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Vasyl Stefanyk Carpathian National University

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Andrei Snarskii^{1,2}, Iryna Ivanova¹, Viacheslav Fedotov¹, Ivan Didur¹

Reciprocity Relation in Thermoelectric Composites: Optimizing Materials for Energy Efficiency and Thermal Management

¹National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine, <u>im_ivan@ukr.net</u>;

²Institute for Information Recording National Academy of Sciences of Ukraine, Kyiv, Ukraine

Effective kinetic properties of two-phase heterogeneous media with thermoelectric properties have been considered. These properties manifest themselves when an electric current and a heat flow coexist in the medium. It is shown that in some cases, it is possible to generalize the reciprocity relations obtained in the absence of thermoelectric phenomena and find invariants (combinations of effective thermoelectric coefficients) with respect to changes in the phase concentration in the two-dimensional case. For the three-dimensional case, using the moving percolation threshold approach in the mean-field theory, it is shown that similar reciprocity relations (invariants) can be approximately satisfied when the percolation threshold is shifted.

Keywords: Thermoelectricity, composites, percolation, kinetic coefficient.

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Introduction

Research of thermoelectric composites is essential for developing and improving materials that can convert thermal energy into electrical energy and vice versa. Such research has been conducted to improve the efficiency, durability and environmental safety of thermoelectric devices [1-5].

The problem of calculating the properties of composites, in particular the calculation of effective coefficients, is a complex problem. The exact solution to the problem of calculating the effective coefficients of thermoelectric media over the entire range of phase concentrations with different values of local coefficients does not have a general exact solution. There are various approximations that allow, in some cases, to obtain relatively accurate concentration expressions for effective coefficients [6-10]. For example, in the case when in a two-phase composite the concentration of one of the phases is much less than the other, Maxwell's

approximation is a good one [6-7]. Another case is a twophase, highly inhomogeneous medium near the percolation threshold; here, a good description is the percolation theory (a geometric analogue of the theory of second-order phase transitions) [10,11]. But in general, in the entire concentration range only an approximate description is possible; the successful mean field approximation or effective medium approximation (EMA) is most frequently used [12,13,9].

In some cases, it is possible to obtain additional ratios for the effective coefficients; for example, for a two-dimensional randomly inhomogeneous medium, the so-called reciprocity relation was obtained for the conductivity problem [14].

Widely used methods for calculating the concentration dependence of effective kinetic coefficients, such as the mean field method, imply a given (once and for all) percolation threshold. In real composites it may be different depending on the method and technology of composite creation. Here we consider a modification of the method that allows taking into account the possibility

of different percolation thresholds. It is shown that in the three-dimensional case it is possible to generalize the reciprocity relations – relations that connect effective conductivity, thermal conductivity and thermoelectric power.

Our paper examines, on the basis of the isomorphism method, a generalization of reciprocity ratios in the case of thermoelectric phenomena and discusses the issue of similar ratios for three-dimensional media with a shifted percolation threshold.

I. Effective coefficients of thermoelectric composites and methods of their calculation

For a single-flow problem (the problem of effective conductivity), when Ohm's law locally takes place, connecting the electric current density - j - and the electric field - E, the coefficient of effective conductivity - σ_e connects their volume-average values

$$j = \sigma E, \langle j \rangle = \sigma_e \langle E \rangle.$$
 (1)

The main characteristic of composites, including for thermoelectric phenomena, is effective coefficients. Let's define them as follows. For thermoelectric phenomena, we write down the local ratio between the densities of electric current - j and heat flow - q, electric field - E and temperature gradient -g = -gradT

$$j = \sigma E + \gamma g$$
, $s = \gamma E + \chi g$, (2)

and in a stationary case

$$div j = 0$$
, $div s = 0$, $rot E = 0$, $rot g = 0$ (3)

Where

$$\gamma = \sigma \alpha, \chi = k/T(1 + ZT), s = q/T, Z = \sigma \cdot \alpha^2/k,$$
 (4)

 α - coefficient of thermo emf, k - coefficient of thermal conductivity and for convenience (symmetry in system (2)) flow is introduced s=q/T.

