Recycling the Independent Field Approximation argument in the far field

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Abstract

The Independent Field Approximation for the entropy production of Laplacian mild diffusional fields is rigorously introduced and discussed. Some new results due to super-convergent algorithms are presented and the meaning of the active zone concept is enlightened.

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1. INTRODUCTION

Diffusion is a very important phenomenon in many natural, biological and industrial processes [1, 5, 6]. To give only a small example, the transport of oxygen in the terminal part of the respiratory system of mammals is due to diffusion [2, 6]. In view of its importance, a number of studies on the influence of the shape of the boundaries has been justified. These studies have been mainly based on important statements from Harmonic Analysis which have been announced these last years [7–9]. In particular, the possible role of an extremely irregular - and eventually fractal - boundary has been extensively studied, as fractals constitute well-suited models of naturally disordered morphologies [3, 5, 6, 12, 13, 15–17].

One of the basic conclusions emerging from these studies is the existence of universal scaling laws culminating in the derivation of interesting expressions for the *impedance* describing the system's linear response. Many of these laws find their origin in Makarov's theorem stating that, whatever the shape of an irregular (simply connected) boundary in two dimensions might be, the *active zone* in which most of the flux generated by a Laplacian field is concentrated, scales as a length [7–9].

The active zone approximation tells us simply that some parts of an irregular surface are not really working, being "passive", so that all thermodynamic properties can be estimated by considering only the "active zone". According to the theorems announced previously, for a Laplacian field this is always a good approximation. This is also the basic conclusion of the present work.

The paper is organized as follows. In Sec 2 we give the basic formulation of irreversible thermodynamics for diffusion on one neutral species of particles. In Sec 3 we give the explicit form of the entropy production and the variational functional for regular boundaries. In Sec 4 we examine the case of irregular boundaries and give the IFA analytical approach, while in Sec 5 we check this numerically by very precise numerical algorithms on rectangular non-scaling geometries which are variants of the initial geometry, and we show that IFA is always a good approximation. In Sec 6 we draw the main conclusions.

2. FORMULATION

Let us now consider the case of diffusion of some neutral species from a flat source of constant concentration c_1 toward an irregular membrane maintained in constant concentration c_2 by means, for instance, of an adsorption mechanism. The temperature of the system T is also kept constant [4].

In this case the entropy production P is

$$P = \int_V \sigma \, d\mathbf{r} \tag{1}$$

where σ is the local entropy production which is defined as the bilinear form

$$\sigma = \mathbf{J} \cdot \mathbf{X} \tag{2}$$

where $\mathbf{J}$ are the corresponding current and $\mathbf{X}$ the thermodynamic force.

For diffusion of one kind of particles the thermodynamic force is given in terms of the chemical potential μ by

$$\mathbf{X} = -\frac{\nabla \mu}{T}, \tag{3}$$

where now

$$\mu = kT \ln c + f(T) \tag{4}$$

c being the solute concentration, k the Boltzmann constant and $f(T)$ is a function of the temperature only.

Furthermore, one has the Fick's law

$$\mathbf{J} = -D\nabla c \tag{5}$$

where

$$D = const. \tag{6}$$

It follows immediately from the continuity equation

$$\frac{\partial \phi}{\partial t} = -div\,\mathbf{J}, \tag{7}$$

that in the steady state, c is a Laplacian field. We have that

$$P = \int_V (-D\nabla c) \cdot \nabla(-\frac{\mu}{T})\ d\mathbf{r}. \tag{8}$$

The full expression for the entropy production in the steady state is then

$$P = Dk \int_V \frac{(\nabla c)^2}{c}\ d\mathbf{r}. \tag{9}$$

On the other hand, one easily sees that the functional

$$Q = \int_V (\nabla c)^2\ d\mathbf{r} \tag{10}$$

is extremal in the steady state [10].

