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Sandia National Laboratories

Reaction-Diffusion in Inhomogeneous Fluids

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Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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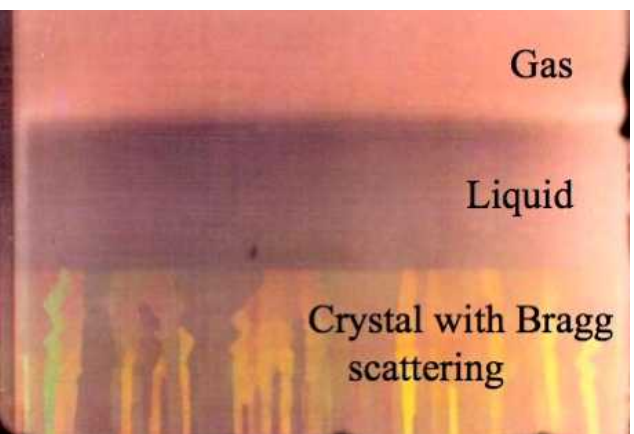
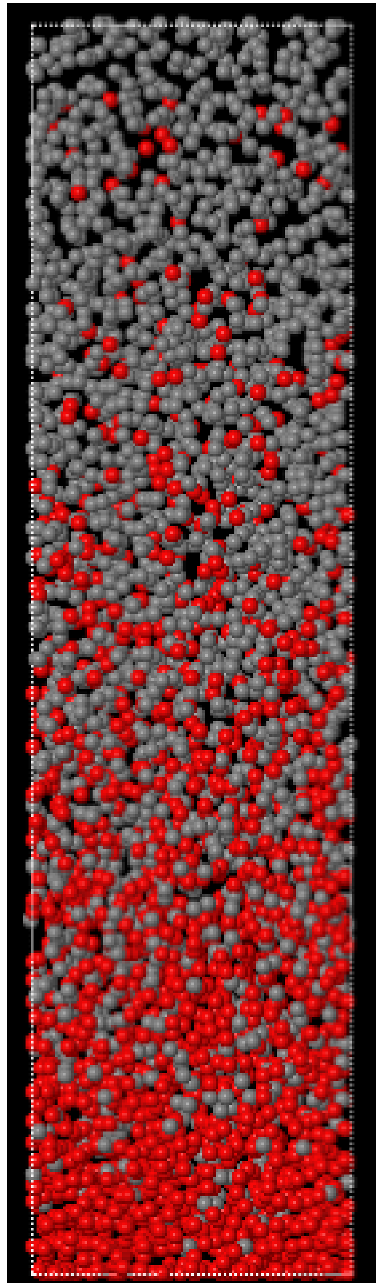
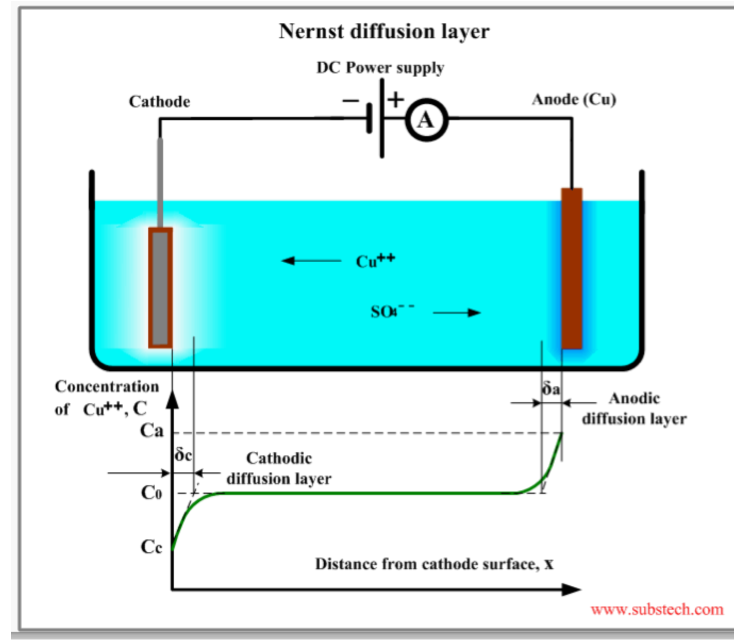
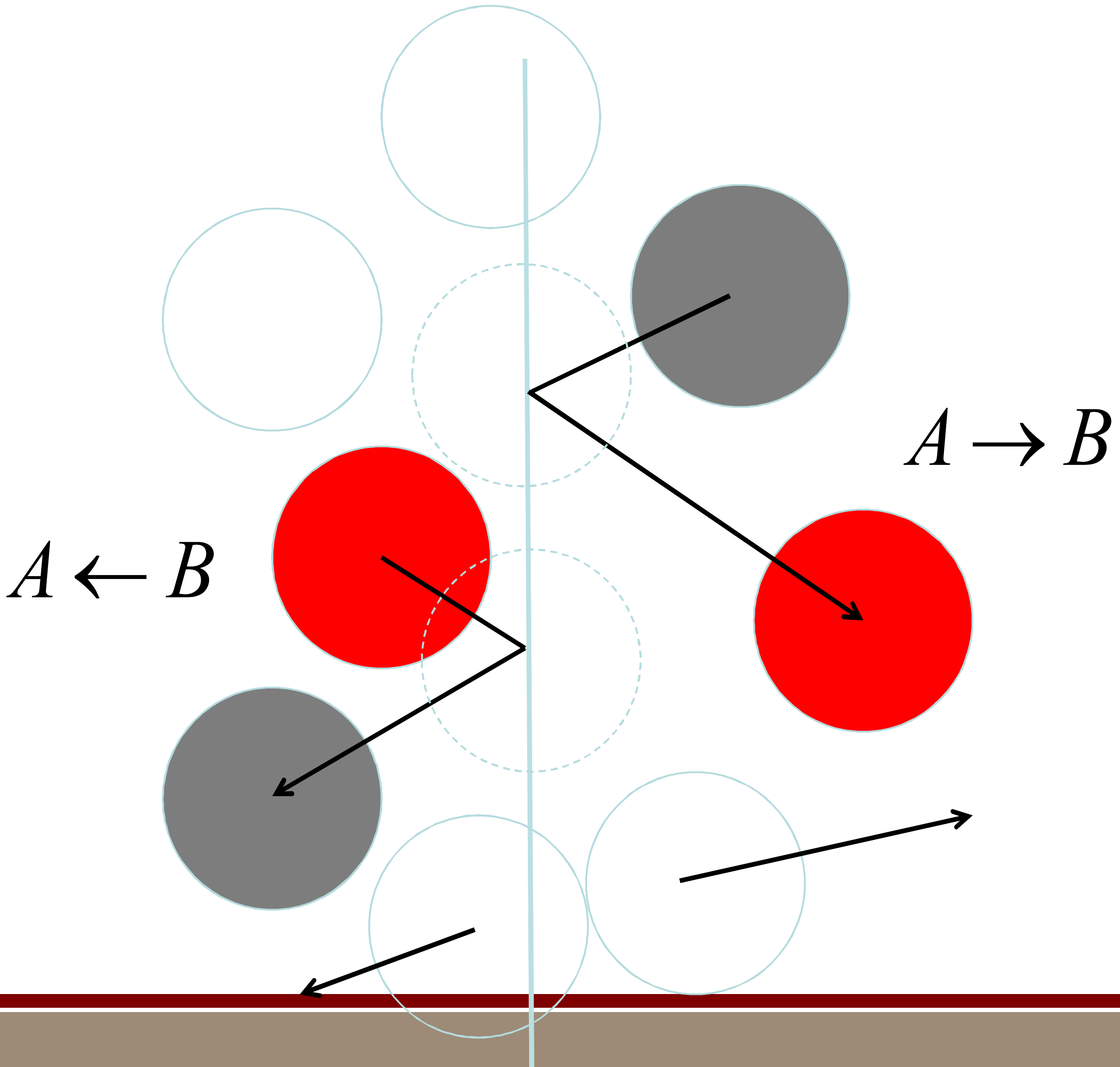

