# **EFFECTIVE THERMAL CONDUCTIVITY AND DIFFUSIVITY IN HETEROGENEOUS MATERIALS**

# Štefan Barta

Department of Physics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, SK-812 19 Bratislava, Slovakia Email: bartas@elf.stuba.sk

# Abstract

The effective heat equation and the formula for the dynamic effective thermal conductivity and diffusivity and the dynamic effective heat capacity of the unit volume in heterogeneous materials are derived.

Key words: stationary effective thermal conductivity, dynamic effective thermal conductivity, dynamic effective heat capacity, equilibrium effective heat capacity

# **1** Introduction

The paper is intended to interprete the effective thermal conductivity and diffusivity in heterogeneous materials. In the connection with the derivation of the heat equation in heterogeneous materials we stated that the effective thermal conductivity measured by a nonstationary method is different from that one measured by a stationary method. Similarly the effective heat capacity of the unit volume measured in an nonequilibrium state is different from that one measured in a equilibrium state. This fact may be a motivation for experimentalists to prove that. The detailed derivation of the heat equation describring the process of heat transport in heterogeneous materials will be published presently. In this paper we will use some theoretical results because the aim of this paper is to describe qualitativity the characteristic features of heat transport in heterogeneous materials.

Heterogeneous material will be considered as the material consisting of the isotropic grains (granules) of different materials. Among these materials there may be also liquid or gaseous material (porous material). The typical representative materials of heterogeneous materials are composite or porous materials. The shape of grains is approximately of the globular form. The grains of the same material will be called a component. All grains of different materials are randomly distributed over the whole sample (random material). Due to this randomness the physical quantities of heterogeneous materials on the submacroscopic level (on the length scale of linear dimension of grains) are not only dependent on space coordinates but they are also random quantities. In the ideal case the physical parameters change discontinuously between the neighbour grains of different materials. But in the real case there is a very thin interlayer in which the physical parameters change continuously between two values of the neighbouring grains belonging to different materials. So we can assume that the physical parameters are a continuous function of the space coordinates.

Therefore, the heat equation of heterogeneous materials on the submacroscopic level reads

$$\gamma(\vec{r})\frac{\partial T}{\partial t} = \nabla\lambda(\vec{r})\nabla T \tag{1}$$

where  $\gamma(\vec{r}) = \rho(\vec{r})c_p(\vec{r})$  is the heat capacity of unit volume,  $\rho(\vec{r})$  is the density,  $c_p(\vec{r})$  is the specific heat capacity at the constant pressure,  $\lambda(\vec{r})$  is thermal conductivity, T is the thermodynamic temperature. The use of phenomenological equation (1) is justified only in he case when the linear dimensions of grains are much larger than the mean free path of carriers which participate on the transport of mass, energy and charge. But on the other hand they have to be much smaller with respect to macroscopic linear dimensions The parameters as  $\gamma(\vec{r}), \rho(\vec{r})$  and  $\lambda(\vec{r})$  characterize the material on the submacroscopic level. However heterogeneous materials on the macroscopic level usually are homogeneous and isotropic, therefore, the physical parameters of heterogeneous materials on the macroscopic level are independent on the space coordinates and they will be called *effective parameters*. The experimentalists suppose that the effective thermophysical parameters can be measured by using the standard stationary or nonstationary methods. Generally such assumption is not correct. The necessary and sufficient conditions for using effective parameters in stationary regime are discussed in Beran's work [1]. All standard stationary or nonstationary methods are based on the solution of the heat equation at the given initial and boundary conditions. These methods can be correctly used only in the case of homogeneous materials. The question arises what is that what one measures if the standard methods are used in the case of heterogeneous materials. For this reason it is necessary to give the interpretation of the effective thermophysical parameters. At first we notice how experimentalist measures the temperature in the case of heterogeneous materials. For example if one measures the temperature by a thermocouple which planary dimensions are  $0.1 \times 0.1 \text{ mm}^2$ . The planary dimensions of the grain are  $1 \times 1 \mu \text{m}^2$ , then the number of grains which are covered by the thermocouple is10<sup>4</sup>. From this fact it follows that the thermocouple measures the average temperature  $\langle T \rangle$  of the 10<sup>4</sup> grains. Similarly the experimentalist measures the average heat current density  $\langle \vec{q} \rangle$  which flows trough the  $10^4$  grains.

