On calculation of effective conductivity of inhomogeneous metals

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Abstract

In the framework of the perturbation theory an expression suitable for calculation of the effective conductivity of 3-D inhomogeneous metals is derived. Formally, the final expression is an exact result, however, a function written as a perturbation series enters the answer. More accurately, when statistical properties of the given inhomogeneous medium are known, our result provides the regular algorithm for calculation of the effective conductivity up to an arbitrary term of the perturbation series. As examples, we examine (i) an isotropic metal whose local conductivity is a Gaussianly distributed random function, (ii) the effective conductivity of polycrystalline metals.

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1 Introduction

Rather often macroscopic properties of stochastically inhomogeneous media, which are isotropic in average, can be described in the framework of different models of effective isotropic medium. Calculation of the effective conductivity (EC) is one of the well-known problems of theory of conductive media. It has been studied theoretically for many years (see, e.g., the review paper by A.G.Fokin [1]). However, in the general case up to now this problem has not been solved yet.

Exact solutions for effective characteristics of stochastically inhomogeneous media can be found very rarely. One of such examples is the calculation of EC of some two-dimensional inhomogeneous media [2]. The existence of this result is due to a specific symmetry transformation allowed by the equations of the problem. Recently in the frequency region of the local impedance (the Leontovich) boundary conditions applicability the exact solution for the effective surface impedance of inhomogeneous metals was obtained [3, 4]. Sometimes effective characteristics can be estimated qualitatively. For example, there are no regular methods allowing us to calculate the effective conductivity of three-dimensional (3-D) polycrystals accurately, but some geometrical reasoning suggested in Ref.[5], allowed the authors to estimate EC of strongly anisotropic polycrystals.

When the exact solution for an effective value \( \psi_{ef} \) of a characteristic \( \psi \) cannot be found, perturbation theory calculations may be useful. In a stochastically inhomogeneous medium \( \psi \) is a stochastic function of position \( \mathbf{r} \). A natural zero order approximation for \( \psi_{ef} \) is \( < \psi > \) that is of \( \psi(\mathbf{r}) \) averaged over all possible realizations of the medium. However, when calculating \( < \psi > \), we do not take into account corrections due to the spatial fluctuations of \( \psi(\mathbf{r}) \).

From our point of view, the most accurate and physically meaningful method to take account of spatial fluctuations goes back to the work of I.M.Lifshitz and L.N.Rosenzweig [6]. They proposed to start from differential equations of the problem coefficients of which
are random functions of position. Averaging these equations we derive equations for the averaged fields, which allow us to determine the effective characteristic. Usually this approach works when the inhomogeneity is small and perturbation theory is applicable. Previously it was used to calculate a lot of static and dynamic characteristics of inhomogeneous media. As an example, we cite Refs. [7, 8, 9, 10, 11]. In all these works only the first nonvanishing term taking account of spatial fluctuations was calculated. For a characteristic $\psi$ this term is of the order of $\langle (\psi - \langle \psi \rangle)^2 \rangle$. Usually, it does not depend on the correlations of the values of $\psi$ in different points of the medium.

It is much more difficult to calculate the corrections of the higher orders in $(\psi(r) - \langle \psi \rangle)$. The calculation involves step by step derivation of equations for each correction of the order $n > 2$. In addition, the high order corrections depend on the statistical properties of the medium.

In this paper with the aid of the perturbation theory we derive an expression suitable for calculation of EC $\sigma_{ef}$ of 3-D inhomogeneous metals. The basic formula for $\sigma_{ef}$ is obtained in Section 2. Formally, in the framework of the perturbation theory applicability, the final expression, Eq.(15), is exact. However, a function written as a perturbation series enters the answer. So, more accurately, when statistical properties of the given inhomogeneous medium are known, our result provides the regular algorithm for calculation of EC up to an arbitrary term of the perturbation series. We also write down the perturbation theory expression for EC of two-dimensional (2-D) conducting media. As an example, we examine an isotropic metal whose local conductivity is a Gaussianly distributed random function, and calculate the forth order correction to the effective conductivity.

In Section 3 we consider polycrystalline metals. To verify our perturbation theory, in Subsection 3.1 we compare the perturbation theory calculation of $\sigma_{ef}$ for 2-D polycrystals with the exact result of [1]. In Subsection 3.2 EC of 3-D polycrystals is discussed. We calculate EC up to the third order term in the parameters of anisotropy and outline the region of the perturbation theory applicability. Also we examine the dependence of the third order term on the statistical properties of the polycrystal.

# 2 Perturbation Theory for Effective Conductivity of 3-D Inhomogeneous Metals

We consider a stochastically inhomogeneous metal that is isotropic and homogeneous in average. The elements of the local conductivity (LC) tensor $\sigma_{ik}$ are stochastic functions of position $r$. By $\langle ... \rangle$ denote the ensemble average over all possible realizations of the medium. The averaged conductivity $\langle \sigma_{ik}(r) \rangle = \langle \sigma \rangle \delta_{ik}$, and

$$\sigma_{ik}(r) = \langle \sigma \rangle (\delta_{ik} + \Delta_{ik}(r)), \quad \langle \Delta_{ik}(r) \rangle = 0. \quad (1)$$

The stochastic tensor $\Delta_{ik}(r)$ describes the spatial fluctuations of LC.

By definition, the effective conductivity $\sigma_{ef}$ is specified by equation:

$$\langle j(r) \rangle = \sigma_{ef} \langle E(r) \rangle, \quad (2)$$

where $\langle j \rangle$ is the macroscopic direct current density and $\langle E \rangle$ is the uniform macroscopic electric field; $j(r)$ and $E(r)$ are the local current density and the local electric field, respectively.
To calculate $\sigma_{ef}$, we write the electrostatics equations

$$\nabla \cdot \mathbf{j} = 0, \quad \nabla \times \mathbf{E} = 0, \quad (3)$$

and the material equation that is the Ohm law. According to Eq.(1)

$$j_i(r) = \langle \sigma \rangle (\delta_{ik} + \Delta_{ik}(r))E_k(r). \quad (4)$$

Because of the tensor $\Delta_{ik}(r)$, Eq.(3) constitute a system of stochastic equations for the local field $E_i(r)$.

