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Minimum entropy production and approximate analytical solutions for transport processes in heterogeneous media

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Abstract:

The Prigogine's Principle of minimum entropy production (PMEP) [1,2], has been rejected as a principle because at the beginning, it just worked with constant phenomenological coefficient materials in heat transport (which do not exist even when the material is pure). However, in the classical irreversible thermodynamics (CIT), it has been proved its wider validity, that is, the PMEP is fulfilled for heterogeneous materials (with position dependence of phenomenological coefficients) for heat transport and thermoelectric effects. So, for the named transport processes performance, near equilibrium, are with minimum entropy production. In this work we show that diffusion is a minimum entropy production transport process too. Moreover, we present different methods to get and to approximate analytical solutions to the transport equations for heterogeneous materials to compute the profiles of the phenomenon. We hope to see the influence of the non-homogeneity in the transport process.

Keywords:

Classical Irreversible Thermodynamics; Entropy production; Near equilibrium; Transport process.

1. Introduction

The variational principle has a long history of success in several physics areas. The most known are Hamilton's principle in Classical Mechanics, principle of least action in Mechanics, Electromagnetic Theory and Quantum Mechanics, Hilbert's action principle in General Relativity and so on. However, the variational principle, as the Prigogine's Principle of Minimum Entropy Production (PMEP) has a different story in Thermodynamics. That is, the scientific community has engaged into a heated and continuous discussion on whether PMEP for the description of stationary states out of equilibrium has general application or it is rather of limited validity[1,3-12]. However, what everyone agrees on is that the stationary states of systems with constant phenomenological coefficients are states with a minimum entropy production [2].

In this work we present a little summary to expose the previous efforts on the PMEP. That is, the range of validity of the PMEP may be expanded by showing that the stationary states of externally constrained solids with internal structure have a minimum global entropy production in two cases, namely, heat transport and thermoelectric effect. The equations obeyed in the stationary states as obtained from the PMEP will coincide with those that follow from the balance equations when the internal structure is introduced through the Onsager coefficients which become functions of position. It is worthy to mention that this brings the heat transport into the realm of the non-Fourier regime [13-14].

Another transport process is diffusion. This is a phenomenon in which substances move from an area of lower concentration to an area of higher concentration due to their kinetic energy. This process has attracted the attention the last few years since it manifests itself in various systems of interest to physics, chemistry, biology, economics, and medicine. For example, in probability theory and statistics, diffusion processes are a class of continuous-time Markov processes with almost surely continuous sample paths [15-18]. Diffusion processes are even used to model and characterise the cognitive and neural process involved in making rapid decisions about objects and events in the environment [19]. Consequently, given the nature of this phenomenon, this work shows the extended validity of the PMEP within the diffusion processes at constant temperature in heterogeneous media.

The most simple transport processes, after named, have something in common: their spatial differential equation for the variable of interest has exactly the same form. However, this transport equation, a second order differential equation, has no constant coefficients. This means that each internal structure in the material or each heterogeneity in media implies different space dependence coefficients. This entails resolving in a particular way each differential equation. Nevertheless, the presented work shows an approximate analytical general solution for transport processes in heterogeneous media.

The organization of the paper runs as follows. In Sec. 2 the basic elements of variational principles are presented to provide the proper background for the subsequent developments. We profit from this in Sec. 3 where we consider the specific case of diffusion transport and examine the cases where the phenomenological coefficient is a constant, where it is chemical potential dependent and the case where the Onsager coefficient depends only on the position. It is shown that in this case the PMEP for the stationary states is satisfied. Section 4 is devoted to three different proposals to get an approximate analytical solution for transport processes in heterogeneous media. We close this work in the final section with some concluding remarks.

2. Variational principle in Classical Irreversible Thermodynamics

As it was mentioned before, the variational principle in Classical Irreversible Thermodynamics (CIT) has had rejection in the past. Their development in dissipative systems has been rather difficult due to the non-self-adjoint property of the differential operators appearing in the dynamic equations. In order to redeem the variational principle, in this short section we remind the bases of Calculus in order to solve the variational problem posed by the PMEP. The extended validity of the PMEP is exposed for the heat transport process and the thermoelectric effect too.

