New classic equations for conductivity and thermopower

Asya S Skal†

The Research Institute, The College of Judea and Samaria, Ariel 44837, Israel

Abstract. All classical equations of kinetic coefficients in physics give only the first response to the external forces and fields. We have constructed new equations for kinetic coefficients, with all responses of the fields and forces, by using the perturbation method, which, customarily, was a mathematical tool for the approximate solution of the equations. Naturally, the recurrent equations which were obtained lead to recurrent solutions, which were found by the Green's function technique. The exact analytical formulae, produced by this method, play the same role for the calculations of kinetic coefficients as the Kirchhoff system of equations does for conductivity. In the framework of this solution one has obtained the upper boundary for fields when the solution is yet converged. We have considered the Hall and Seebeck coefficients and the elastic moduli (Skal A S 1997 *Physica* **A** to be published), and suggested that all other kinetic and transport coefficients may be rewritten in this way. On the basis of the formulae obtained, numerical calculations of the Hall and Seebeck coefficients are presented. The new universality classes for the Hall and Seebeck coefficients and the upper bond of the critical Hall conductivity exponent for all orders of a magnetic field contributions are obtained.

1. Introduction

Much of our understanding of the physics of polycrystalline films, powder semiconductors and composite media comes from the percolation theory. The interest in this problem stems largely from the fact that percolation is, by far, the best understood type of quenched disorder. The current through composite media depends on both the nature of the inhomogeneities and their spatial arrangement. If there is some component of inhomogeneity which is distributed spatially randomly, the electric current will flow by a percolation process [2]. In the powdered semiconductors one can consider a power layer where the effective resistivity of layers is dominated by the grain-to-grain contact resistances. If the value of the contact resistance can take a range of values due to fluctuations in barrier height and/or variations in the contact area, then the current will flow along paths that offer minimum resistance. A variation of the barrier height will lead to a wide variation in contact resistance, and the wider the range of contact resistance is the more significant the percolation will be. In the limit of a very wide range of contact resistances, the overall effective resistivity will be determined by the critical resistance at the percolation threshold level. These treatments derive expressions for kinetic coefficients of a composite material in terms of the properties of its constituents.

The original effective medium theory [3] gives results which differ from the percolation theory near the threshold, and therefore we will discuss the theoretical treatment of the Hall effect and thermopower in percolation systems [1, 4]. Instead of linear-response properties

† E-mail address: Skal@research.yosh.ac.il

to coupled fields, which lead to exact relations among kinetic coefficients [5], we adopt the approximation [1, 4] of assuming that the local conductivity, the thermoconductivity and the Young modules are zeroth-order quantities, while the Hall and the Seebeck coefficients and the Poisson ratio are first-order quantities. However, the perturbation theory allows us to obtain new recurrence equations with recurrent solutions for all orders of responses of the Hall and Seebeck coefficients, the Poisson ratio for conductivity in a magnetic field, the thermopower and elasticity of disordered systems.

Composite media have been around for a very long time, and it sometimes seems that we already know everything about their physical property. In this paper we shall attempt to show that there are some new classical equations for transport and kinetic coefficients, which lead to recurrence solutions. We shall focus on three subareas, namely magnetotransport, the thermopower and the elastic properties [1] of composite media, but we will suggest that it can also be applied to other kinetic coefficients. We shall discuss problems which are described by Laplacian or second-order finite difference operators, and generalize the numerical-simulation scheme using our analytical results.

2. The phenomenological equation in a magnetic field

The theory of the behaviour of a classical electron gas in combined electric and magnetic fields was developed by Gans [6], and was extended by Sommerfeld and Frank [7], Davis [8] and Seitz [9]. On the basis of Lorentz' transport theory, Gans [6] treated the case in which the applied electric and magnetic fields are normal. He examined the results to first order in the applied electrostatic field and to an arbitrary order in the magnetic field, and found that he could sum the series corresponding to sums over various orders of the magnetic field. Sommerfeld and Frank [7] subsequently obtained the same results but more concisely, Davis [8] and Seitz [9] generalized Gans' treatment of the problem for the case in which the electric and magnetic fields are oriented randomly relative to one another. In the approximation where the current varies linearly with the electrostatic field, and it varies with the magnetic field, up to quadratic terms, they obtained

$$\underline{I} = \sigma \underline{E} + \alpha H [\underline{E} \times \underline{H}] + \beta H^2 [\underline{E} \times \underline{H}]. \tag{1}$$

This is the only high order of a magnetic field equation known in literature, and it corresponds to our more complicated recurrence equation (9).

The existing theoretical discussion about composite materials is mostly limited to low-density approximations, as pointed out in [10–12]. The experimental literature of this field was given in [13–18].

In the effective medium theory the conductivity reaches zero at a volume fraction of $\frac{1}{3}$ (this can be compared with the percolation threshold), but the effective Hall coefficient never differs from the local Hall coefficient of the conducting component R_1 by more than a factor of 2 ($R^e = 2R_1$, $R_2/R_1 \mapsto 1$). Kirkpatrick suggested that the Hall coefficient should be proportional to the inverse of the percolation probability $R^e(p) = P^{-1}(p)R_1$. This suggestion received great criticism because it implied that the dead ends occurring in the infinite cluster contribute to the Hall coefficient even though they do not carry current or appear on the surface of a sample. A picture, which seems unrealistic for customary percolation, was explained by the starry sky model [4].

The difference between results of the effective-medium theory is often due to involving the different averaging procedures. The difference between our results and the effective-medium theory results lies in the fact that we have developed exact analytical formulae for the mentioned kinetic coefficients, using the Green's function technique. The formulae

produced by this method play the same role for the calculations of kinetic coefficients as the Kirchhoff system of equations does for conductivity, and therefore, the numerous errors of the critical exponents calculations lie in the same error bar.

3. The new equations for conductivity in a magnetic field

An equation can be introduced for the current density $\underline{j}(r)$ in disordered systems, whose discontinuous scale is larger than the free path of the charge carriers, and whose free path is larger than the cyclotron radius. In this case we can consider the local conductivity $\sigma(r)$, and the local Hall coefficient $R(r)$ at each point of the sample. A new analytical result is obtained for the perturbation theory of the current density in a magnetic field, whose formula exactly corresponds with (2) to first order.