We write $\mathbf{j}(r)$ and $\mathbf{E}(r)$ as $j = \langle j \rangle + \delta j$ and $E = \langle E \rangle + \delta E \Rightarrow \langle j \rangle = \langle 0 \rangle$; $\delta j$ and $\delta E$ are position dependent stochastic current and stochastic field, respectively. Substituting these expressions in Eq.(4) we obtain after averaging

$$\langle j_i \rangle = \langle \sigma \rangle (E_i > + J_i), \quad J_i = \langle \Delta_{ik}(r)\delta E_k(r) \rangle. \quad (5)$$

Comparing Eq.(2) and Eq.(5), we see that the uniform vector $\mathbf{J}$ defines the contribution of the spatial fluctuations of LC to the value of EC.

Subtracting Eq.(5) from Eq.(4) we have

$$\delta j_i = \langle \sigma \rangle (\delta E_i + \Delta_{ik} < E_k > + D_i), \quad D_i = \Delta_{ik}\delta E_k - J_i. \quad (6)$$

The components of the vector $\mathbf{D}$ at least quadratic in powers of the elements of the tensor $\Delta_{ik}$. When calculating EC up to the first nonvanishing term taking account of spatial fluctuations, the vector $\mathbf{D}$ in Eq.(6) has to be omitted. However, just this vector defines corrections of higher orders.

To calculate the vector $\mathbf{J}$ we use the perturbation theory. We present the stochastic field $\delta E_i(r)$ as a series in powers of the elements of the stochastic tensor $\Delta_{ik}(r)$:

$$\delta E_i(r) = \sum_{n=1}^{\infty} \delta E_i^{(n)}(r). \quad (7.a)$$

and seek the vector $J_i$ as the series

$$J_i = \sum_{n=2}^{\infty} J_i^{(n)}, \quad J_i^{(n)} = \langle \Delta_{jk}(r)\delta E_i^{(n-1)}(r) \rangle. \quad (7.b)$$

With regard to Eq.(6) from the electrostatic equations (3) it follows that the Fourier coefficient of the stochastic field $\delta E_i(r)$ is $\delta E_i(k) = -\kappa_i\kappa_j(\Delta_{jk}(k) < E_k > + D_j(k))$, where $\kappa_i = k_i/k$. Consequently, the Fourier coefficients of $\delta E_i^{(n)}(r)$ are

$$\delta E_i^{(1)}(k) = -\kappa_i\kappa_j\Delta_{jk}(k) < E_k > \quad \text{and} \quad \delta E_i^{(n)}(k) |_{n>1} = -\kappa_i\kappa_jD_j^{(n)}(k), \quad (8)$$

where $D_j^{(n)}(k)$ is the Fourier coefficient of $D_j^{(n)}(r) = \Delta_{jk}(r)\delta E_k^{(n-1)}(r) - J_j^{(n)}$.

Equations (7) and (8) allow us to write the n-th term of the series (7.b) as a sum of the lower orders terms $J_i^{(m)} (2 \leq m < n)$. Indeed, for $n \geq 2$ from Eq.(8) it follows that

$$\delta E_i^{(n)}(r) = -\left\{ \int \int d^3k nd^3k_{n-1} q_{ijn}^{(n)} \Delta_{jn} \delta E_{l_{m-1}}^{(n-1)}(k_n - k_{n-1})e^{ik_n r} \right\}, \quad (9)$$

where $q_{ik}^{(n)} = \kappa_i^{(n)}\kappa_k^{(n)}$. 

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Next, we use Eq.(9) to write down the expression for $\delta E_i^{(n-1)}(r)$. We Fourier analyze $\delta E_i^{(n-1)}(r)$ and substitute the result in Eq.(9). Then the term proportional to $J_i^{(n-1)}$ appears in the right-hand side of Eq.(9) and the Fourier coefficient $\delta E_i^{(n-2)}(k)$ enters the integral term of this equation.

The next steps are obvious. In successive order we decrease the superscripts in the expressions for the stochastic fields $\delta \mathbf{E}^{(m)}$ entering the integral term of Eq.(9). At the last step the coefficient $\delta \mathbf{E}^{(1)}(k_1)$ defined by Eq.(8) enters the equation.

If we use the expression for $\delta E_i^{(n)}(r)$ obtained as the result of the aforementioned decreasing procedure when calculating $J_i^{(n+1)}$ and replace the superscript $(n + 1)$ by $m$, we have

$$\sum_{l=2}^{m} w_{ik}^{(m-l)} J_k^{(l)} = -3w_{ik}^{(m)} < E_k >. \quad (10)$$

In Eq.(10) $w_{ik}^{(0)} = \delta_{ik}$, $w_{ik}^{(1)} = - < \Delta_{ik}(r) > /3 = 0$ and for $n \geq 2$

$$w_{ik}^{(n)} = (-1)^n \frac{1}{3(2\pi)^{3(n-1)}} \int ... \int d^3r_1 ... d^3r_{n-1} \int ... \int d^3k_1 ... d^3k_{n-1} q_{1i1}^{(1)} ... q_{n-1i-1}^{(n-1)} \times$$

$$< \Delta_{il}(r) \Delta_{jil2}(r_1) ... \Delta_{jn-1i}(r_{n-1}) > e^{i\mathbf{k}_1(r-r_1)} e^{i\mathbf{k}_2(r_1-r_2)} ... e^{i\mathbf{k}_{n-1}(r_{n-2}-r_{n-1})} \quad (11)$$

When the medium is isotropic in average, the moments $< \Delta_{il}(r) \Delta_{jil2}(r_1) ... \Delta_{jn-1i}(r_{n-1}) >$ depend only on the modulus of the differences between the vectors $r_i$ entering the average. Then the elements of the tensors $w_{ik}^{(n)}$ do not depend on position. Since all isotropic uniform second rank tensors reduce themselves to the unit tensor $\delta_{ik}$, the only possible form of all the tensors $w_{ik}^{(n)} (n \geq 2)$ is

$$w_{ik}^{(n)} = w^{(n)} \delta_{ik}; \quad w^{(n)} = \frac{1}{3} w_{ii}^{(n)} \quad (12)$$

where $w_{ii}^{(n)}$ is the trace of the matrix $w_{ik}^{(n)}$. We also have $w^{(0)} = 1$ and $w^{(1)} = 0$.