In the sequel we will be interested in the behaviour of P as given by eq.(9) under the condition that, as stated above, c satisfies in the steady state Laplace's equation

$$\nabla^2 c = 0. \tag{11}$$

3. REGULAR BOUNDARIES

Before we address the role of complex boundaries we evaluate both c and P in the simple reference case of a two-dimensional box of height L_y and length (diameter) L_x submitted to Dirichlet conditions along the y direction and to zero-flux ones along the x direction. The solution of eq.(11) is then trivially given as a linear concentration profile

$$c(y) = \frac{c_1 - c_2}{L_y} y + c_2, \tag{12}$$

where $c_1 = c(L_y)$, and $c_2 = c(0)$. The entropy production can be calculated exactly, yielding

$$P = DkL_x \frac{1}{L_y}(c_2 - c_1) \ln \frac{c_2}{c_1}. \tag{13}$$

We notice that P diverges for the absorbing boundary condition $c_2 = 0$ on $y = 0$. For fixed c_1 and c_2 it is inversely proportional to the size L_y.

Continuing along the same lines, one can readily perform the integration in eq.(10), leading to the following expression for the variational functional in terms of geometry

$$Q = \frac{L_x}{L_y}(c_2 - c_1)^2. \tag{14}$$

Notice that unlike the entropy production [eq.(9)], the variational functional no more diverges for the absorbing boundary condition $c_2 = 0$ on $y = 0$ usually adopted in the literature.

4. IRREGULAR BOUNDARIES: ANALYTIC APPROACH

The simplest setting in which possible effects of complex geometry on entropy production can be identified is given in Fig.1. A concentration difference $c_1 - c_2$ is applied across the vertical boundaries of a cell, over a characteristic length L_y. The cell obeys to zero-flux boundary conditions along the horizontal direction x, but there is now an anomaly consisting of extending the horizontal characteristic length L_x by a bump in the middle. An essential feature of the Laplacian field is to diverge in the open corners created by this bump and this makes the treatement of the problem nontrivial. These singularities are, however, integrable (see [12, 13, 15–17]).

We have shown in [16], that the entropy production would keep the structure of eq.(13) as far as y depencence goes, but the proportionality factor L_x would be modulated on the grounds of Makarov's theorem by an additional size-independent factor A depending on geometry and on concentrations only:

$$P = DkA(c_1, c_2; g)L_x \frac{1}{L_y}(c_2 - c_1)\ln\frac{c_2}{c_1}. \tag{15}$$

Under the same conditions the variational functional Q takes the form

$$Q = B(g)L_x \frac{1}{L_y}(c_2 - c_1)^2, \tag{16}$$

where now the constant B depends on geometry only.

Clearly, $A(c_1, c_2; g) = 1$ and $B(g) = 1$ for a flat membrane [cf. eqs. (13) and (14)]. As it turns out, $A(c_1, c_2; g) < 1$ and $B(g) < 1$ for a nonflat surface owing to the curvature of the equipotential lines arising from the geometric irregularities of the membrane. This means that a system bounded by an irregular membrane possesses the same entropy production as a smaller system with regular boundaries.

To estimate A and B we have applied the active zone concept [16]. We have first observed that there are connections between these quantities. In the case of *mild diffusion*, where

$$|(c_2 - c_1)/c_1| = O(\varepsilon), \quad \varepsilon << 1, \tag{17}$$

we have from eq.(15), eq.(16) that

$$P \sim \varepsilon^2, \quad \varepsilon << 1, \tag{18}$$

and

$$Q \sim \varepsilon^2, \quad \varepsilon << 1. \tag{19}$$

Furthermore,

$$B(g) \sim \lim_{c_2 \to c_1} A^{mild}(c_1, c_2; g) \tag{20}$$

up to a proportionality factor of Dk/c_1.

The situation is *very different* for *strong diffusion*, where

$$|(c_2 - c_1)/c_1| = O(1), \quad c_1 = O(1). \tag{21}$$

As the previous arguments do not apply, this case has only be analyzed numerically until now in [16]. The case of strong diffusion is not analyzed at all in the present work.

