

L.P. Bulat, I.A. Nefedova



L.P. Bulat

Saint-Petersburg National Research University ITMO
9, Lomonosov Str., Saint-Petersburg,
191002, Russian Federation



I.A. Nefedova

**NONLOCAL TRANSPORT PHENOMENA
IN SEMICONDUCTORS**

The content of “nonlocality” concept in theory of transport phenomena is discussed. Nonlinear and nonlocal phenomena in thermoelectricity are compared. Finite element method is used to calculate the characteristic length of change in temperature and nonlocality length for a semiconductor “cone-plate” contact. It is shown that the presence of nonlinear phenomena brings about the emergence of nonlocal phenomena and vice versa.

Key words: nonlocal transport phenomena, nonlinear transport phenomena, thermoelectric phenomena, semiconductors, solids, finite element method.

Conventional theory of transport phenomena in solids, liquids and gases employs a well-known Boltzmann equation derived as far back as 1872. In almost all cases, local solutions of this equation are considered. In the strict sense, classical Boltzmann equation has its domain of applicability, and the problem of correctness of local solutions in each case demands verification and justification [1-3]. In monograph [1] and a cycle of works (see, for instance, [2, 3]) the fundamental concepts of a generalized Boltzmann gas-kinetic theory as part of nonlocal physics are developed. It is established that theory of transport phenomena can be considered within a unified theory based on nonlocal description [2]. Moreover, a generalized nonlocal quantum kinetics and gas-hydrodynamics is applicable to mathematical simulation of the vast class of objects – from galaxies to atoms [2, 3]. A large number of applied problems can be considered with the aid of a generalized Boltzmann nonlocal theory of transport, starting from study of various turbulent flows, application of generalized quantum mechanics and quantum hydrodynamics for the analysis of nanostructures, to theory of dark energy and matter evolution after the Big Bang [1-3].

What is the essence of nonlocality of transport phenomena in semiconductors and solids in general?

Let some function $f(x)$ and derivative $\partial\varphi(x)/\partial x$ are related by the relation [4]

$$f(x) = \int_{-\infty}^{+\infty} K(x-x') \frac{\partial\varphi(x')}{\partial x'} dx'. \quad (1)$$

Relation (1) between $f(x)$ and $\partial\varphi(x)/\partial x$ is inherently linear, rather than local, since the value $f(x)$ at point x depends on the value of derivative $\partial\varphi(x)/\partial x$ at other points [4]. A nonlocal bond nucleus $K(x-x')$ must possess the property $K(x-x') \rightarrow 0$ at $x-x' \rightarrow \infty$.

It is easy to verify [4] that if the nucleus is of the form $K(x-x') = K_0\delta(x-x')$ where $\delta(x-x')$ is a δ -function, then formula (1) goes over into $f(x) = -K_0 d\varphi/dx$, i.e. the relation acquires a local character. In other words, if some function $f(x)$ depends only on the first derivative (derivatives) of other function with respect to coordinates, then function $f(x)$ is local.

As is known, under thermodynamic equilibrium conditions temperature T and electrochemical potential $\mu = \mu_0 - e\varphi$ at each sample point are constant (μ_0 and φ are chemical and electrical potentials, respectively, e is electron charge). If, however, these conditions are not satisfied, the following spatial derivatives of temperature and electrochemical potential must be different from zero [4]:

