

Theory of Disordered Systems

Prof. Dr. Igor Sokolov

Lecture 2: Perturbation theories and EMA

In this lecture we discuss the simplest question on how e.g. the effective conductivity of a (*truly*) disordered mixture of materials with different conductances can be obtained within simple perturbative approaches as well as within the effective medium approximation (a kind of a mean field approximation). The perturbative theories are effective when the fluctuation of the local conductance is (in some specific sense) small. This is the case either for the low contrast between the components (e.g. in a two-component medium $|\sigma_1 - \sigma_2| \ll \sigma_{1,2}$) or for low concentration of one of the components.

1 Low contrast

The discussion follows Landau+Lifshitz, vol. VIII, chapter II, §9. We consider first the case when

$$\sigma(\mathbf{r}) = \bar{\sigma} + \delta\sigma(\mathbf{r})$$

with $|\delta\sigma(\mathbf{r})| \ll \bar{\sigma}$ (see L+L, VIII, p.52). $\bar{\sigma}$ can be considered as arithmetic (volume) mean of the corresponding conductivity, so that $\langle\delta\sigma(\mathbf{r})\rangle = 0$. Then

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0 + \delta\mathbf{E}(\mathbf{r}).$$

The mean deviation $\langle\delta\mathbf{E}(\mathbf{r})\rangle = 0$. Moreover, in a fully disordered system showing the isotropy on the average, $\delta\mathbf{E}(\mathbf{r})$ is isotropic. The mean current density

$$\langle\mathbf{j}(\mathbf{r})\rangle = \langle(\bar{\sigma} + \delta\sigma(\mathbf{r}))(\mathbf{E}_0 + \delta\mathbf{E}(\mathbf{r}))\rangle = \bar{\sigma}\mathbf{E}_0 + \langle\delta\sigma(\mathbf{r})\delta\mathbf{E}(\mathbf{r})\rangle :$$

the first non-vanishing correction is of the second order in $\delta\sigma(\mathbf{r})$ (since $\delta\mathbf{E}(\mathbf{r})$ is caused by $\delta\sigma(\mathbf{r})$). The mean current flows in the direction of the mean electric field \mathbf{E}_0 , i.e. parallel to the x -axis, so that (since $\delta\sigma(\mathbf{r})$ is a scalar)

$$\langle\delta\mathbf{j}(\mathbf{r})\rangle = \bar{\sigma}E_0\mathbf{e}_x + \langle\delta\sigma(\mathbf{r})\delta E_x(\mathbf{r})\rangle\mathbf{e}_x. \quad (1)$$

To find the connection between $\delta\sigma(\mathbf{r})$ and $\delta\mathbf{E}(\mathbf{r})$ we use the fact that

$$\operatorname{div} \mathbf{j}(\mathbf{r}) = 0$$

and that $\mathbf{j} = \sigma(\mathbf{r})\mathbf{E}(\mathbf{r})$, so that in the first order in “deltas”

$$\bar{\sigma} \operatorname{div} \delta\mathbf{E}(\mathbf{r}) + \mathbf{E}_0 \operatorname{grad} \delta\sigma(\mathbf{r}) = 0,$$

or

$$\operatorname{div} \delta\mathbf{E}(\mathbf{r}) = -\frac{\mathbf{E}_0}{\bar{\sigma}} \operatorname{grad} \delta\sigma(\mathbf{r}).$$

Since the direction of \mathbf{E}_0 is parallel to the x -axis the scalar product in the r.h.s. can be rewritten:

$$\operatorname{div} \delta\mathbf{E}(\mathbf{r}) = -\frac{E_0}{\bar{\sigma}} \frac{\partial}{\partial x} \delta\sigma(\mathbf{r}).$$

Since

$$\operatorname{div} \delta\mathbf{E} = \frac{\partial \delta E_x}{\partial x} + \frac{\partial \delta E_y}{\partial y} + \dots$$

and since in an isotropic system all these partial derivatives are *typically* equal (a somewhat uncontrolled assumption in which our vague understanding of what is “disordered” is mathematically transformed), we get

$$\operatorname{div} \delta\mathbf{E} = d \frac{\partial \delta E_x}{\partial x}$$

where d is the dimension of space (number of partial derivatives entering the divergence). Then

$$\frac{\partial \delta E_x}{\partial x} = -\frac{E_0}{d\bar{\sigma}} \frac{\partial}{\partial x} \delta\sigma(\mathbf{r}).$$