2.1. Variational principle

Let us consider a functional of the form

$$v[y(x)] = \int_{x_0}^{x_1} F(x, y,\ y')dx, \qquad (1)$$

where v is a functional dependent on a continuous function $[y(x)]$ in such a way that to each function $[y(x)]$ of a certain class of functions there corresponds a value v. The boundary points of the admissible curves will be considered fixed, and the function $F(x, y,\ y')$ will be taken as differentiable.

The necessary condition for the functional v to be an extremum is that its variation δv vanishes. Thus, for functional of Eq. (1) the condition takes the form

$$\int_{x_0}^{x_1} (\frac{dF}{dy} - \frac{d}{dx}\frac{dF}{dy'})\delta y\, dx\ =\ 0. \qquad (2)$$

Hence, the Euler-Lagange equation is

$$\frac{dF}{dy} - \frac{d}{dx}\frac{dF}{dy'} \equiv 0, \qquad (3)$$

on the curve $y(x)$ which extremizes the functional under consideration [20].

2.2. Heat transport process

Heat transport is one of the most common processes experienced daily and one of the most studied since its dissipative nature. Let us consider a rigid heat-conducting solid whose thermodynamic variable space is constituted by the specific internal energy u. Within the CIT if the local specific entropy depends solely on this variable $s = s(u)$ and the internal energy is determined by the internal energy conservation equation

$$\rho\frac{du}{dt} = \rho C_v \frac{dT}{dt} = -\ \nabla \cdot \bar{q}\ , \qquad (4)$$

(where $\bar{q}$ is the heat flux and it has been used that for a rigid heat-conducting solid, $u = C_v T$, with C_v the constant volume heat capacity) the time evolution equation for the entropy is

$$\rho\frac{ds}{dt} + \nabla \cdot \frac{\bar{q}}{T} = \bar{q} \cdot (\nabla\frac{1}{T}). \qquad (5)$$

Here, it is identified the entropy production, σ, and the entropy flux, $\bar{J_s}$, as

$\sigma = \bar{q} \cdot (\nabla \frac{1}{T})$ and $\bar{J}_s = \frac{\bar{q}}{T}$. (6)

It is considered the usual assumption of CIT of a linear relationship between the heat flux and its conjugate thermodynamic force,

$\bar{q} = L_{qq} \nabla \frac{1}{T}$, (7)

with L_{qq} is the Onsager coefficient (phenomenological coefficient). Then, from Eqs. (4) and (7) the stationary transport equation is

$\nabla \cdot (L_{qq} \nabla \frac{1}{T}) = 0.$ (8)

In order to show the validity of the PMEP, this principle is as follows: the non-equilibrium stationary states, reached by the system when it is subjected to given boundary conditions, is one of minimum global entropy production, that is

$\delta \int \sigma \, dV = 0.$ (9)

where V is the system volume. The validity extension of the PMEP is revealed with the examination the stationary states and their relation with the PMEP when specific dependences of the coefficient L_{qq} in Eq. (7) are assumed.

It is extremely known that with constant phenomenological coefficients the Euler equation that follows from the PMEP is the same as that coming from the energy conservation equation [2]. This is why the principle is considered as a limited one since there are no materials or systems with this kind of phenomenological coefficients even when the system is made of just one element. The latter because elements have their own internal structure. It has also been accepted that phenomenological coefficients depend on the temperature. The Fourier regime is a particular case such that $L_{qq} = \lambda T^2$, with a constant thermal conductivity λ. Even more, there are many experimental publications showing the temperature dependence of the Onsager coefficients for different materials. However, the PMEP is not satisfied. This leads us to conclude that temperature dependence is not the correct assumption.

Last, the new range of applicability of the PMEP is when the Onsager coefficient, is a direct function of position, $L_{qq} = L_{qq}(\bar{r})$. The motivation of this assumption is that the system of interest is an inhomogeneous material in some sense [21]. Thereupon, the Euler equation that follows from the PMEP is exactly the same as the one resulting from the energy equation for stationary states. It is worth mentioning that this transport regime is of non-Fourier type [13].

