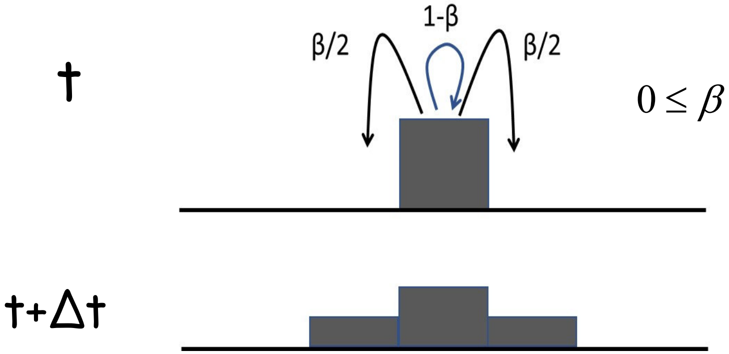
The fourth order diffusion equation and mass conservation requirements.

COLMEA IM-UFRJ
2022

Luiz Bevilacqua

DISCRETE APPROACH TO DIFFUSION PHENOMENA

Symmetric Diffusion-Retention



$0 \le \beta \le 1$

$$q_n^t = (1-\beta)\, q_n^{t-1} + \frac{\beta}{2} q_{n-1}^{t-1} + \frac{\beta}{2} q_{n+1}^{t-1}$$

$$q_n^{t+1} = (1-\beta)\, q_n^{t} + \frac{\beta}{2} q_{n-1}^{t} + \frac{\beta}{2} q_{n+1}^{t}$$

$$\Delta q_n^t = q_n^{t+1} - q_n^t$$

$$\Delta q_n^{t+\Delta t} = \left\{ \beta \Delta^2 q_n - (1-\beta)\, \beta \Delta^4 q_n \right\}^t$$

$$\frac{\Delta q_n^{t+\Delta t}}{\Delta t} = \left\{ \beta \frac{\Delta x^2}{\Delta t} \frac{\Delta^2 q_n}{\Delta x^2} - (1-\beta)\, \beta \frac{\Delta x^4}{\Delta t} \frac{\Delta^4 q_n}{\Delta x^4} \right\}^t$$

BI-FLUX DIFFUSION PROCESS

This is a bi-flux process consisting of two microstates spreading simultaneously but interconnected through the parameter β

$$\lim_{\substack{\Delta t\to 0\\ \Delta x\to 0}}\left\{\frac{\Delta q_n^{t+\Delta t}}{\Delta t}+\left\{-\beta\left\{\frac{\Delta x^2}{\Delta t}\right\}\frac{\Delta^2 q_n}{\Delta x^2}+(1-\beta)\left\{\beta\frac{\Delta x^4}{\Delta t}\right\}\frac{\Delta^4 q_n}{\Delta x^4}\right\}=0\right\}^t$$

$$\lim_{\substack{\Delta t\to 0\\ \Delta x\to 0}}\left\{\frac{\Delta x^2}{\Delta t}\right\}=D \qquad \lim_{\substack{\Delta t\to 0\\ \Delta x\to 0}}\left\{\beta\frac{\Delta x^4}{\Delta t}\right\}=\beta R$$

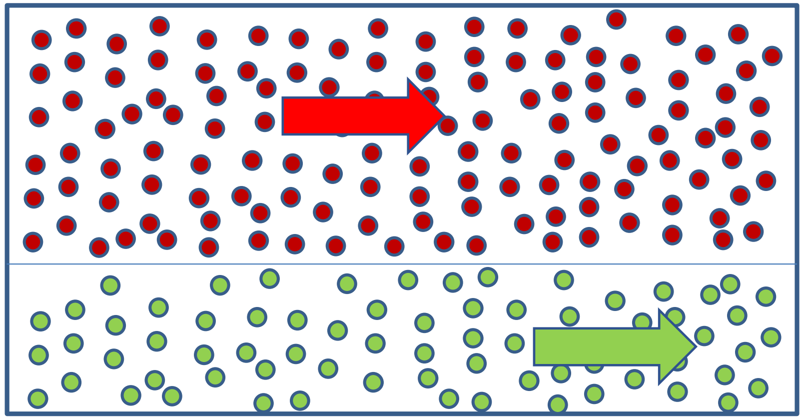
Main flux (Fickian) is driven by a potential such that $\langle\bar{x}\rangle \propto t^{1/2}$

Subsidiary fkux is driven by a potential such that $\langle\bar{x}\rangle \propto t^{1/4}$

BI-FLUX DIFFUSION PROCESS IN HOMOGENEOUS MEDIA

Solution for β=const, time independent parameters D, R and β

$$\frac{\partial q}{\partial t} = \beta D \frac{\partial^2 q}{\partial x^2} - (1-\beta)\beta R \frac{\partial^4 q}{\partial x^4}$$



t_n

Fickian flux

$$\mathbf{\Psi}_1 = -D\frac{\partial q}{\partial x}\mathbf{n}$$

Subsidiary flux

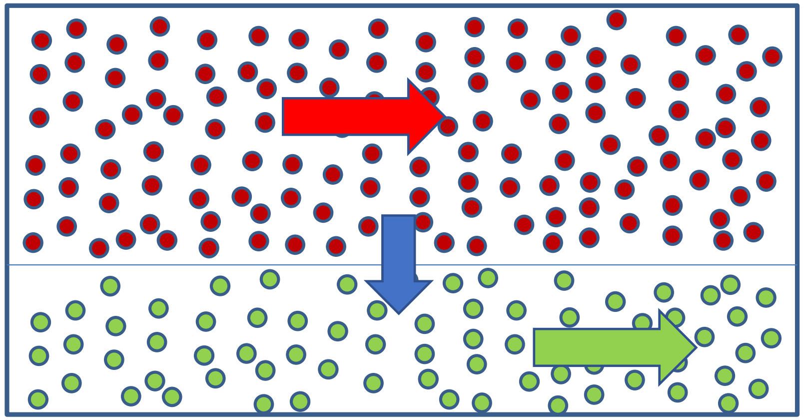
$$\mathbf{\Psi}_2 = \beta R\frac{\partial^3 q}{\partial x^3}\mathbf{n}$$

β = const.

D → Diffusion coeficiente R → Reactivity β → fraction in the Fickian flux

BI-FLUX DIFFUSION PROCESS β=β(t)

Complex diffusion for β= β(t) time dependent energy states



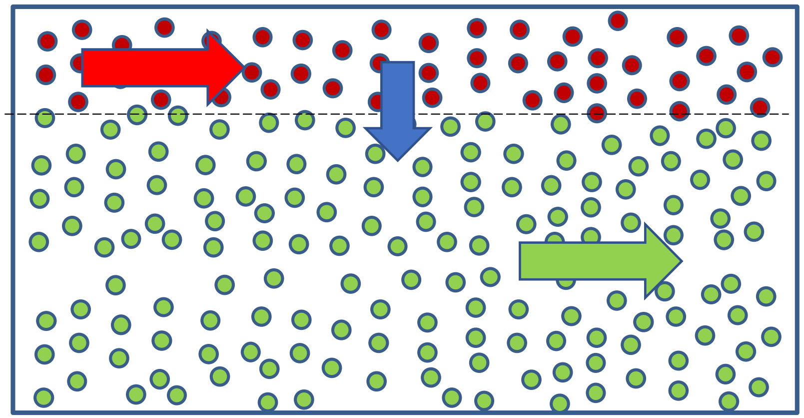
t_n

Fickian flux

$$\boldsymbol{\Psi}_1 = -D\frac{\partial q}{\partial x}\mathbf{n}$$

Subsidiary flux

$$\boldsymbol{\Psi}_2 = \beta R\frac{\partial^3 q}{\partial x^3}\mathbf{n}$$



$t_m > t_n$

β = β(t)

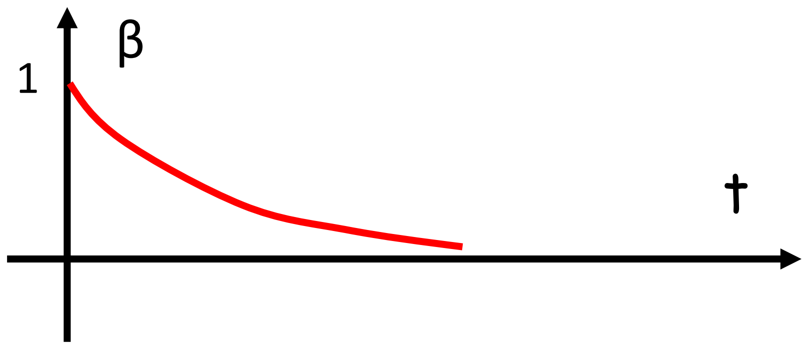
$$\boldsymbol{\Psi}_0 \,\square\, \frac{\partial \beta}{\partial t}$$