Taking account of Eq.(12) we write down Eqs.(10) for all $2 \leq m < \infty$:

$$J_i^{(2)} = -3w^{(2)} < E_i >, \quad \text{if} \ m = 2; \quad (13.a)$$

$$w^{(1)} J_i^{(2)} + J_i^{(3)} = -3w^{(3)} < E_i >, \quad \text{if} \ m = 3; \quad (13.b)$$

$$w^{(2)} J_i^{(2)} + w^{(1)} J_i^{(3)} + J_i^{(4)} = -3w^{(4)} < E_i >, \quad \text{if} \ m = 4; \quad (13.c)$$

$$w^{(3)} J_i^{(2)} + w^{(2)} J_i^{(3)} + w^{(1)} J_i^{(4)} + J_i^{(5)} = -3w^{(5)} < E_i >, \quad \text{if} \ m = 5 \quad (13.d)$$

and so on. We add together all these equations. Then according to Eq.(7.b) we obtain

$$T_3 J_i = -3(T_3 - 1) < E_i >, \quad T_3 = \sum_{m=0}^{\infty} w^{(m)}. \quad (14)$$

Consequently, $J_i = 3(1/T_3 - 1) < E_i >$. Finally, with regard to Eq.(2) and Eq.(5) we have

$$\sigma_{ef} = < \sigma > (3/T_3 - 2). \quad (15)$$
Together with Eq.(15) we would like to present the expression for EC of 2-D inhomogeneous metals. Repeating the previous calculations with regard to the dimensionality of the problem, we obtain

$$\sigma_{ef} = \sigma(2/T_2 - 1), \quad T_2 = \sum_{m=0}^{\infty} v^{(m)}$$  \hspace{1cm} (16.a)

where again \(v^{(0)} = 1, v^{(1)} = 0\) and for \(n \geq 2\) we have

$$v^{(n)} = (-1)^n \frac{1}{4(2\pi)^{2(n-1)}} \int \ldots \int d^2 r_1 \ldots d^2 r_{n-1} \int \ldots \int d^2 k_1 \ldots d^2 k_{n-1} q^{(1)}_{1j_1} \ldots q^{(n-1)}_{n-1j_{n-1}} \times \nonumber$$

$$< \Delta_{d_1}(r) \Delta_{j_1}(r_1) \ldots \Delta_{j_{n-1}}(r_{n-1}) > e^{ik_1(r-r_1)} e^{ik_2(r_1-r_2)} \ldots e^{ik_{n-1}(r_{n-2}-r_{n-1})}, \hspace{1cm} (16.b)$$

\(r_n\) and \(k_n\) are 2-D position and wave vectors, respectively.

Equations (15) and (16) are the basic formulas we use when calculating EC within the framework of the perturbation theory. These formulas look rather simple. However, usually even for rather simple models of inhomogeneous conducting media we can calculate \(T_3\) (or \(T_2\)) up to the desirable order in powers of the parameters of inhomogeneity only.

It can appear that no significant simplification has been done. However, when the perturbation theory is applicable, Eq.(15) and Eq.(16) provide a regular method for calculation of the high order terms in the expression for EC.

In the end of this Section as an example, we examine an isotropic metal with Gaussian inhomogeneities. This example is rather simple, since, first, for isotropic metals the expressions for \(w^{(n)}\) are simplified, and, second, the form of \(n\)-point averages entering these expressions are known.

We suppose that LC is \(\sigma_{ik}(r) = \langle \sigma > (1+\Delta(r)) \delta_{ik}\), where \(\Delta(r)\) is a strictly stationary, zero-mean Gaussian process \([12]\). Then the two-point average is

$$\langle \Delta(r) \Delta(r_1) > = \Delta^2 W_G(|r - r_1|), \hspace{1cm} (17.a)$$

where \(\Delta^2 = \langle \Delta^2(r) \rangle\), and the Gaussian correlation function \(W_G(r)\) and its Fourier coefficient \(W_G(k)\) are

$$W_G(r) = e^{-r^2/a^2} \text{ and } W_G(k) = \frac{a^3}{(2\sqrt{\pi})^3} e^{-(ka)^2/4}, \hspace{1cm} (17.b)$$

\(a\) is the correlation radius. Next, the average of a product of an odd number of \(\Delta(r)\) vanishes, and the average of an even number of \(\Delta(r)\) is given by the sum of the products of the averages of pairs of the \(\Delta(r)\)’s taken in all possible ways, irrespective of order, e.g.

$$\langle \Delta(r) \Delta(r_1) \Delta(r_2) \Delta(r_3) > = \Delta^4(W_G(|r - r_1|)W_G(|r_2 - r_3|) + W_G(|r - r_2|)W_G(|r_1 - r_3|) \nonumber$$

$$+ W_G(|r - r_3|)W_G(|r_1 - r_2|)). \hspace{1cm} (17.c)$$

For this particular medium in the sum \(T_3\) all the terms \(w^{(2n-1)} = 0\). We use Eq.(11) and Eq.(12) to calculate \(w^{(2)}\) and \(w^{(4)}\). Then

$$w^{(2)} = \frac{\Delta^2}{9} \int d^2 k W_G(k). \hspace{1cm} (18)$$
Being the value of $W_G(r)$ when $r = 0$, the integral in right-hand side of Eq.(18) is equal to one. Thus, $w^{(2)} = \Delta^2/9$. Note, Eq.(18) is valid not only in the case of Gaussian inhomogeneities, but for any random zero-mean function $\Delta(r)$. Consequently, always the first (quadratic in fluctuations of LC) correction to EC is independent of the form of the correlation function (see, for example, [13]).