Finally, it can be stated that the PMEP is not of limited validity and the heat transport process is an optimized process developed under the minimum entropy production criteria.

2.3 Thermoelectric effect

After the results presented in the previous subsection, the guiding idea was that there exists a relationship between inhomogeneity (structuring), minimum entropy production and performance which may be fruitfully exploited for designing more efficient thermoelectric semiconductor devices [22].

Let be a semiconductor material subjected to an external temperature difference which brings an electric potential difference. Regarding local equilibrium, the first assumption is that the entropy density, s, depends on the total energy density, u, and the number density of charge carriers, n, that is $s = s(u, n)$. In accordance with the CIT, the time evolution of the local specific entropy is

$\frac{ds}{dt} = - \nabla \cdot (\frac{\bar{J}_u}{T} - \frac{\bar{\mu}\bar{J}}{eT}) + (\bar{J}_u \cdot \nabla \frac{1}{T} - \bar{J} \cdot \nabla \frac{\bar{\mu}}{eT}),$ (10)

where $\bar{J}_u$ being the total energy flux , $\bar{J}$ being the electric charge flux, $T = T(\bar{r})$ is the position dependent temperature, $\bar{\mu} = \bar{\mu}(\bar{r})$ being the position dependent electrochemical potential, e the electron charge. The above equation is compared with the entropy balance equation

$\frac{ds}{dt} = - \nabla \cdot \bar{J}_s + \sigma.$ (11)

This allow us to identify the entropy flux, $\bar{J}_s$ and the entropy production, σ, as

$\bar{J}_s = \frac{\bar{J}_u}{T} - \frac{\bar{\mu}\bar{J}}{eT},$ (12)

$\sigma = \bar{J}_u \cdot \nabla \frac{1}{T} - \bar{J} \cdot \nabla \frac{\bar{\mu}}{eT}.$ (13)

The linear laws that relate thermodynamic forces and fluxes are

$$\overline{J_u} = L_{11}\nabla\frac{1}{T} + L_{12}\nabla\frac{\bar{\mu}}{eT}, \qquad (14)$$

$$\overline{J} = L_{21}\nabla\frac{1}{T} + L_{22}\nabla\frac{\bar{\mu}}{eT}, \qquad (15)$$

where L_{ij} $(i, j = 1,\ 2)$ are the transport coefficients which fulfills the Onsager reciprocity relation, that is, $L_{12} = L_{21}$ and the positive definite character of the entropy production is guaranteed if, $L_{ii} > 0$ and $L_{11}L_{22} \geq L_{12}^2$. It is worthy to mention that for thermoelectric processes there are cross effects as it can be seen in fluxes (Eqs. (14) and (15)).

In order to show the validity of the PMEP, it is required to get the same transport equations from the energy and mass conservation equations that from the PMEP. Since this process involves cross effects, it is necessary to use the generalized variational principle. Therefore , the corresponding Euler equations, Eq. (3), are computed with two different physical fields, that is, $y \in \{1/T,\ \bar{\mu}/T\}$.

Despite the fact that the thermoelectric process is a cross effects phenomena, the conclusions obtained for the heat transport process are the same. That is, when the phenomenological coefficients are constant quantities the transport equations that correspond to the non-equilibrium stationary states of the system and that follow from the mass and energy conservation equations match with the ones coming from the PMEP. But, when the assumption is that phenomenological coefficients depend on the temperature or electrochemical potential, the PMEP is not satisfied. However, regarding a thermoelectric material with an heterogeneous structure, it is justified that the Onsager coefficients have a position dependence, i.e., $L_{ij} = L_{ij}(\bar{r})$. The result is that the pair of equations from the PMEP is the same as the ones derived from the conservation equations in the stationary non-equilibrium state [14].

Hence, it has been emphasized that the non-equilibrium stationary states of the inhomogeneous thermoelectric material are states of minimum entropy production.

3. Variational principle in diffusion process

The processes exposed before are transport processes as diffusion. Diffusion process is a passive movement of particles from a region of higher concentration to another region of lower concentration. This is a phenomenon of interest for biology, physics, chemistry, economy and medical sciences.