If the application of the standard methods for measuring the effective thermophysical parameters is justified then the Fourier's law in the case of heterogeneous materials has the following form

$$\langle \vec{q} \rangle = -\lambda_{eff}^d \nabla \langle T \rangle \tag{2}$$

where  $\lambda_{eff}^{d}$  is the dynamic effective thermal conductivity, which is measured by the nonstationary standard method. In the case of the stationary standard method the Fourier's law can be written in the form

$$\langle \vec{q} \rangle = -\lambda_{eff}^{st} \nabla \langle T \rangle \tag{3}$$

where  $\lambda_{e\!f\!f}^{st}$  is the stationary effective thermal conductivity. The heat equation reads

$$\gamma_{eff}^{d} \frac{\partial \langle T \rangle}{\partial t} = \lambda_{eff}^{d} \Delta \langle T \rangle \tag{4}$$

where  $\gamma_{eff}^{d}$  is the dynamic effective heat capacity of the unit volume. Relations (2), (3) and (4) will be derived later on. The parameter  $\gamma_{eff}^{d}$ , as opposed to the equilibrium heat

capacity of the unit volume  $\gamma_{eff}^{eq}$ , is the transport coefficient similarly as the  $\lambda_{eff}^{d}$ . According to the mixing rule we can write

$$\gamma_{eff}^{eq} = \langle \gamma(\vec{r}) \rangle = \sum_{i=1}^{n} c_i \rho_i c_{pi}$$
<sup>(5)</sup>

where  $c_i \frac{V_i}{V}$  is the volume fraction of the  $i^{th}$ -component,  $c_{pi}$  is the specific heat capacity at the constant pressure of the  $i^{th}$ -component,  $\rho_i$  is the density of the  $i^{th}$ component,  $V_i$  is the volume of the  $i^{th}$ -component, V is the total volume. Generally the statistics of the structure of heterogeneous material on the submacroscopic level is very often unknown and only the volume fractions may be known from the manufacturing process. If the heterogeneous material on the macroscopic level is a homogeneous one it is possible to use the Assumption: The probability of the occupation of the certain place with the grain of the  $i^{th}$ -component is equal to its volume fraction  $c_i$ .

# 2 Theory

#### 2.1 Nonstationary case

One of the aims of this paper is to derive the effective heat equation and the relations for the dynamic and stationary effective thermal conductivity and for dynamic effective heat capacity of the unit volume. These relations are very important especially for technologists. Knowing the relations for effective parameters, it is possible to produce composite materials with the prescribed values of the parameters (materal "tailoring").

For the above-mentioned aims it is necessary at first to solve stochastic equation (1). To the purpose of solving equation (1) we apply the Laplace's transformation on equations (1) and (4):

$$p\tilde{T} - T(\vec{r}, 0) = \nabla a(\vec{r}) \cdot \nabla \tilde{T} + \frac{\nabla \gamma(\vec{r})}{\gamma(\vec{r})} a(\vec{r}) \cdot \nabla \tilde{T}$$
(6)

and

$$p\tilde{T}_{p} - T(\vec{r}, 0) = a_{p}\Delta\tilde{T}_{p}$$
<sup>(7)</sup>

where  $a(\vec{r}) = \frac{\lambda(\vec{r})}{\gamma(\vec{r})}$  is the thermal diffusivity,  $a_p = \frac{\lambda_p}{\gamma_p^d}$  is the dynamic effective

diffusivity,  $\tilde{T}_p = \frac{\langle \tilde{T} \rangle}{f}$ ,  $\gamma_p^d = f \gamma_{eff}^d$ ,  $\lambda_p^d = f \lambda_{eff}^d$ , f is the free parameter independent on time-space coordinates. It will be determined later on. After some complicated calculation one obtains

$$\nabla \widetilde{T} = \frac{1}{1 + g \frac{\beta(\vec{r})a(\vec{r}) - a_p}{a_p}} \nabla \widetilde{T}_p$$
(8)

and

$$\widetilde{T} = \frac{1}{1+g} \frac{\beta(\vec{r})a(\vec{r})-a_p}{a_p} \widetilde{T}_p$$
(9)