Our calculations showed that $w^{(4)} = \Delta^4(\pi - 20/9)/9$. Then according to Eq.(14) and Eq.(15) up to the terms of the order of $\Delta^4$ we have

$$T_3^{(G)} = 1 + \frac{1}{9} \left\{ \Delta^2 + \Delta^4(\pi - \frac{20}{9}) \right\}, \quad \sigma_{ef}^{(G)} = \langle \sigma \rangle \left\{ 1 - \frac{1}{3} \left[ \Delta^2 + \Delta^4(\pi - \frac{7}{3}) \right] \right\}. \quad (19)$$

For Gaussianly distributed random function $\Delta(r)$ it is rather simple to calculate $\sigma_{ef}^{(G)}$ up to the higher order terms in $\Delta^2$. However, we failed trying to obtain a general formula for these terms.

### 3 The Effective Conductivity of Polycrystals

Polycrystals are widespread case of inhomogeneous media, where the inhomogeneity is due to different orientations of discrete single crystal grains. Anisotropic properties of each grain are described by tensor characteristics. If crystallographic axes of the grains are randomly rotated with respect to a fixed set of laboratory axes, the characteristics of the medium measured in the laboratory coordinate system are stochastic tensor functions of position. However, the invariants of the tensors are the same for all the grains and do not depend on position. Consequently, effective characteristics of polycrystals have to be expressed in terms of the invariants of the tensors that describe the phenomenon. When a polycrystal is isotropic in average (it is untextured), its effective characteristics are isotropic tensors. For example, EC of an untextured polycrystal is $\sigma_{ik}^{ef} = \sigma_{ef}\delta_{ik}$.

#### 3.1 Two-dimensional Polycrystals

For 2-D polycrystal there is the exact solution for $\sigma_{ef}$ found by Dykhne [2]. We use the Dykhne formula to verify the calculations of Section 2, comparing the perturbation theory results with the expansion of the exact solution in powers of the parameter defining the anisotropy of LC. We do not find out a procedure allowing us to calculate an arbitrary term of the perturbation series. Therefore we only checked the first and the second terms taking account of spatial fluctuations. This exercise, being a test for our theory, outlined the way of calculation of high-order terms in the expression for EC of 3-D polycrystals.

Let $\sigma_{ik}$ be the single crystal 2-D conductivity tensor, and let $\sigma_1$ and $\sigma_2$ be its principle values. We set

$$\bar{\sigma} = \frac{1}{2}(\sigma_1 + \sigma_2), \quad \Delta = \frac{(\sigma_1 - \sigma_2)}{\sigma_1 + \sigma_2}, \quad (20)$$

where $\bar{\sigma}$ is the mean conductivity, and the dimensionless parameter $\Delta$ ($|\Delta| < 1$) defines the deviation of the principle conductivities from $\bar{\sigma}$: $\sigma_1 = \bar{\sigma}(1 + \Delta)$ and $\sigma_2 = \bar{\sigma}(1 - \Delta)$. Being the first order invariant of the tensor $\sigma_{ik}$, the mean conductivity is independent of position. Evidently, $\bar{\sigma} = \langle \sigma \rangle$.

According to Dykhne, EC of a 2-D polycrystal does not depend on correlations between stochastic functions $\Delta_{ik}(r)$ at different positions: $\sigma_{ef} = \sqrt{\sigma_1\sigma_2}$. Note, $\sigma_1\sigma_2$ being the determinant of the tensor $\sigma_{ik}$, is its invariant.
We rewrite the Dykhne formula as

$$\sigma_{ef} = \sigma \sqrt{(1 - \Delta^2)} = \sigma (1 - \frac{\Delta^2}{2} - \frac{\Delta^4}{8} ... )$$

(21)

and compare the terms of the series (21) with the result obtained with the aid of Eqs.(16).

To start the calculation we write the local conductivity tensor with respect to the laboratory coordinate system: \( \sigma_{ik} = \sigma (\delta_{ik} + \Delta_{ik}(r)) \), where

\[
\Delta_{ik}(r) = \Delta Z_{ik}(r); \quad Z_{ik} = (\alpha_{i1}\alpha_{k1} - \alpha_{i2}\alpha_{k2}),
\]

(22)

and \( \alpha_{ik} = \alpha_{ik}(r) \) is 2-D rotation matrix that defines the orientation of the crystallographic axes of the grain containing the point \( r \) with respect to the laboratory axes. The elements of 2-D rotation matrix depend on one angle only. Let it be the angle \( \psi \). The value of \( \psi \) is a stochastic function of position.

With regard to Eqs.(16) when calculating EC of 2-D polycrystals up to the terms of the order of \( \Delta^4 \), we need to calculate the terms \( v^{(n)} \) \((n = 2, 3, 4)\) of the series (16.a) for \( T_2 \). Consequently, first, we must define the second, the third and the fourth moments of the stochastic tensor function \( \Delta_{ik}(r) \). The general statistical properties of polycrystals were discussed in Ref.[9]. Here we discuss them briefly, paying attention to calculation of the high-order moments.

The only property of the medium that affects the ensemble averages is the rotations of the crystallographic axes of the grains. Then ensemble average becomes the average over all possible rotations of the crystallites. We assume that in the ensemble the angles defining the rotations of different grains are statistically independent. When calculating the second order two-point correlator \( \langle \Delta_{ik}(r)\Delta_{li}(r_1) \rangle \) entering the expression for \( v^{(2)} \), there are two cases to consider:

1. \( r \) and \( r_1 \) are in the same grain;
2. \( r \) and \( r_1 \) are in different grains.

