The minimum entropy production principle and heat transport in solids with internal structure.

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Abstract: Much has been discussed whether the minimum entropy production principle (MEPP), has general application or whether it is of rather limited validity. In particular, it has been concluded that for systems with constant phenomenological Onsager coefficients the entropy production can only decrease in time until a minimum is reached when the system is in the stationary state, but this is still under debate. In this work heat transport in solids with internal structure within the framework of a two temperature description. The time evolution equations for such system are derived through the usual methods of irreversible thermodynamics and also from the MEPP. We find that both sets of stationary equations coincide without imposing any restriction on the phenomenological coefficients other than those coming from the internal structuring of the solid. We exemplify this finding with the case of pure Aluminum subjected to a heat pulse.

Heat conduction process and MEPP

Differential equations describing the heat conduction process are derived from the first law of thermodynamics and the Fourier's law, namely

$$\rho c \frac{\partial T}{\partial t} + \nabla \cdot q = 0 , \qquad q = L_{qq} \nabla \frac{1}{T}, \qquad (1)$$

and from the principle of minimum entropy production

$$\delta \int \sigma \, dV = 0 , \qquad \sigma = q \cdot \nabla \frac{1}{T} \qquad (2)$$

$$\sigma_T - \frac{d\sigma_{T'}}{dx} = 0. \qquad (3)$$

- First observation

According to de Groot and Mazur [1] affirmed : "Stationary non equilibrium states have the important property that under certain conditions, they are characterized by a minimum entropy production, compatible with the external constrains imposed on the system. This property is valid only if the phenomenological coefficients are supposed to be constants."

The principal assumption is $L_{qq} = cte$. Then, the equation of energy conservation in the stationary state is at grips with the solution of the variational problem, namely

$$T\nabla^2 T - 2(\nabla T)^2 = 0 \qquad (4)$$

Since the principal assumption is so restricting on systems, it has been tempting to think that stationary state for real heat conduction systems, from variational principle, may be achieved by the dependence of the phenomenological coefficients.

- Second observation

Assuming that the phenomenological coefficients depends on temperature, $L_{qq} = L_{qq}(T)$, from the energy conservation in the stationary state one gets

$$2L_{qq}(T)(\nabla T)^2 - T(\nabla T)^2 \nabla L_{qq}(T) - L_{qq}(T)T\nabla^2 T = 0 \qquad (5)$$

On the othe hand, from the MEPP the result is

$$2L_{qq}(T)(\nabla T)^2 - \frac{1}{2}T(\nabla T)^2 \nabla L_{qq}(T) - L_{qq}(T)T\nabla^2 T = 0 \qquad (6)$$

There is a little difference in the coefficient of the second term which comes from the temperature dependence of the Onsager coefficient. In this case the energy balance equation and the Mepp do not yield the same result.

- Third observation

An alternative assumption is that the Onsager coefficient depends on position , $L_{qq} = L_{qq}(x)$, which means that the system of interest is an inhomogeneous material. In this case we get the same temperature distribution from two different ways, the MEPP and the energy conservation equation.

$$2L_{qq}(x)(\nabla T)^2 - T(\nabla T)\nabla L_{qq}(x) - L_{qq}(x)T\nabla^2 T = 0 \qquad (7)$$

Two temperature model

The two temperature model is a proposal to explain no-Fourier heat transport in a rigid solid where the main assumption is to consider that this behaviour is due to the consideration of non-homogeneous materials.

The system consists of a rigid heat conducting solid with an internal structure in which two coupled irreversible processes take place: on the one hand, processes that occur at a macroscopic length scale, that is at a length scale of the same order of magnitude as the characteristic length of the system itself L; on the other hand, processes that occur at a length scale of the same order of magnitude as the characteristic length of the internal structure. The starting assumption is that the total internal energy of the system can be divided into two parts, each one corresponding to the above two dissipative processes, $u_T = u_M + u_m$, where u stands for the internal energy and the labels T, M and m denote total, macroscopic and microscopic processes, respectively. Defining two quasi-temperatures through the known caloric relation, u=CT with C the heat capacity at constant volume, we have the following

$$T_M = \frac{u_M}{c_M} \qquad and \qquad T_m = \frac{u_m}{c_m} \qquad (8)$$

The macro-temperature, T_M, is an average temperature that describes the processes that occur in the bulk and the micro-temperature, T_m, describes the changes that frequently and slightly separate the system from the average temporal evolution due to the emergence of effects originating from the microstructure. Assuming that the thermodynamic space of variables is constituted by the internal energies u_M and u_m in such a way that the entropy is a function of them, the equations for the entropy production and the dissipative fluxes read, respectively, as