Then thermoelectric effective coefficients connect volume-average local thermodynamic flows and thermodynamic forces

$$\langle j \rangle = \sigma_e \langle E \rangle + \gamma_e \langle g \rangle,$$
 (5)

$$\langle s \rangle = \gamma_e \langle E \rangle + \chi_e \langle g \rangle$$

where $\langle ... \rangle = 1/V \int_V ... dV$ and it is assumed that the size of the averaging (sample) is much larger than the correlation length.

For the two-dimensional case of a two-phase single-flow problem, for example, a conductivity problem in the absence of a temperature gradient, i.e. in the absence of thermoelectric phenomena, when Ohm's law $j = \sigma E$ locally takes place, in [14] a reciprocity relation was obtained that relates the effective conductivity at different conductivity values

$$\sigma_e(p) \cdot \sigma_e(1-p) = \sigma_1 \sigma_2, \tag{6}$$

where σ_1 and σ_2 are conductivities of the first and second phases and p is the concentration of the first phase.

To determine σ_e in the entire concentration range, EMA can be used; for the conductivity problem, it is often called the Bruggeman-Landauer approximation [7,8]. This approximation can be written as

$$\frac{\sigma_{e} - \sigma_{1}}{(d - 1)\sigma_{e} + \sigma_{1}} p + \frac{\sigma_{e} - \sigma_{2}}{(d - 1)\sigma_{e} + \sigma_{2}} (1 - p) = 0$$
 (7)

where d=2,3 is the dimension of the problem.

Naturally, the problem of finding the effective conductivity (single-flow problem) is much simpler than the problem of finding the thermoelectric effective coefficients (double-flow problem). If we are talking about finding the effective coefficients in a thermoelectric system in the EMA approximation, then for this it is necessary to find a generalization of (7) for the case of double-flow systems. One of the possible ways [7,15] is to introduce matrices of local - $\hat{\Omega}_i$ and effective - $\hat{\Omega}_e$ kinetic coefficients

$$\widehat{\Omega}_{i} = \begin{pmatrix} \sigma_{i} & \sigma_{i}, \alpha_{i} \\ \sigma_{i}, \alpha_{i} & k_{i}^{1+Z_{i}T} \end{pmatrix}, \widehat{\Omega}_{e} = \begin{pmatrix} \sigma_{e} & \sigma_{i}, \alpha_{i} \\ \sigma_{e}, \alpha_{e} & k_{e}^{1+Z_{e}T} \end{pmatrix}, \tag{8}$$

where i=1,2 signifies the phase number.

Now (2) can be written as

$$\binom{j}{s} = \binom{\sigma}{\gamma} \binom{\gamma}{\ell} \binom{E}{a}, \tag{9}$$

And by analogy with (7), we can write EMA in the form

$$\frac{\widehat{\Omega}_e - \widehat{\Omega}_1}{2\widehat{\Omega}_e + \widehat{\Omega}_1} p + \frac{\widehat{\Omega}_e - \widehat{\Omega}_2}{2\widehat{\Omega}_e + \widehat{\Omega}_2} (1 - p) = 0, \tag{10}$$

Solving the system of equations written in matrix form (10) allows us to find the concentration dependences of thermoelectric effective coefficients and their dependence on local coefficients values in the mean field approximation.

II. Isomorphism method

In [2,10,11], another version of the analysis of thermoelectric phenomena in composites was proposed. It was shown that the problem of calculating the thermoelectric effective coefficients of two-phase systems (two-flow system) can be reduced to the problem of calculating the effective coefficients of a single-flow system. In other words, from the concentration behavior of the effective conductivity (in a problem without thermoelectric phenomena), one can concentration behavior of the effective thermoelectric coefficients in an inhomogeneous medium of the same geometric structure (the same phase arrangement). The method of reducing a two-flow problem to a single-flow one is usually called the isomorphism method. The isomorphism method can be written in different

mathematical schemes (see, for example, [10]).