The detailed calculations will be published presently. Using the reverse transformation in relation (8) and (9) then one can write

$$\nabla T = \frac{1}{1 + g \frac{\beta(\vec{r})a(\vec{r}) - a_p}{a_p}} \nabla T_p$$
(10)

and

$$T = \frac{1}{1+g} \frac{\beta(\vec{r})a(\vec{r}) - a_p}{a_p} T_p$$
(11)

Relations (8) and (9) are approximately valid in the case of weakly heterogeneity. With the help of relation (10) we can calculate the heat current density

$$\vec{q} = -\lambda(\vec{r})\nabla T = -\frac{\lambda(\vec{r})}{1+g}\frac{\beta(\vec{r})a(\vec{r})-a_p}{a_p}\nabla T_p = -\lambda_p^d \nabla T_p$$
(12)

After averaging relation (12) one obtains

$$\langle \vec{q} \rangle = -\langle \frac{\lambda(\vec{r})}{1 + g \frac{\beta(\vec{r})a(\vec{r}) - a_p}{a_p}} \rangle \nabla T_p = -\lambda_p^d \nabla T_p = -\lambda_{eff}^d \nabla \langle T \rangle$$
(13)

where

$$\lambda_{eff}^{d} = \left\langle \frac{\lambda(\vec{r})}{1 + g \frac{\beta(\vec{r})a(\vec{r}) - a_{p}}{a_{p}}} \right\rangle \frac{1}{\left\langle \frac{1}{1 + g \frac{\beta(\vec{r})a(\vec{r}) - a_{p}}{a_{p}}} \right\rangle}$$
(14)

is the dynamic effective thermal conductivity. In relation (13) we used average relation (10). Further it can be shown using relation (11) the following relation

$$\langle \gamma(\vec{r}) \frac{\partial T}{\partial t} \rangle = \gamma_{eff}^{d} \frac{\partial \langle T \rangle}{\partial t}$$
(15)

where

$$\gamma_{eff}^{d} = \left\langle \frac{\gamma(\vec{r}\,)}{1+g\,\frac{\beta(\vec{r}\,)a(\vec{r}\,)-a_{p}}{a_{p}}} \right\rangle \frac{1}{\left\langle \frac{1}{1+g\,\frac{\beta(\vec{r}\,)a(\vec{r}\,)-a_{p}}{a_{p}}} \right\rangle} \tag{16}$$

is the dynamic effective heat capacity of the unit volume. The dynamic effective thermal diffusivity is expressed by the relation

$$a_{p} = \frac{\lambda_{p}^{d}}{\gamma_{p}^{d}} = \frac{f\lambda_{p}^{d}}{f\gamma_{p}^{d}} = \frac{\lambda_{eff}^{d}}{\gamma_{eff}^{d}}.$$
 Considering relations (14) and (16) one can write

$$\langle \frac{\gamma(\vec{r})}{1+g} \frac{\beta(\vec{r})a(\vec{r})-a_p}{a_p} \rangle a_p = \langle \frac{\lambda(\vec{r})}{1+g} \frac{\beta(\vec{r})a(\vec{r})-a_p}{a_p} \rangle$$
(17)

From equation (17) we calculate the  $a_p$  and introduce it into relation (14) and (16) and in this way we can calculate the  $\lambda_{eff}^d$  and  $\gamma_{eff}^d$ . As it was alredy mentioned if the heterogeneous material on the macroscopic level is a homogeneous one the effective parameters are independent on space coordinates. Averaging equation (1) one obtains

$$\langle \gamma(\vec{r}) \frac{\partial T}{\partial t} \rangle = \nabla \langle \lambda(\vec{r}) \nabla T \rangle \tag{18}$$

Introducing relations (13) and (15) into equation (18) we obtain equation (4). In this way equation (4) is justified.