When H is small enough, the Hall current density can be represented as a vector product $\underline{\lambda}(r) \times \underline{E}(r)$ where $\underline{E} = -\nabla\varphi$ is an electric field and $\underline{\lambda}(r)$ is the local Hall conductivity. The equation for the current density in such a system may be written as:

$$\underline{j}(r) = \sigma(r)\nabla\varphi(r) + \sigma^{-1}(r)\underline{\lambda}(r) \times \underline{j}(r) \tag{2}$$

where $\lambda(r) = \sigma^2(r)R(r)\underline{H}$ represents a conductor in which the conductivity tensor is isotropic and $|\lambda(r)| \ll \sigma(r)$.

Consider a cubic sample with side lengths L_{x_m}, $m = 1, 2, 3$ with an applied electric field $\underline{E}$ along the x_m-axis and $\varphi_m(r)$ denoting the electrical potential, and $\underline{j}_m(r)$ being the current density. In the presence of a weak magnetic field the Lorentz force $\underline{F}_1$ is considered in the perturbation theory as the first-order response, whereas the Ohmic current density $\underline{j}_o(r)$ is considered as a zeroth-order response of a magnetic field. As a first step of the approximation, one obtains the Hall current density $\underline{j}_1(r)$, therefore the new, full current density is equal to $\underline{j}(r) = \underline{j}_o(r) + \underline{j}_1(r)$, in addition to a new electrical potential $\varphi(r) = \varphi_o(r) + \varphi_1(r)$. As k step results, one obtains a new Lorentz force $\underline{F}_k$ ad infinitum. The full current density and the full electrical potential can be described in powers of $\underline{H}$ (or $\lambda(r)$) as

$$\underline{j}_m(r) = \underline{j}_{0,m}(r) + \underline{j}_{1,m}(r) + \cdots + \underline{j}_{k,m}(r) \tag{3}$$

$$\varphi_m(r) = \varphi_{0,m}(r) + \varphi_{1,m}(r) + \cdots + \varphi_{k,m}(r). \tag{4}$$

For the boundary condition of the potential one obtains

$$\varphi_{0,m}(r)_{r\in B} = Ex_m \tag{5}$$

$$\varphi_{k,m}(r)_{r\in B} = 0 \tag{6}$$

where B is the boundary of the sample.

Now we must substitute $\underline{j}(r)$ from the right-hand side into the left-hand side of equation (1). If one repeats this operation k times, one obtains the equation:

$$\underline{j}(r) = \sigma(r)\nabla\varphi(r) + \sigma(r)^0\underline{\lambda}(r) \times \nabla\varphi(r) + \sigma(r)^{-1} \times \underline{\lambda}(r) \times \underline{\lambda}(r) \times \nabla\varphi(r)$$
$$+ \sigma(r)^{-(k-1)}\underline{\lambda}(r) \times \cdots \times \underline{\lambda}(r) \times \nabla\varphi(r) + \cdots. \tag{7}$$

Substituting (4) into (7) and separating the orders in $\underline{\lambda}(r)$ yields

$$\underline{j}_{0,m}(r) = \sigma(r)\nabla\varphi_0(r)$$

$$\underline{j}_{1,m}(r) = \sigma(r)\nabla\varphi_1(r) + \sigma^0(r)\underline{\lambda}(r) \times \nabla\varphi_{0,m}(r)$$

$$\underline{j}_{k,m}(r) = \sigma(r)\nabla\varphi_k(r) + \sigma^0(r)\underline{\lambda}(r) \times \nabla\varphi_{k-1,m}(r) + \cdots$$
$$+ \sigma^{-(k-1)}(r)\underline{\lambda}(r) \times \cdots \times \underline{\lambda}(r) \times \nabla\varphi_{0,m}(r). \tag{8}$$

The system of equations can be rewritten in a recurrent form for the projection of the current density on the n-axis:

$$j_{o,m}^n(r) = \sigma(r)\nabla_n\varphi_{0,m}(r)$$
$$j_{1,m}^n(r) = \sigma(r)\nabla_n\varphi_{1,m}(r) + \sigma^{-1}(r)[\underline{\lambda}(r) \times \underline{j}_{0,m}(r)]_n \tag{9}$$
$$j_{k,m}^n(r) = \sigma(r)\nabla_n\varphi_{k,m}(r) + \sigma^{-1}(r)[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]_n.$$

This allows us to use the Green's function to calculate (9) from the beginning, step by step. Now we introduce the Green's function $G(r, r')$ by the equation:

$$\nabla_n(\sigma(r)\nabla_n G(r, r')) = \delta^3(r - r') \tag{10}$$

with the boundary condition:

$$G(r, r')_{r\in B} = 0. \tag{11}$$

Summation over repeated indices is implied. The Green's function method can be applied to a potential with zero boundary conditions. For this purpose one can introduce a new potential $\varphi'_{0,m}(r)$ as:

$$\varphi'_{0,m}(r) = \varphi_{0,m}(r) - Ex_m \qquad \varphi'_{0,m}(r)_{r\in B} = 0. \tag{12}$$

Since $\nabla_n j_{0,m}^n(r) = 0$, $\nabla_n(\sigma(r)\nabla_n\varphi_{0,m}(r)) = 0$, this can be rewritten as:

$$\nabla_n(\sigma(r)\nabla_n\varphi'_{0,m}(r)) = -\nabla_n(\sigma(r)\nabla_n(Ex_m)). \tag{13}$$

Using the Green's function one can find for $\varphi'_{0,m}(r)$ and simultaneously for $\varphi_{0,m}(r)$,

$$\varphi_{0,m}(r) = Ex_m + \varphi'_{0,m}(r) = Ex_m + \int G(r, r')\nabla'_n[\sigma(r')\nabla'_n(Ex'_m)]\,\mathrm{d}V$$

$$= Ex_m - E\int \sigma(r')\nabla'_m G(r, r')\,\mathrm{d}V' \tag{14}$$

and since $\nabla_n(Ex_m) = E\delta_m^n$, also for $j_{0,m}^n(r)$

$$j_{0,m}^n(r) = \sigma(r)\nabla_n\varphi_{0,m}(r) = E\sigma(r)\delta_m^n + E\int \sigma(r)\sigma(r')\nabla_n\nabla'_m G(r, r')\,\mathrm{d}V'. \tag{15}$$

For further application, the integral may be expressed in another form

$$\int \sigma(r)\sigma(r')\nabla_n\nabla'_m G(r, r')\,\mathrm{d}V' = E^{-1}j_{0,m}^n(r) - \sigma(r)\delta_m^n. \tag{16}$$

This formula allows integrating multiplication of the gradient of the Green's function at two local conductivities. The result is the total current to zeroth order.