Here we will consider this method as proposed ([17], see detail in [10]). To reduce a two-flow system to a single-flow system, multiply the second relation in (2) by a constant *K* and add it to the first

$$j + Ks = (\sigma + K\gamma)E + (\gamma + K\gamma)g. \tag{11}$$

Rewriting (11) in the form

$$j + Ks = (\sigma + K\gamma)(E + \omega \cdot g), \ \omega = \frac{\gamma + K\gamma}{\sigma + K\gamma}$$
 (12)

one can introduce a new flow (current) – i and a new field – ε

$$i = j + Ks, \quad \varepsilon = E + \omega \cdot g.$$
 (13)

In the stationary case we are considering, currents and fields fulfill conditions (3). The introduced current – i and field – ε must fulfill the same conditions.

$$div i = 0, rot \varepsilon = 0.$$
 (14).

Because the introduced constant - K by definition does not depend on the coordinates, the condition (14) for the current is satisfied automatically, due to the fulfillment of (3). As for the factor - ω in (12), since at different points of the medium the local coefficients takes on different values (in the two-phase case this is - σ_1 , σ_2 , α_1 , α_2 , k_1 , k_2 ,) generally speaking, it depends on the coordinates. However, it is possible to satisfy the condition of constancy of this factor (make it independent of the coordinates) by requiring that the constant - K be a solution to the equation

$$\frac{\gamma_1 + K\chi_1}{\sigma_1 + K\gamma_1} = \frac{\gamma_2 + K\chi_2}{\sigma_2 + K\gamma_2} \tag{15}$$

The solution to equation (15) determines two possible constants - K_I , K_{II} and the corresponding constants - ω_I and ω_{II}

$$K_{I,II} = \frac{\chi_2 \sigma_1 - \chi_1 \sigma_2 \pm \sqrt{(\chi_2 \sigma_1 - \chi_1 \sigma_2)^2 - 4(\chi_1 \gamma_2 - \chi_2 \gamma_1)(\gamma_1 \sigma_2 - \gamma_2 \sigma_1)}}{2(\chi_1 \gamma_2 - \chi_2 \gamma_1)}$$
(16)

Now (13) can be written as a single-flow system

$$i(r) = f(r) \cdot \varepsilon(r),$$
 (17)

where "current" and "field" obey conditions (14) and the effective coefficient of which is determined similarly to (5)

$$\langle i \rangle = f^e \langle \varepsilon \rangle. \tag{18}$$

The resulting system differs from (1) only in notation. Thus, if we know the concentration behavior of conductivity in problem (1) (in a single-flow problem), then a simple change of notation gives us an expression for f^e . Note that there are actually two systems (18), one for K_I, ω_I , the second for K_{II}, ω_{II} . Local coefficients (analogues of conductivity) of the first and second phases K_{II} , and K_{II} are related to the local coefficients of the TE system in the following way

$$f_{1,I} = \sigma_1 + K_I \gamma_1, \ f_{2,I} = \sigma_2 + K_I \gamma_2,$$
 (19)

respectively, with - K_I , ω_I for the first system and with - K_{II} , ω_{II} for the second.

Now, in order to find the effective thermoelectric coefficients, it is necessary to write (11) in averaged form

$$\langle j \rangle + K_I \langle s \rangle = f_I^e (\langle E \rangle + \omega_I \langle g \rangle),$$

$$\langle j \rangle + K_{II} \langle s \rangle = f_{II}^e (\langle E \rangle + \omega_{II} \langle g \rangle),$$
 (20)

where

$$f_I^e = f_I^e(f_{1,I}, f_{2,I}, p), f_{II}^e = f_{II}^e(f_{1,II}, f_{2,II}, p),$$

and to rewrite similarly to (5)

$$\langle j \rangle = \frac{\kappa_{II} f_I^e - \kappa_I f_I^e}{\kappa_{II} - \kappa_I} \langle E \rangle + \frac{\kappa_{II} f_I^e \omega_I - \kappa_I f_{II}^e \omega_{II}}{\kappa_{II} - \kappa_I} \langle g \rangle,$$

$$\langle s \rangle = \frac{f_{II}^e - f_I^e}{\kappa_{II} - \kappa_I} \langle E \rangle + \frac{f_{II}^e \omega_{II} - f_I^e \omega_I}{\kappa_{II} - \kappa_I} \langle g \rangle \tag{21}$$

Where $K_{II}\omega_I = K_I\omega_{II} = -1$.