$$\sigma = -\frac{1}{T_M}\left(q_M \frac{\frac{\partial T_M}{\partial x}}{T_M}\right) - \frac{1}{T_m}\left(q_m \frac{\frac{\partial T_m}{\partial x}}{T_m}\right) \qquad (9)$$

$$-q_M = L_{11}\frac{\frac{\partial T_M}{\partial x}}{T_M^2} + L_{12}\frac{\frac{\partial T_m}{\partial x}}{T_m^2} \; ; \; -q_m = L_{21}\frac{\frac{\partial T_M}{\partial x}}{T_M^2} + L_{22}\frac{\frac{\partial T_m}{\partial x}}{T_m^2}$$

where $L_{ij}(x)$ are phenomenological coefficients. The comparison of the two temperature model for structured solids (aluminum, meat, and foam like structures) with experimental results has shown that the model reproduces well the non-Fourier behavior in two cases, non-equilibrium states which do not satisfy the Onsager reciprocity relations and also states satisfying the Onsager relations. The results obtained also reveal that the non-Fourier behavior of the structured material comes from the influence of the microtemperature which contains the information of the microstructure and that the Fourier description of heat transport is blind to the details of the microstructure [2]. More over, the profile of the entropy production for different times in the case of pure Aluminum can be seen in Figure (1). We note that the region near the thermally excited boundary ($x = L$) is where more entropy is being produced. Also we observe that the entropy production for the early stages of the time evolution is greater than that for later times as the system approaches the stationary state. This suggests that the stationary state will obey a minimum entropy production principle as shown bellow.
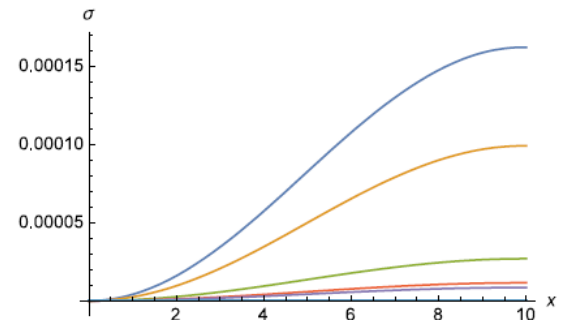

Figure 1. Entropy production profile at different times for pure Aluminum. Blue: 100, Orange: 120, Green: 150, Red: 180, Purple:220.

If the variational principle is applied to this model, we find the amazing fact that energy balance equation and MEPP yield the same result.

$$L_{11}\left(-2\frac{(\nabla T_M)^2}{T_M^3} + \frac{\nabla^2 T_M}{T_M^2}\right) + \frac{\nabla T_M}{T_M^2}\nabla L_{11}$$
$$+ L_{12}\left(-2\frac{(\nabla T_m)^2}{T_m^3} + \frac{\nabla^2 T_m}{T_m^2}\right) + \frac{\nabla T_m}{T_m^2}\nabla L_{12} = 0 \qquad (10)$$

$$L_{21}\left(-2\frac{(\nabla T_M)^2}{T_M^3} + \frac{\nabla^2 T_M}{T_M^2}\right) + \frac{\nabla T_M}{T_M^2}\nabla L_{21}$$
$$+ L_{22}\left(-2\frac{(\nabla T_m)^2}{T_m^3} + \frac{\nabla^2 T_m}{T_m^2}\right) + \frac{\nabla T_m}{T_m^2}\nabla L_{22} = 0 \qquad (11)$$

Conclusions

As can be seen, the transport equations obtained from the energy balance equation and the variational principle coincide if the transport coefficients depend directly on the position, $L_{ij} = L_{ij}(x)$. This means that the microstructure of materials plays an indispensable role in the transport of energy and therefore in the entropy production, making the latter a minimum.

Refereces
[1] S.R de Groot and P. Mazur, **Non-Equilibrium Thermodynamics**, Dover Publications Inc. New York.
[2] R.E Gonzalez-Narvaez, M. López de Haro, and F. Vázquez, **Internal structure and heat conduction in rigid solids: a two temperature approach,** J. Non-Equilib. Thermodyn. 2021. On revisión.