Since $\nabla_n j_{k,m}^n(r) = 0$ then from (9):

$$\nabla_n[\sigma(r)\nabla_n\varphi_{k,m}(r)] = -\nabla_n\{\sigma^{-1}(r)[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]_n\}$$
$$\varphi_{k,m}(r) = -\int_{V'} \sigma^{-1}(r')[\underline{\lambda}(r') \times \underline{j}_{k-1,m}(r')]_s\nabla'_s G(r, r')\,\mathrm{d}V' \tag{17}$$

and then by using (16):

$$\int \sigma(r)\nabla_n\varphi_{k,m}(r)\,\mathrm{d}V = \int_V \sigma^{-2}(r)[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]_s\,\mathrm{d}V \int_{V'} \sigma(r)\sigma(r')\nabla_n\nabla'_s G(r, r')\,\mathrm{d}V'$$

$$= \int [E^{-1}j_{0,n}^s(r) - \sigma(r)\delta_s^n]_s[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]_s\sigma^{-2}(r)\,\mathrm{d}V. \tag{18}$$

One can calculate the current $\langle j_{k,m}^n(r) \rangle$:

$$\int j_{k,m}^n(r)\,\mathrm{d}V = \int \sigma(r)\nabla_n\varphi_{k,m}(r)\,\mathrm{d}V + \int_V \sigma^{-1}(r)[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]_n\,\mathrm{d}V$$

$$= E^{-1}\int \sigma^{-2}(r)j_{0,n}^s[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]_s\,\mathrm{d}V - \int \sigma^{-1}(r)[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]_n\,\mathrm{d}V$$

$$+ \int \sigma^{-1}(r)[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]_n\,\mathrm{d}V. \tag{19}$$

The last two terms cancel and for $\langle j_{k,m}^n(r) \rangle$ one obtains:

$$\langle j_{k,m}^n(r) \rangle = \int j_{k,m}^n(r)\,\mathrm{d}V = E^{-1}\int_V \sigma^{-2}(r)j_{0,n}(r)[\underline{\lambda}(r) \times \underline{j}_{k-1,m}(r)]\,\mathrm{d}V. \tag{20}$$

This recurrence formula allows us to calculate each subsequent current from its previous value. For example, for effective magnetoresistance one can write

$$\Delta\rho_{m,n}(p) = \frac{\int_V \underline{j}_{0,n}(r)[\underline{H} \times \underline{j}_{1,n}(r)]R(r)\,\mathrm{d}V}{\sigma_n^{\mathrm{eff}}(p)\sigma_m^{\mathrm{eff}}(p)E^2}. \tag{21}$$

It is interesting to compare Bergman's [19] formula (5) for the magnetoconductivity with our result (21). The only difference is that Bergman did not complete his calculation because he did not use a formula like (16) for integrating the Green's function.

Now one can rewrite the result in a common integral equation form

$$\langle j_m^n(r) - j_{0,m}^n(r) \rangle = \left\langle \sum_{k=2}^{\infty} j_{k-1,m}^n(r) \right\rangle$$

$$= E^{-1}\int_V \left(\underline{j}_{0,n}(r)\left[\underline{H} \times \sum_{k=1}^{\infty} \underline{j}_{k-1,m}(r) \right] \right)R(r)\,\mathrm{d}V$$

$$= E^{-1}\int_V (\underline{j}_{0,n}(r)[\underline{H} \times \underline{j}_m(r)])R(r)\,\mathrm{d}V. \tag{22}$$

In [4] it was shown that the Hall coefficient for $k = 1$ can be obtained without calculating the current density in the presence of a magnetic field

$$R^{\mathrm{eff}}(p) = \frac{\langle \underline{j}_1(r) \rangle}{(\sigma_x^{\mathrm{eff}}(p)\sigma_y^{\mathrm{eff}}(p)U_xU_yHL)}$$

$$= \int_V \frac{(\underline{j}_0(r)[\underline{j}_0'(r) \times \underline{H}])R(r)\,\mathrm{d}V}{\sigma_x^{\mathrm{eff}}(p)\sigma_y^{\mathrm{eff}}(p)U_xU_yLH} \tag{23}$$

where $\underline{j}_0(r)$ and $\underline{j}_0'(r)$ are the current density obtained from the equation $\nabla(\sigma(r)\nabla U(r)) = 0$ with boundary conditions along the x-axis for a potential difference U_x and along the y-axis for a potential difference U_y, $\sigma(r)$ and $R(r)$ are the local values of the conductivity and the Hall coefficient, $\sigma_x^{\mathrm{eff}}(p)$ and $\sigma_y^{\mathrm{eff}}(p)$ are the effective conductivities along these axes and L is the length of the sample along the magnetic field $\underline{H}$.

When we consider this solution we can calculate two values:

(i) the effective Hall potential drop when the Hall circuit is disrupted;

(ii) the effective Hall current when it is not disrupted.