$$\begin{aligned} & \frac{\partial T}{\partial x}, \frac{\partial T}{\partial y}, \frac{\partial T}{\partial z}, \frac{\partial^2 T}{\partial x^2}, \frac{\partial^2 T}{\partial y^2}, \frac{\partial^2 T}{\partial z^2}, \frac{\partial^2 T}{\partial x \partial y}, \frac{\partial^2 T}{\partial x \partial z}, \frac{\partial^2 T}{\partial y \partial z}, \frac{\partial^3 T}{\partial x^3}, \frac{\partial^3 T}{\partial y^3}, \frac{\partial^3 T}{\partial z^3}, \\ & \frac{\partial^3 T}{\partial x^2 \partial y}, \frac{\partial^3 T}{\partial x^2 \partial z}, \frac{\partial^3 T}{\partial x \partial y^2}, \frac{\partial^3 T}{\partial x \partial z^2}, \frac{\partial^3 T}{\partial x \partial y \partial z}, \frac{\partial^3 T}{\partial y^2 \partial z}, \frac{\partial^3 T}{\partial y \partial z^2}, \dots \\ & \frac{\partial \mu}{\partial x}, \frac{\partial \mu}{\partial y}, \frac{\partial \mu}{\partial z}, \frac{\partial^2 \mu}{\partial x^2}, \frac{\partial^2 \mu}{\partial y^2}, \frac{\partial^2 \mu}{\partial z^2}, \frac{\partial^2 \mu}{\partial x \partial y}, \frac{\partial^2 \mu}{\partial x \partial z}, \frac{\partial^2 \mu}{\partial y \partial z}, \frac{\partial^3 \mu}{\partial x^3}, \frac{\partial^3 \mu}{\partial y^3}, \frac{\partial^3 \mu}{\partial z^3}, \\ & \frac{\partial^3 \mu}{\partial x^2 \partial y}, \frac{\partial^3 \mu}{\partial x^2 \partial z}, \frac{\partial^3 \mu}{\partial x \partial y^2}, \frac{\partial^3 \mu}{\partial x \partial z^2}, \frac{\partial^3 \mu}{\partial x \partial y \partial z}, \frac{\partial^3 \mu}{\partial y^2 \partial z}, \frac{\partial^3 \mu}{\partial y \partial z^2}, \dots \end{aligned} \quad (2)$$

Of course, higher-order derivatives with respect to coordinates can be nonzero, too. The vectors of current density and heat flux

$$\vec{j} = \{j_x, j_y, j_z\}, \quad \vec{q} = \{q_x, q_y, q_z\}$$

must be functions of derivatives of temperature and chemical potential with respect to coordinates [4]:

$$j_k = f_k^j(\dots), \quad q_k = f_k^q(\dots), \quad (3)$$

where three dots in brackets mean a collection of spatial derivatives (2).

In the lectures by A.G. Samoilovich [4] it was assumed that with small deviations from thermodynamic equilibrium the expressions for current and heat flux densities (3) will comprise only linear summands, and will not involve quadratic, cubic and higher degrees of spatial derivatives of temperature and electrochemical potential. Thus, in (3) only linear summands will be left with quadratic, cubic, etc. higher derivatives with respect to coordinates.

However, direct solution of the Boltzmann equation and calculation of current density and heat flux density for semiconductors dependent on not very small temperature gradients [5-8] has shown that nonlinear and nonlocal terms in equations for fluxes are of the same order. Therefore, at least in the model assumed in [5-8], the presence of nonlinear summands automatically brings about the emergence of nonlocal terms, and, vice versa, the presence of nonlocal summands automatically causes the emergence of nonlinear terms. In one-dimensional geometry, solution of the Boltzmann equation was obtained with electron scattering on acoustic phonons or ionized impurities by two methods: perturbation theory and variation [5-8]. Both methods yield the expressions for current density and heat flux density. If we restrict ourselves to conventional linear and local summands and the first nonlinear and nonlocal terms, then the equation for current density for a single-dimensional problem can be represented as follows:

$$\begin{aligned} j = & -\sigma \frac{d\mu}{dx} - \sigma\alpha \frac{dT}{dx} + \\ & + a_1 \left(\frac{dT}{dx} \right)^3 + a_2 \left(\frac{dT}{dx} \right)^2 \frac{d\mu}{dx} + a_3 \frac{dT}{dx} \left(\frac{d\mu}{dx} \right)^2 + a_4 \left(\frac{d\mu}{dx} \right)^3 + \\ & + a_5 \frac{d^2 T}{dx^2} \frac{dT}{dx} + a_6 \frac{d^2 T}{dx^2} \frac{d\mu}{dx} + a_7 \frac{dT}{dx} \frac{d^2 \mu}{dx^2} + a_8 \frac{d^2 \mu}{dx^2} \frac{d\mu}{dx} + a_9 \frac{d^3 T}{dx^3} + a_{10} \frac{d^3 \mu}{dx^3}, \end{aligned} \quad (4)$$

where σ and α are known electric conductivity and Seebeck coefficients (in the anisotropic case – second-rank tensors), a_k are kinetic coefficients characterizing nonlinear and nonlocal phenomena. The analytical expressions for coefficients a_k for different cases are given in [6, 7].