Integrating this equation (and noting that the integration constant vanishes since $\delta E_x = 0$ for $\delta\sigma = 0$) we get

$$\delta E_x = -\frac{E_0}{d\bar{\sigma}} \delta\sigma(\mathbf{r}).$$

Inserting this into Eq.(1) we get

$$\langle \mathbf{j}(\mathbf{r}) \rangle = \bar{\sigma} \mathbf{E}_0 + \frac{\mathbf{E}_0}{d\bar{\sigma}} \langle \delta\sigma^2(\mathbf{r}) \rangle$$

so that

$$\sigma^* = \bar{\sigma} - \frac{\langle \delta\sigma^2(\mathbf{r}) \rangle}{d\bar{\sigma}}.$$

Note that the minus sign here is quite plausible and complies with the inequality $\sigma^* \leq \langle \sigma \rangle$. The corrections appear in the second order of perturbation theory.

2 Dilute solution at arbitrary contrast

We consider now a different situation which corresponds e.g. to an emulsion, a dilute mixture of spherical droplets of different radii r_i with conductivity σ_2 in the matrix of conductivity σ_1 . Different variants of the corresponding results are known under names Maxwell(1873)-, Clausius(1879)-Mossotti(1850)-, Lorenz(1880)-Lorentz(1880)- or Maxwell-Garnett(1904) - relations. The most general form (not discussed here) is usually quoted as Maxwell-Garnett (MG) one.

Let us consider a single spherical inclusion (“particle”) in an otherwise homogeneous medium. The electric field far from the particle is homogeneous and equals \mathbf{E}_0 . Finding the corresponding potential in the presence of the particle is a typical problem of electrostatics (change \mathbf{j} for \mathbf{D} for the divergence-free field, and you get it!).

The electric field inside the sphere is homogeneous, and the field outside of it is a combination of the homogeneous external field \mathbf{E}_0 and of the dipole field. Thus, the potentials inside the sphere, ϕ_i and outside the sphere ϕ_e are given by

$$\begin{aligned}\phi_i(\mathbf{r}) &= -B\mathbf{E}_0\mathbf{r} \\ \phi_e(\mathbf{r}) &= -\mathbf{E}_0\mathbf{r} + A\mathbf{E}_0\frac{\mathbf{r}}{r^3}\end{aligned}$$

with the constants A and B which have to be determined from the boundary conditions at the boundary of the sphere: the continuity of the potential

$$\phi_i(\mathbf{r}) = \phi_e(\mathbf{r})$$

and the continuity of the normal component of the current $j_{i,\perp} = j_{e,\perp}$. Using the fact that $\mathbf{j} = \sigma(\mathbf{r})\mathbf{E}(\mathbf{r})$ the last one can be rewritten as

$$\sigma_1 \frac{\partial \phi_i}{\partial r} = \sigma_2 \frac{\partial \phi_e}{\partial r}$$

at the boundary. The result in three dimensions for the field inside the sphere reads:

$$\mathbf{E}_i = \frac{3\sigma_2}{2\sigma_2 + \sigma_1} \mathbf{E}_0,$$

(see e.g. Landau+Lifshitz, vol. VIII, chapter II, §8). In d dimensions we have

$$\mathbf{E}_i = \frac{d\sigma_2}{(d-1)\sigma_2 + \sigma_1} \mathbf{E}_0. \quad (2)$$

Let us now consider the integral

$$\frac{1}{V} \int (\mathbf{j} - \sigma_2 \mathbf{E}) d\mathbf{r} = \mathbf{J} - \sigma_2 \mathbf{E}_0$$

(the notation follows our Lecture 1). The integrand differs from zero only within the spheres, since in the matrix $\mathbf{j} = \sigma_2 \mathbf{E}$. If the spheres lie very far from each other, the external field felt by each sphere does not differ considerably from \mathbf{E}_0 since the dipole contributions from other inclusions decay quite fast with the distance between them, and therefore the fields inside all these spheres can be approximated by \mathbf{E}_i given by Eq.(2). Therefore our integral is

$$\mathbf{J} - \sigma_2 \mathbf{E}_0 = \frac{1}{V} \int_{\Omega} (\sigma_1 \mathbf{E}_i - \sigma_2 \mathbf{E}_i) d\mathbf{r} = \nu \frac{d(\sigma_1 - \sigma_2)\sigma_2}{(d-1)\sigma_2 + \sigma_1} \mathbf{E}_0$$

where the integration runs over the total volume Ω inside the inclusions, and ν is the quotient of volume inside these inclusions and the total volume of the system. Therefore

$$\mathbf{J} = \sigma_2 \mathbf{E}_0 + \nu \frac{d(\sigma_1 - \sigma_2)\sigma_2}{(d-1)\sigma_2 + \sigma_1} \mathbf{E}_0$$

and

$$\sigma^* = \sigma_2 + \nu \frac{d(\sigma_1 - \sigma_2)\sigma_2}{(d-1)\sigma_2 + \sigma_1}. \quad (3)$$