We denote the probability of the case 1 by \( W_2(|r - r_1|) \). Then \( 1 - W_2 \) is the probability of the case 2. The fact that the probability \( W_2 \) depends on \( r \) and \( r_1 \) only through \( |r - r_1| \) is the consequence of our assumption that the polycrystalline medium is isotropic and statistically homogeneous.

Let \( \psi \) and \( \psi_1 \) be the angles defining the orientation of the crystallographic axes in the grain containing the point \( r \). In the case 1 the rotations defined by the angles \( \psi \) and \( \psi_1 \) are identically equal. So, these both angles define one specific rotation. In this case the second order two-point correlator \( \langle \Delta_{ik}(r)\Delta_{li}(r_1) \rangle \) reduces to the second order one-point correlator \( S_{ik:li} = \langle \Delta_{ik}(r)\Delta_{li}(r) \rangle \). This is an isotropic second-rank tensor: \( S_{ik:li} = S \delta_{kl} \). As far as \( \Delta_{ii} = 0 \), \( \Delta_{ik}\Delta_{ki} = 2\Delta^2 \) is the only nonzero second order invariant of the tensor \( \Delta_{m}(r) \). Then \( S = \Delta^2 \).

Because all the rotations are assumed to be independent, in the case 2 we have

\[
\langle \Delta_{ik}(r)\Delta_{li}(r_1) \rangle = \langle \Delta_{ik}(r) \rangle \langle \Delta_{li}(r_1) \rangle = 0.
\]

Consequently, the case 2 does not contribute to the value of the second order two-point correlator \( \langle \Delta_{ik}(r)\Delta_{li}(r_1) \rangle \). Thus

\[
\langle \Delta_{ik}(r)\Delta_{li}(r_1) \rangle = \Delta^2 W_2(|r - r_1|)\delta_{kl}.
\]

(23)

Next, it is evident that the three-point average \( \langle \Delta_{ik}(r)\Delta_{lm}(r_1)\Delta_{ni}(r_2) \rangle \) is not equal to zero only if all the three vectors \( r, r_1 \) and \( r_2 \) are in the same grain. Let us denote the probability of this event as \( W_3 = W_3(|r - r_1|, |r - r_2|, |r_1 - r_2|) \). Then

\[
\langle \Delta_{ik}(r)\Delta_{lm}(r_1)\Delta_{ni}(r_2) \rangle = S_{ik:lm:ni}W_3(|r - r_1|, |r - r_2|, |r_1 - r_2|).
\]

(24)
where $S_{ik;lm;ni} = \langle \Delta_{ik}(r) \Delta_{lm}(r) \Delta_{ni}(r) \rangle$ is the third order one-point average. It is clear that $S_{ik;lm;ni}$ is the isotropic forth-rank tensor. One can easily verify that in the 2-D case all the invariants of the tensor $\Delta_{ik} \Delta_{lm} \Delta_{ni}$ are equal to zero. Then, without calculations we can state that all the elements of the tensor $S_{ik;lm;ni}$ vanish. As a result, $v^{(3)} = 0$, and the third order correction to EC vanishes.

Finally, it is clear that there are only two possibilities when the four-point average
$\langle \Delta_{ik}(r) \Delta_{lm}(r_1) \Delta_{np}(r_2) \Delta_{qi}(r_3) \rangle$ is not equal to zero. Namely,
1. Each of the pairs of the four vectors, but not all of them simultaneously, are in the same grain.
2. All the four vectors are in the same grain.

For the case 1 by $W_4([r_a, r_b], [r_c, r_d])$ we denote the joint conditional probability for the vectors $r_a$ and $r_b$ to get in the same grain, and, simultaneously, for the vectors $r_c$ and $r_d$ to get in some other grain. The probability $W_4([r_a, r_b], [r_c, r_d])$ excludes the possibility for all the four vectors to be in the same grain. Evidently, since all the rotations of the grains are independent, in the case 1 the four-point average is a product of two one-point averages of the second order. Next, by $W_4([r, r_1, r_2, r_3])$ we denote the probability of the case 2. Then

\[
\langle \Delta_{ik}(r) \Delta_{lm}(r_1) \Delta_{np}(r_2) \Delta_{qi}(r_3) \rangle = W_4([r, r_1], [r_2, r_3])S_{ik,lm}S_{np,qi} + W_4([r_1, r_3], [r_2, r_3])S_{ik,lm}S_{np,qi} + W_4([r, r_1], [r_2, r_3])R_{ik,lm, np,qi},
\]

where

\[
S_{ik,lm} = \langle \Delta_{ik}(r) \Delta_{lm}(r) \rangle, \quad (25.b)
\]

\[
R_{ik,lm, np,qi} = \langle \Delta_{ik}(r) \Delta_{lm}(r)(r) \Delta_{np}(r) \Delta_{qi}(r) \rangle. \quad (25.c)
\]

Let us calculate the elements of the isotropic tensors $S_{ik;lm}$ and $R_{ik,lm, np,qi}$. Taking account of the symmetry properties with respect to interchanges of the indices, we see that the isotropic forth rank tensor $S_{ik;lm}$ must have the form $S_{ik;lm} = a \delta_{ik} \delta_{lm} + b (\delta_{il} \delta_{km} + \delta_{im} \delta_{kl})$. To determine the values of $a$ and $b$ we calculate the two independent invariants of the tensor $\Delta_{ik} \Delta_{lm}$. They are the contractions $\Delta_{kk} \Delta_{ll} = 0$ and $\Delta_{ik} \Delta_{ki} = 2 \Delta^2$. Then

\[
S_{ik;lm} = \frac{\Delta^2}{2} (-\delta_{ik} \delta_{lm} + \delta_{il} \delta_{km} + \delta_{im} \delta_{kl}). \quad (26.a)
\]

If we use the explicit form of the tensor $\Delta_{ik}$ (see Eq.(22)), it is easy to see that in the 2-D case the sixth rank tensor

\[
R_{ik,lm, np,qi} = S_{ik, qi} S_{lm, np} = \Delta^2 \delta_{kq} S_{lm, np}. \quad (26.b)
\]

Now we are ready to calculate the terms $v^{(2)}$ and $v^{(4)}$ of the sum $T_2$. The same as when deriving Eq.(18), with the aid of Eq.(23) we obtain $v^{(2)} = \Delta^2/4$. As usual, the first correction term is independent of the form of the correlation function $W_2(r)$.