Thus, according to (21), the effective coefficients of thermoelectric systems are expressed as follows through the effective coefficient of a single-flow system f_I^e , f_{II}^e

$$\sigma_e = \frac{\kappa_{II} f_I^e - \kappa_I f_{II}^e}{\kappa_{II} - \kappa_I}, \quad \gamma_e = \frac{f_{II}^e - f_I^e}{\kappa_{II} - \kappa_I}, \quad \chi_e = \frac{f_{II}^e \omega_{II} - f_I^e \omega_I}{\kappa_{II} - \kappa_I}$$
(22)

Note that the concentration dependence σ_e from (22) is found taking into account thermoelectric phenomena and, naturally, does not coincide, generally speaking, with the concentration dependence of the effective coefficient - σ_e (5) of a single-flow system.

III. Reciprocity relations for twodimensionally inhomogeneous media with thermoelectric phenomena

To find the thermoelectric analogy of reciprocity relations in the thermoelectric system, we rewrite (6) in the form

$$f_I^e(p)f_I^e(1-p) = f_I^e(1/2)^2,$$

$$f_{II}^e(p)f_{II}^e(1-p) = f_{II}^e(1/2)^2.$$
 (23)

Relations (23) already contain certain ratios for thermoelectric effective coefficients. To write them down explicitly, we can express f_I^e , f_{II}^e through thermoelectric effective coefficient; this can be done, for example, like

this

Substituting (24) into (23), we find TE analogues of the reciprocity relations

$$f_I^e(p) = \sigma_e + K_I \sigma_e \alpha_e, \ f_{II}^e(p) = \sigma_e + K_{II} \sigma_e \alpha_e,$$
 (24)

$$\sigma_{e}(p)[1 + K_{I}\alpha_{e}(p)] \cdot \sigma_{e}(1 - p)[1 + K_{I}\alpha_{e}(1 - p)] = \{\sigma_{e}(1/2)[1 + K_{I}\alpha_{e}(1/2)]\}^{2},$$

$$\sigma_{e}(p)[1 + K_{II}\alpha_{e}(p)] \cdot \sigma_{e}(1 - p)[1 + K_{II}\alpha_{e}(1 - p)] = \{\sigma_{e}(1/2)[1 + K_{II}\alpha_{e}(1/2)]\}^{2},$$
(25)

To illustrate the obtained relations, we give a numerical example; for this we write (25) in normalized form

$$\Lambda_I(p) = \frac{\sigma_e(p)[1 + K_I \alpha_e(p)] \cdot \sigma_e(1-p)[1 + K_I \alpha_e(1-p)]}{\{\sigma_e(1/2)[1 + K_I \alpha_e(1/2)]\}^2},$$

$$\Lambda_{II}(p) = \frac{\sigma_e(p)[1 + K_{II}\alpha_e(p)] \cdot \sigma_e(1-p)[1 + K_{II}\alpha_e(1-p)]}{\{\sigma_e(1/2)[1 + K_{II}\alpha_e(1/2)]\}^2}.$$
 (26)

where, if the reciprocity relations are satisfied, the normalized expressions - $\Lambda_I(p)$ and - $\Lambda_{II}(p)$ do not depend on concentration, i.e. equal to a constant, in this case unity.

For comparison, we write similar expressions for the effective conductivity and thermo-emf coefficient

$$\Lambda \sigma(p) = \frac{\sigma_e(p)\sigma_e(1-p)}{|\sigma_e(p_c=1/2)|^2}, \quad \Lambda \alpha(p) = \frac{\alpha_e(p)\alpha_e(1-p)}{|\alpha_e(p_c=1/2)|^2}$$
(27)

We take the concentration dependences for thermoelectric effective coefficient from the two-dimensional EMA. Let us take the numerical values of the local coefficients thermoelectric coefficients for the second phase to be close to the values for a semiconductor with a good quality factor (for example, p-Bi₂Te₃) $\sigma_2 = 10^5 Ohm^{(-1)}m^{(-1)}$, $\alpha_2 = 2 \cdot 10^{(-4)}V/K$, $k_2 = 1W/m \cdot K$, at T = 300K with the quality factor of the second phase $Z_2T = 1.2$ [18]. And we will choose the first phase as metal, i.e. with a practically zero value of the local thermo-emf coefficient $-\sigma_1 = 5 \cdot 10^6 Ohm^{(-1)}m^{(-1)}$, $\alpha_1 = 0 V/K$, $k_1 = 40W/m \cdot K$.

