PQI-5776

Aula 8 – Dissolução de partícula esférica

título

Aplicação

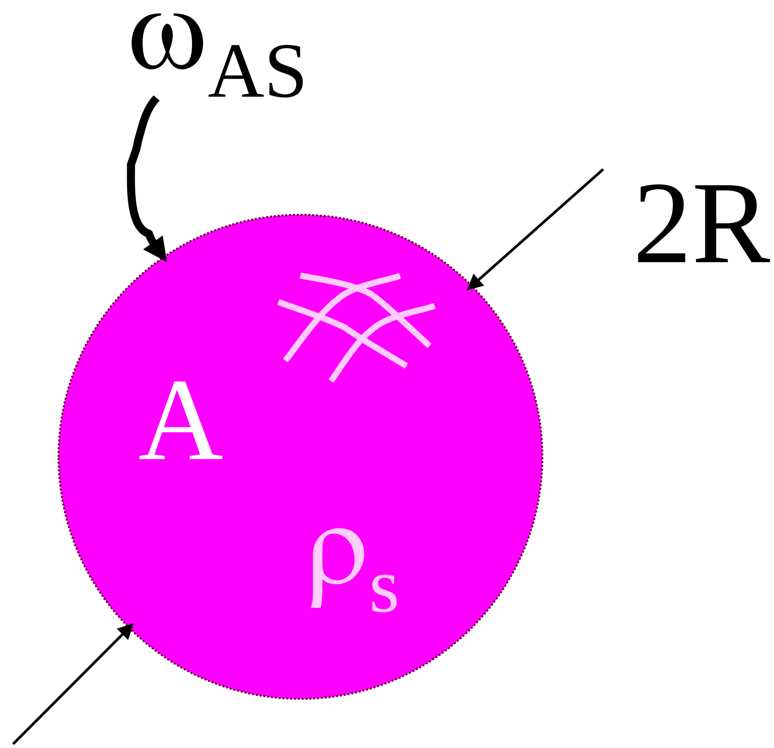
B (fluido)

$v \approx 0$

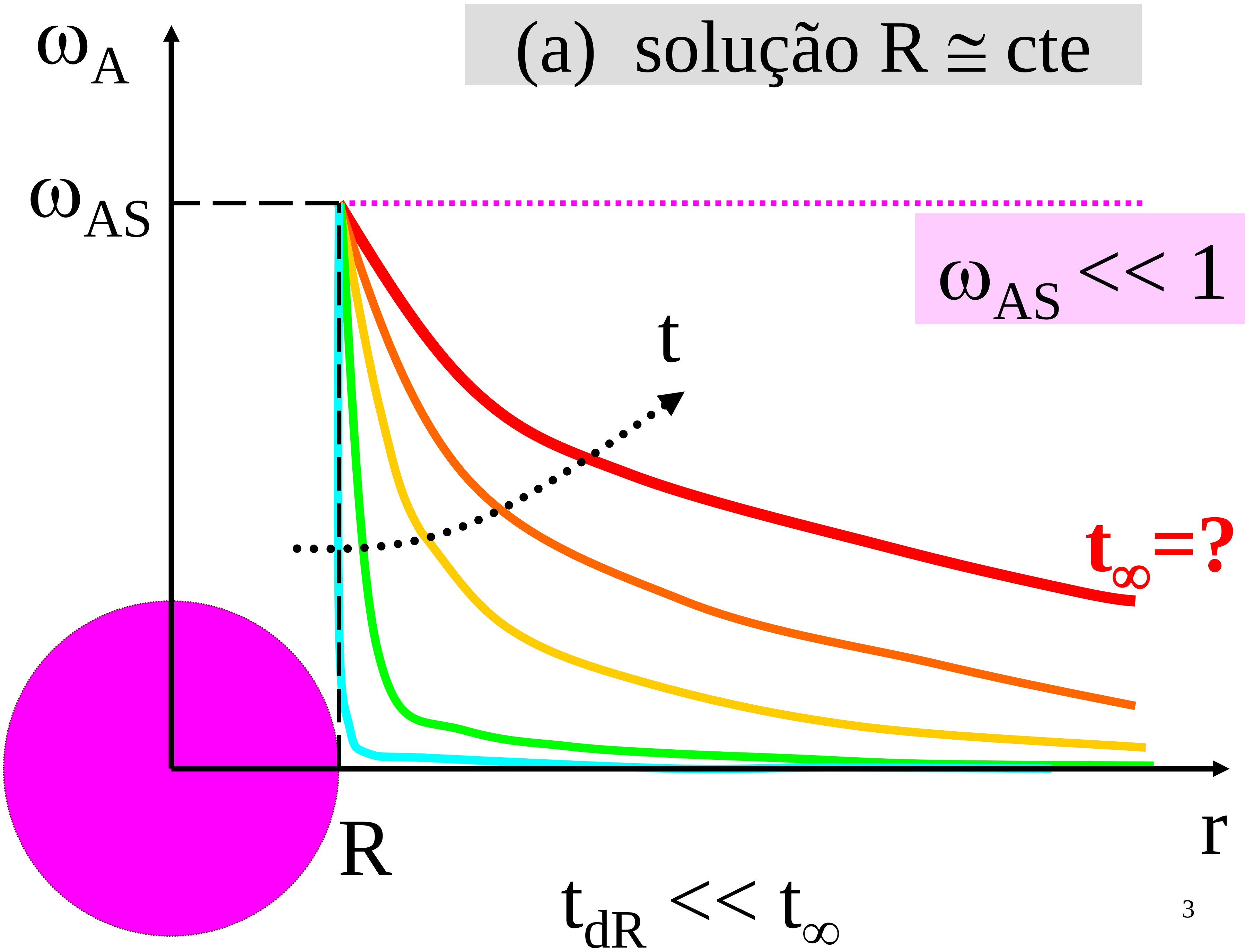
ρ

D_{AB}

p e T ctes



secagem,
evaporação de uma gota,
dissolução de um fármaco


(a) solução R ≅ cte
ω_A
ω_{AS}
$\omega_{AS} << 1$
t
$t_\infty = ?$
R
r
$t_{dR} << t_\infty$