In the remaining part of this section we focus on the case of *mild diffusion*. Our purpose is to illustrate how to estimate B and A analytically in this limit. To this end we follow the "independent field approximation" (IFA). This is a coarse-graining argument based on a compartmentalization of the full continuous space in which diffusion takes place into a finite number of properly selected nonoverlapping and not interacting rectangular regions, where one can write down closed expressions for the entropy production and the variational functional supposing linear concentration profiles. The nonlinearity of the field arising from the irregularities of the boundaries is thus approximated by piecewise linear functions, entailing discontinuities of the equipotential lines at the boundaries between the cells.

Let us illustrate how the IFA works for the first fractal generation of the cell (Fig. 2) and for two geometries (a) and (b) corresponding to two different geometries. We separate the cell into three rectangles shown in the figure. Accepting linear concentration profiles in each of the side parts (i) and (iii), one finds for the entropy production, applying eq.(13) with $L_x = \ell$ and $L_y = 2\ell$

$$P^{(i)} = P^{(iii)} = \frac{1}{2} Dk(c_2 - c_1) \ln \frac{c_2}{c_1}. \tag{22}$$

Accepting furthermore a linear half penetration inside the pore (that is, a linear concentration profile until the middle of the pore [13, 16], thereby neglecting the remaining passive zone), one has for the central region (ii) from eq.(13) with $L_x = \ell$ and $L_y = 5\ell/2$

$$P^{(ii)} = \frac{2}{5} Dk(c_2 - c_1) \ln \frac{c_2}{c_1}. \tag{23}$$

The total entropy production of the cell becomes

$$P^{tot} = \frac{7}{5} Dk(c_2 - c_1) \ln \frac{c_2}{c_1}. \tag{24}$$

Applying now eq.(15), eq.(16) for the whole cell with $L_x = 3\ell$ and $L_y = 2\ell$ we find [remember that we deal here with mild diffusion, see eq.(20)]

$$P^{tot} = \frac{3}{2} DkB(g)(c_2 - c_1) \ln \frac{c_2}{c_1}. \tag{25}$$

Comparison with eq.(24) leads to

$$\frac{3}{2} B(g) = \frac{7}{5}, \tag{26}$$

that is

$$B_a(g) = \frac{14}{15} \simeq 0.9333. \tag{27}$$

Continuing in the same manner one finds

$$B_b(g) = \frac{20}{21} \simeq 0.9524. \tag{28}$$

As also stressed out in [16], although crude, this evaluation gives some insight on the physical origin of B(g). On the other hand, the argument of half-penetration of the field in the pore is expected to hold better when the distance of the source of particles from the entrance of the pore is larger than the depth of the geometrical irregularity. One thus expects an improvement of the quality of the predictions from geometry (a) to (b), a fact that has been confirmed numerically in [16].

Notice finally that the entropy production [eq.(9)] remains invariant under a *homotechy* transformation of all the lengths $L_x \to \lambda L_x$, $L_y \to \lambda L_y$ in two dimensions, as one sees from eq.(15). In particular, no characteristic length scale subsists in the expression for the entropy production.

5. IRREGULAR BOUNDARIES: NUMERICAL APPROACH

For the numerical investigation of eq.(11) we have used a modified version of the finite difference (overrelaxation scheme) algorithm used in [15–17] for the detection of the Makarov regime. This algorithm is thus tailormade for extremely precise calculations on the Laplacian field. The main improvement here is that one can also vary the distance of the irregular membrane from the flat membrane, as well as the depth of the pore!

The Laplace's equation for non-scaling fractal geometries which are variants of an initial fractal generator, is resolved by finite difference overrelaxation algorithm [10, 11], with a very fine mesh of the lattice for the finite differences, namely $\ell = 300$ and $L_x = 900$. The depth of the pore varies from 150, to 300 and then to 600 length units.

Using the above results one may estimate the factor B with a very good precision (up to four significant digits). We obtain

$$B_a^{ph}(g) \simeq 0.9738, \tag{29}$$

for geometry (a),

$$B_b^{ph}(g) \simeq 0.9824 \tag{30}$$

for geometry (b), where the superscript "ph" stands for "phenomenological". Comparing with eq.(27), eq.(28) we see that B_a differs from B_a^{ph} by 6 % and B_b differs from B_b^{ph} by 4 %.