The first line in Eq. (4) corresponds to a conventional generalized Ohm’s law which in a vector form is given by

$$\vec{j}^{(o)} = \hat{\sigma}\vec{E} - \hat{\sigma}\hat{\alpha}\nabla T, \quad (5)$$

where $\vec{E} = \frac{1}{e}\nabla\mu$ is a generalized intensity of the electric field.

Note that Eq. (4) involves not quadratic, but only cubic combinations of derivatives of temperature and electrochemical potential, and also third, rather than second, derivatives of temperature and electrochemical potential with respect to coordinate. It is due to symmetry requirements, i.e. in a one-dimensional or isotropic case, replacement of temperature gradient direction or electric field intensity should not lead to a change in current density or heat flux value. At the same time, in the case of a sample having no inversion centre an equation of (4) type must also involve quadratic terms. This fact yields a variety of new nonlinear and nonlocal phenomena in the samples having no inversion centre. Even in cubic crystals a variety of new effects can appear [9-11].

Apart from linear and local, Eq. (4) also involves nonlinear and nonlocal terms, i.e. actually we have in (4) an expansion in small parameters. Physically, it means that each of the two lengths, namely characteristic length of temperature change L_T and nonlocality length in temperature L_{Tloc}

$$L_T = T\left(\frac{dT}{dx}\right)^{-1}, \quad L_{Tloc} = T\left(\frac{d^2T}{dx^2}\right)^{-1}, \quad (6)$$

are large as compared to current carrier cooling length L_0 [6-8]

$$L_T \geq L_0, \quad L_{Tloc} \geq L_0. \quad (7)$$

Eq.(4) has been written for a one-dimensional geometry. In a real three-dimensional problem the respective equation must also include summands comprising all, among them cross derivatives with respect to different coordinates (2).

Thus, if characteristic lengths (6) are not very large as compared to charge carrier cooling length, then, as it follows from solving the Boltzmann equation in a one-dimensional model [5-8], Eq. (4) must comprise nonlocal terms. To check the conditions whereby in a real three-dimensional model the nonlinear (nonlocal) phenomena must become apparent, we made a calculation using finite element method of the temperature field for a semiconductor “cone-plate” contact [12] which is often realized in various applied problems.

In the present paper, computer simulation method is used to study possible emergence of nonlocal thermoelectric phenomena in a real three-dimensional geometry. As a geometrical model, “truncated cone-plate” structure is employed (Fig. 1). Such a structure is interesting for the following reasons: 1) it simulates properly real contacts in the bulk nanostructured and composite materials [13]; 2) it describes properly particle contacts for spark plasma sintering method (SPS-method) showing good promise for creation of efficient thermoelectric nanomaterials [14]; 3) such a structure is used in thermoelements “with cold contacts” offering high thermoelectric figure of merit [15].

Let the Joule heat be used for heating “truncated cone-plate” contact, with electric voltage applied between the cone base and the lower part of the plate for electric current generation (Fig. 1).

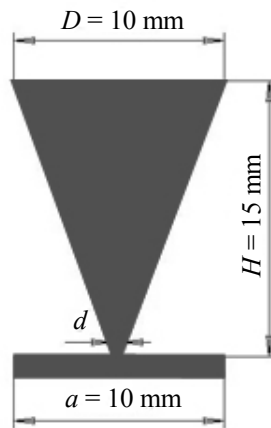


Fig. 1. Model geometry.

The basic equations of the problem include energy balance equation

$$\operatorname{div}(-\kappa \nabla T) = Q \tag{8}$$

and current-continuity equation

$$\operatorname{div}(\sigma \vec{E}) = 0, \tag{9}$$

where Q is heat source power (Joule heat).