Let us consider a diffusion process at constant temperature. In accordance to CIT, the entropy density, s, depends on the particle number density (concentration) , n, i.e., $s = s(n)$. In this case, the time evolution of the local specific entropy is

$$\frac{ds}{dt} = \frac{\partial s}{\partial n}\frac{dn}{dt} \quad \ni \quad \frac{\partial s}{\partial n} = -\frac{\mu}{T} \quad and \quad , \frac{dn}{dt} = -\frac{1}{e}\nabla \cdot \bar{J} \qquad (16)$$

where μ is the chemical potential, T being the constant temperature and $\bar{J}$ the particle flux. The third equation is the continuity equation. Therefore, the evolution of the specific entropy is

$$\frac{ds}{dt} = \nabla \cdot \left(\frac{\mu}{eT}\bar{J}\right) - \bar{J} \cdot \nabla\frac{\mu}{eT}. \qquad (17)$$

The comparison between the last expression with Eq. (11) lead us to identify the entropy flux, $\overline{J_s}$ and the entropy production, σ, as

$$\overline{J_s} = -\frac{\mu}{eT}\bar{J}, \qquad (18)$$

$$\sigma = -\bar{J} \cdot \nabla\frac{\mu}{eT}. \qquad (19)$$

In order to simplify the compute, let be $\mu^* = \mu(\bar{r})/eT$. The linear law that relates flux and the thermodynamic force is

$$\bar{J} = L\nabla\frac{\mu}{eT} = L\nabla\mu^* \qquad (20)$$

where L is the Onsager coefficient in this diffusion process at constant temperature, which implies that entropy production is rewritten as

$$\sigma = -L(\nabla\mu^*)^2. \qquad (21)$$

For sake of simplicity, let's be restricted to one dimension, x. To test the validity of the PMEP with diffusion process, let begin with constant phenomenological coefficient, i.e., $L = cte$. From the conservation equation in the stationary state, Eq. (16),

$$0 = \frac{\partial}{\partial x}J = L\frac{\partial^2}{\partial x^2}\mu^* \quad \Rightarrow \quad 0 = \frac{\partial^2}{\partial x^2}\mu^*.$$

This is the second Fick's law. With the variational principle, the Euler-Lagrange equation, Eq. (3), with $F = \sigma$ and $y = \mu^{*}$

$$\frac{d\sigma}{d\mu^{*}} - \frac{d}{dx}\frac{d\sigma}{d\mu^{*}} = 0 - 2L\frac{d}{dx}\frac{\partial}{\partial x}\mu^{*} \quad \Rightarrow \frac{\partial^{2}}{\partial x^{2}}\mu^{*} = 0.$$

There is a perfect coincidence between the two last expressions. Hence, the diffusion process satisfies the PMEP when the Onsager coefficient is constant. It is worth mentioning Fick's equation obeys the PMEP, while on the contrary, Fourier's regime does not.

In the case, when $L = L(\mu^{*})$, the conservation equation in the stationary state, Eq. (16), is

$$0 = \frac{\partial}{\partial x}J \quad \Rightarrow \quad 0 = \frac{dL}{d\mu^{*}}\left(\frac{\partial}{\partial x}\mu^{*}\right)^{2} + L\frac{\partial^{2}}{\partial x^{2}}\mu^{*}.$$

From the PMEP,

$$\frac{d\sigma}{d\mu^{*}} - \frac{d}{dx}\frac{d\sigma}{d\mu^{*}} =- \frac{dL}{d\mu^{*}}\left(\frac{\partial}{\partial x}\mu^{*}\right)^{2} + 2L\frac{\partial^{2}}{\partial x^{2}}\mu^{*} + 2\frac{dL}{d\mu^{*}}\left(\frac{\partial}{\partial x}\mu^{*}\right)^{2} = 0 \quad \Rightarrow \frac{dL}{d\mu^{*}}\left(\frac{\partial}{\partial x}\mu^{*}\right)^{2} + 2L\frac{\partial^{2}}{\partial x^{2}}\mu^{*} = 0.$$

It is clear that the last two expressions, in this case, are different in the coefficient of the second term. Therefore, the assumption of a chemical potential dependence of the Onsager coefficient does not lead to the correct transport equation in the stationary state for the diffusion process.