The hidden flux
Migration between
the energy states

β=1 t=0 $$\frac{\partial q}{\partial t} = D\frac{\partial^2 q}{\partial x^2}$$ Fick

1>β>0 t>0 $$\frac{\partial q}{\partial t} = \beta(t) D\frac{\partial^2 q}{\partial x^2} - \left(1-\beta(t)\right)\beta(t) R(t)\frac{\partial^4 q}{\partial x^4}$$ Bi-flux

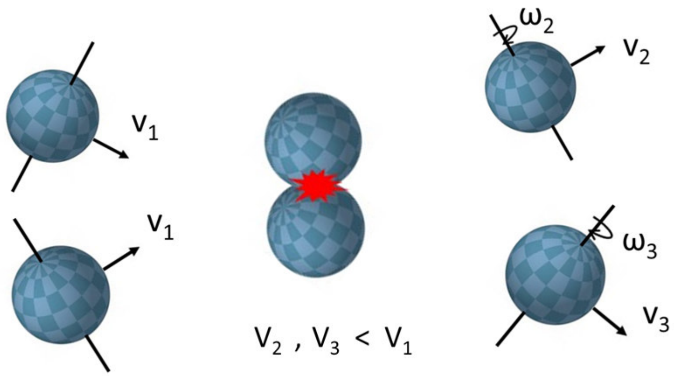
β=0 t→∞ $$\frac{\partial q}{\partial t} = 0$$ Steady state. Maximum ω-entropy



ENERGY EXCHANGE IN A PARTICULAR UNIVERSE

Ψ_1

$\beta = 1$



Ψ_2

$\beta < 1$

Microstate 1
Primary energy state

Microstate 2
Secondary energy state

THE REACTIVITY PARAMETER R AND THE FRACTION β

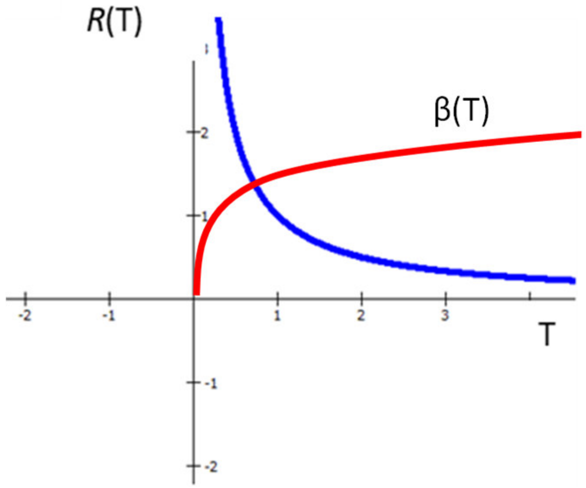
<u>It has been shown through the analysis of inverse problems (Silva Neto, Knupp, Wyse and others) that R=R(β).</u>

1. The variation δβ is related to (-δR) the negative sign meaning that *δβ* decreases as *δR* increases.
2. The variation δβ is proporcional to β.

$$\delta\beta = \beta \frac{(-\delta R)}{R_0}$$

$$\beta = \exp\left(-\frac{R}{R_0}\right)$$

$$R = -R_0 \ln \beta$$



GOVERNING EQUATION: ADIABATIC PROCESSES

The governing equation for particles dispersing in a homogeneous media distributed into a sequence of decaying energy states.

$$p_1 = \beta \qquad p_2 = (1-\beta) \qquad R = -R_0 \ln \beta = -R_0 \ln p_1$$

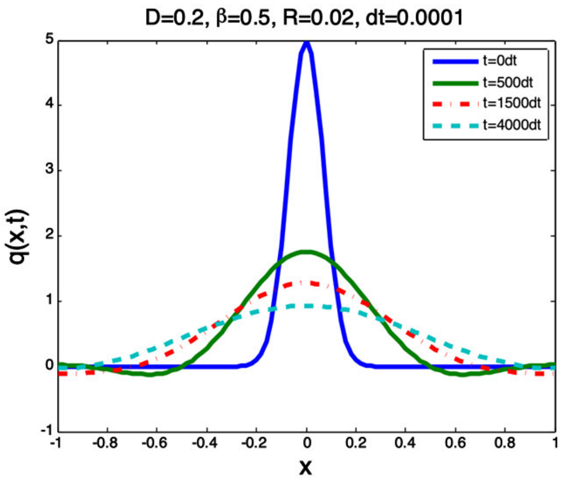
Ω-ENTROPY

$$\frac{\partial q}{\partial t} = p_1 D \frac{\partial^2 q}{\partial x^2} + p_2 R_0 p_1 \ln p_1 \frac{\partial^4 q}{\partial x^4}$$

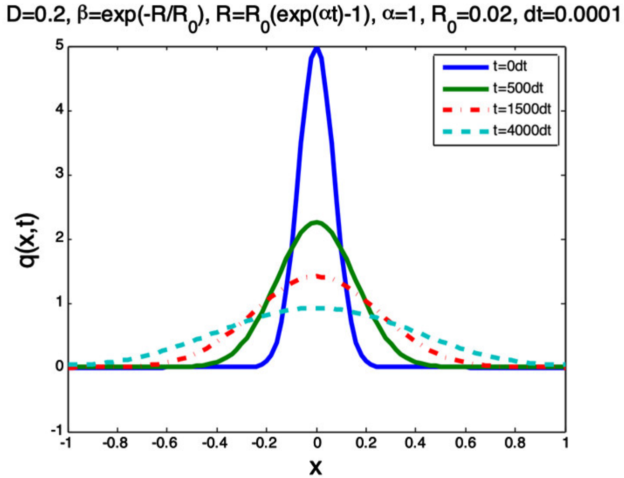
$$\mathbf{\Psi}_1 = -D\frac{\partial q}{\partial x}\mathbf{n} \qquad \mathbf{\Psi}_2 = -R_0 p_1 \ln p_1 \frac{\partial^3 q}{\partial x^3}\mathbf{n} \qquad \lim_{p_1 \to 0} \mathbf{\Psi}_2 \to 0$$

p_1, p_2 and R **are time dependent** parameters

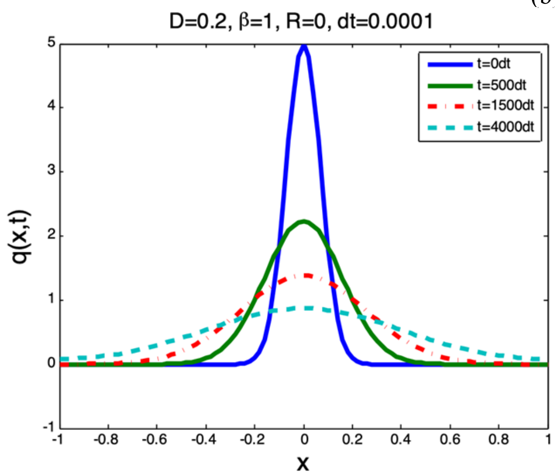
Energy exchange in a biflux diffusion process consisting of particles of the same nature split into two distinct microstates, L.Bevilacqua, M.Jiang, JBSMSE



(a)



(b)



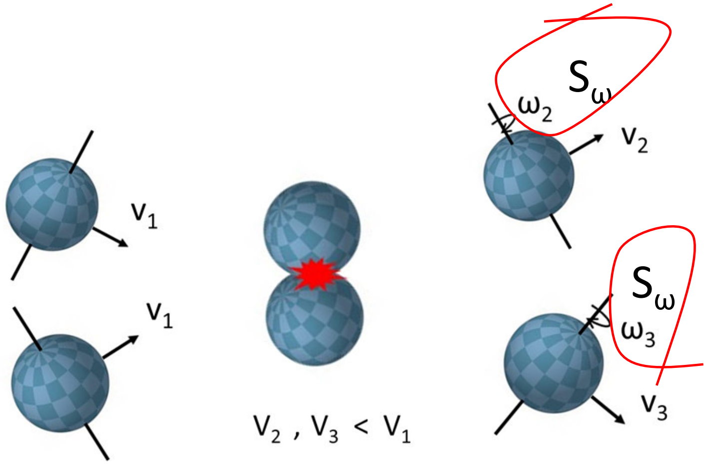
(c)