Obviously, the effective Hall potential drop is equal to the sum of the Lorentz battery $\underline{E}_L(r)$ on each point of the sample. The random distribution of the values and orientations of the Lorentz battery can be obtained by using the Ohmic density of the current $j_0^x(r)$, calculated by iteration of the Kirchhoff system of equations, with boundary conditions

applied, for example, to the x-axis. In this case the Lorentz battery is equal to the value $\underline{E}_L(r) = R(r)\underline{j}_0^x(r) \times \underline{H}$. There are difficulties in summing up these batteries because of their random orientation, and not because of their random values. In order to overcome these difficulties, it is necessary to change the vector field of the Lorentz battery to the field of Hall current density outside Hall circuit. As shown in [4], by using the well known reciprocity theorem, the Hall current density in an outside Hall circuit (which came from the Lorentz battery on each point of the sample) is equal to a subintegral value in equation (23). One may summarize it as an integral form (23) because each part of the Hall current density is parallel in an outside circuit.

It is important to understand that our method divides the full Hall current density in the sample into two parts. The first part of the current, which is proportional to $j_0^y(r)$, has a path to the boundary along a percolation cluster, while the second part does not have this possibility. One must recalculate the Kirchhoff system of equations, with the other boundary conditions applied to the y-axis in the event that a magnetic field is applied along the z-axis. As a result one obtains the current density $\underline{j}_0^y(r)$. By using integral (5) in the zero step of approximation ($k = 0$), one obtains the first part of the Hall current, which has a path to the Hall contacts, because $j_0^y(r)$ was put through the Hall contacts. One may claim that this is the exact result of the zero step of the approximation, because the second part was influenced by only the changes in the Ohmic density of the currents. Therefore it needs the recurrence formulae (20) for all responses of a magnetic field. Our Green's function method [4] corresponds, mathematically, to the precise summarization of the Lorentz batteries, but not to the new kind of the effective medium approximations.

However, the theory cannot be completed without an answer to a very important question. One needs to find the condition when the solution of equation (7) converges. The recurrence form of the solution equation (20) enables us to obtain an exact answer for this question.

One can rewrite equation (20) as an inequality for the first-order solution

$$\int \underline{j}_1^y(r)\,\mathrm{d}V = E^{-1} \int (\underline{j}_0^x(r)[\underline{H} \times \underline{j}_0^y(r)])\,R(r)\,\mathrm{d}V$$

$$= \int ([\underline{j}_0^x(r) \times \underline{H}]\underline{j}_0^y(r))\,R(r)\,\mathrm{d}V < \max\left(\frac{|[\underline{j}_0^x(r) \times \underline{H}]R(r)|}{E}\right) \int |\underline{j}_0^y(r)|\,\mathrm{d}V.$$

$$(24)$$

The second-order solution gives the inequality

$$\int j_2^y(r)\,\mathrm{d}V = \int ([\underline{j}_1^x(r) \times \underline{H}]j_0^y(r)R(r)\,\mathrm{d}V$$

$$< \max\left(\frac{|[\underline{j}_0^x(r) \times \underline{H}]R(r)|}{E}\right)^2 \int |\underline{j}_0^y(r)|\,\mathrm{d}V. \qquad (25)$$

The common case k is

$$\int j_k^y(r)\,\mathrm{d}V = \int ([\underline{j}_0^x(r) \times \underline{H}]\underline{j}_{k-1}^y(r))\,R(r)\,\mathrm{d}V$$

$$< \max\left(\frac{|[\underline{j}_0^x(r) \times \underline{H}]R(r)|}{E}\right)^k \int |j_0^y(r)|\,\mathrm{d}V. \qquad (26)$$

In the magnetic field if the first term in the inequality

$$\max\left(\frac{|[\underline{j}_0^x(r) \times \underline{H}]R(r)|}{E}\right) < 1 \tag{27}$$

then $\langle j_k^y(r)\rangle \to 0$ as $k \to \pm\infty$ and solution (20) is converged.

4. The new equations for thermopower

There is literature [21–25] on the thermopower of inhomogeneous aggregates, consisting of two or more distinct phases, separated by sharp boundaries. It is obvious that the thermoelectric properties of homogeneous materials are superior to those of inhomogeneous composites. This is suggested by the calculation of the thermoelectrical properties of a composite rod constructed of two pieces of dissimilar material in parallel or in series [21]. There may be an application of such composites: for example, a second phase might be introduced to improve the mechanical properties of the material. The theory that has been discussed may assist the interpretation of experiments on such materials [23].

With the Green's function technique used in the appendix, one can obtain the Seebeck coefficient constructed by the perturbation theory. This leads, again [4], to a recurrent system of equations, assuming that the media can be described by local thermoconductivity $k(r)$, temperature $T(r)$, and the Seebeck coefficient $\alpha(r)$. It is possible to write the system of equations for the thermocurrent $\underline{j}(r)$ and thermal flux $\underline{u}(r)$ as follows

$$\underline{j}(r) = \sigma(r)\underline{\nabla}\varphi(r) - \sigma(r)\alpha(r)\underline{\nabla}T(r) \tag{28a}$$

$$\underline{u}(r) = \kappa(r)\underline{\nabla}T(r) - \sigma(r)\alpha(r)T(r)\underline{\nabla}\varphi(r). \tag{28b}$$

Suppose that the opposite edges of the sample are electrically connected and the thermoelectric current is measured. The temperatures of the edges are held at T_1 and T_2. The boundary conditions for $\varphi(r)$ and $T(r)$ are:

$$\varphi(r)_{r\in B} = 0 \qquad T(r)_{r\in B} = \frac{(T_2 - T_1)x_m}{L}. \tag{29}$$

In the zeroth-order sequence for α we can neglect the second term of equation (1b) and obtain:

$$\underline{j}_0(r) = \sigma(r)\underline{\nabla}\varphi_0(r) - \sigma(r)\alpha(r)\underline{\nabla}T_0(r) \tag{30a}$$

and

$$\underline{u}_0(r) = \kappa(r)\underline{\nabla}T_0(r). \tag{30b}$$

Now we can write a sequence for α with values $T(r)$ and $u(r)$:

$$T(r) = T_0(r) + T_1(r) + T_2(r) + \cdots$$
$$\underline{u}(r) = \underline{u}_0(r) + \underline{u}_1(r) + \underline{u}_2(r) + \cdots. \tag{31}$$

Substituting sequences (31) into systems (28), one can obtain equations of all the orders of α. Equation (30b), for the temperature distribution, is similar to that of the electric current with conductivity $\kappa(r)$. On a lattice it can be solved by integrating Kirchhoff's equations.