In the real world, the diffusion process takes place in inhomogeneous media. This allows to assume that Onsager coefficient has a position dependence, that is, $L = L(x)$. The comparison between the transport equations coming from the conservation equation and from the variational principle is the same transport equation,

$$\frac{dL(x)}{dx}\left(\frac{\partial}{\partial x}\mu^{*}\right) + L(x)\frac{\partial^{2}}{\partial x^{2}}\mu^{*} = 0. \qquad (22)$$

The main conclusion of this section is that the non-equilibrium stationary states for the diffusion process evolve to equilibrium with minimum entropy production.

It has been shown the extended validity of the PMEP for different kinds of transport process, it means that heat transport, thermoelectric effect and diffusion process near equilibrium evolve to the equilibrium states with the entropy production cutted down to the minimum.

4. Approximate analytical solutions for transport processes in heterogeneous media.

The last section was devoted to the transport process. As it can be seen before, for simple transport process, which do not include cross effects, the resulting dimensionless transport equation, restricted to one dimension, x, has two possible forms

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(D(x)\frac{\partial T}{\partial x}\right), \qquad (23)$$

and the most general is

$$C(x)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(K(x)\frac{\partial T}{\partial x}\right), \qquad (24)$$

where T is the transport variable to solve and $x \in [0, 1]$. The inhomogeneity of the system dictates the functions $D(x)$, $C(x)$, and $K(x)$ which are positive and continuous functions with position dependence. All that give a second order differential equation with no constant coefficients. Given the infinite possibilities in the internal structure of a system, what follows is an attempt to find a general procedure in order to get the solution of the most general transport equation.

4.1 Linear case, heterogeneous media.

This section is devoted to compute an approximate analytical time-dependent solution of Eq. (23) with a particular $D(x)$. Namely, the linear function $D(x)$ is,

$$D(x) = mx + b. \qquad (25)$$

The assumed boundary conditions are Dirichlet-Dirichlet,

$$T(0, t) = T_{0} \quad and \quad T(1, t) = T_{1}, \qquad (26)$$

where T_0, and T_1 are the values of the variable T at the borders of the one-dimensional system. Since the boundary conditions are constant, it is clear that this equation has a stationary solution, $T_{ss}(x)$. Then, the transient part will be necessarily vanish at the borders, because the general solution will be written as a superposition of the stationary part plus a transient part,

$$T(x,t) = T_{ss}(x) + T_{tr}(x,t). \qquad (27)$$

Beginning with the stationary solutions of Eq. (23), notice that the time derivative disappears at the stationary state, and therefore the transport equation, Eq. (23), reduces to

$$\frac{d}{dx}(D(x)\frac{dT}{dx}) = 0. \qquad (28)$$

The above equation can be integrated by standard methods of solution of ordinary differential equations. A straightforward calculation shows that

$$T_{ss}(x) = T_0 + (T_0 - T_1)\frac{ln\,((mx+b)/b)}{ln\,((m+b/b))}. \qquad (29)$$

In order to obtain the time-dependent temperature profile $T(x,t)$, for arbitrary initial conditions, the separation of variables technique is applied and eventually the solution as a series of eigenfunctions of the problem is given.

The time-dependent temperature profile, can be written as $T(x,t) = \rho(x)\tau(t)$. Therefore, replacing this supposition into Eq. (23) the separated differential equations to be solved are

$$\frac{d\tau}{dt} =- k^2\tau, \quad \text{and} \quad \frac{\partial}{\partial x}(D(x)\frac{\partial\rho}{\partial x}) =- k^2\rho\,, \qquad (30)$$

with k, the separation constant. The time-dependent part of the solution, $\tau(t)$, is given by

$$\tau(t) = e^{-k^2 t}. \qquad (31)$$

On the other hand, the solution for the spatial dependence is not so simple, but it can be computed in terms of Bessel functions. In order to see that this is the case, a change of variable is needed, namely