#### 2.2 Stationary case

In the stationary case the heat equation according to equations (1) and (4) has the form

$$\nabla \lambda(\vec{r}) \nabla T = 0 \text{ and } \Delta T_p = 0 \tag{19}$$

It can be shown, after some calculations [2] and [3], that the solution of equations (19) is expressed in the form

$$\nabla \boldsymbol{T} = \frac{1}{1 + \boldsymbol{g} \frac{\boldsymbol{\lambda}(\vec{\boldsymbol{r}}) - \boldsymbol{\lambda}_{eff}^{st}}{\boldsymbol{\lambda}_{eff}^{st}}} \nabla \boldsymbol{T}_{p}$$
(20)

With the help of equation (20) one can write

$$\vec{q} = -\frac{\lambda(\vec{r})}{1 + g \frac{\lambda(\vec{r}) - \lambda_{eff}^{st}}{\lambda_{eff}^{st}}} \nabla T_p$$
(21)

Averaging relation (21) one obtains

$$\langle \vec{q} \rangle = -\langle \frac{\lambda(\vec{r}\,)}{1 + g \, \frac{\lambda(\vec{r}\,) - \lambda_{eff}^{st}}{\lambda_{eff}^{st}}} \rangle \nabla T_p = -\lambda_{eff}^{st} \, \nabla \langle T \rangle$$
(22)

where

$$\lambda_{eff}^{st} = \left\langle \frac{\lambda(\vec{r})}{1 + g \frac{\lambda(\vec{r}) - \lambda_{eff}^{st}}{\lambda_{eff}^{st}}} \right\rangle \frac{1}{\left\langle 1 + g \frac{\lambda(\vec{r}) - \lambda_{eff}^{st}}{\lambda_{eff}^{st}} \right\rangle}$$
(23)

is the stationary effective thermal conductivity. In relation (22) we used averaged relation (20). Relation (23) can be written in the following form

$$\langle \frac{\lambda(\vec{r}) - \lambda_{eff}^{st}}{1 + g \frac{\lambda(\vec{r}) - \lambda_{eff}^{st}}{\lambda_{eff}^{st}}} \rangle = 0$$
(24)

From equation (24) one can calculate the  $\lambda_{eff}^{st}$ .

#### **3 Binary system**

#### 3.1 Stationary case

For the binary system relation (24) is expressed in the form

$$c_{1} \frac{\lambda_{1} - \lambda_{eff}^{st}}{1 + g \frac{\lambda_{1} - \lambda_{eff}^{st}}{\lambda_{eff}^{st}}} + c_{2} \frac{\lambda_{2} - \lambda_{eff}^{st}}{1 + g \frac{\lambda_{2} - \lambda_{eff}^{st}}{\lambda_{eff}^{st}}} = 0$$
(25)

From equation (25) we can calculate the  $\lambda_{eff}^{st}$ :

$$\boldsymbol{\lambda}_{eff}^{st} = \frac{\boldsymbol{c}_1(\boldsymbol{\lambda}_1 - \boldsymbol{\lambda}_2) + (1 - \boldsymbol{g})\boldsymbol{\lambda}_2 - \boldsymbol{g}\boldsymbol{\lambda}_1}{2(1 - \boldsymbol{g})} + \sqrt{\left[\frac{\boldsymbol{c}_1(\boldsymbol{\lambda}_1 - \boldsymbol{\lambda}_2) + (1 - \boldsymbol{g})\boldsymbol{\lambda}_2 - \boldsymbol{g}\boldsymbol{\lambda}_1}{2(1 - \boldsymbol{g})}\right]^2 + \frac{\boldsymbol{g}}{1 - \boldsymbol{g}}\boldsymbol{\lambda}_1\boldsymbol{\lambda}_2}$$
(26)

In relation (26) we used the relation  $c_1 + c_2 = 1$ . The solution of equation (25) can be analyzed in two limiting cases:

•  $\lambda_2 = 0$ , then the solution of equation (25) is the following:

If 
$$\boldsymbol{c}_1 \leq \boldsymbol{g}$$
, then  $\lambda_{eff}^{st} = 0$  (27)

If 
$$\boldsymbol{c}_1 > \boldsymbol{g}$$
, then  $\lambda_{eff}^{st} = \frac{\boldsymbol{\kappa}_1}{1-\boldsymbol{g}} (\boldsymbol{c}_1 - \boldsymbol{c}_{1k})$  (28)

Where  $c_{1k} = g$  is the critical volume fraction (percolation threshold). For  $c_1 < c_{1k}$  the grains of the first component form clusters which are separated from each other and, therefore, a sample is thermally non-conducting ( $\lambda_{eff}^{st} = 0$ ). At  $c_1 = c_{1k} = g$  some clusters connect themselves together and form a percolation cluster, which is spread out through the whole sample. From this moment  $\lambda_{eff}^{st}$  is increasing with the volume fraction  $c_1$  (relation (28)). This effect is called a percolation and at the  $c_1 = c_{1k}$  the percolation phase transition takes place.

•  $\lambda_1 = 0$ , then the solution of equation (25) is the following:

If 
$$\boldsymbol{c}_2 \leq \boldsymbol{g}$$
, then  $\lambda_{eff}^{st} = 0$  (29)

If 
$$\boldsymbol{c}_2 > \boldsymbol{g}$$
, then  $\lambda_{ef}^{st} = \frac{\lambda_2}{1-\boldsymbol{g}} (\boldsymbol{c}_2 - \boldsymbol{c}_{2k})$  (30)

Where  $c_{2k} = g$  is the percolation threshold. These results may be interpreted by the similar way as in the case  $\lambda_2 = 0$ .

### 3.2 Nonstationary case

For binary system equation (17) can be expressed in the following form

$$\langle c_1 \frac{\gamma_1}{1+g \frac{\beta_1 a_1 - a_p}{a_p}} + c_2 \frac{\gamma_2}{1+g \frac{\beta_2 a_2 - a_p}{a_p}} \rangle a_p = c_1 \frac{\lambda_1}{1+g \frac{\beta_1 a_1 - a_p}{a_p}} + c_2 \frac{\lambda_2}{1+g \frac{\beta_2 a_2 - a_p}{a_p}}$$
(31)

From equation (31) one can calculate the  $a_p$ . Until now the parameters  $\{\beta_i\}$  were considered as the free parameters. Now we determine them according to the percolation process:

• Let us consider the case when  $\lambda_2 = 0$ , then equation (31) after some arrangement has the form

$$a_{p}\left\{a_{p}-\frac{\lambda_{1}}{\gamma_{1}(1-g)}\frac{c_{1}\left[(1-g)\gamma_{1}+g\gamma_{2}\beta_{1}\right]-g\gamma_{2}\beta_{1}}{c_{1}\gamma_{1}+c_{2}\gamma_{2}}\right\}=0$$
We put
$$(32)$$

We put

$$\beta_1 = \frac{\gamma_1}{\gamma_2},\tag{33}$$

then equation (32) will be similar to the equation for  $\lambda_{eff}^{st}$ . Because  $a_p > 0$ , then the solution of equation (32) is the following:

If 
$$c_1 \leq g$$
, then  $a_p = 0$ . If  $c_1 > g$ , then  $a_p = \frac{\lambda_1}{(1-g)(c_1\gamma_1 + c_2\gamma_2)}(c_1 - g)$ .

It can be shown that the dynamical effective heat capacity of the unit volume, in the case when the  $\lambda_2 = 0$ , is non-zero in the whole interval of the  $c_1$  and, therefore, for the  $a_p = 0$  the  $\lambda_{eff}^d = 0$ .