ENERGY EXCHANGE IN A PARTICULAR UNIVERSE

Our particular universe

$\boldsymbol{\Psi_1}$

$$U_1 \propto |\mathbf{v}_1|^2$$



$\boldsymbol{\Psi_2}$

$$U_2 \propto |\mathbf{v}_2|^2 + S_\omega$$

Hidden energy

ENERGY EXCHANGE IN A PARTICULAR UNIVERSE

In an isolated system the total specific kinetic energy is given by

$$\Phi = U_1 + U_2 = \underbrace{E_1 + E_2}_{\text{Active energy}} + \underbrace{p_2 S_\omega\left(p_1\right)}_{\text{Rotational energy}}$$

$$E_1 = p_1 \left|\mathbf{\Psi}_1\right|^2 \big/ 2q \qquad \lim_{t\to\infty} p_1(t) \to 0 \qquad \lim_{t\to\infty} E_1 \to 0$$

$$E_2 = p_2 \left|\mathbf{\Psi}_2\right|^2 \big/ 2q \qquad \lim_{t\to\infty} p_2(t) \to 1 \qquad \lim_{t\to\infty} \left|\mathbf{\Psi}_2\right| \propto \lim_{t\to\infty} R_0 p_1 \ln p_1 \to 0 \qquad \lim_{t\to\infty} E_2 \to 0$$

Therefore

$$\lim_{t\to\infty}\left(U_1 + U_2\right) = S_\omega(0)$$

ACTIVE ENERGY DISTRIBUTION

$$\Phi - p_2 S_\omega(p_1) = E_1 + E_2$$

$$\left[\Phi - p_2 S_\omega(p_1)\right] = \frac{p_1}{2q} D^2 \left(\frac{\partial q}{\partial x}\right)^2 + \frac{(1-p_1)}{2q} R_0^2 (p_1 \ln p_1)^2 \left(\frac{\partial^3 q}{\partial x^3}\right)^2$$

$$\mathbf{\Psi}_1 = -D\frac{\partial q}{\partial x}\mathbf{n}$$

$$\mathbf{\Psi}_2 = -R_0 p_1 \ln p_1 \frac{\partial^3 q}{\partial x^3}\mathbf{n}$$

In the domain $-\infty < x < \infty$

$$\int_{-\infty}^{+\infty} \left[\Phi - (1-p_1) S_\omega(p_1)\right] dx = \frac{p_1 D^2}{2} \int_{-\infty}^{+\infty} \frac{1}{q}\left(\frac{\partial q}{\partial x}\right)^2 dx + \frac{(1-p_1)(p_1 \ln p_1)^2 R_0^2}{2} \int_{-\infty}^{+\infty} \frac{1}{q}\left(\frac{\partial^3 q}{\partial x^3}\right)^2 dx$$

$$\Upsilon = \int_{-\infty}^{+\infty} \left[\Phi - (1-p_1) S_\omega(p_1)\right] dx \Big/ \int_{-\infty}^{+\infty} \Phi_0 dx \le 1$$

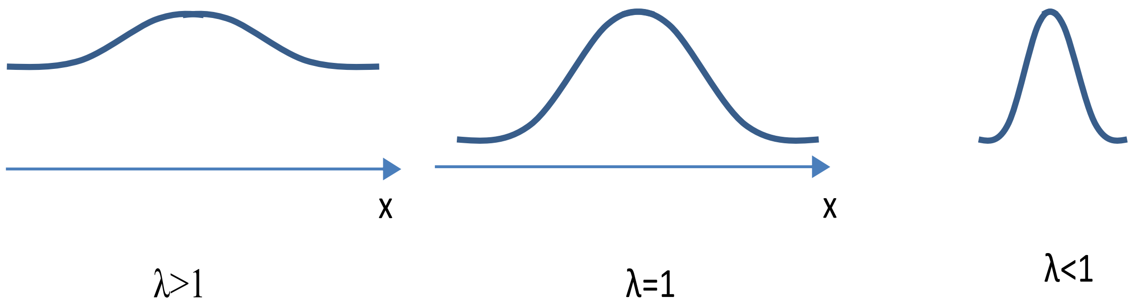
$$\Phi_0 = \frac{D^2}{2} \int_{-\infty}^{+} \frac{1}{q}\left(\frac{\partial q}{\partial x}\right)^2 dx^2$$

Fickian process

ACTIVE ENERGY DISTRIBUTION

$$\Upsilon = p_1 + (1-p_1)(p_1 \ln p_1)^2 \frac{R_0^2}{D^2}\left(\int_{-\infty}^{+\infty} \frac{1}{q}\left(\frac{\partial^3 q}{\partial x^3}\right)^2 dx \Big/ \int_{-\infty}^{+\infty} \frac{1}{q}\left(\frac{\partial q}{\partial x}\right)^2 dx \right) \leq 1$$

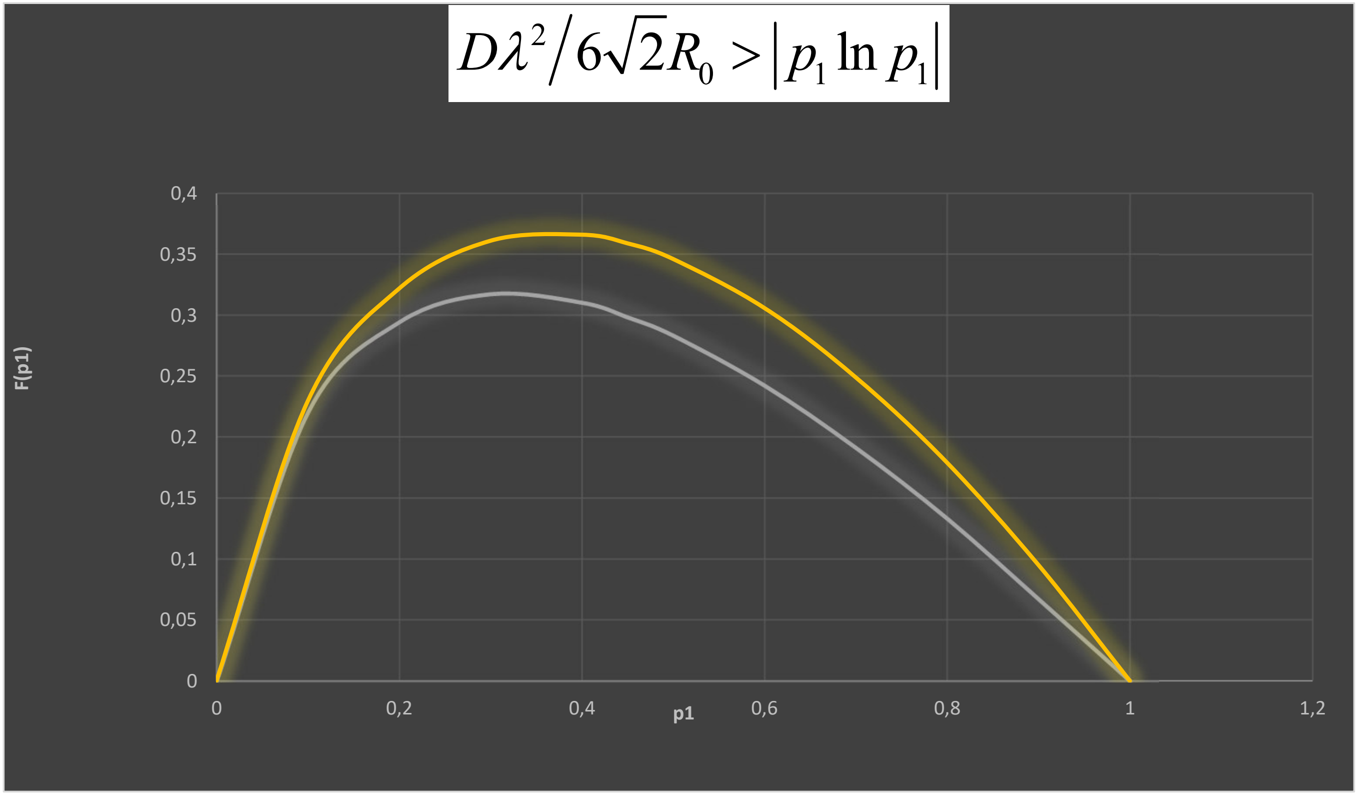
Density distribution $q(x) \approx \exp(-(x/\lambda)^2)$. The distribution spreads out with increasing values of λ.