$$u = 2\sqrt{D(x)} = 2\sqrt{mx + b},$$

which lead to do another change, that is, $\rho(x) \to \hat{\rho}(u) = \hat{\rho}\,(2\sqrt{mx + b})$, such that, the equation ruling the behavior of $\hat{\rho}$ can be written as

$$u^2\frac{d^2\hat{\rho}}{du^2} + u\frac{d\hat{\rho}}{du} + \hat{k}^2\hat{\rho} = 0, \qquad (32)$$

where $\hat{k} = k/m$. The Eq. (32) is the well known Bessel equation [23]. The most general solution for a fixed k, is given by,

$$\rho(x) = AJ_0(\frac{2k}{m}\sqrt{mx + b}) - BN_0(\frac{2k}{m}\sqrt{mx + b}), \qquad (33)$$

where J_0 is the are the Bessel function of first kind of order zero and N_0 is the Bessel function of second kind of order zero , A and B are constants that will be further fixed by means of the initial conditions. It should be mentioned that the sign in B is placed just by convenience as we will see below.

With the purpose of the admitted values for the separation constant k, i.e., the eigenvalues of the problem, notice that, due to the fact that we are looking for the transient solution of the problem, we should impose the following boundary conditions for ρ,

$$\rho(0) = \rho(1) = 0\,. \qquad (34)$$

The above is required because we have already imposed the boundary conditions for T in the stationary part, T_{ss} . Then, the transient part will necessarily vanish at the borders, because the general solution will be written as a superposition of the stationary part plus a transient part, Eq. (27).

Thus, the conditions in Eq. (34) lead to

$$J_0(a)N_0(\xi a) = J_0(\xi a)N_0(a), \qquad (35)$$

with $a = 2k\sqrt{b}/m$ and $\xi = \sqrt{(m + b)/b}$. Condition in Eq. (35) determines the admitted values of the separation constant k, or equivalently, the admitted values of a. It is not hard to see that such an equation has infinitely many solutions for a, which are countable and will be denoted by a_l for l a natural number. In other words, we say that a_l denotes the l`th root of the function

$$f(x) = J_0(x)N_0(\xi x) - J_0(\xi x)N_0(x)\,. \qquad (36)$$

The roots of $f(x)$ cannot be written exactly in an analytical form. But , it is possible to have an approximate expression for a_l for large l,[24]

$$a_l \approx \frac{l\pi}{\xi-1} + \frac{\xi-1}{8\pi\xi}\frac{1}{l} + O(l^{-3}). \qquad (37)$$

Thus, the admitted values for k in terms of the zeros a_l of the function $f(x)$ are

$$k_l = \frac{ma_l}{2\sqrt{b}}. \qquad (38)$$

Another result from the conditions of Eq. (34) is that A and B are not independent from each other. More over, It is important to state at this point that the set of functions, with l a natural number, is

$$\rho_l(x) = N_0(a_l)J_0(a_l\sqrt{\frac{mx+b}{b}}) - J_0(a_l)N_0(a_l\sqrt{\frac{mx+b}{b}}) \quad . \qquad (39)$$

All this allows to write down the transient solution $T_{tr}(x, t)$ as a series of these eigenfunctions as follows (recalling the solution for $\tau(t)$ given in Eq. (31)).

$$T_{tr}(x,\ t) = \sum_{l=1}^{\infty} C_l\rho_l(x)exp(\frac{m^2a_l^2t}{4b}). \qquad (40)$$

4.1 General case, heterogeneous media.

4.4.1. Analytical approach to the transport equation with time dependent boundary conditions in inhomogeneous materials.

The other dimensionless transport equation is Eq. (24). The assumed boundary conditions are time independent as follows

$$T(0,t) = T_0 + a'e^{iwt}, \qquad \text{and} \qquad T(1,t) = T_1, \qquad (41)$$

where T_0 and T_1 are the values of the variable T at the borders of the one-dimensional system. The constant a' stands for the amplitude of the variable oscillations at one of the border of the system, oscillations whose frequency is denoted by w.