As can be seen from Fig. 1, the concentration dependence of $\Lambda_I(p)$ and $\Lambda_{II}(p)$ is absent, while the expressions $\Lambda\sigma(p)$ and $\Lambda\alpha(p)$ significantly depend on concentration. Thus, expressions (26) are indeed thermoelectric analogues of reciprocity relations.

IV. Effective Medium Approximation problem for composites with various percolation thresholds

Unlike, for example, the critical indices that characterize the concentration behavior of the effective coefficient in the critical region of percolation theory, which are universal (i.e., depending only on the dimensionality of the problem), the percolation threshold - p_c for different composites (and when modeling on different lattices) can have different values [6,11].

For the standard version of EMA (7), with large heterogeneity (σ_1, σ_2) in a certain concentration region, there is a sharp change in the concentration dependence of the effective conductivity. These concentration values are compared with the percolation threshold - p_c in percolation media in the critical region. In the standard

version of EMA (7), these values p_c are implicitly included in the equation; in two- and three-dimensional cases they are equal

$$p_c(2d) = 1/2, \quad p_c(3d) = 1/3$$
 (28)

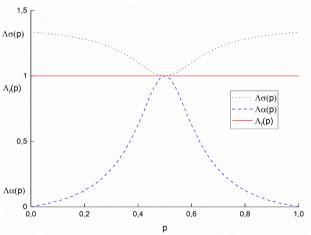


Fig. 1. Functions of concentration dependencies $\Lambda_I(p)$ (red online), $\Lambda\alpha(p)$ (Blue online), $\Lambda\sigma(p)$ (Black online).

To describe situations when, for example, there is a need to describe experimental data obtained for a medium with a percolation threshold different from those indicated, a modification of EMA for the three-dimensional case was proposed in [19], which allows one to set the percolation threshold. This modification can be written in the form [20]

$$\frac{\frac{\sigma_e - \sigma_1}{2\sigma_e + \sigma_1}}{1 + c(p, \tilde{p}_c) \frac{\sigma_e - \sigma_1}{2\sigma_e + \sigma_1}} p + \frac{\frac{\sigma_e - \sigma_2}{2\sigma_e + \sigma_2}}{1 + c(p, \tilde{p}_c) \frac{\sigma_e - \sigma_2}{2\sigma_e + \sigma_2}} (1 - p) = 0$$
 (29)

where $c(p, \tilde{p}_c)$ is Sarychev-Vinogradov term that can be written as

$$c(p, \tilde{p}_c) = (1 - 3\tilde{p}_c) \left(\frac{p}{\tilde{p}_c}\right)^{\tilde{p}_c} \left(\frac{1 - p}{1 - \tilde{p}_c}\right)^{1 - \tilde{p}_c}$$
(30)

In [20-22], the modified approximation (29-30) was used to calculate the effective properties of magnetic elastomers, in which restructuring occurs in an external magnetic field. To describe this restructuring, the concept of a moving percolation threshold was introduced based on (30).

When describing thermoelectric properties, the EMA modification can be used to study the possibility of the existence of reciprocity relations at different values of the percolation threshold.

V. Reciprocity relations in threedimensional thermoelectric composites with a shifted percolation threshold

It should be immediately emphasized that the issue of reciprocity relations is considered within the framework of an approximate theory - modified EMA.

Let's first consider a single-flow problem. Similarly to (24), we introduce a normalized relation for $\sigma_e(p)\sigma_e(1-p)$

$$\Lambda\sigma(p,\tilde{p}_c) = \frac{\sigma_e(p)\sigma_e(1-p)}{[\sigma_e(p_c=\tilde{p}_c)]^2},\tag{31}$$

where \tilde{p}_c is a given percolation threshold in the description of the concentration dependence $\sigma_e(p)$ within the framework of a modified EMA, when the effective conductivity depends on the given percolation threshold. Naturally, when given - $\tilde{p}_c = 1/3$, the modified EMA transforms into its standard form (7). Note that the value of effective conductivity at any concentration value (even far from the percolation threshold) also depends on the value of the given - \tilde{p}_c .