The boundary conditions were selected as follows: the lateral surfaces of cone and plate are thermally and electrically isolated, the temperatures of cone base and plate outer face are thermostated at equal temperature T_0 , with constant electric voltage U_0 maintained between them, and cross-linking in temperature and thermal flux made in contact area. The boundary conditions of this kind correspond, for instance, to situation whereby the Benedicks effect arises [6-8].

Comsol Multiphysics software package was used to calculate and visualize the distribution of temperature field and temperature gradient. For certainty, *n-Ge* sample with parameters $k = 60.2 \text{ W/(m}\cdot\text{K)}$, $\sigma = 10 \text{ S/m}$ was considered. Temperature $T_0 = 300 \text{ K}$, voltage U_0 assumed the values: 50, 75, 100, 125 and 130 V. Geometric dimensions $D = 10 \text{ mm}$, $H = 15 \text{ mm}$, $a = 10 \text{ mm}$ were assigned (Fig. 1).

The calculated data are represented in Figs. 2 – 3.

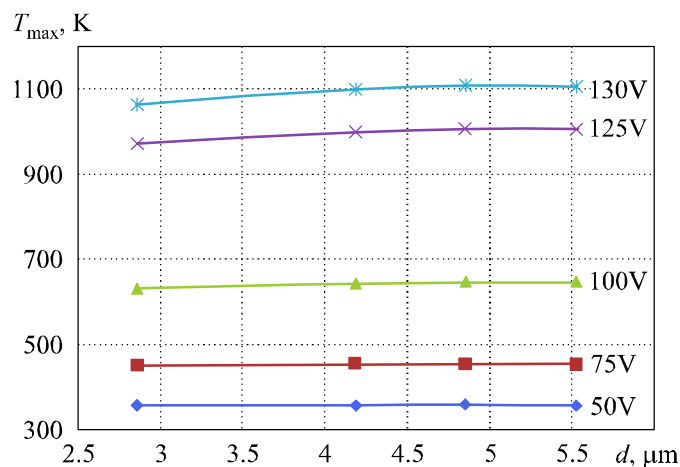


Fig. 2. Dependences of maximum temperature at contact point on contact plane diameter.

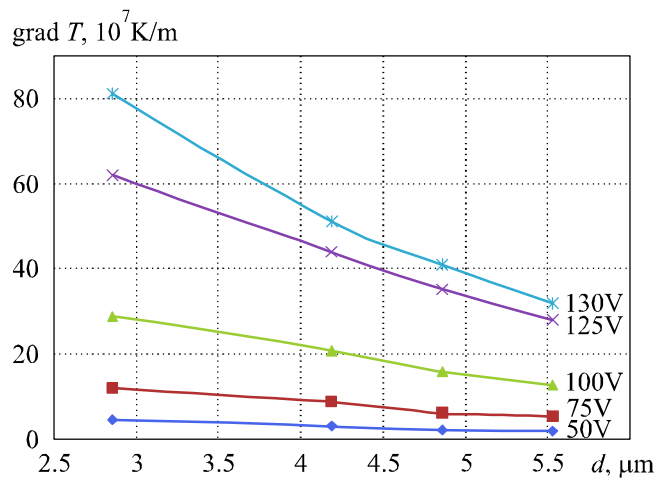


Fig. 3. Dependences of temperature gradient at contact point on contact plane diameter.

Calculations have shown that as long as geometric dimensions D , H and a are large as compared to neck diameter d (Fig. 1), these dimensions have no effect on the temperature field in contact area.

From Fig. 2 it is seen that maximum temperature in contact area is almost independent of neck diameter at a fixed voltage. It increases with voltage, and in this model at a voltage of 130 V maximum contact temperature becomes comparable to germanium melting point ($T_{melt} = 937\text{ }^{\circ}\text{C}$). Naturally, temperature gradient reduces with increase in contact plane diameter and grows with increase in applied voltage (Fig. 3).

Knowing temperature gradient, one can determine characteristic length of its change L_T and temperature nonlocality length L_{Tloc} . These results are represented in Figs. 4 – 5.

