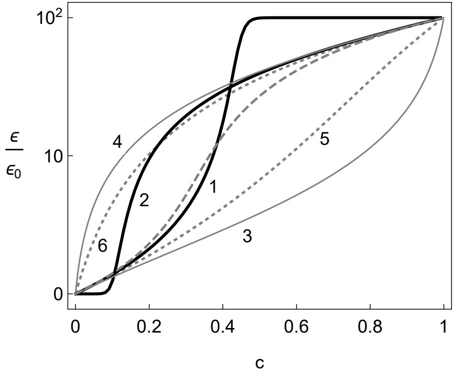


Figure: The concentration dependence of ε according to: the new low- (22) and high-concentration (23) rules (thick solid lines 1 and 2, respectively); Hashin-Shtrikman bottom and upper bounds (thin solid lines 3 and 4); CGA (10) (dashed line); original ABM low- (12) and high-concentration (14) rules (dotted lines 5 and 6). The only parameter used $\varepsilon_1/\varepsilon_0 = 10^2$.

Conclusion

- The classical asymmetrical Bruggeman model (ABM) mixing rules are, in general, physically inconsistent and applicable only for diluted (with respect to one of the constituents) systems with low dielectric contrast between the constituents.
- The overall changes in ε due to addition of an infinitesimal portion of one constituent include the contributions from both constituents (inclusions and the host medium) and depend on the state of the system before the addition.
- The new generalized differential mixing rules are, again, applicable only in certain concentration ranges because beyond those they do not satisfy the Hashin-Shtrikman bounds.
- The results obtained can be generalized to macroscopically homogeneous and isotropic systems with quasistatic complex permittivities of the constituents.

Thank you for your attention!