equacionamento

$$\frac{\partial \rho \varphi}{\partial t} + \operatorname{div} \rho \vec{v} \varphi = -\operatorname{div} \vec{j}_\phi + \dot{\sigma}_{V_\phi}$$

$$\varphi = \omega_A$$

$$\underbrace{\frac{\partial \rho \omega_A}{\partial t}}_{\substack{=0 \\ st.st.}} + \operatorname{div} \underbrace{\rho \vec{v}}_{\vec{n}} \omega_A = -\operatorname{div} \overbrace{\vec{n}_A - \vec{n}\,\omega_A}^{\vec{j}_A} + \underbrace{r_A}_{\substack{=0 \\ s/reação}}$$

$$\operatorname{div} \vec{n}_A = 0$$

$$\vec{n}_A = \vec{j}_A + \overbrace{\vec{n}_A + \underbrace{\vec{n}_B}_{=0}}^{\vec{n}} \omega_A = \vec{j}_A + \vec{n}_A \ \omega_A$$

$$\vec{n}_A (1 - \underbrace{\omega_A}_{<<1}) = \vec{j}_A$$

$$\vec{n}_A \approx \vec{j}_A$$

$$\operatorname{div} \vec{j}_A = 0$$

modelo

$$\operatorname{div}\vec{j}_A = 0$$

$$\vec{j}_A = -\rho D_{AB}\,\vec{\operatorname{grad}}\,\omega_A$$

$$\operatorname{div}(-)\underbrace{\rho D_{AB}}_{p;T\ \text{ctes}}\,\vec{\operatorname{grad}}\,\omega_A = -\rho D_{AB}\,\operatorname{Lap}\,\omega_A = 0$$

$$\operatorname{Lap}\,\omega_A = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\omega_A}{\partial r}\right) + \ldots = 0$$

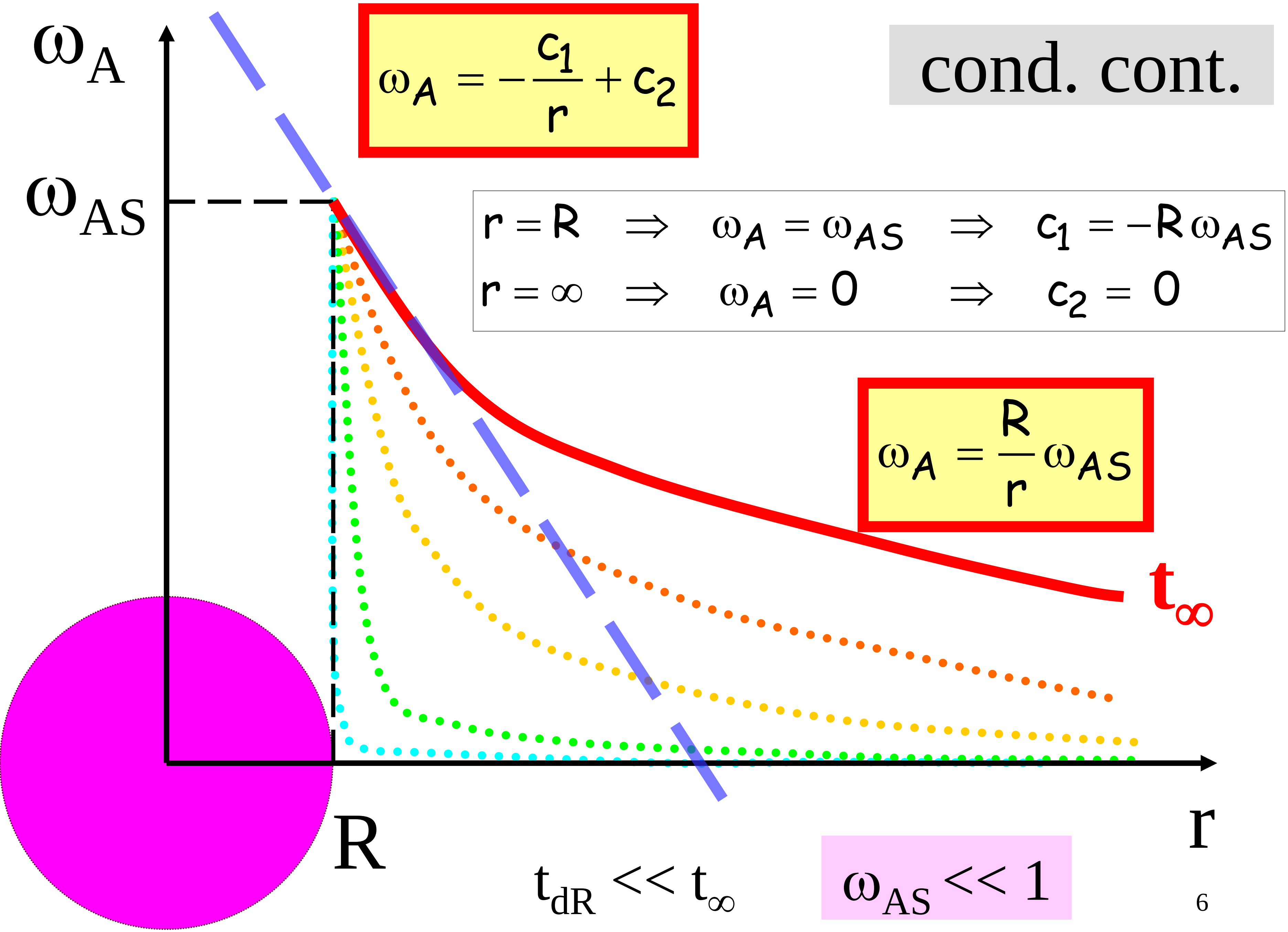
$$\frac{d}{dr}\left(r^2\frac{d\omega_A}{dr}\right) = 0$$