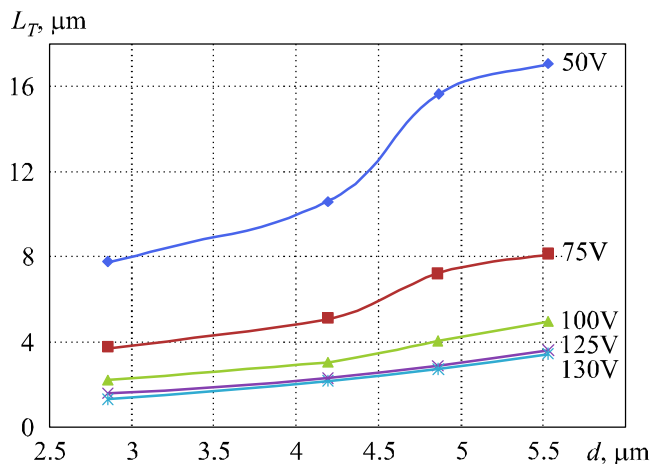


Fig. 4. Dependences of characteristic length of temperature change on contact plane diameter.

From Fig. 4 it is seen that the lowest L_T value in the model under consideration is achieved with a minimum contact diameter $d = 2.8\text{ }\mu\text{m}$ and varies from $1.3\text{ }\mu\text{m}$ to $7.8\text{ }\mu\text{m}$, whereas cooling length for $n\text{-Ge}$ $L_0 = 1.7\text{ }\mu\text{m}$ [8]. It means that cooling length and characteristic length of temperature change are quite comparable. That is, under conditions at hand the processes of heat and electric charge transport become nonlinear. Now, inequality $L_0 \ll L_T$ is not satisfied, and we have no right to use conventional linear transport equations, such as generalized Ohm's and Fourier's laws [12].

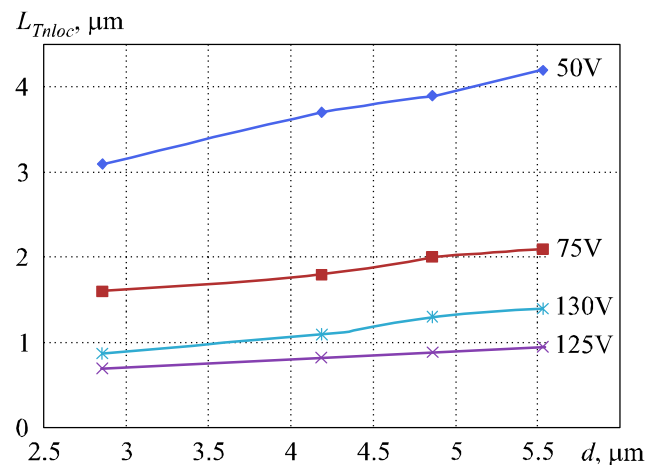


Fig. 5. Dependences of temperature nonlocality length on contact plane diameter.

An important role of nonlocality is illustrated in Fig. 5. We see that minimum values of nonlocality length L_{Tnloc} are also achieved with a minimum contact diameter $d = 2.8 \mu\text{m}$ and make $(0.7 - 0.9) \mu\text{m}$, i.e. 2 – 7 times less than nonlinearity length L_T under the same conditions. Thus, computer simulation proves theoretical conclusions within a one-dimensional model [5-8] that the presence of nonlinear transport phenomena automatically brings about the emergence of nonlocal phenomena and vice versa, the presence of nonlocal summands automatically causes the emergence of nonlinear terms. Moreover, nonlocal phenomena can be even more important, like in the case under consideration, when the following inequality is satisfied

$$L_{Tnloc} < L_T. \tag{10}$$

Inequality (10) means that situations are possible when one can ignore the nonlinear phenomena ($L_o \ll L_T$), but must already take into account the nonlocal effects ($L_{Tnloc} \sim L_T$). In general, in each specific case it is necessary to check the relative role of nonlinear and nonlocal phenomena using, for instance computer simulation.