In first order, one obtains:

$$\underline{j}_1(r) = \sigma(r)\underline{\nabla}\varphi_1(r) - \alpha(r)\sigma(r)\underline{\nabla}T_0(r)$$
$$\underline{u}_1(r) = \kappa(r)\underline{\nabla}T_1(r) + \alpha(r)\sigma(r)T_0(r)\underline{\nabla}\varphi_1(r). \tag{32}$$

Therefore, the boundary condition, with potential equal to zero can be rewritten as:

$$\varphi(r)_{r \in B} = 0 \Rightarrow \varphi_0(r) \equiv 0$$

thus the second term in equation (3*b*) equals zero (also in the first-order equation (32)) and $T_1(r) = T_0(r)$. The zero term in a row for α equals the first one, and our task is now to find the second term.

The equation for the second term is as follows

$$\underline{j}_2(r) = \sigma(r)\underline{\nabla}\varphi_2(r) + \alpha(r)\sigma(r)\underline{\nabla}T_1(r) \tag{33a}$$

$$\underline{u}_2(r) = \kappa(r)\underline{\nabla}T_2(r) + \alpha(r)\sigma(r)T_0(r)\underline{\nabla}\varphi_1(r) + \alpha(r)\sigma(r)T_1(r)\underline{\nabla}\varphi_0(r). \tag{33b}$$

The last term equals zero, because $\nabla\varphi_0(r) = 0$. From the equation $\nabla u_2(r) = 0$, one can obtain $T_2(r)$ as a function of $T_1(r) = T_0(r)$ and $\varphi_1(r)$

$$\underline{\nabla}(\kappa(r)\underline{\nabla}T_2(r)) = \underline{\nabla}(\alpha(r)\sigma(r)T_0(r)\underline{\nabla}\varphi_1(r))$$

$$T_2(r) = \int G(r, r')\underline{\nabla}(\alpha(r')\sigma(r')T_0(r')\underline{\nabla}\varphi_1(r')) \, \mathrm{d}V'. \tag{34}$$

Using row (28*a*), one obtains the equation for thermocurrent density in the form:

$$\underline{j}_1(r) = \sigma(r)\underline{\nabla}\varphi_1(r) - \alpha(r)\sigma(r)\underline{\nabla}T_0(r)$$

$$\underline{j}_2(r) = \sigma(r)\underline{\nabla}\varphi_2(r) - \alpha(r)\sigma(r)\underline{\nabla}T_1(r)$$

$$\vdots \tag{35}$$

$$\underline{j}_k(r) = \sigma(r)\underline{\nabla}\varphi_k(r) - \alpha(r)\sigma(r)\underline{\nabla}T_{k-1}(r).$$

Since $\nabla j_k(r) = 0$ and using the Green's function, one can calculate the potential:

$$\varphi_k(r) = \int G(r, r')\underline{\nabla}(\sigma(r')\alpha(r')\underline{\nabla}T_{k-1}(r')) \, \mathrm{d}V'. \tag{36}$$

Using (A7) one can obtain the mean value of thermocurrent

$$\langle j_k(r) \rangle = \int \alpha(r)\nabla T_{k-1}(r) \int \sigma(r)\sigma(r')\nabla\nabla'G(r, r') \, \mathrm{d}V \, \mathrm{d}V' - \int \alpha(r)\sigma(r)\nabla T_{k-1}(r) \, \mathrm{d}V$$

$$= E^{-1} \int \alpha(r)(j_0(r)\nabla T_{k-1}(r)) \, \mathrm{d}V. \tag{37}$$

Thermocurrent $\langle j_1(r) \rangle$ can be obtained from temperature $T_0(r)$, which is easy to calculate from Kirchoff's system of equations.

Thermocurrent $\langle j_2(r) \rangle$ can be calculated by using $T_1(r)$, but $T_1(r) = T_0(r)$ and the first-order result is equal to the zeroth-order result.

The third order in many physical situations is very small, but in the particular cases it can be important. Formula (37) offers the possibility of calculating the contributions of all orders of α to thermocurrent from the temperature distribution.

5. Numerical analysis of the Hall and Seebeck coefficients and the effective medium theory

On the basis of the formulae obtained, a computer program was created and the Hall and Seebeck coefficient was calculated for a three-dimensional lattice consisting of $25 \times 25 \times 25$ sites.

Using a random Gaussian potential model and potential level W_0 one can calculate the probability

$$p = \int_{-\infty}^{W_0} F(W)\,\mathrm{d}W \qquad W(r) = \int K(r-r')f(r')\,\mathrm{d}r' \tag{38}$$

for the conductivity σ_1, the Hall coefficient R_1, the thermal conductivity k_1 and the Seebeck coefficient α_1 of the component 1 at $W > W_0$ and the probability $1 - p$ for those of the component $2(\sigma_2, R_2, k_2, \alpha_2)$. $f(r)$ is a random Gaussian function with correlator $f(r)f(r') = \delta(r-r')$ and $K(r) = \exp(r/r_0)$ where r_0 is a correlative radius. This model seems to be better than site percolation for continuum percolation and for comparison with experiment.

In order to calculate the Hall coefficient, the following algorithm and boundary conditions have been assumed.

(1) Periodic boundary conditions are assumed for all surfaces of the cube without contacts:

(i) the surface passes through the sites of the lattice; (ii) the cube is mirrored at the boundary.

(2) The electrical contacts are situated on the surfaces $x = 0$ and $x = L$, and their potentials are assumed to be $U_{x=0} = 0$ and $U_{x=L} = 1$. The iteration formula for calculating the potential connected with each given site, follows from Kirchhoff's current law. After the iteration procedure has ended, every site can be associated with three current components j_x, j_y and j_z, which are calculated as a half sum of currents in the bonds adjoining this site.

(3) The procedure for calculating $\sigma_y^{\mathrm{eff}}(p)$ is the same as in (2), but the contacts are situated on the surfaces $y = 0$ and $y = L$, and every site can now be associated with three current components, j_x^1, j_y^1 and j_z^1.