Start by noticing that if $a' = 0$, Eq. (24) would have a stationary solution $T_{ss}(x)$ which can be obtained in the same way as the previous section. Thus, it is convenient to define $T_{sp}(x,t) = T(x,t) - T_{ss}(x)$, where $T_{sp}(x,t)$ satisfies Eq. (24) with boundary conditions

$$T(0,t) = a'e^{iwt}, \qquad \text{and} \qquad T(1,t) = 0. \qquad (42)$$

In order to solve Eq. (24) with boundary conditions of Eq. (42) the separation of variables technique is used [23]. The assumption is the $T_{sp}(x,t) = R(x)\tau(t)$, then

$$\frac{d\tau}{dt} =- k^2\tau, \qquad \text{and} \qquad \frac{\partial}{\partial x}(K(x)\frac{\partial R}{\partial x}) =- k^2C(x)R(x)\,, \qquad (43)$$

where the k the separation constant. The time-dependent part of the solution, $\tau(t)$, is given by Eq. (31).

The solution for the spatial part cannot be exactly determined but an approximation can be obtained. It is proposed a change of variable, $u = \mu(x)$, where $\mu(x)$ is a function to be determined but it is assumed to be continuous and invertible. Thus

$$\frac{d}{dx}(K(x)\frac{d}{dx}) = \mu'(x)\frac{d}{du}(K(x)\mu'(x)\frac{d}{du}),$$

Now, in other to keep the differential operator as simple as possible, the following condition is imposed $u = \mu(x) = K(x)\mu'(x)$. This imposition allows to solve for the function

$$\mu(x) = exp(\int_0^x \frac{dy}{K(y)}). \qquad (44)$$

If $\mu(0) = 1$ and that $\mu(1)$ takes the value

$$b = \mu(1) = exp(\int_0^1 \frac{dy}{K(y)}) = e^{N_0}$$

where can be observed that $\mu(x)$ continuous, invertible and that is a well defined function for all $u \in [1,\ b]$. Under this changes, if $R(x) \rightarrow \rho(u)$, the differential equation for the spatial part, Eq. (43), can be written as

$$u\frac{d}{du}(u\frac{d\rho}{du}) =- k^2D(u)\rho(u) \ni D(u) = K(\mu^{-1}(u))C(\mu^{-1}(u)). \qquad (45)$$

The new function $D(u)$ can be expressed as

$$D(u) = d_0u^2 + \beta(u), \tag{46}$$

for some positive continuous function $\beta(u)$, then the Eq. (45)

$$u^2\rho''(u) + u\rho'(u) + k_0^2u^2\rho(u) =- k^2\beta(u)\rho(u), \tag{47}$$

where the constant $k_0^2 = d_0k^2$. The Eq. (47) is almost the Bessel equation. In the particular case of $\beta(u) = 0$ for all u, then Eq. (47) reduces to

$$u^2\rho_0''(u) + u\rho_0'(u) + (k_0^2u^2 + \nu_0^2)\rho_0(u) = 0, \tag{48}$$

which is the well known Bessel equation of order $\nu_0^2 = 0$. Consequently, the solution of Eq. (48) is

$$\rho_0(u) = A_0J_0(k_0u) + B_0N_0(k_0u), \tag{49}$$

with A_0 and B_0 constants fixed by the boundary conditions of Eq. (42). The boundary conditions for $\rho_0(u)$ are

$$\rho_0(1) = a \quad \text{and} \quad \rho_0(b) = 0. \tag{50}$$

Notice that, Eq. (49) is valid when $\beta(u) = 0$. In other case, adopting the above boundary conditions for the function $\rho_0(u)$, without loss of generality, $\rho(u)$ can be written as

$$\rho(u) = \rho_0(u) + \phi(u), \tag{51}$$

so that the differential equation for the function $\phi(u)$ is

$$u^2\phi''(u) + u\phi'(u) + (k_0^2u^2 + \nu_0^2)\phi(u) = g(u) - k^2\beta(u)\phi(u), \tag{52}$$

such that $g(u) =- k^2\beta(u)\rho(u)$. Notice that Eq.(52) is an inhomogeneous ordinary differential equation. Therefore, this differential equation can be transformed into an integral one by means of the Green's function of the homogeneous problem, Eq. (48), [25]. Consequently, the Green's function, $G_0(u,v)$, satisfies