• Let us consider the case when  $\lambda_1 = 0$ . If we will proceed in a similar way as in the case  $\lambda_2 = 0$ , we come to the equation

$$a_{p}\left\{a_{p}-\frac{\lambda_{2}}{\gamma_{2}(1-g)}\frac{c_{2}\left[(1-g)\gamma_{2}+g\gamma_{1}\beta_{2}\right]-g\gamma_{1}\beta_{2}}{c_{1}\gamma_{1}+c_{2}\gamma_{2}}\right\}=0$$
(34)

We put

$$\beta_2 = \frac{\gamma_2}{\gamma_1},\tag{35}$$

then equation (34) has the following solution

If 
$$c_2 \leq g$$
, then  $a_p = 0$ . If  $c_2 > g$ , then  $a_p = \frac{\lambda_2}{(1-g)(c_1\gamma_1 + c_2\gamma_2)}(c_2 - g)$ .

Again we can state that the dynamical heat capacity of the unit volume, in the case of  $\lambda_1 = 0$ , is nonzero in the whole interval of  $c_2$  and, therefore, for  $a_p = 0$ , the  $\lambda_{eff}^d = 0$ .

# **4** Conclusion

In the conclusion we summarize all theoretical results: From the equation (31) we can calculate the  $a_p$ 

$$a_{p} = \frac{d}{2} + \sqrt{\frac{d^{2}}{4} + e}$$
where
(36)

$$d = \frac{c_1\lambda_1 + c_2\lambda_2 - g(\lambda_1 + \lambda_2)}{(1-g)(c_1\beta\gamma_1 + c_2\gamma_2)}, \text{ and } e = \frac{g}{1-g}\frac{\lambda_1\lambda_2}{\gamma_1\gamma_2}\frac{c_1\gamma_2 + c_2\gamma_1}{c_1\gamma_1 + c_2\gamma_2}$$

The dynamical effective thermal conductity: From relations (14), (33) and (35) it can be written:

$$\lambda_{eff}^{d} = \frac{c_{1} \frac{\lambda_{1}}{(1-g)a_{p} + g\gamma_{2}\lambda_{1}} + c_{2} \frac{\lambda_{2}}{(1-g)a_{p} + g\gamma_{1}\lambda_{2}}}{c_{1} \frac{1}{(1-g)a_{p} + g\gamma_{2}\lambda_{1}} + c_{2} \frac{1}{(1-g)a_{p} + g\gamma_{1}\lambda_{2}}}$$
(37)

The dynamical effective heat capacity of the unit volume: From relations (16), (33) and (35) it can be written:

$$\gamma_{eff}^{d} = \frac{c_{1} \frac{\gamma_{1}}{(1-g)a_{p} + g\gamma_{2}\lambda_{1}} + c_{2} \frac{\gamma_{2}}{(1-g)a_{p} + g\gamma_{1}\lambda_{2}}}{c_{1} \frac{1}{(1-g)a_{p} + g\gamma_{2}\lambda_{1}} + c_{2} \frac{1}{(1-g)a_{p} + g\gamma_{1}\lambda_{2}}}$$
(38)

Comparing relations (26) and (37) we come to conclusion that  $\lambda_{eff}^d \neq \lambda_{eff}^{st}$ . From relation (38) it is obvious that  $\gamma_{eff}^d \neq \gamma_{eff}^{eq}$ , where

$$\gamma_{eff}^{eq} = \sum_{i=1}^{n} c_i \rho_i c_{pi}, \qquad (39)$$

where n is the number of components.

## Acknowledgement

Authors wish to thank the Slovak Science Grant Agency for the financial support under the contract 8304/01.

# References

- Beran M.J, 1974 Application of Statistical Theories for the Determination of Thermal, Electrical and Magnetic Properties of Heterogeneous Materials. In *Composite Materials, Vol.2* (New York, Academic Press) p.209.
- [2] Barta Š, Dieška P, 2002 Effective Thermal Conductivity of Particulate Composite Materials, *Metallic Materials*, **40**, 2002, p.99.
- [3] Barta Š, Dieška P, 2002 Effective Thermal Conductivity of Fibrous Composite Materials, *Metallic Materials*, **41**, 2003, p.223.