$$r^2\frac{d\omega_A}{dr} = c_1$$

$$d\omega_A = \frac{c_1}{r^2}dr$$

$$\omega_A = -\frac{c_1}{r} + c_2$$

perfil


ω_A
ω_{AS}
$\omega_A = -\frac{c_1}{r} + c_2$
cond. cont.
$r = R \Rightarrow \omega_A = \omega_{AS} \Rightarrow c_1 = -R\,\omega_{AS}$
$r = \infty \Rightarrow \omega_A = 0 \Rightarrow c_2 = 0$
$\omega_A = \frac{R}{r}\omega_{AS}$
t_∞
R
r
$t_{dR} << t_\infty$
$\omega_{AS} << 1$

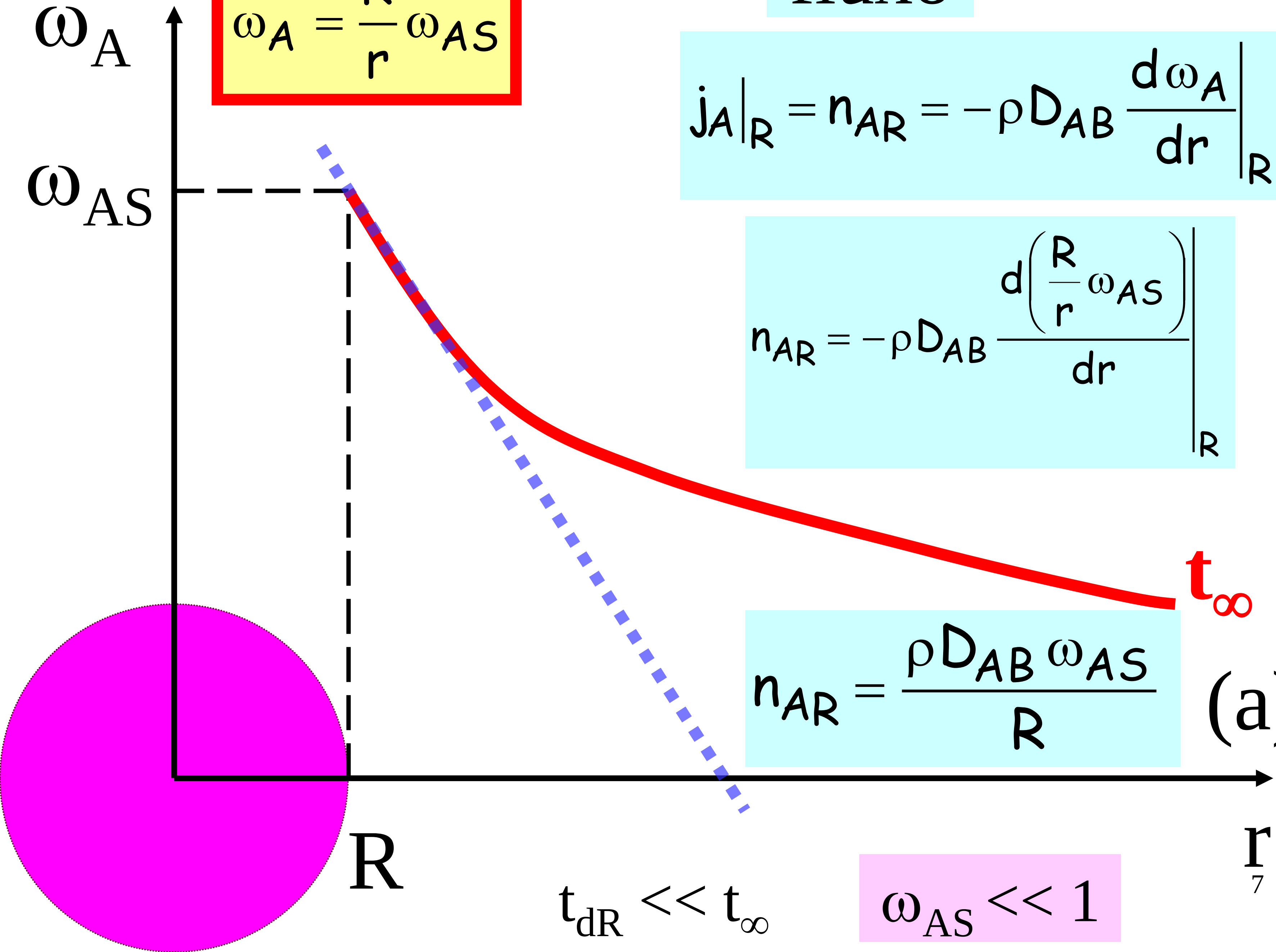
$$\omega_A = \frac{R}{r}\omega_{AS}$$

fluxo

$$j_A\big|_R = n_{AR} = -\rho D_{AB}\left.\frac{d\omega_A}{dr}\right|_R$$

$$n_{AR} = -\rho D_{AB}\left.\frac{d\left(\frac{R}{r}\omega_{AS}\right)}{dr}\right|_R$$