Figure 2 shows the concentration behavior $\Lambda \sigma(p)$, and it is clear that $\Lambda \sigma(p)$ is closer to the constant, when the given percolation threshold is closer to the value $\frac{1}{2}$.

Let us rewrite (25) in general form, when the normalization (right-hand side) is a function of the specified percolation threshold

$$\sigma_{e}(p)[1 + K_{I}\alpha_{e}(p)] \cdot \sigma_{e}(1 - p)[1 + K_{I}\alpha_{e}(1 - p)] = \{\sigma_{e}(\tilde{p}_{c})[1 + K_{I}\alpha_{e}(p\tilde{p}_{c})]\}^{2},$$

$$\sigma_{e}(p)[1 + K_{II}\alpha_{e}(p)] \cdot \sigma_{e}(1 - p)[1 + K_{II}\alpha_{e}(1 - p)] = \{\sigma_{e}(\tilde{p}_{c})[1 + K_{II}\alpha_{e}(p\tilde{p}_{c})]\}^{2}$$
(32)

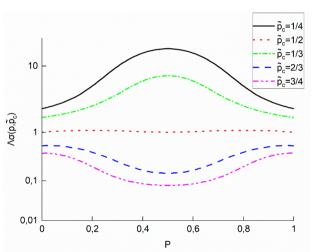


Fig. 2. Concentration dependency of function $\Lambda\sigma(p, \tilde{p}_c)$ at different concentration value $\tilde{p}_c = 1/4$ (Black online), $\tilde{p}_c = 1/4$ (Red online), $\tilde{p}_c = 1/3$ (Green online), $\tilde{p}_c = 2/3$ (Blue online), $\tilde{p}_c = 3/4$ (Magenta online).

And similarly to (26), let's consider the normalized relations - $\Lambda_I(p, \tilde{p}_c)$, $\Lambda_{II}(p, \tilde{p}_c)$, which will now depend on the given percolation threshold

$$\Lambda_I(p, \tilde{p}_c) = \frac{\sigma_e(p)[1+K_I\alpha_e(p)]\cdot\sigma_e(1-p)[1+K_I\alpha_e(1-p)]}{\{\sigma_e(\tilde{p}_c)[1+K_I\alpha_e(p\tilde{p}_c)]\}^2}$$

$$\Lambda_{II}(p, \tilde{p}_c) = \frac{\sigma_e(p)[1 + K_{II}\alpha_e(p)] \cdot \sigma_e(1 - p)[1 + K_{II}\alpha_e(1 - p)]}{\{\sigma_e(\tilde{p}_c)[1 + K_{II}\alpha_e(p\tilde{p}_c)]\}^2}.$$
 (33)

and similar relations for effective conductivity (31) and thermo-emf

$$\Lambda\alpha(p,\tilde{p}_c) = \frac{\alpha_e(p)\alpha_e(1-p)}{[\alpha_e(p_c=1/2)]^2}.$$
 (34)

Note that the thermoelectrics effective coefficients in the three-dimensional case under consideration in (31-34) were obtained by the isomorphism method in the modified EMA approximation (29-30).

In Fig.3 concentration dependences are shown - $\Lambda_I(p, \tilde{p}_c)$, $\Lambda_{II}(p, \tilde{p}_c)$ at different values \tilde{p}_c .

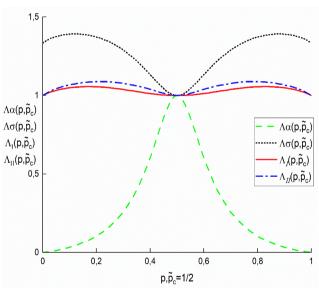


Fig. 3. Concentration dependencies of functions $\Lambda_I(p, \tilde{p}_c)$ (Red online), $\Lambda_{II}(p, \tilde{p}_c)$ (Blue online), $\Lambda\sigma(p, \tilde{p}_c)$ (Black online), $\Lambda\alpha(p, \tilde{p}_c)$ (Green online).

As can be seen from Fig.3, as in the single-flow threedimensional case, the reciprocity relations for thermoelectric effective coefficients systems are fulfilled the better, the closer the specified flow threshold is to ½.