$$u^2\frac{d^2G_0(u,v)}{du^2} + u\frac{dG_0(u,v)}{du} + (k_0^2u^2 + \nu_0^2)G_0(u,v) = \delta(v), \tag{53}$$

with boundary conditions $G_0(1,v) = a$ and $G_0(b,v) = 0$. Then, the equation for $\phi(u)$ is

$$\phi(u) = \int_1^b G_0(u,v)(g(v) - k^2\beta(v)\phi(v))dv. \tag{54}$$

Let rename some functions, that is

$$f(u) = \int_1^b G_0(u,v)g(v)dv, \quad \text{and} \quad \widehat{K}(u,v) =- k^2G_0(u,v)\beta(v), \tag{55}$$

In such a way that function $\phi(u)$ can be rewritten as

$$\phi(u) = f(u) + \int_1^b \widehat{K}(u,v)\phi(v)dv. \tag{56}$$

The solution of $\phi(u)$ can be computed with the Neumann series

$$\phi(u) = \sum_{n=0}^{\infty} \phi_n(u), \tag{57}$$

with

$$\phi_n(u) = \int_1^b\int_1^b\cdots\int_1^b \widehat{K}(u,t_1)\,\widehat{K}(t_1,t_2)\cdots\widehat{K}(t_{n-1},t_n)f(t_1)dt_1dt_2\cdots dt_n, \tag{58}$$

for $n \geq 1$ and $f(u) = \phi_0(u)$.

4.4.2. General case heterogeneous media. Potential series.

Another alternative to find the solution of the spatial part of the differential equation, Eq. (43), are the potential series [23],

$$\frac{\partial}{\partial x}\left(K(x)\frac{\partial R}{\partial x}\right) =- k^2C(x)R(x)$$

The first assumption is that continuous functions $C(x)$, and $K(x)$ can be expressed as

$$K(x) = \sum_{n=0}^{\infty} K_nx^n, \quad \text{and} \quad C(x) = \sum_{n=0}^{\infty} C_nx^n, \tag{59}$$

as well as the solution

$$R(x) = \sum_{p=0}^{\infty} r_p x^p, \qquad (60)$$

where r_p are the target coefficients to find. After the replacing of the Eqs. (59) and (60) in Eq. (43), the result is

$$(2K_0 r_2 + k^2 r_0 C_0 + K_1 r_1)x^2 + \sum_{p'=3}^{\infty} [K_0 r_{p'} p'(p' - 1) + k^2 r_{p'-2} C_0 + K_{p'-1} r_1 (p' - 1)] x^{p'}$$

$$\sum_{p=2}^{\infty} \left\{ \left[r_p p(p - 1) \sum_{n=1}^{\infty} K_n + r_p p \sum_{n=1}^{\infty} n K_n + k^2 r_{p-2} \sum_{n=1}^{\infty} C_n \right] x^n \right\} x^p = 0, \quad (61)$$

with $p' = p + 1$. The coefficients r_o and r_1 are determined by the boundary conditions. The other values for the solution of the Eq. (60) are

$$r_2 = - \frac{k^2 r_0 C_0 + K_1 r_1}{2K_0},$$

$$r_p = - \frac{k^2 r_{p'-2} C_0 + K_{p'-1} r_1 (p'-1) + \sum_{n=1}^{p'-2} r_{p'-n} (p'-n)(p'-1) K_n + k^2 r_{p'-n-2} C_n}{K_0 r_{p'} p'(p'-1)}, \ \forall\, p' = p + n \in [3, \infty) \qquad (62)$$

5. Concluding remarks

In this work, we have presented the extension of the PMEP for another transport process, that is, diffusion transport process at constant temperature. It means that non-equilibrium states for diffusion processes run out to equilibrium states within a minimum entropy production criteria within non-homogenous media.

Moreover, it was identified that in the case of heat transport processes as well as diffusion phenomena, transport equations for heterogeneous media have the same differential equations forms. It means, transport equations are second order differential equations with no constant coefficients. It implies that for each internal structure or non-homogeneous region a particular solution method is required to get the solution. In order to avoid this treatment, different alternatives to get general approximated solutions were exposed.

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