ACTIVE ENERGY DISTRIBUTION

Now let us assume the density distribution is of the order:

$q \Box \exp\left(-x/\lambda\right)^2$ we get $D\lambda^2/6\sqrt{2}R_0 > \left|p_1 \ln p_1\right|$



APPLICATIONS

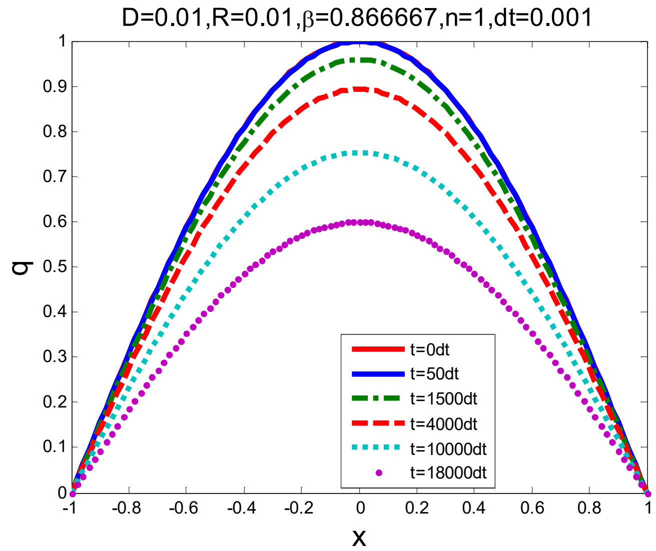
A solution in the search of a problem

Capital flow
Population dynamics, Epidemics
Biochemical reactions

***Nature*, 517, 227-230 (2015)**
The heat released during catalytic turnover enhances the diffusion of an enzyme
Clement Riedel1 , Ronen Gabizon , Christian A. M. Wilson, Kambiz Hamadani1, Konstantinos Tsekouras , Susan Marqusee, Steve Presse & Carlos Bustamante

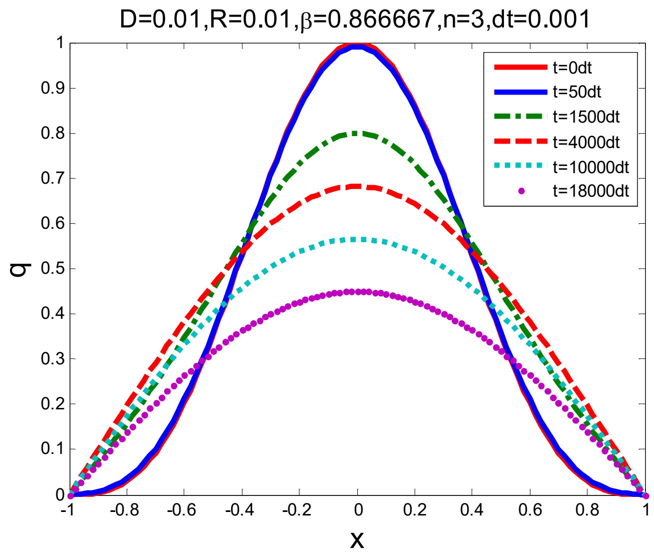
$$D = D_0 + \frac{2\gamma Q}{3\zeta^2} mV = D_0 + \alpha V$$

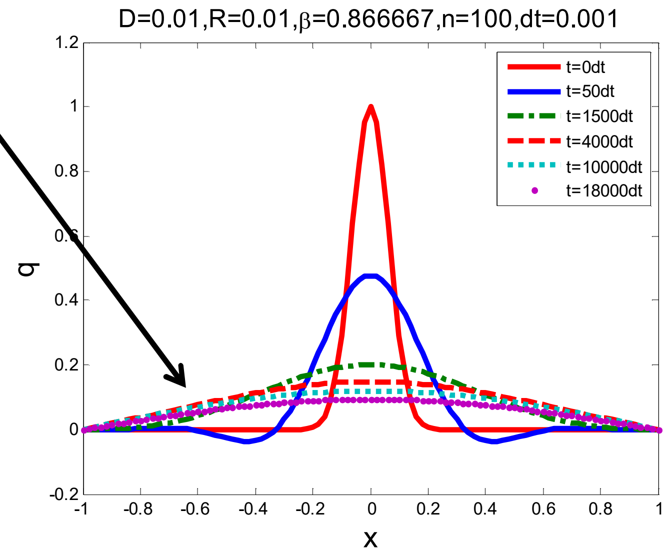
IS THERE A CRITICAL N? $Q(X,0)=(COS(0.5\pi X))^N$



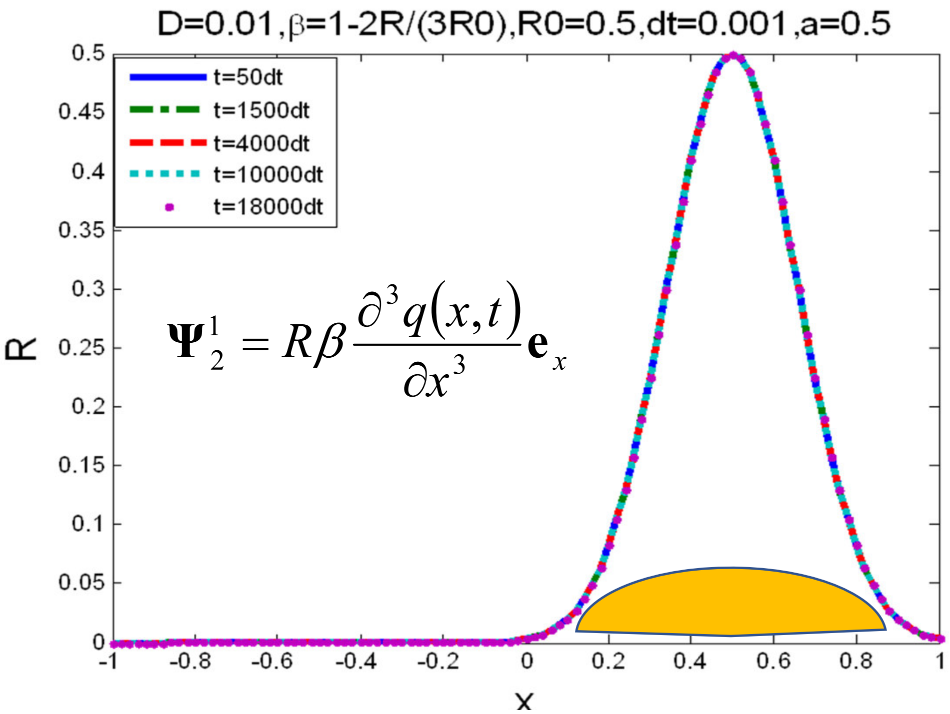
The mass preservation principle depends on the concentration factor

Minimum formation only for $n>n_{crit}$





MEIOS NÃO HOMOGÊNEOS – AÇÃO DE FEROMÔNIO



Distribuição do feromônio no substrato (-1,1)

$$\frac{\partial q(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\beta D \frac{\partial q(x,t)}{\partial x}\right] - \frac{\partial}{\partial x}\left[(1-\beta) R\beta \frac{\partial^3 q(x,t)}{\partial x^3}\right]$$