VI. Discussion

Two- and three-dimensional random media (composites) with different percolation thresholds are considered. For a two-dimensional medium in the standard case, an analogue for thermoelectric effective coefficients has been rigorously found.

In the three-dimensional case, when studying

reciprocity relations for both the single-flow case (conductivity) and the two-flow case (thermoelectric phenomena), one has to resort to a modification of the standard method for calculating the effective coefficient, which allows one to consider media with different, predetermined percolation thresholds. Within the framework of the modified EMA, the existence of approximate reciprocity relations for thermoelectric phenomena in media with a percolation threshold of ½ was shown.

A separate question is the study of the possibility of the existence of analogues of the reciprocity relation in the problem of elasticity, when the composite consists of two chaotically situated phases with different values of local elastic moduli. The problem is complicated by the fact that in the simplest two-dimensional case, the EMA approximation (also called the Budyansky approximation in this problem) [15] does not give the percolation threshold of ½, which would seem logical for a mutually equivalent arrangement of phases. Therefore, the question of the existence of reciprocity relations for effective elastic moduli is of interest already in the two-dimensional case.

Conclusions

Experimental determination of the concentration dependence of the differential thermoelectric power coefficient is more complicated than, for example, determining specific conductivity. The obtained reciprocity relations allow us to relate these coefficients to each other, which can also be used for the correct design of thermoelectric composites, optimization of their characteristics and increasing the efficiency of thermoelectric devices.

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Snarskii A.O. – Dr.Sc., Professor, Department of General Physics, Faculty of Physics and Mathematics;

Ivanova I.M. – Ph.D., Associate Porfessor Department of General Physics, Faculty of Physics and Mathematics;

Fedotov V.V. – Senior Lecturer, Department of General Physics, Faculty of Physics and Mathematics;

Didur I.V. – Student, Department of General Physics, Faculty of Physics and Mathematics.

- [1] J. Huang, J.P. Male, Y. Sun, R. Gurunathan, P. Huang, G. J. Snyder, Y. Lin, *Effective reduction of matrix thermal conductivity through composite softening*, Newton, 1, 100008 (2025); https://doi.org/10.1016/j.newton.2024.100008.
- [2] N.D. Wood, L.J. Gillie, D.J. Cooke, M. Molinari, A Review of Key Properties of Thermoelectric Composites of Polymers and Inorganic Materials, Materials, 15, 8672, (2022); https://doi.org/10.3390/ma15238672.
- [3] T. Parashchuk, O. Cherniushok, O. Smitiukh, O. Marchuk, K. T. Wojciechowski, *Structure Evolution and Bonding Inhomogeneity toward High Thermoelectric Performance in Cu2CoSnS4-xSex Materials*, Chem. Mater., 35, 4772 (2023); https://doi.org/10.1021/acs.chemmater.3c00586.
- [4] A. Kosonowski, A. Kumar, T. Parashchuk, R. Cardoso-Gil, K. T. Wojciechowski, *Thermal conductivity of PbTe–CoSb₃ bulk polycrystalline composite: role of microstructure and interface thermal resistance*, Dalton Trans., 50, 1261 (2021), https://doi.org/10.1039/D0DT03752D.
- [5] Ashutosh Kumar, Preeti Bhumla, Artur Kosonowski, Karol Wolski, Szczepan Zapotoczny, Saswata Bhattacharya,* and Krzysztof T. Wojciechowski, *Synergistic Effect of Work Function and Acoustic Impedance Mismatch for Improved Thermoelectric Performance in GeTe-WC Composite*, ACS Appl. Mater. Interfaces, 14, 44527 (2022); https://doi.org/10.1021/acsami.2c11369.
- [6] S. Torquato, Random Heterogeneous Materials. Microstructure and Macroscopic Properties, (Springer Verlag: New York, USA, 2002) https://doi.org/10.1115/1.1483342.
- [7] B. Ya. Balagurov Electrophysical Properties in composites. (Leland 2015) 752 p.
- [8] I.V. Andrianov, J. Awrejcewicz, V.V. Danishevskyy, *Asymptotical Mechanics of Composites*, (Springer: Cham, Germany, 2018) 313. https://doi.org/10.1007/978-3-319-65786-8.
- [9] T.C. Choy, *Effective medium theory: principles and applications*, (Oxford University Press: Oxford, UK, 2016) https://doi.org/10.1093/acprof:oso/9780198705093.001.0001.
- [10] A.A. Snarskii, I.V. Bezsudnov, V.A. Sevryukov, A. Morozovskiy, J. Malinsky, *Transport Processes in Macroscopically Disordered Media*. From Mean Field Theory to Percolation, (Springer Verlag: New York, USA, 2016); https://doi.org/10.1007/978-1-4419-8291-9.
- [11] D. Stauffer, A. Aharon. Introduction To Percolation Theory 2nd ed. (CRC Press, 2018).
- [12] V.D. Bruggeman, Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen Ann. Phys. 416 (7), 636, (1935); https://doi.org/10.1002/andp.19354160705.
- [13] R. Landauer, *The Electrical Resistance of Binary Metallic Mixtures*, J. Appl. Phys., 23, 779 (1952); https://doi.org/10.1063/1.1702301.
- [14] A. M. Dykhne, Contluctivity of a Two-dimensional Two-phase System, Sov. Phys. JETP, 32(1), 65 (1971).
- [15] J. P. Straley, *Thermoelectric properties of inhomogeneous materials*, J.Phys.D: Applied Physics, 14(11), 2101, (1981); https://doi.org/10.1088/0022-3727/14/11/017.
- [16] V. Halpern, The Thermopower of Binary Mixtures J.Phys.C, 16 (7), L217(1983).
- [17] A. M. Dykhne, Private communication (1980).