(4) The products $j_x j_y^1$ and $-j_y j_x^1$, multiplied by the Hall coefficients R_1 or R_2 at these points, are summed for every site of the lattice.

The procedure for calculating the Seebeck coefficient is identical.

The dependence of conductivity and Hall and Seebeck coefficients on p and for various ratios of σ_1/σ_2, R_1/R_2, and k_1/k_2 is illustrated in figures 1–5. Figure 1 illustrates the concentration dependence conductivity and the Hall coefficient for various ratios σ_1/σ_2 and R_1/R_2. In figure 1 the behaviour of the percolation probability $P(p)$ is shown by the heavy curve. There is an interesting feature in the behaviour of conductivity and the reciprocal Hall coefficient which can be seen in figure 1. The maximum distance between the conductivities and reciprocal coefficients curves is denoted by A. This distance is a function of the conductivity ratio. At $\sigma_2/\sigma_1 > 10^{-5}$, the curves differ greatly and A increases to its maximum value. In this case quantitative agreement is achieved for the high-density impurity conductor $\mathrm{Na}_x\mathrm{WO}_3$ [28], for which the reciprocal Hall coefficient is observed to correspond with $P(p)$. When the ratio σ_2/σ_1 rises, A decreases smoothly to 0 at $\sigma_2/\sigma_1 > 0.5$. This behaviour of the distance A can be used to estimate the conductivity ratio of the experimental data constituents in heterogeneous materials.

Cohen and Jortner [10] generalized the effective medium theory (EMT) to treat situations in which the conductivity is a tensor quantity everywhere, as must occur in the presence of a magnetic field and then applied to several liquid semiconducting systems. Their analysis was generalized for thermopower by Webman *et al* [12] for a random mixture of two components, where conductivity σ_1, thermoconductivity k_1 and Hall and Seebeck coefficients R_1 and α_1 occupy a volume fraction p and σ_2, k_2, R_2, and α_2 occupy a volume fraction $1 - p$.

Let us compare the results predicted by EMT with our calculation. The broken curves in figures 2–4 correspond to the data obtained by Cohen and Jortner's formulae. As Kirkpatrick
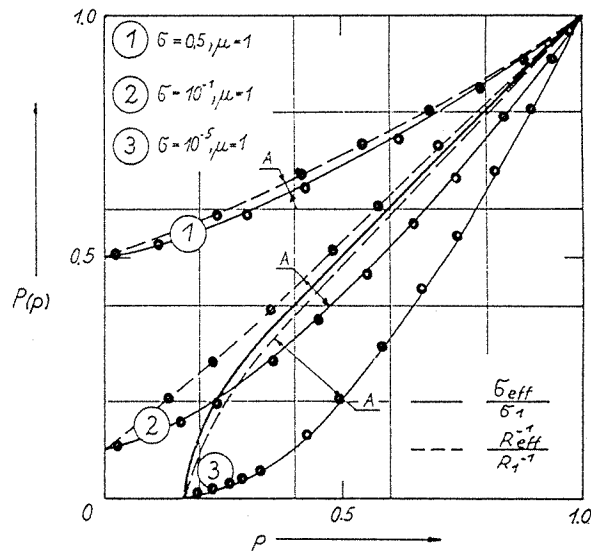
Figure 1. The effective conductivity (the heavy curves with the circles) and the effective reciprocal Hall coefficient (dotted curves with the circles) for the Hall mobility $\mu = \mu_2/\mu_1 = 1$ and the different values $\sigma = \sigma_2/\sigma_1$. The percolation probability $P(p)$ is presented by the heavy curve.
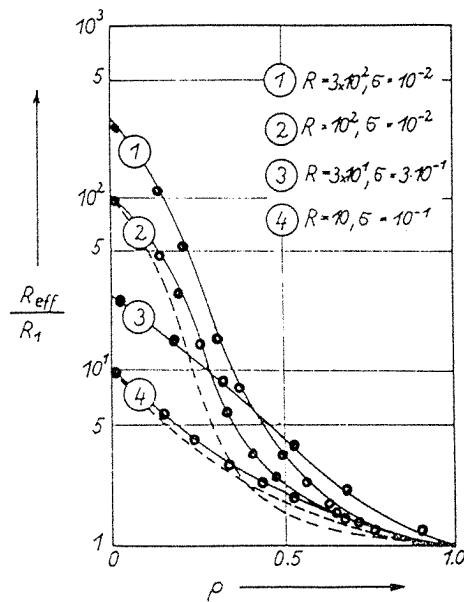

Figure 2. The reciprocal Hall coefficient for the different values $\sigma = \sigma_2/\sigma_1$ and $R = R_2/R_1$. Predictions of EMT are shown by the broken curves.

[9] pointed out, one can obtain an accurate analytical EMT calculation of conductivity problem outside the critical region. The numerical results presented show that the EMT is also accurate for the Hall and Seebeck coefficients and that the critical region in which it fails (see figure 3) covers only a modes range of concentrations.