$$n_{AR} = \frac{\rho D_{AB}\,\omega_{AS}}{R}$$



$\omega_{AS} << 1$

(b) Coeficiente convectivo

$$n_{AR} = \frac{\rho D_{AB} \omega_{AS}}{R} = k\rho(\omega_{AS} - \underbrace{\omega_{A\infty}}_{=0})$$

$$k = \frac{D_{AB}}{R}$$

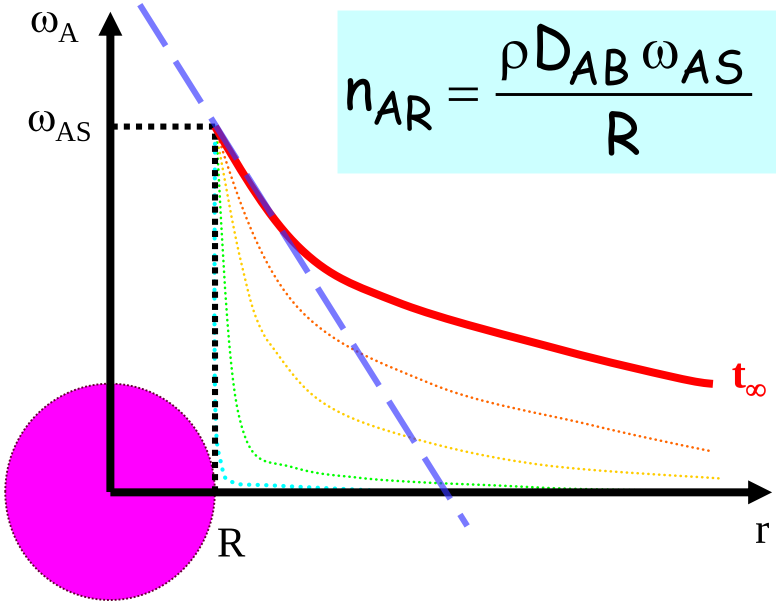
$$\frac{kR}{D_{AB}} = 1$$

$$\frac{kD}{D_{AB}} = 2 = Sh$$

Se as partículas forem muito pequenas mesmo que $v \neq 0$ não se observa movimento relativo então Sh = 2 e Nu = 2 também. No caso geral:

$$Sh = 2 + 0{,}6 Re^{1/2} Sc^{1/3}$$

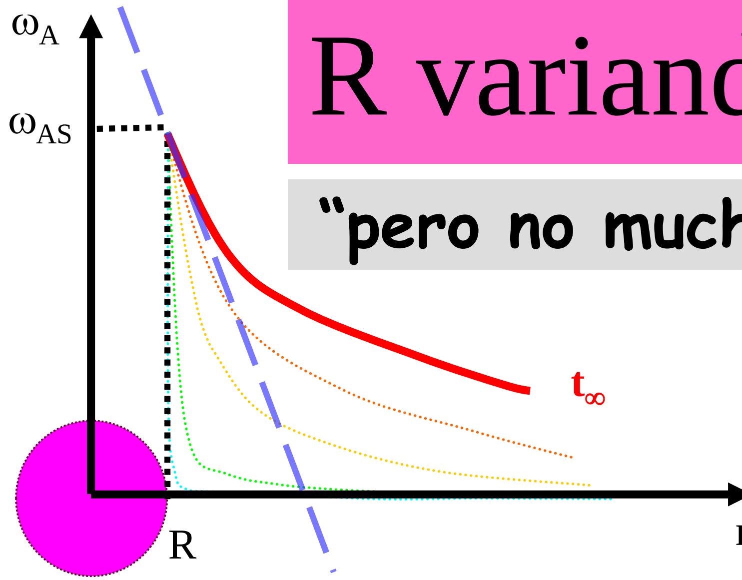
Sherwood



$$n_{AR} = \frac{\rho D_{AB}\,\omega_{AS}}{R}$$

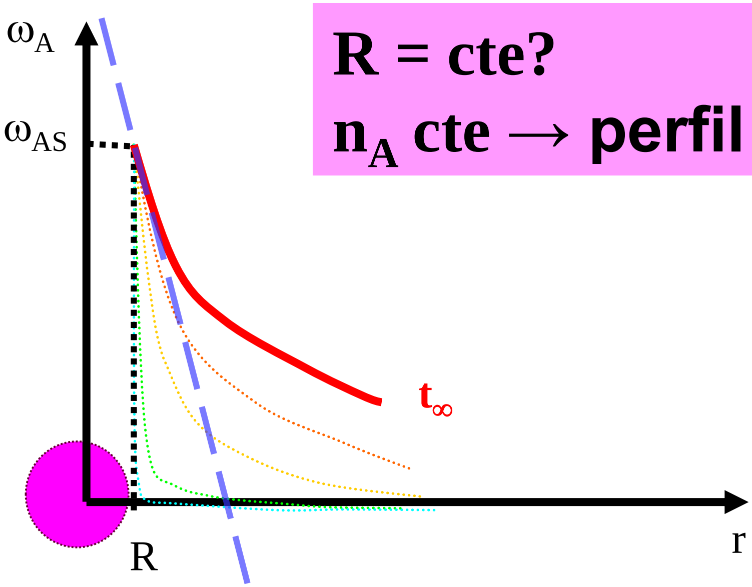
R variando

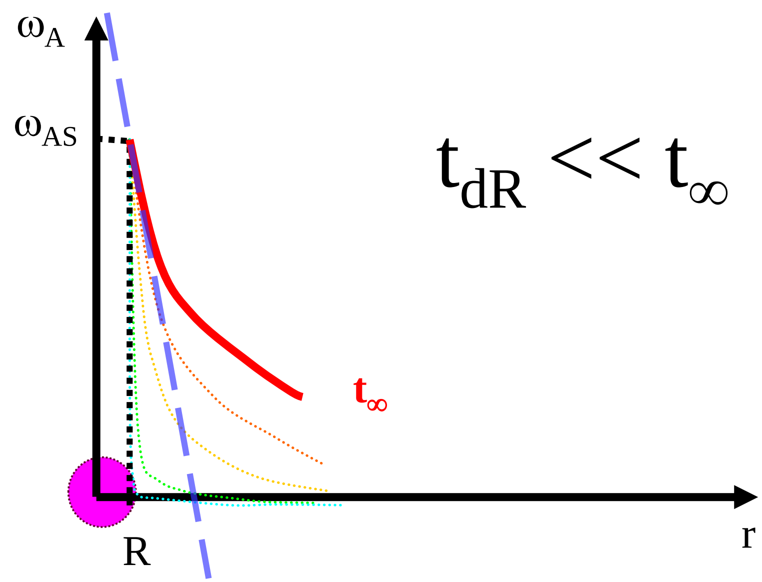
"pero no mucho"



R = cte?

n_A cte → perfil cte?





$t_{dR} << t_{\infty}$

"quase" estacionário

$\omega_{AS} << 1$

(c)Tempo para dissolução total

pseudo-permanente

n_{AR} aumenta mas a área diminui

$$\frac{dm_A}{dt} = -An_{AR} = \frac{d(\rho_s V)}{dt} = \rho_s \frac{d(4/3\pi R^3)}{dt} = -4\pi R^2 n_{AR}$$

$$\rho_s \frac{4}{3}\frac{d(R^3)}{dt} = -4R^2\left[\frac{\rho D_{AB}\,\omega_{AS}}{R}\right] \qquad \rho_s \frac{3}{3R}R^2 dR = -\rho D_{AB}\,\omega_{AS}\,dt$$

$$\frac{\rho_s}{\rho D_{AB}\,\omega_{AS}} R\,dR = -dt \qquad \int_R^0 \frac{\rho_s}{\rho D_{AB}\,\omega_{AS}} R\,dR = -\int_0^t dt$$

$$t = \frac{R^2\,\rho_s}{2\rho D_{AB}\,\omega_{AS}} \qquad t \approx m^{2/3}$$

numéricos

ácido benzóico sólido em água; R = 1 cm

D_{AB} = 10^{-5} cm^2/s; ρ_S ~ 1 g/cm^3; ρ ~ 1 g/cm^3

solubilidade = 2,5 g/l = 0,0025 g/cm^3 $\rightarrow$ ω_{AS} = 0,0025

$$t_{diss} = \frac{1^2 .1}{2.1.10^{-5}.0,0025} = 2.10^7 s \approx 5000 h$$

iodo sólido em ar; R = 1 cm

D_{AB} = 10^{-1} cm^2/s; ρ_S ~ 1 g/cm^3; ρ ~ 0,001 g/cm^3

p^V_{I2} = 0,5 mmHg ; x_{AS} = $6,6.10^{-4}$ $\rightarrow$ ω_{AS} = $5,7.10^{-3}$

$$t_{diss} = \frac{1^2 .1}{2.10^{-3}.10^{-1}.5,7.10^{-3}} = 10^6 s \approx 300 h$$

(d) Transiente

$$\frac{\partial \rho \omega_A}{\partial t} + \operatorname{div} \underbrace{\rho \vec{v}}_{\vec{n}} \omega_A = -\operatorname{div} \overbrace{\vec{j}_A}^{\vec{n}_A - \vec{n}\,\omega_A} + \underbrace{r_A}_{=0 \text{ s/reação}}$$

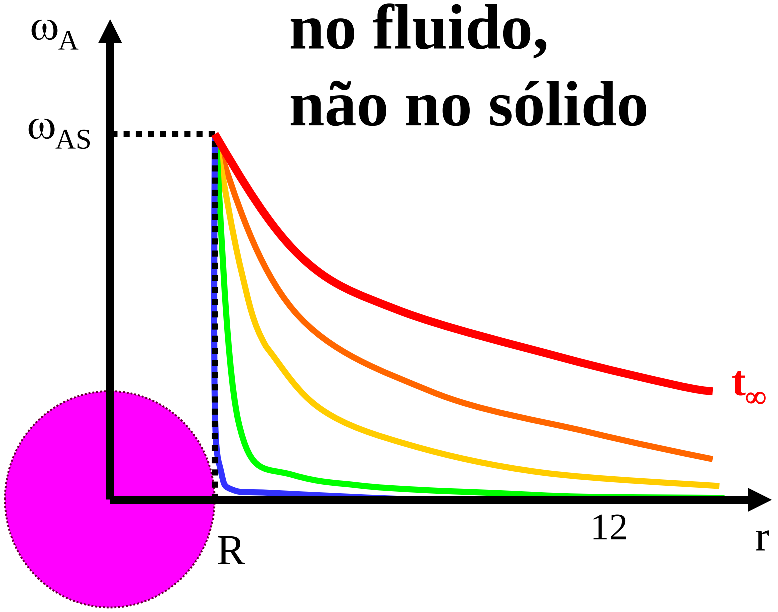
$$\rho \frac{\partial \omega_A}{\partial t} + \omega_A \underbrace{\frac{\partial \rho}{\partial t}}_{=0} = -\operatorname{div} \vec{n}_A = -\operatorname{div} \vec{j}_A = -\rho D_{AB} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \omega_A}{\partial r} \right)$$