- [18] D.M. Rowe Thermoelectrics Handbook (Macro to Nano). (Boca-Raton: Taylor Francis, 2006).
- [19] A.K. Sarychev, A.P. Vinogradov, *Effective Medium Theory for the Magnetoconductivity Tensor of Disordered Materials*, Phys. Stat. Sol. (b) (1983);https://doi.org/10.1002/pssb.2221170252.
- [20] A. A. Snarskii, M. Shamonin, P. Yuskevich, *Effect of magnetic-field-induced restructuring on the elastic properties of magnetoactive elastomers*, Journal of Magnetism and Magnetic Materials, 517, 167392 (2021)https://doi.org/10.1016/j.jmmm.2020.167392.
- [21] A.A. Snarskii, D. Zorinets, M. Shamonin, V. M. Kalita, *Theoretical method for calculation of effective properties of composite materials with reconfigurable microstructure: Electric and magnetic phenomena*, Physica A: Statistical Mechanics and its Applications, 535 (C) (2019); https://doi.org/10.1016/j.physa.2019.122467.
- [22] A. A. Snarskii, M. Shamonin, P. Yuskevich, D.V. Saveliev, I.A. Belyaeva, *Induced anisotropy in composite materials with reconfigurable microstructure: Effective medium model with movable percolation threshold*, Physica A: Statistical Mechanics and its Applications, 560 (C), (2020); https://doi.org/10.1016/j.physa.2020.125170.

А.О. Снарський^{1,2}, І.М. Іванова¹, В.В. Федотов¹, І.В. Дідур¹

Співвідношення взаємності в термоелектричних композитах: оптимізація матеріалів для енергоефективності та управління тепловою енергією

¹Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», м. Київ, Україна, <u>im ivan@ukr.net</u>

²Інститут реєстрації інформації Національної академії наук України, м. Київ, Україна

Були розглянуті ефективні кінетичні властивості двофазних гетерогенних середовищ з різними термоелектричними властивостями. Ці властивості проявляють себе, коли електричний струм та тепловий потік співіснують у цьому середовищі. Показано, що в деяких випадках виявляється можливим узагальнити співвідношення взаємності, отримані за відсутності термолектричних явищ, і знайти інваріанти (комбінації ефективних термоелектричних коефіцієнтів) відносно зміни концентрації у двовимірному випадку. У тривимірному випадку, використовуючи підхід рухомого порогу протікання у теорії середнього поля, показано,що схожі співвідношення взаємності (інваріанти) можуть бути наближено задоволені, коли поріг протікання зсувається

Ключові слова: Термоелектрика, композити, протікання, кінетичний коефіцієнт.