I.C.: $q(x,0) = 0.25(1+\cos(\pi x)),$

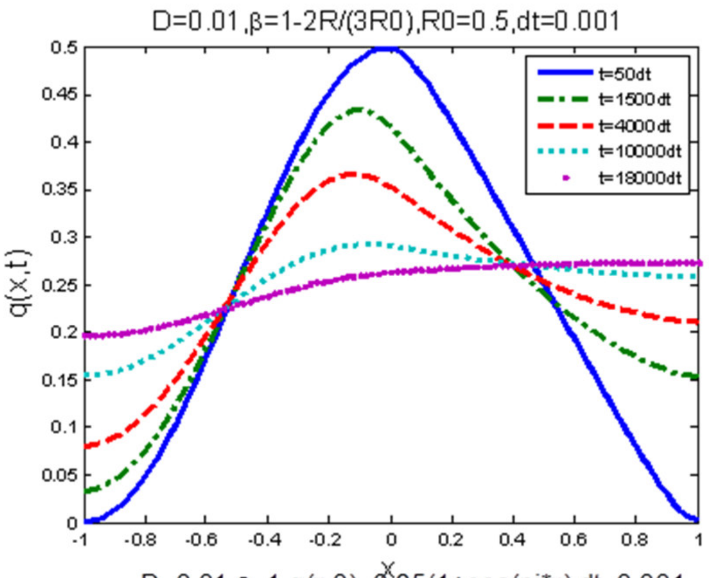
B.C.: $\partial q(-1,t)/\partial x = 0 \qquad \partial q(1,t)/\partial x = 0$

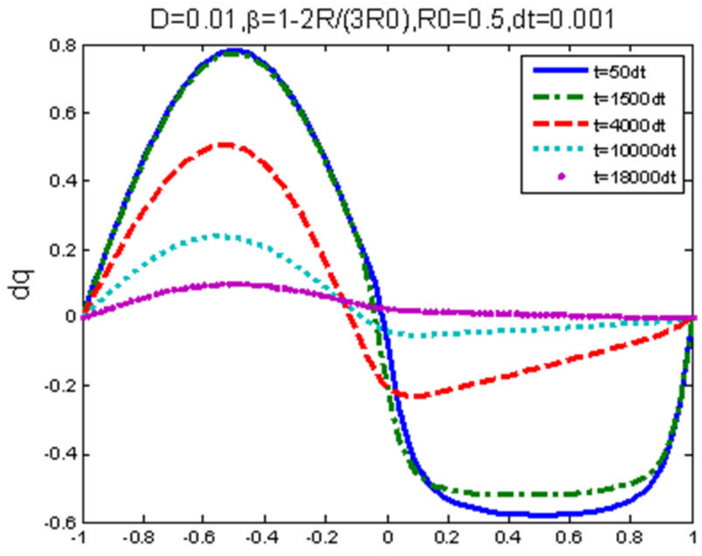
$\partial^3 q(-1,t)/\partial x^3 = 0 \qquad \partial^3 q(1,t)/\partial x^3 = 0$

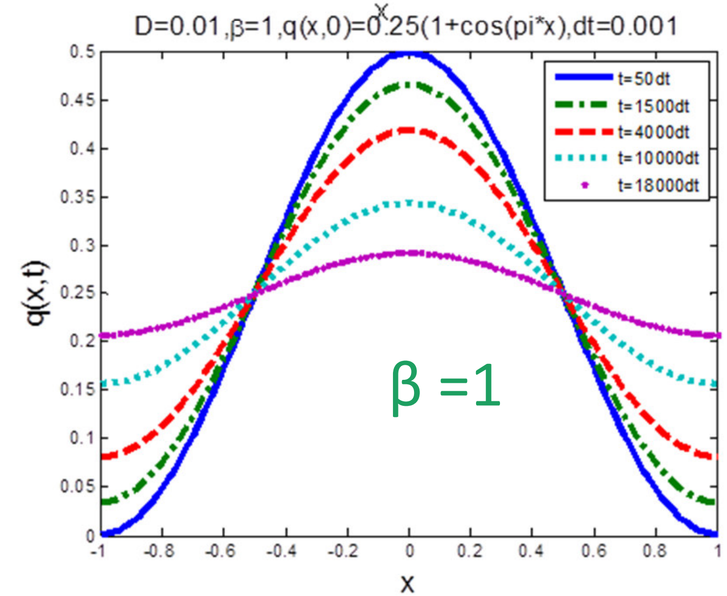
$$\beta(x) = 1 - 2R(x)/3R_0$$

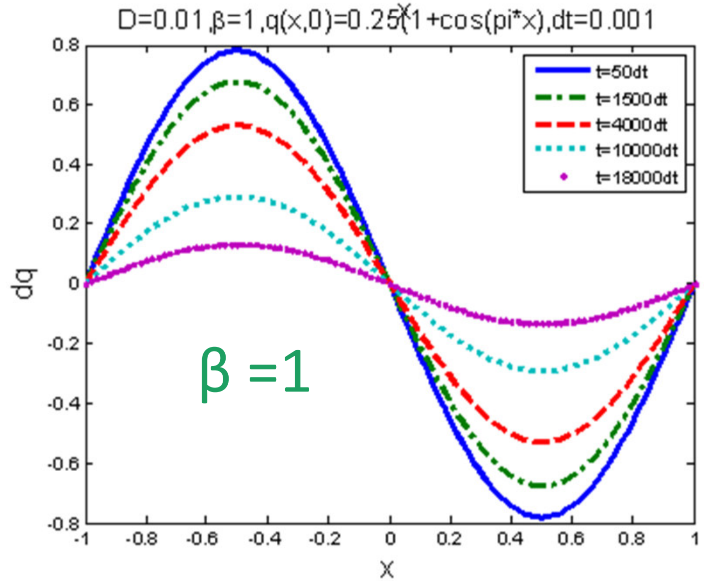
$$R(x) = R_0 \exp(-20(x-0.5)^2),$$

$R_0 = 0.5 \qquad D=0.01$

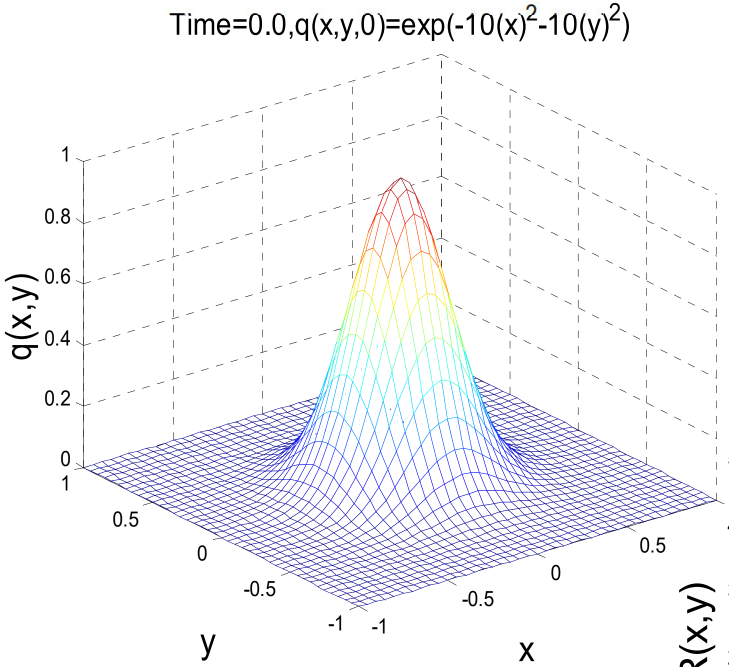

D=0.01,β=1-2R/(3R0),R0=0.5,dt=0.001
q(x,t)
x
t=50dt
t=1500dt
t=4000dt
t=10000dt
t=18000dt


D=0.01,β=1-2R/(3R0),R0=0.5,dt=0.001
dq
x
t=50dt
t=1500dt
t=4000dt
t=10000dt
t=18000dt


D=0.01,β=1,q(x,0)=0.25(1+cos(pi*x),dt=0.001
q(x,t)
x
t=50dt
t=1500dt
t=4000dt
t=10000dt
t=18000dt
β =1