$$\frac{\partial \omega_A}{\partial t} + D_{AB} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \omega_A}{\partial r} \right) = 0$$

$t \le 0$	$\omega_A = \omega_{A\infty} = 0$
$r = R$	$\omega_A = \omega_{AS}$
$r = \infty$	$\omega_A = 0$

$$\xi = \frac{r - R}{2\sqrt{D_{AB} t}}$$

no fluido, não no sólido



$$\frac{\partial \omega_A}{\partial t} + D_{AB}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\omega_A}{\partial r}\right)=0$$

$$\frac{d\varpi}{d\xi} = \Omega \frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2 \frac{d\varpi}{d\xi}\right)$$

$$t \le 0 \qquad \omega_A = \omega_{A\infty} = 0$$
$$r = R \qquad \omega_A = \omega_{AS}$$
$$r = \infty \qquad \omega_A = 0$$

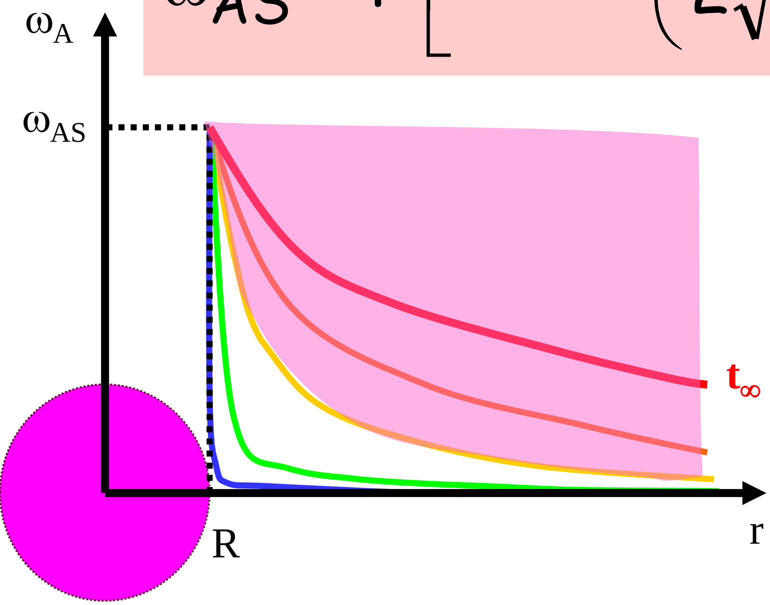
combinando

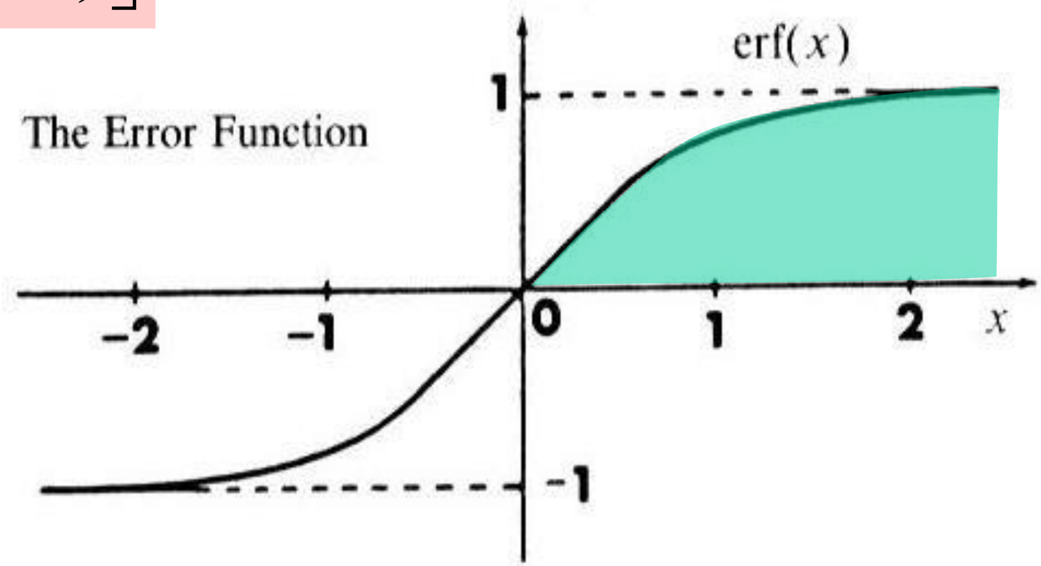
$$\xi = \frac{r-R}{2\sqrt{D_{AB}t}} \qquad \varpi = \frac{\omega_A}{\omega_{AS}}$$

$$\xi = \infty \qquad \varpi = 0$$
$$\xi = 0 \qquad \varpi = 1$$
$$\xi = \infty \qquad \varpi = 0$$

$$\varpi = \frac{R}{r}\left[1 - \mathrm{erf}(x)\right]$$

$$\frac{\omega_A}{\omega_{AS}} = \frac{R}{r}\left[1 - \mathrm{erf}\left(\frac{r-R}{2\sqrt{D_{AB}t}}\right)\right]$$