The best formula for thermopower, which gives the correct value of the threshold, was
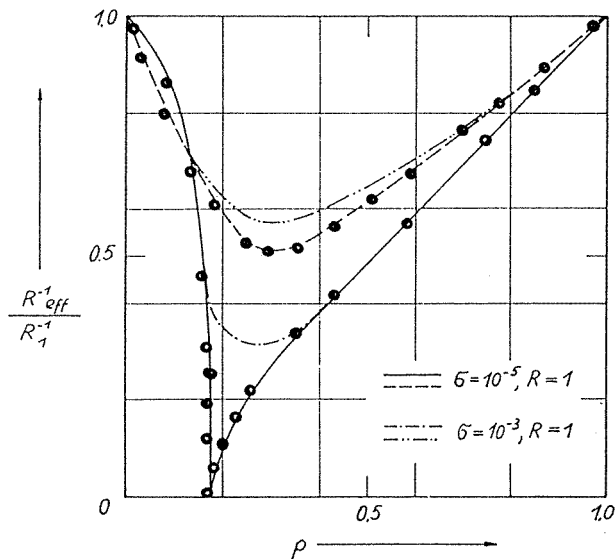
Figure 3. The reciprocal Hall coefficient for the different values $\sigma = \sigma_2/\sigma_1$ and $R = R_2/R_1$. Predictions of EMT are shown by the broken curves and chain curves.
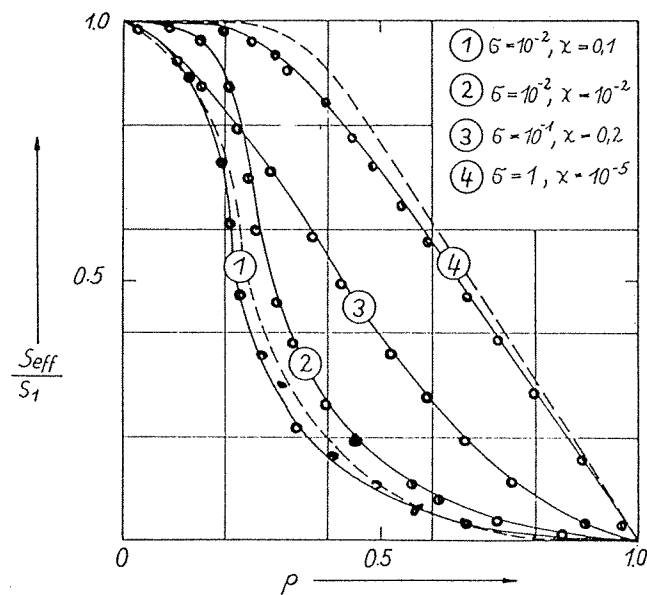

Figure 4. The effective Seebeck coefficient for the different values $\sigma = \sigma_2/\sigma_1$ and $\chi = k_2/k_1$. Predictions of EMT are shown by the broken curves.

presented by Straley [26] and Halpern [27]

$$\alpha^{\text{eff}}(p) = (\alpha_2 - \alpha_1)[(k^{\text{eff}}(p)/\sigma^{\text{eff}}(p) - k_1/\sigma_1)/(k_2/\sigma_2 - k_1/\sigma_1)] + \alpha_1. \tag{39}$$

The physical meaning of this formula at $k_1 \cong k_2$, where the formula becomes strong, is that the Seebeck coefficient is proportional to the difference between the effective resistance
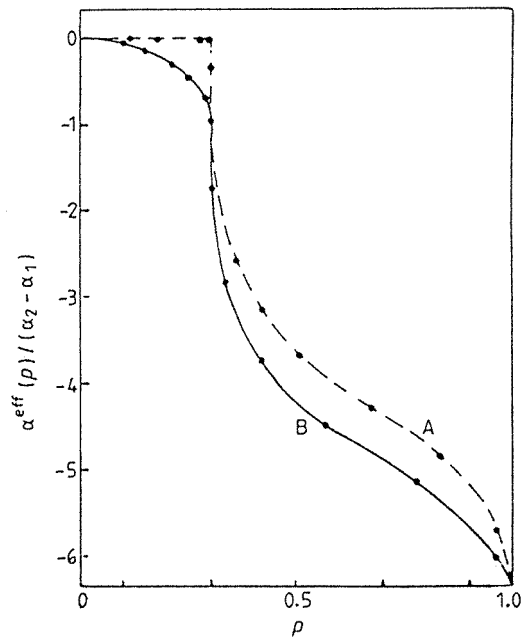
Figure 5. The effective Seebeck coefficient for (A) $\sigma_1/\sigma_2 = k_1/k_2 = 10^5$; (B) $\sigma_1/\sigma_2 = 10^5$; $k_1/k_2 = 1.001$.

and the resistance of component 1. In this particular case the critical exponent of the Seebeck coefficient is equal to the conductivity exponent t and therefore both the thermopower and the conductivity belong to the same universality class. Formula (39) was verified by a computer calculation using integrals (37). Our calculation shows that this formula is extremely accurate for both two- and three-dimensional spaces, and for both sides of the threshold but does not work for the ratio $k_1/k_2 \gg 1$, whereas for the $k_1/\sigma_1 = k_2/\sigma_2$ it becomes meaningless, since both the numerator and the denominator become equal to zero. Figure 5 presents the two different curves with different critical exponents for both extreme cases. All other cases lie in short intervals between them. When the ratio $k_1/k_2 \gg 1$, the 'special' nodes appear and the thermopower belongs to the new universality class.

6. An upper bound of the critical Hall conductivity exponent for the contributions of all orders to the current density in a magnetic field

An upper bound of the critical Hall conductivity exponent for the contributions of all orders of the Hall effect to the current density in a magnetic field can be obtained by using both equation (23) and equation (27).

As follows from numerical calculation of equation (23) [4], the Hall conductivity $G^{\mathrm{eff}}(p)$ critical exponent for the case when $R_1/R_2 \to 1$ can be presented for both sides of the threshold by the formula

$$G^{\mathrm{eff}}(p) \propto |p - p_c|^\tau \qquad \tau_1 = 2t - g \qquad g = 0.6 \tag{40}$$

where t is the conductivity critical exponent and g is the Hall coefficient critical exponent [21].

In order to calculate the upper bound of the critical Halls conductivity exponent τ_k, one needs to use equation (27) related to $\langle f_k^y(r) \rangle$, which leads to the formula

$$\tau_k \leqslant 2t - g. \tag{41}$$

Our numerical calculations have shown that one can obtain a new universality class for the Hall coefficient critical exponent for both sides of the threshold when $R_2/R_1 \to 1$. In the opposite case, the situation is more complicated. For $p > p_c$ the former case holds but for $p < p_c$ the Hall coefficient and conductivity belong to the same universality class $\tau_1 = 2t$ if $R_2 \gg R_1$.

7. Conclusion

We have developed exact analytical formulae for the mentioned kinetic coefficients, using the Green's function technique. The formulae produced by this method play the same role for the calculations of kinetic coefficients as the Kirchhoff system of equations does for conductivity, therefore the numerous errors of the critical exponents calculations lie in the same error bar. These formulae give contribution of all orders of the Hall effect to the current density.