To calculate $v^{(4)}$ we substitute Eqs.(25) and Eqs.(26) in Eq.(16.b) for $n = 4$ and calculate the contraction entering the integrand of the left-hand side of this equation. Then

\[
v^{(4)} = \frac{\Delta^4}{16} \sum_{q=1}^{3} X(q). \quad (27.a)
\]
where

\[ X^{(1)} = \int \int \int d^2 r_1 d^2 r_2 d^2 r_3 \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r}_2 - \mathbf{r}_3) W_4([\mathbf{r}, \mathbf{r}_1, [\mathbf{r}_2, \mathbf{r}_3]), \quad (27.b) \]

\[ X^{(2)} = \frac{1}{(2\pi)^2} \int \int \int d^2 r_1 d^2 r_2 d^2 r_3 \int \int d^2 k_1 d^2 k_3 e^{i k_1 (\mathbf{r} - \mathbf{r}_1)} e^{i k_3 (\mathbf{r}_2 - \mathbf{r}_3)} \times [2(\bar{\kappa}^{(1)} \bar{\kappa}^{(3)})^2 - 1] \delta(\mathbf{r}_1 - \mathbf{r}_2) W_4([\mathbf{r}, \mathbf{r}_2], [\mathbf{r}_1, \mathbf{r}_3]), \quad (27.c) \]

and

\[ X^{(3)} = \frac{2}{(2\pi)^2} \int \int \int d^2 r_1 d^2 r_2 d^2 r_3 \int \int d^2 k_1 d^2 k_3 e^{i k_1 (\mathbf{r} - \mathbf{r}_1)} e^{i k_3 (\mathbf{r}_2 - \mathbf{r}_3)} \times (\bar{\kappa}^{(1)} \bar{\kappa}^{(3)})^2 \delta(\mathbf{r}_1 - \mathbf{r}_2) [W_4([\mathbf{r}, \mathbf{r}_3], [\mathbf{r}_1, \mathbf{r}_2]) + W_4([\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3])]. \quad (27.d) \]

Because of the presence of the \( \delta \)-functions in the integrand of the expression for \( X^{(1)} \), we have \( X^{(1)} = W_4([\mathbf{r}, \mathbf{r}], [\mathbf{r}, \mathbf{r}]) \). Thus, \( \mathbf{r} = \mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}_3 \), and, consequently, all the four vectors are in the same grain. However, according to the definition, the probability \( W_4([\mathbf{r}_a, \mathbf{r}_b], [\mathbf{r}_c, \mathbf{r}_d]) \) is not equal to zero only if the vectors \( \mathbf{r}_a \) and \( \mathbf{r}_b \) are in the same grain, but the vectors \( \mathbf{r}_c \) and \( \mathbf{r}_d \) are in some other grain. Then \( X^{(4)} = 0 \). The same argumentation is valid when calculating \( X^{(2)} \). Really, after integration over \( \mathbf{r}_2 \), the probability \( W_4([\mathbf{r}, \mathbf{r}_1], [\mathbf{r}_1, \mathbf{r}_3]) \) enters the integrand. This probability is equal to zero too. Then \( X^{(2)} = 0 \).

As a result, only the third term \( X^{(3)} \) of the sum (27.a) contributes to \( v^{(4)} \). In the integrand of Eq.(27.d) the sum of probabilities \( W_4([\mathbf{r}, \mathbf{r}_3], [\mathbf{r}_1, \mathbf{r}_2]) + W_4([\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3]) \) defines the combined probability for the pairs of the vectors \( \mathbf{r}, \mathbf{r}_3 \) and \( \mathbf{r}_1, \mathbf{r}_2 \) be in the same grains not making difference between the cases when the first and the second pairs get in one or distinct grains. This combined probability can be expressed in terms of the probability \( W_2 \). Namely, \( W_4([\mathbf{r}, \mathbf{r}_3], [\mathbf{r}_1, \mathbf{r}_2]) + W_4([\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3]) = W_2(|\mathbf{r} - \mathbf{r}_3|) W_2(|\mathbf{r}_1 - \mathbf{r}_2|) \).

When substituting this equality in Eq.(27.d) and performing the integrations, we obtain

\[ v^{(4)} = \frac{\Delta^4}{8}. \]

Finally, with regard to Eqs.(18) up to the terms of the order of \( \Delta^4 \) we have

\[ T_2 = 1 + \frac{\Delta^2}{4} + \frac{\Delta^4}{8} \quad \text{and} \quad \sigma_{ef} = \bar{\sigma}(1 - \frac{\Delta^2}{2} - \frac{\Delta^4}{8}). \quad (28) \]

(compare with Eq.(21)). We see that within the accuracy of calculation EC is the same as the one defined by the Dykhne formula.

The results of this subsection can be formulated as follows: we verified the perturbation theory of Section 2 and find out the forms of the correlators (see Eqs.(23), (24) and (25)) entering the integrands of the terms of the series \( T_2 \). With regard to the dimensionality of the problem, the same form of the correlators must be used when calculating EC of 3-D polycrystals.