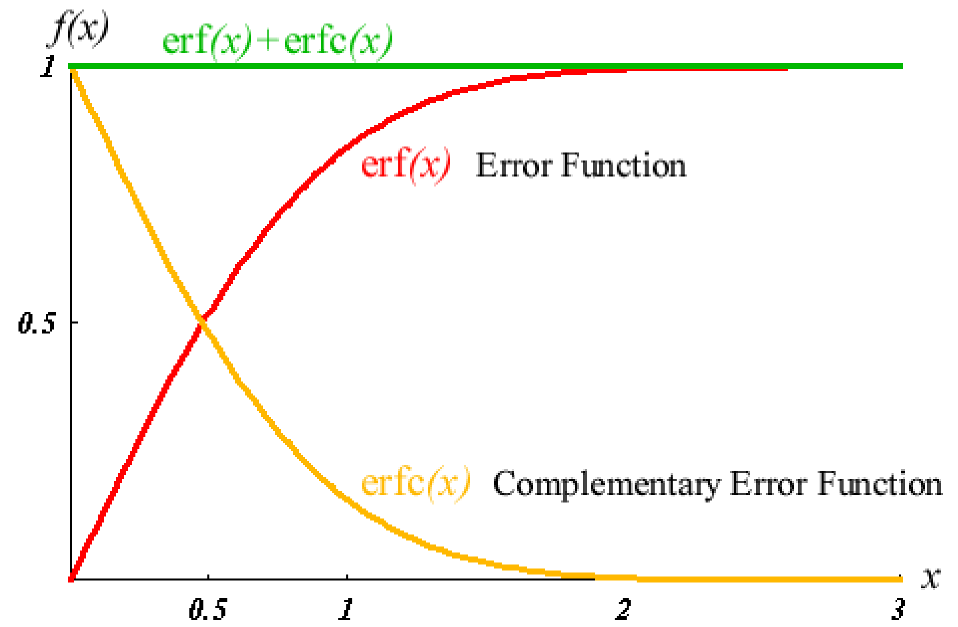
Error Function

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\xi^2}\, d\xi,$$

$$\operatorname{erf} \infty = 1,$$

$$\operatorname{erf}(-x) = -\operatorname{erf} x.$$

$$\operatorname{erfc} x = 1 - \operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-\xi^2}\, d\xi.$$



Para x << 1

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)n!}.$$

Derivadas

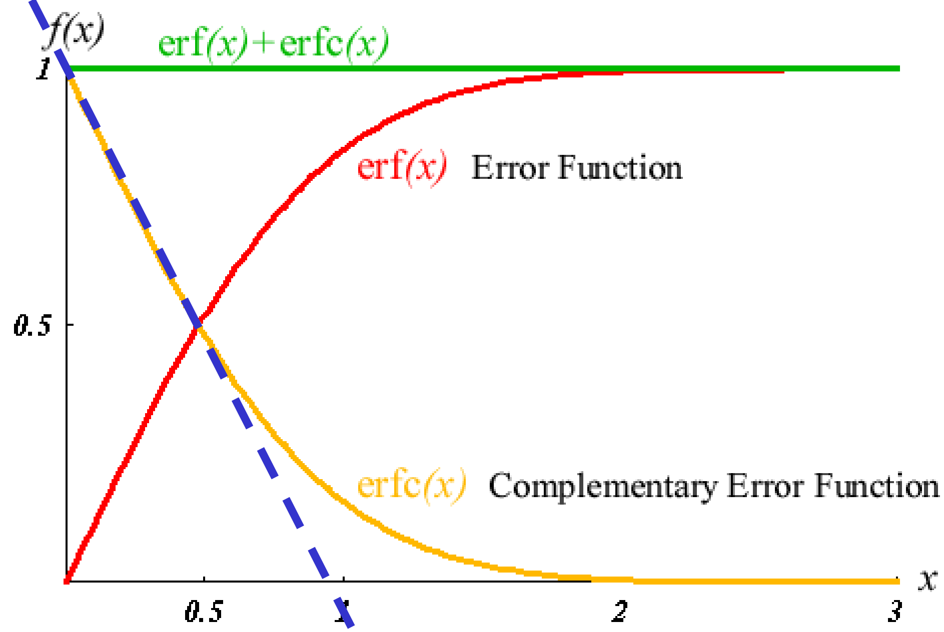
$$\Phi_n(x) = \frac{d^n}{dx^n} \operatorname{erf} x,$$

$$\Phi_1(x) = \frac{2}{\sqrt{\pi}} e^{-x^2},$$

$$\Phi_2(x) = -\frac{4}{\sqrt{\pi}} x e^{-x^2},$$

fluxo

$$\omega_A = \frac{R\omega_{AS}}{r}\left[1 - \mathrm{erf}\left(\frac{r-R}{2\sqrt{D_{AB}t}}\right)\right]$$



$$j_A\big|_R = n_{AR} = -\rho D_{AB}\left.\frac{d\omega_A}{dr}\right|_R$$

$$n_{AR} = -\rho D_{AB}\frac{d}{dr}\left\{\frac{R\omega_{AS}}{r}\left[1-\mathrm{erf}\left(\frac{r-R}{2\sqrt{D_{AB}t}}\right)\right]\right\}_R =$$