When the ratio $k_1/k_2 \gg 1$, the 'special' nodes appear and the thermopower belongs to the new universality class.

Acknowledgments

Appendix

Consider a cubic sample with side lengths L_{x_m}, $m = 1, 2, 3$ with an applied electric field E along the x_m-axis. $\varphi_m(r)$ denotes the electrical potential and $j_m(r)$ denotes the current density.

For the boundary condition of the potential one obtains:

$$\varphi_{0,m}(r)_{r \in B} = E x_m \tag{A1}$$

where B is the boundary of the sample.

Now we introduce the Green's function $G(r, r')$ by the equation:

$$\nabla_n(\sigma(r)\nabla_n G(r, r')) = \delta^3(r - r') \tag{A2}$$

with the boundary condition

$$G(r, r')_{r \in B} = 0. \tag{A3}$$

Summation over repeated indices is implied. The Green's function method can be applied to the potential with zero boundary conditions. For this purpose one can introduce a new potential $\varphi'_{0,m}(r)$ as:

$$\varphi'_{0,m}(r) = \varphi_{0,m}(r) - E x_m \qquad \text{where} \qquad \varphi'_{0,m}(r)_{r \in B} = 0$$

since $\nabla_n j^n_{0,m}(r) = 0$, $\nabla_n(\sigma(r)\nabla_n \varphi_{0,m}(r)) = 0$.

This can be rewritten as:

$$\nabla_n(\sigma(r)\nabla_n \varphi'_{0,m}(r)) = -\nabla_n(\sigma(r)\nabla_n(E x_m)). \tag{A4}$$

Using the Green's function one can find a solution for $\varphi'_{0,m}(r)$ and simultaneously, for $\varphi_{0,m}(r)$

$$\varphi_{0,m}(r) = Ex_m + \varphi'_{0,m}(r) = Ex_m + \int G(r,r')\nabla'(\sigma(r')\nabla'(Ex'_m))\,\mathrm{d}V'$$

$$= Ex_m - E\int \sigma(r')\nabla'_m G(r,r')\,\mathrm{d}V' \tag{A5}$$

and since $\nabla_n(Ex_m) = E\delta^n_m$, for $j^n_{0,m}(r)$ one obtains

$$j^n_{0,m}(r) = \sigma(r)\nabla_n\varphi_{0,m}(r) = E\sigma(r)\delta^n_m + E\int \sigma(r)\sigma(r')\nabla_n\nabla'_m G(r,r')\,\mathrm{d}V'. \tag{A6}$$

For further application, the integral may be expressed in another form

$$E\int \sigma(r)\sigma(r')\nabla_n\nabla'_m G(r,r')\,\mathrm{d}V' = E^{-1}j^n_{0,m}(r) - \sigma(r)\delta^n_m. \tag{A7}$$

This formula allows integrating multiplication of the gradient of the Green's function at two local conductivities. The result is the total current to zeroth order.

References

[1] Skal A S 1997 The starry sky model part 3: A new equilibrium equation and two kinds of the 'special' elastic nodes *Physica* **242A** 13
[2] Stauffer D and Aharony A 1994 *Introduction to Percolation Theory* (London: Taylor and Francis)
[3] Webman I and Jortner J 1977 *Phys. Rev.* B **16** 2959
   Even V and Jortner J 1972 *Phys. Rev. Lett.* **28** 31
   Even V and Jortner J 1973 *Phys. Rev.* B **8** 2536
[4] Skal A S 1981 *Sov. Phys. Dokl. Acad. Sci.* **260** 602
   Skal A S 1982 *Phil. Mag.* B **3** 335
   Skal A S 1993 *Phys. Lett.* A **182** 157
   Skal A S 1994 *Mod. Phys. Lett.* B **8** 1045
   Skal A S 1996 *Physica* **234A** 1–21
[5] Milgrom M and Shtrikman S 1989 *Phys. Rev.* B **40** 5991
[6] Gans R 1906 *Ann. Phys., Lpz.* **20** 293
[7] Sommerfeld A and Frank N H 1931 *Rev. Mod. Phys.* **3** 1
[8] Davis L 1939 *Phys. Rev.* **56** 93
[9] Seitz F 1950 *Phys. Rev.* **79** 372
[10] Cohen M H and Jortner J 1973 *Phys. Rev.* A **10** 978
[11] Zallen R and Scher H 1971 *Phys. Rev.* B **4** 4471
[12] Webman I, Jortner J and Cohen M H 1975 *Phys. Rev.* B **11** 2885
[13] Stroud D and Pan F P 1979 *Phys. Rev.* B **20** 455
[14] Bandyopadhyay B, Lindenfeld P, Mclean W L and Sin H K 1982 *Phys. Rev.* B **26** 3476
[15] Palevski A, Rappaport M, Kapitulnik Z, Fried A and Deutscher G 1984 *J. Physique Lett.* **45** L367
[16] Orton J W and Powell M J 1980 *Prog. Phys.* **43** 1263
[17] Kapitulnik A, Palevski A and Deutscher G 1986 *Bull. Am. Phys. Soc.* **31** 594
[18] Dai V, Palevski A and Deutscher G 1987 *Phys. Rev.* B **36** 790
[19] Bergman D J 1987 *Phil. Mag.* **56** 983
[20] Kirkpatrick S 1973 *Rev. Mod. Phys.* **45** 574
[21] Airapetiants C V 1958 *Sov. Phys. Tech. Phys.* **2** 429
[22] Reeynolds J A and Hough J M 1957 *Proc. Phys. Soc.* B **70** 769
[23] Herring C 1960 *J. Appl. Phys.* **31** 1939
[24] Foiles C L 1979 *J. Phys. F: Met. Phys.* **9** 2381
[25] Lightsey P A 1972 *Thesis* Cornell University
[26] Straley J P 1982 *J. Phys. C: Solid State Phys.* **13** 819
[27] Halpern V 1983 *J. Phys. C: Solid State Phys.* **16** L217
[28] Lightsey P A 1972 *Thesis* Cornell University