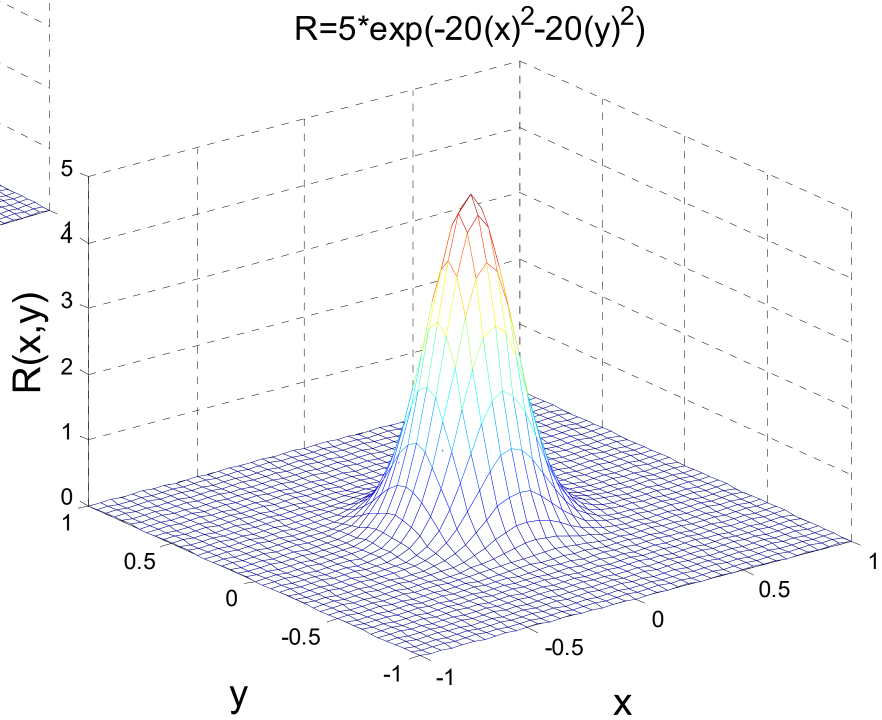

D=0.01,β=1,q(x,0)=0.25(1+cos(pi*x),dt=0.001
dq
x
t=50dt
t=1500dt
t=4000dt
t=10000dt
t=18000dt
β =1

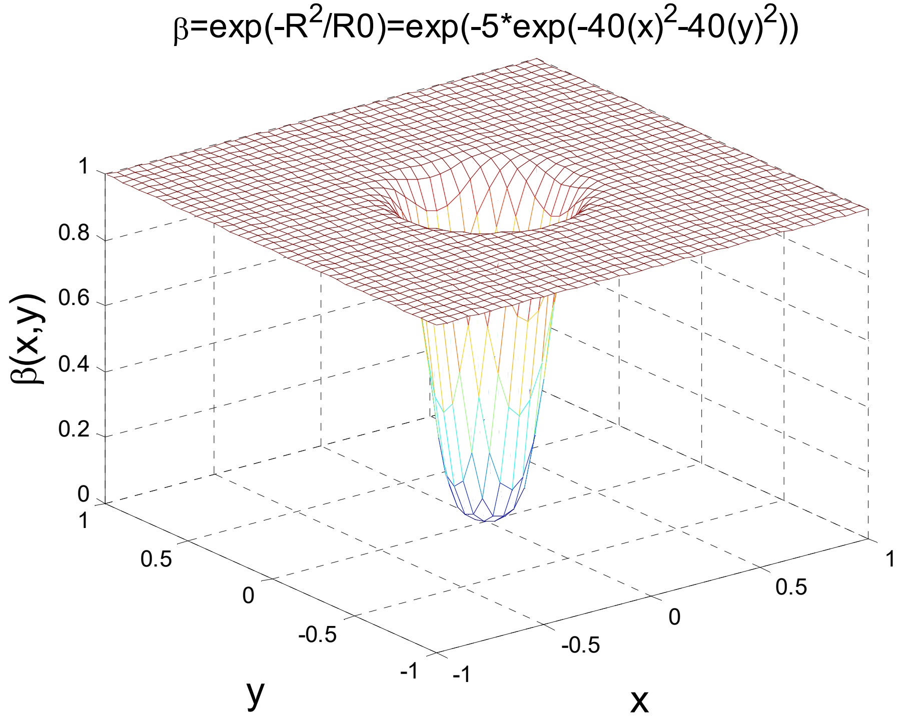
CONCENTRATION EVOLUTION IN 2D ANISOTROPIC MEDIUM: EXAMPLE 2



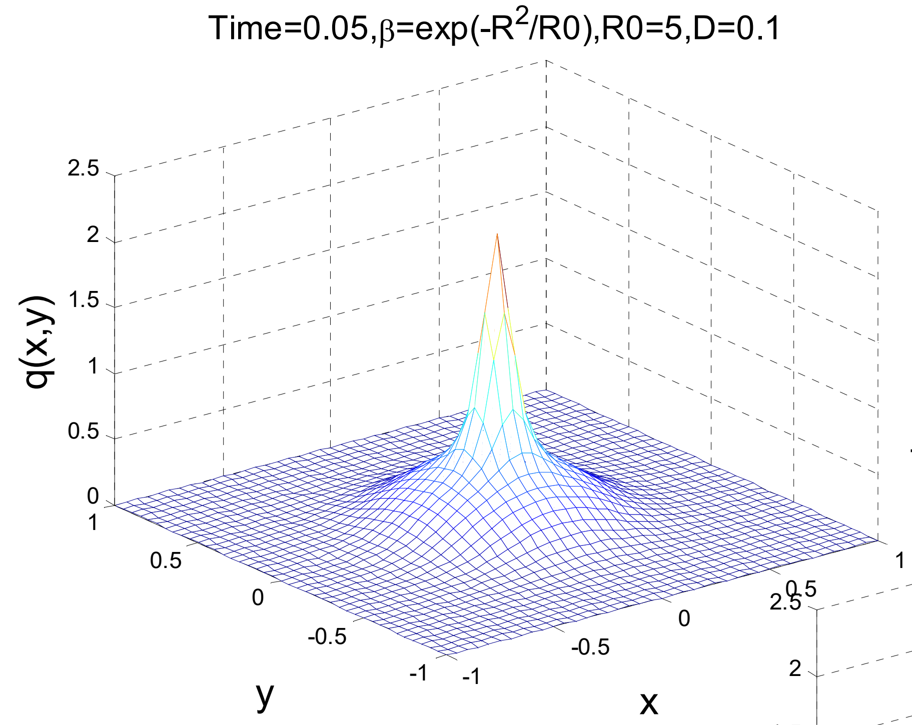
Initial Conditions

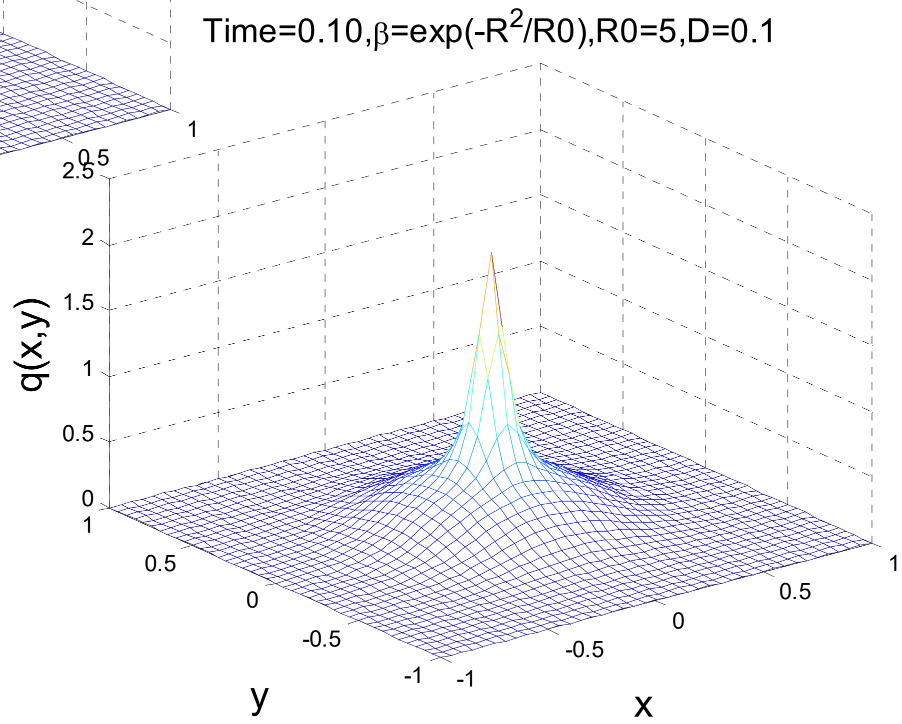
R(x,y)