$$= -\rho D_{AB}\left\{-\frac{R\omega_{AS}}{r^2}\left[1-\mathrm{erf}\left(\frac{r-R}{2\sqrt{D_{AB}t}}\right)\right] + \frac{R\omega_{AS}}{r}\left[0 - \frac{2}{\sqrt{\pi}}e^{-\left(\frac{r-R}{2\sqrt{D_{AB}t}}\right)^2}\frac{1}{(-)2\sqrt{D_{AB}t}}\right]\right\}_R$$

$$n_{AR} = -\rho D_{AB}\left\{-\frac{R\omega_{AS}}{R^2}[1-0] + \frac{R\omega_{AS}}{R}\left[0 + \frac{2}{\sqrt{\pi}}e^{-0^2}\frac{1}{2\sqrt{D_{AB}t}}\right]\right\}$$

$$n_{AR} = \underbrace{\frac{\rho D_{AB}\omega_{AS}}{R}}_{st.st.}\left(1 + \underbrace{\frac{R}{\sqrt{\pi D_{AB} t}}}_{trans.}\right)$$

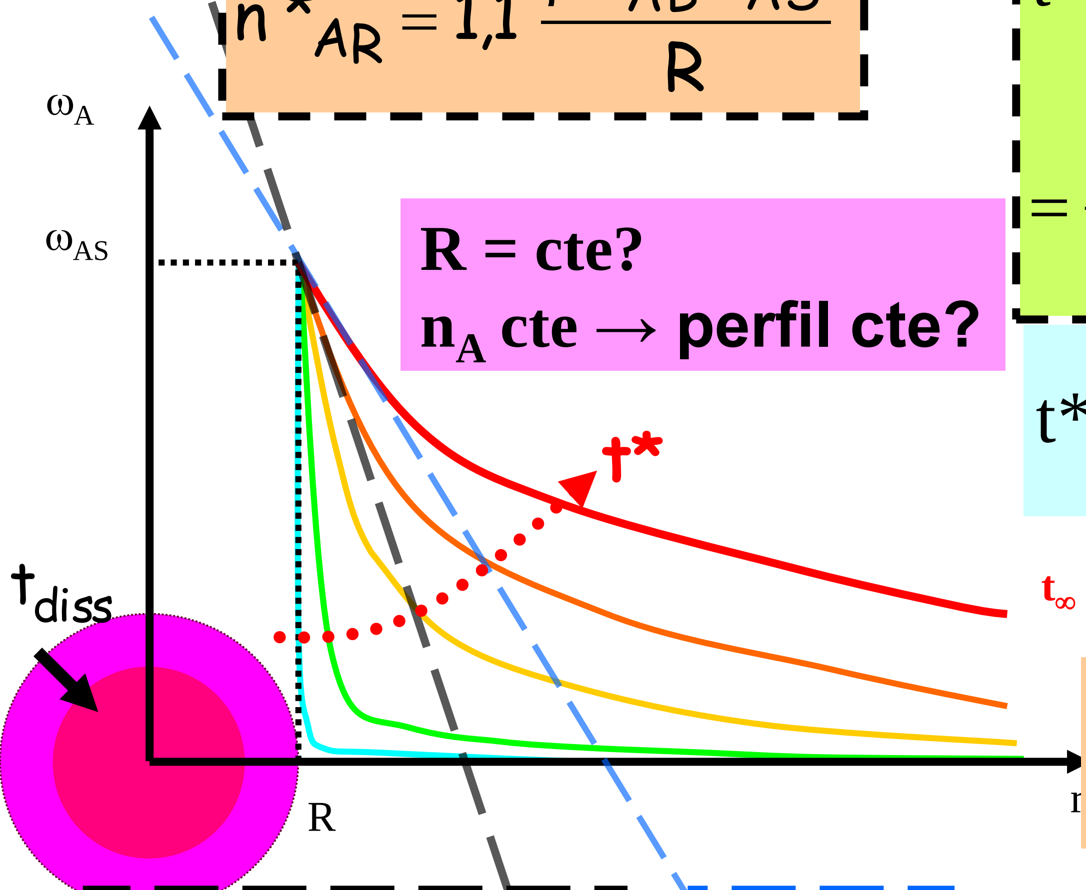
$$t = \frac{R^2}{\pi D_{AB}}\left[\frac{R\, n_{AR}}{\rho D_{AB}\omega_{AS}} - 1\right]^{-2}$$

$$n^*_{AR} = 1{,}1\,\frac{\rho D_{AB}\omega_{AS}}{R}$$

$$t^* = \frac{R^2}{\pi D_{AB}}\left[1{,}1 - 1\right]^{-2} = \frac{100\,R^2}{\pi D_{AB}} = \frac{100\,.1^2}{\pi D_{AB}} \approx \frac{32}{D_{AB}}$$

R = cte?

n_A cte → perfil cte?



$$t^* = \frac{32}{10^{-5}} = 3.10^5\,s \approx 900\,h$$

$$t_{diss} \approx 5000\,h$$

$$\sim 18\%$$

$$t^* = \frac{32}{10^{-1}} = 320s \approx 0{,}12\,h$$

$$t_{diss} \approx 300\,h$$

$$\sim 0{,}03\%$$

$$n^*_{AR} = 1{,}1\,n_{AR\,st.st.}$$

$$n_{AR\,st.st.}$$