### 3.2 Three-dimensional Polycrystals

Let a polycrystal be composed from 3-D single crystal grains. The local conductivity tensor is defined by Eq.(1). If the polycrystal is isotropic in average, \( < \sigma > = \bar{\sigma} = \)
\( (\sigma_1 + \sigma_2 + \sigma_3)/3, \sigma_i \ (i = 1, 2, 3) \) are the principal values of the single crystal conductivity tensor. The principle values of the tensor \( \Delta_{ik} \) are

\[
\Delta_1 = \frac{(2\sigma_1 - \sigma_2 - \sigma_3)}{(\sigma_1 + \sigma_2 + \sigma_3)}; \quad \Delta_2 = \frac{(2\sigma_2 - \sigma_1 - \sigma_3)}{(\sigma_1 + \sigma_2 + \sigma_3)}; \quad \Delta_3 = \frac{(2\sigma_3 - \sigma_1 - \sigma_2)}{(\sigma_1 + \sigma_2 + \sigma_3)}.
\]  

(29.a)

Since \( \Delta_1 + \Delta_2 + \Delta_3 = 0 \), the anisotropy of LC of a 3-D polycrystal is defined by two independent parameters. With respect to the laboratory coordinate system

\[
\Delta_{ik} = \Delta_1 \alpha_{i1} \alpha_{k1} + \Delta_2 \alpha_{i2} \alpha_{k2} + \Delta_3 \alpha_{i3} \alpha_{k3},
\]  

(29.b)

where \( \alpha_{ik} \) is the 3-D rotation matrix, whose elements are stochastic functions of position.

In what follows we calculate the third order fluctuation correction to EC of 3-D poly-

crystals. In contrast to the 2-D case, this correction does not vanish. To perform the calculation up we need to define the terms \( w^{(2)} \) and \( w^{(3)} \) of the series \( T_3 \) (see Eq.(14) and Eq.(15)).

W e calculate the two-point average entering the expression for \( w^{(2)} \) the same as in Subsection 3.1. With regard to the dimensionality of the problem \( \langle \Delta_{ik}(r) \Delta_{kl}(r_1) \rangle = D_2 W_2(|r - r_1|)\delta_{kl}/3 \) where \( D_2 \) is the second-order invariant of the tensor \( \Delta_{ik} \). \( D_2 = \Delta_{ik} \Delta_{ki} \).

Then with the aid of Eq.(11) and Eq.(12) we have \( w^{(2)} = D_2/27 \). Again the quadratic term of the series \( T_3 \) and, consequently, the quadratic correction to EC do not depend on the form of the correlation function.

When calculating \( w^{(3)} \) we use Eq.(24) to calculate the three-point average \( \langle \Delta_{ik}(r) \Delta_{lm}(r_1) \Delta_{ni}(r_2) \rangle \).

This average does not vanish only if all the three vectors \( r, r_1 \) and \( r_2 \) are in the same grain. As in the 2-D case, the elements of the isotropic forth rank tensor \( S_{ik;lm;ni} \) have to be expressed in terms of the invariants of the tensor \( \Delta_{ik} \Delta_{lm} \Delta_{ni} \). However, in contrast to the 2-D case, only one of two independent invariants of this tensor is equal to zero. Namely, \( \Delta_{ik} \Delta_{kl} \Delta_{li} = 0 \), but \( \Delta_{ik} \Delta_{kl} \Delta_{li} = D_3 \), where \( D_3 = \Delta_1^3 + \Delta_2^3 + \Delta_3^3 \). Then taking into account the symmetry properties of the tensor \( S_{ik;lm;ni} \) we have

\[
S_{ik;lm;ni} = \frac{D_3}{30}[2\delta_{kn} \delta_{lm} + 3(\delta_{kl} \delta_{nm} + \delta_{km} \delta_{nl})].
\]  

(30.a)

The probability \( W_3 \) for the three vectors \( r, r_1 \) and \( r_2 \) to be in the same grain can be expressed in terms of the probabilities \( W_2 \). Indeed, let us choose one of the three vectors \( r, r_1 \) and \( r_2 \). Since all the choices are equiprobable, the probability to choose one definite vector is equal to 1/3. Let it be the vector \( r \). Then the joint conditional probability of choosing the vector \( r \), and finding vector \( r_1 \) in the same grain with the vector \( r \), and finding vector \( r_2 \) in the same grain with the vector \( r \) is \( W_2(|r - r_1|)W_2(|r - r_2|)/3 \). Now it is easy to see that

\[
W_3 = \frac{1}{3}(W_2(|r - r_1|)W_2(|r - r_2|) + W_2(|r_1 - r|)W_2(|r_1 - r_2|) + W_2(|r_2 - r|)W_2(|r_2 - r_1|)).
\]  

(30.b)

When we take into account Eqs.(30) and substitute Eq.(24) in Eq.(12), after integration over position vectors and over the angles in the double integral over the wave vectors \( k_1 \) and \( k_2 \), we obtain

\[
w^{(3)} = \frac{-D_3}{405} \left\{ \frac{17}{3} - J \right\},
\]  

(31.a)
\[ J = 2\pi^2 \int_0^\infty \int_0^\infty dk_1 dk_2 W_2(k_1)W_2(k_2) \left\{ 1 - \frac{(k_1^2 - k_2^2)^2}{2k_1 q_2(k_1^2 + k_2^2)} \ln \left| (k_1 + k_2)/(k_1 - k_2) \right| \right\}. \]  

(31.b)

Then up to the third order term in the anisotropy we have

\[ T_3 = 1 + w^{(2)} + w^{(3)}, \quad \sigma_{\text{ef}} = \sigma \left[ 1 - \frac{D_2}{9} + \frac{D_3}{135} \left( \frac{17}{3} - j \right) \right]. \]  

(32)

From Eq.(32) it is clearly seen that EC of a 3-D polycrystal depends on the statistical properties of the medium. Of course, this is the well-known result. However, now we can estimate the influence of the form of the correlation function on the value of \( \sigma_{\text{ef}} \). To do this we evaluated \( J \) for several choices of \( W_2(r) \). The obtained results were

1. \( J = 0.028 \), when \( W_2 = \exp(-r^2/a^2) \);
2. \( J = 0.136 \), when \( W_2 = \exp(-r/a) \);
3. \( J = 0.052 \), when \( W_2 = 1/(1 + r^2/a^2) \).