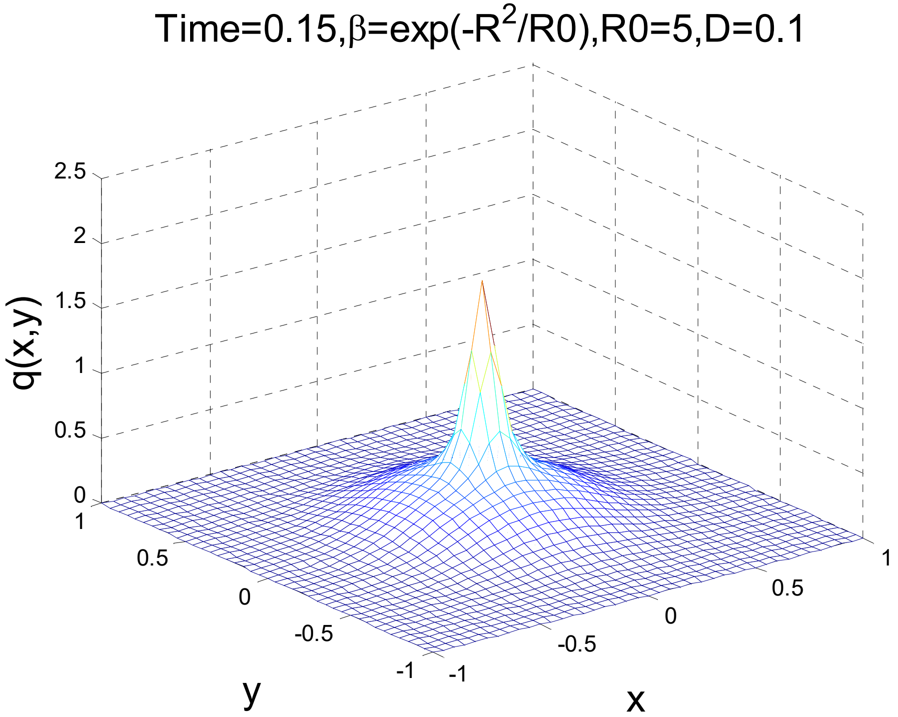




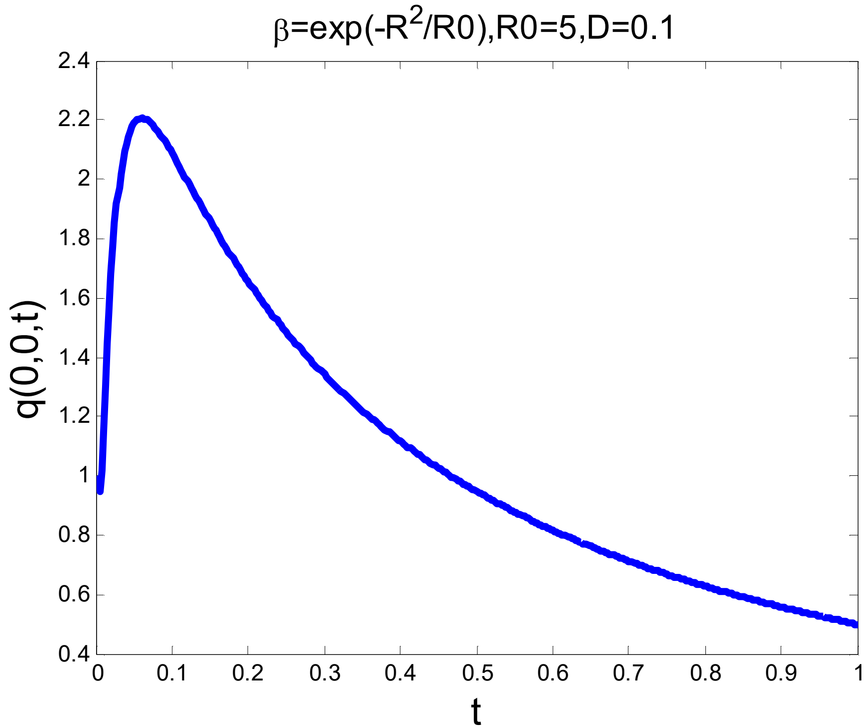
β=exp(-R2/R0)=exp(-5*exp(-40(x)2-40(y)2))
β(x,y)
1
0.8
0.6
0.4
0.2
0
1
0.5
0
-0.5
-1
y
-1
-0.5
0
0.5
1
x


Time=0.05,β=exp(-R^2/R0),R0=5,D=0.1
q(x,y)
2.5
2
1.5
1
0.5
0
1
0.5
0
-0.5
-1
y
-1
-0.5
0
0.5
1
x


Time=0.10,β=exp(-R^2/R0),R0=5,D=0.1
q(x,y)
2.5
2
1.5
1
0.5
0
1
0.5
0
-0.5
-1
y
-1
-0.5
0
0.5
1
x

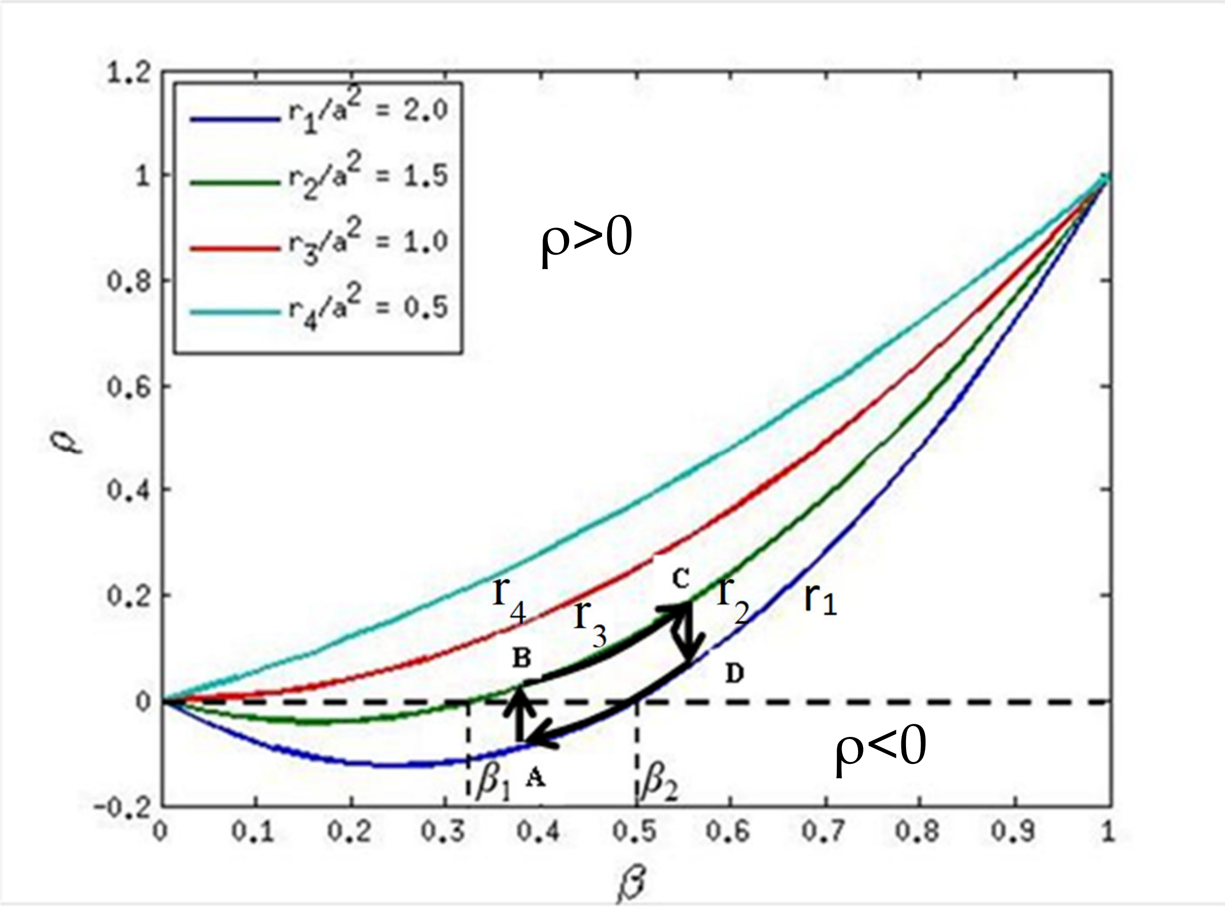


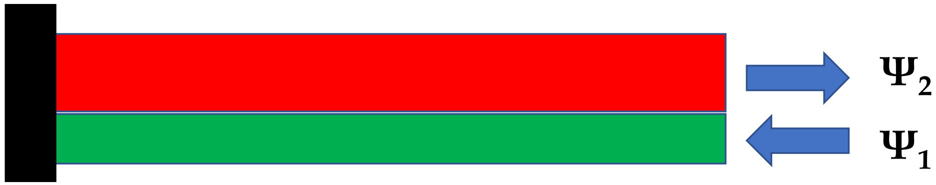
Time=0.15,β=exp(-R^2/R0),R0=5,D=0.1
q(x,y)
2.5
2
1.5
1
0.5
0
1
0.5
0
-0.5
-1
-1
-0.5
0
0.5
1
y
x