There is a further point to be made. In the present model we calculated only the temperature field and were not interested in the electric field arising in the sample. In thermoelectric problems, the presence of temperature field brings about the appearance of corresponding electric (thermoelectric) field. And, in general, apart from nonlinearity and nonlocality lengths related to temperature (5), one should consider similar nonlinearity and nonlocality lengths due to electrochemical potential. However, if we restrict ourselves to thermoelectric problems, then in conformity with Seebecks’s formula, characteristic nonlinearity and nonlocality lengths related to temperature and electrochemical potential, respectively, must be of the same order of magnitude [7]. Therefore, for the estimates it is sufficient to be restricted to the above approach. Certainly, for correct calculation of kinetic coefficients with regard to nonlinear and nonlocal phenomena, one should solve a self-consistent system of equations comprising energy balance equation and current-continuity equation with regard to the Seebeck and Peltier effects.

Mesoscopic and nanostructures are known to be promising thermoelectric materials. In such materials, the size of inhomogeneities (for instance, nanograins) can become comparable not only to characteristic length of temperature change, but also to nonlocality length. The effect of nonlocal phenomena on heat and electrotransport in semiconductor nanostructures has not been studied so far.

References

1. B.V. Alexeev, *Generalized Boltzmann Physical Kinetics* (Elsevier: 2004), 368 p.
2. B.V. Alexeev, Generalized Quantum Hydrodynamics and Principles of Non-Local Physics, *J. Nanoelectronics and Optoelectronics* **3** (2), 143 – 158 (2008).
3. B.V. Alexeev, Solution of the Dark Matter Problem in the Frame of the Non-Local Physics, *arXiv:1007.2800*, 2012
4. A.G. Samoilovich, *Thermoelectric and Thermomagnetic Methods of Energy Conversion* (compendium of lectures) (Chernivtsi: 2006), 227 p.
5. L.P. Bulat, Effect of Temperature Gradient on Electron Distribution Function in Semiconductors, *Semiconductors* **7** (11), 2181 – 2186 (1977).
6. L.P. Bulat, Thermoelectricity under Large Temperature Gradients, *J. Thermoelectricity* **4**, 3 – 34 (1997).
7. L.I. Anatyshuk, L.P. Bulat, *Semiconductors under Extreme Temperature Conditions* (Saint-Petersburg: Nauka, 2001), 224 p.
8. L.I. Anatyshuk, L.P. Bulat, Thermoelectric Phenomena under Large Temperature Gradients. In “*Thermoelectrics Handbook: Macro to Nano-Structured Materials*”. Ed. by D.M. Rowe. CRC Press, 2006, Chapter 3.
9. L.P. Bulat, E.I. Demchishin, Sasaki Phenomenon Thermoelectric Analogue and its Application to Thin Film Sensors, *Int. J. Electronics* **73** (5), 881-882 (1992).
10. L.P. Bulat, E.I. Demchishin, New Nonlinear Thermomagnetic Effects in Films and Sensors Based on These Effects, *Int. J. Electronics* **76** (5), 805-808 (1994).
11. L.I. Anatyshuk, L.P. Bulat, New Nonlinear Thermoelectric, Heat-Conducting and Thermomagnetic Effects and their Classification, *J. Thermoelectricity* **1**, 41 – 55 (1998).
12. L.P. Bulat, I.A. Nefedova, On the Linear Thermoelectric Effects, *Bulletin of the International Academy of Refrigeration* **6**, 54-56 (2012).
13. L.P. Bulat, D.A. Pshenai-Severin, Tunneling Effect on Thermoelectric Figure of Merit of Bulk Nanostructured Materials, *Physics of the Solid State* **52** (3), 452 – 458 (2010).
14. L.P. Bulat, I.A. Drabkin, V.V. Karatayev, V.B. Osvenskii, Yu.N. Parkhomenko, M.G. Lavrentev, A.I. Sorokin, D.A. Pshenai-Severin, V.D. Blank, G.I. Pivovarov, V.T. Bublik, N.Yu. Tabachkova, Structure and Transport Properties of Bulk Nano-Thermoelectrics Based on $Bi_xSb_{2-x}Te_3$ Fabricated by SPS Method, *J. Electronic Materials*, 2013 (in press).
15. U. Ghoshal, S. Ghoshal, C. McDowell and L. Shi, Enhanced Thermoelectric Cooling at Cold Junction Interfaces, *Appl. Phys. Letters* **80** (16), 3006 – 3008 (2002).

Submitted 05.03.2013.