For all the examined forms of the correlation function the value of \( J \) is very small. Consequently, although the value of the third order term in the expression for EC depends on the form of the correlation function, this dependence is very weak.

Concluding this subsection, let us estimate when the low order perturbation theory calculations are sufficient. In Ref.[14] it was shown that the effective conductivity is restricted by inequalities \( \langle \mathbf{j}^2 \rangle / \langle \mathbf{\sigma}^{-1} \rangle \mathbf{j} \leq \sigma_{\text{ef}} \leq \mathbf{e} \mathbf{\sigma} \mathbf{e} / \langle \mathbf{e}^2 \rangle \), where \( \mathbf{\sigma}^{-1} \) is the inverse of the local conductivity tensor \( \mathbf{\sigma} ; \mathbf{j} \) and \( \mathbf{e} \) are arbitrary test vectors of dimension of the current density and the electric field, respectively. If as the test vectors we choose a direct current \( \mathbf{j}_0 \) and a uniform electric field \( \mathbf{e}_0 \), we obtain

\[ \frac{1}{\langle \rho \rangle} \leq \sigma_{\text{ef}} \leq \langle \sigma \rangle. \]  

(33)

In polycrystals \( \langle \sigma \rangle \) is equal to the mean conductivity \( (\sigma_1 + \sigma_2 + \sigma_3)/3 \) and \( \langle \rho \rangle \) is equal to the mean resistivity \( (\sigma_1^{-1} + \sigma_2^{-1} + \sigma_3^{-1})/3 \).

For simplicity, let us examine a uniaxial metal: \( \sigma_1 = \sigma_2 \). According to Eq.(29.a) in this case \( \Delta_1 = \Delta_2 = \Delta = (\sigma_1 - \sigma_3)/(2\sigma_1 + \sigma_3) \), and \( \Delta_3 = -2\Delta \). Then \(-1 < \Delta < 1/2 \), when \( 0 < \sigma_1/\sigma_3 < \infty \). In Fig.1 following Eq.(33) we plot the lower and the upper bound of the ratio \( \sigma_{\text{ef}}/\sigma \) as function of \( \Delta \) as well as the values of \( \sigma_{\text{ef}}/\sigma \) calculated with the aid of Eq.(32). If \(-.2 < \Delta < .2 \) (or \( 4/7 < \sigma_1/\sigma_3 < 2 \)), the difference between the lower bound for EC and its upper bound is less than 10 percents. It is reasonable to assume that the perturbation theory results are applicable not only if \( |\sigma_1/\sigma_3 - 1| \ll 1 \), but at least for all \( \sigma_1/\sigma_3 \) from the aforementioned interval. The Table 1 based on data from [14] shows that rather often the perturbation theory calculations are sufficient when estimating EC.

We would like to note that when comparing the calculated value of \( \sigma_{\text{ef}} \) with experimental results, one must have in mind that in our calculations only the inhomogeneity due to different orientations of polycrystalline grains was taken into account. Of course, in real polycrystals there are other sources of inhomogeneity too. For example, we do not take into account the real structure of the boundaries of the grains. This simplification is justified when the grains are sufficiently large and the properties of the boundaries of the grains do not affect the result significantly.

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Fig.1. The lower bound (dashed line) and the value of $\sigma_{ef}/\sigma$ (full line) for uniaxial polycrystals as functions of the parameter $\Delta$. Always the ratio $\sigma_{ef}/\sigma < 1$. The value of $\sigma_{ef}/\sigma$ is calculated with the accuracy up to $\Delta^3$. 
Fig. 1
| Metall     | Components of conductivity tensor $\times 10^6$ (Ohm $\times$ cm)$^{-1}$ | $\Delta$   | $\sigma_{eff}/\overline{\sigma}$ |
|-----------|-------------------------------------------------------------------------|------------|-----------------------------------|
| Beryllium | $\sigma_1 = \sigma_2 = 0.319$                                          | 0.044      | 0.999                             |
|           | $\sigma_3 = 0.279$                                                     |            |                                   |
| Bismuth   | $\sigma_1 = \sigma_2 = 0.0092$                                         | 0.078      | 0.996                             |
|           | $\sigma_3 = 0.0072$                                                    |            |                                   |
| Galium    | $\sigma_1 = 0.0578$                                                   | $\Delta_1 = -0.1467$ | 0.85     |
|           | $\sigma_2 = 0.1274$                                                   | $\Delta_2 = 0.8809$ |          |
|           | $\sigma_3 = 0.018$                                                    |            |                                   |
| Cadmium   | $\sigma_1 = \sigma_2 = 0.1475$                                         | 0.067      | 0.997                             |
|           | $\sigma_3 = 0.1196$                                                   |            |                                   |
| Magnesium | $\sigma_1 = \sigma_2 = 0.221$                                         | 0.062      | 0.997                             |
|           | $\sigma_3 = 0.2646$                                                   |            |                                   |
| Tin       | $\sigma_1 = \sigma_2 = 0.101$                                         | 0.114      | 0.991                             |
|           | $\sigma_3 = 0.07$                                                     |            |                                   |
| Mercury   | $\sigma_1 = \sigma_2 = 0.043$                                         | -0.096     | 0.998                             |
| (−45° C)  | $\sigma_3 = 0.056$                                                    |            |                                   |
| Stibium   | $\sigma_1 = \sigma_2 = 0.024$                                         | -0.061     | 0.998                             |
|           | $\sigma_3 = 0.028$                                                    |            |                                   |
| Zink      | $\sigma_1 = \sigma_2 = 0.172$                                         | 0.012      | 0.999                             |
|           | $\sigma_3 = 0.165$                                                    |            |                                   |