β=exp(-R^2/R0),R0=5,D=0.1
q(0,0,t)
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
t

FLUXO DE CAPITAL





Condições iniciais:

$$q(x,0) = p_0 \cosh\left(\frac{x}{a}\right)$$

$$q(x,t) = p_0 \exp(\rho t)\cosh\left(\frac{x}{a}\right)$$

$$\rho = \frac{D\beta}{a^2}\left(1-(1-\beta)\frac{r}{a^2}\right) \qquad r=R/D$$

ρ>0 densificação

ρ<0 rarefação

ρ=0 estagnação

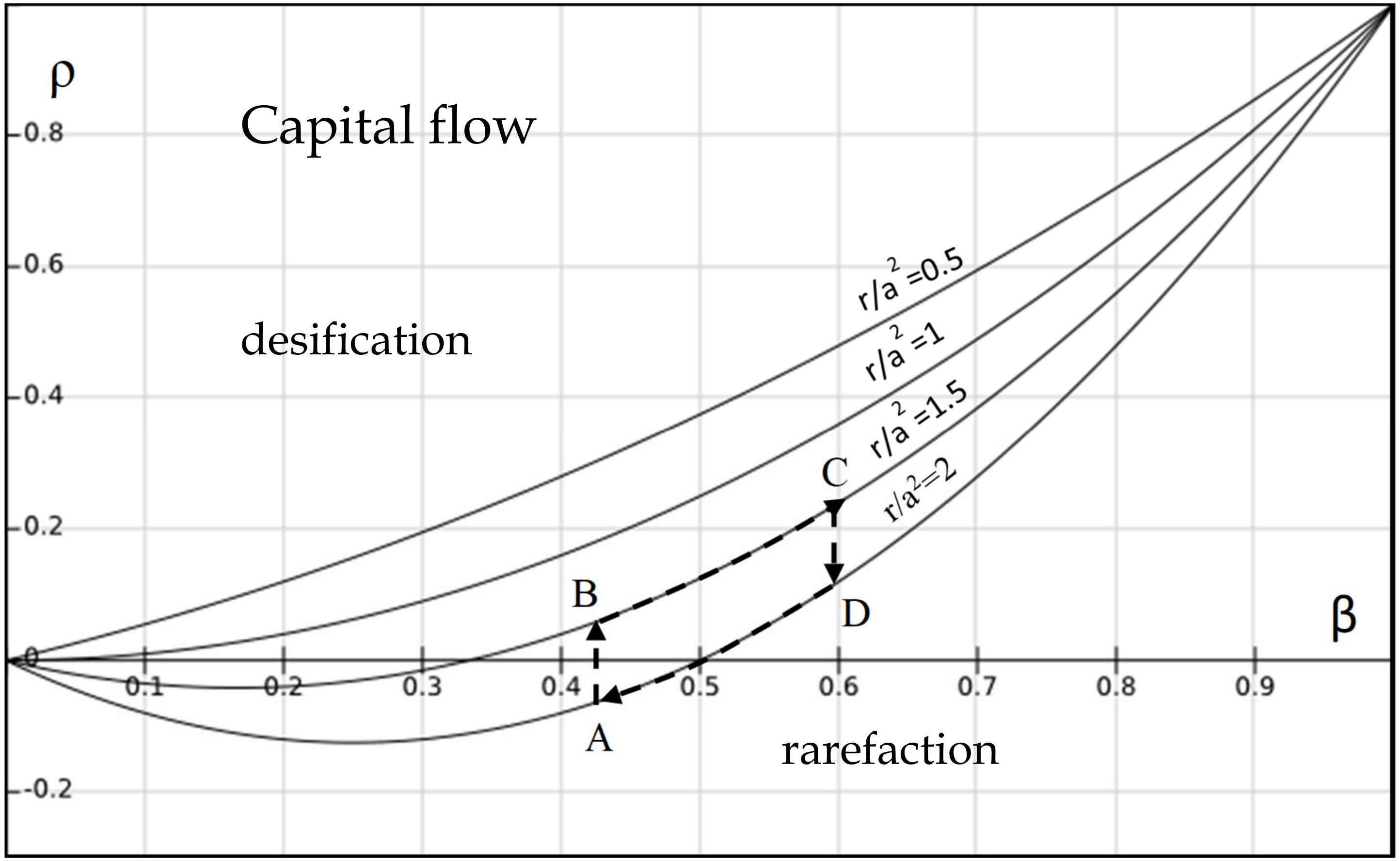
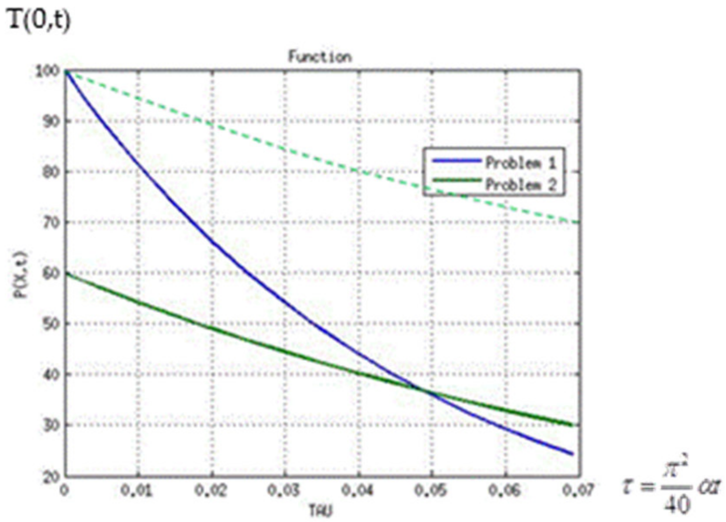


Fig.8. Variação do expoente ρ com β correspondendo à fração de entrada de capital para diferentes valores de $r = R / D$. Na região acima de AB há crescimento econômico, $\rho > 0$. A região abaixo de AB corresponde ao encolhimento econômico $\rho<0$ e os pontos sobre AB correspondem à estagnação $\rho = 0$.

MPEMBA EFFECT

Does hot water freezes quicker than cold water?



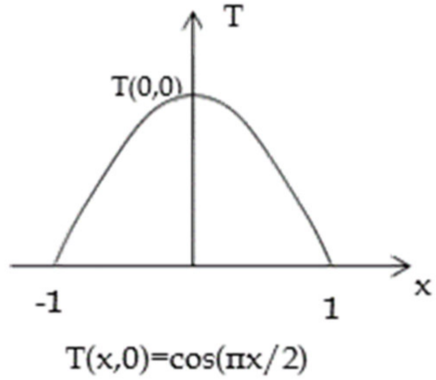


Fig.7. Problem 1: cooling a conductive material according to the bi-flux theory with $\gamma/\alpha=24/\pi^2$ and $\beta=0.58$ with $T(0,0)=100^0C$, blue curve; Problem 2: cooling a conductive material according to the classical heat equation with $T(0,0)=60^0C$ and $T(0,0)= 100^0C$, green curves.

FREEZING BY HEATING

I am deeply indebted to several collaborators who have helped to develop the diffusion theory presented here:

Augusto Galeão, Maosheng Jiang, Antonio Silva Neto, Diego Knupp, J.R. Faria, A.P.P. Wyse, A.J.B. Santos, L. Bevilacqua, and F.P. Costa João Flávio Vieira Vasconcellos, Jader Lugon Junior, Gisele Moraes Marinho, Paulo Gomes Watts, Luciano G. da Silva, J.G.Simas,Ana P. Rio Doce, Flavio Pireonbom.

Also the support of the following research institutions and projects were fundamental to carry on our work:
FINEP Convenio:01.16.0071.00, CNPq for the continued support through the senior research grant, NIDF-Petrobras Project, CAPES-INMETRO, CNPq-TWAS, IEA-USP,

In the Search of the Big-Glub

Heading towards the End...