This equation holds for small ν (large distances between the spheres) but for arbitrary contrast (i.e. for arbitrary difference between σ_1 and σ_2). It evidently has a structure of the first order perturbation theory fully disregarding the interactions between different inclusions. The approximation can be generalized to multicomponent systems and leads to the one with the sum over different components,

$$\sigma^* = \sigma_{\text{matrix}} + \sum_i \nu_i \frac{d(\sigma_i - \sigma_{\text{matrix}})\sigma_{\text{matrix}}}{(d-1)\sigma_{\text{matrix}} + \sigma_i}.$$

3 Effective medium approximation (EMA)

We now consider a self-consistent approximation for calculation of the effective conductance of a mixture (D.A.G. Bruggeman, Annalen der Physik, 5

Folge, **24**, 636 (1935)). The method delivers a good interpolation formula between the results of perturbation approaches when one or another medium is considered as a matrix.

Let us consider our mixture and take a small spherical (in 2d - circular) domain of it as a probe. This one belongs to the domain with conductivity σ_1 with probability ν or to the domain with conductivity σ_2 with probability $1 - \nu$. Let us consider the rest of the disordered medium as a homogeneous and isotropic medium with the effective conductivity σ^* .

The field inside the test domain is then equal to

$$\begin{aligned}\mathbf{E}_1 &= \frac{d\sigma^*}{(d-1)\sigma^* + \sigma_1} \mathbf{E}_0 && \text{with probability } \nu \\ \mathbf{E}_2 &= \frac{d\sigma^*}{(d-1)\sigma^* + \sigma_2} \mathbf{E}_0 && \text{with probability } 1 - \nu\end{aligned}$$

The averaged field in the probe domain has to be equal to the volume mean of the electric field,

$$\nu \mathbf{E}_1 + (1 - \nu) \mathbf{E}_2 = \mathbf{E}_0,$$

which delivers the self-consistency condition. Putting all this together we get

$$\nu \frac{d\sigma^*}{(d-1)\sigma^* + \sigma_1} + (1 - \nu) \frac{d\sigma^*}{(d-1)\sigma^* + \sigma_2} = 1,$$

or in general (e.g. for a multicomponent system or for a system with continuously changing $\sigma(\mathbf{r})$)

$$\left\langle \frac{d\sigma^*}{(d-1)\sigma^* + \sigma} \right\rangle_\sigma = 1 \tag{4}$$

which is considered as an equation for σ^* . The average here can be considered either as a volume average or as an average over the distribution $p(\sigma)$:

$$\int \frac{d\sigma^*}{(d-1)\sigma^* + \sigma} p(\sigma) d\sigma.$$

Eq.(4) can be rewritten in the form

$$\left\langle \frac{\sigma^* - \sigma}{(d-1)\sigma^* + \sigma} \right\rangle_\sigma = 0.$$

For two-component medium in the limiting cases $\nu \rightarrow 0, 1$ the result coincides with the Maxwell-Garnett one, and for $\delta\sigma$ small delivers our second-order formula, Sec. 2.1 (prove this!).

In $d = 2$ for a two-component medium with $\nu = 1/2$ it gives

$$\sigma^* = \sqrt{\sigma_1 \sigma_2}$$

which coincides with the exact result following solely from the isotropy on the average and the invariance under renaming $1 \leftrightarrow 2$.

For a medium with infinite contrast (e.g. for a mixture of a conductor with $\sigma_1 = \sigma$ and a dielectric with $\sigma_2 = 0$ in proportion ν to $1 - \nu$) EMA predicts the percolation transition at $\nu = 1/d$: it gives

$$\sigma^* = \frac{d\nu - 1}{d - 1} \sigma$$

for $\nu > 1/d$ and negative values of σ^* for $\nu < 1/d$, which are interpreted as the transition to a non-conducting state.