For geometry (c) (double depth) we find

$$B_c^{ph}(g) \simeq 0.9738, \tag{31}$$

for geometry (d) (half depth) we find

$$B_d^{ph}(g) \simeq 0.9750, \tag{32}$$

for geometry (e) (double depth) we find

$$B_e^{ph}(g) \simeq 0.9824, \tag{33}$$

for geometry (f) (half depth) we find

$$B_f^{ph}(g) \simeq 0.9832. \tag{34}$$

We observe that deepening the pore by a factor two, leave almost invariant the factor B, that is, the active zone.

By limiting the depth of the pore in its half value, we obtain a little "more efficient" geometry. This calculation gives some further physical inshight in the notion of the factor B. The bigger B is, the more the surface is active!

6. CONLUSIONS AND DISCUSSION

The tendency to decrease dissipation with increasing boundary fragmenation is confirmed for non-scaling rectangular geometries which are variants of an initial fractal generator, by ultra-precise numerical algorithms of finite differences.

The basic result reported here is that the active zone argument is always a good approximation.

The author believes that the most challenging future problem should be to extend this formalism so as to incorporate growth [5, 6, 18] as, for instance, in diffusion limited aggregation (DLA) or viscous fingering related problems, and/or chemical deposition in one of the boundaries. Different directions of research could also be envisaged [14].

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7. FIGURE CAPTIONS

Fig.1. Schematic representation of the diffusion cell for the first fractal iteration of a fractal generator. The dimensions of the cell as well as the boundary conditions are also indicated.

Fig.2. Schematic representation of the coarse-graining procedure associated with the IFA, for geometries (a) and (b) of the first fractal iteration of a fractal generator.

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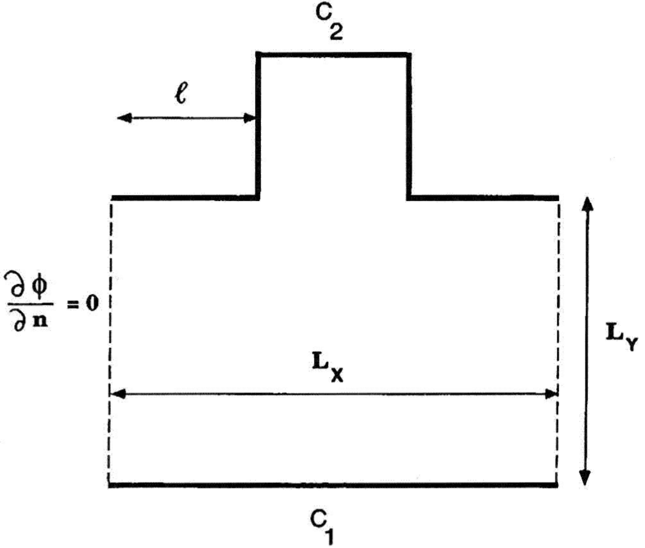
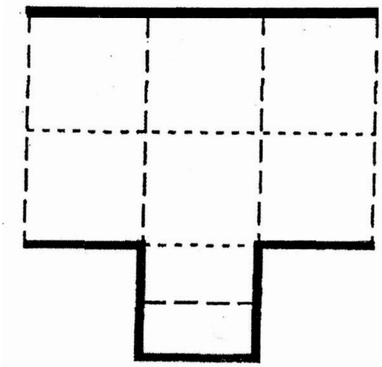
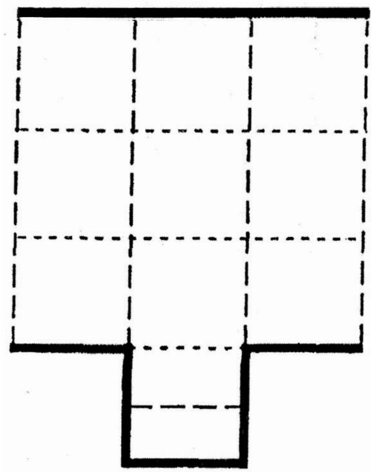


C_2
ℓ
$\frac{\partial \phi}{\partial \mathbf{n}} = 0$
L_Y
L_X
C_1



(a)



(b)