Gas
Liquid
Crystal with Bragg scattering




Nernst diffusion layer
DC Power supply
Cathode
Anode (Cu)
A
Cu^{++}
SO_4^{--}
Concentration of Cu^{++}, C
Ca
δc
Cathodic diffusion layer
Co
Cc
δa
Anodic diffusion layer
Distance from cathode surface, x
www.substech.com

Reaction- (color) diffusion

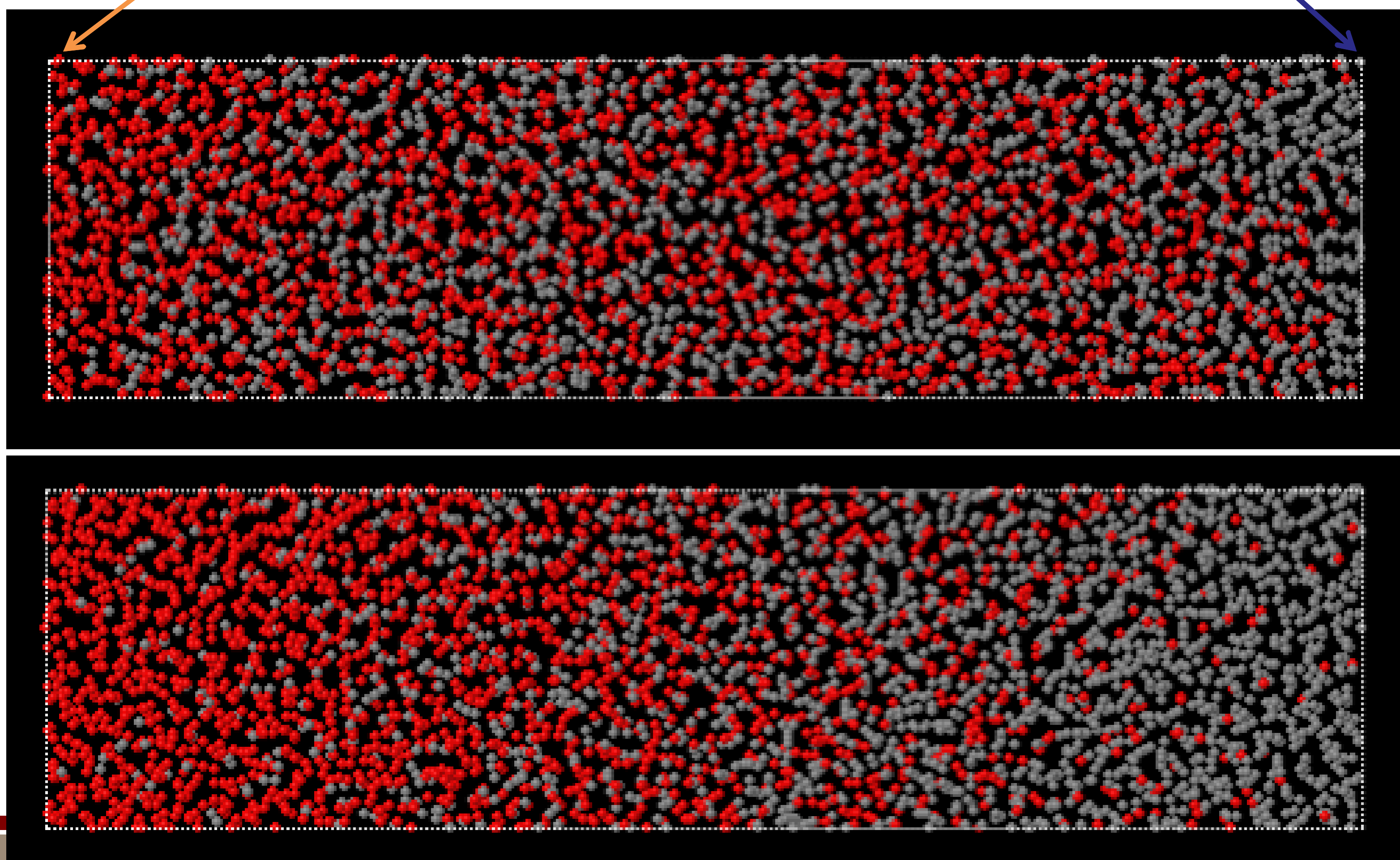


Reaction-color diffusion (PBC)

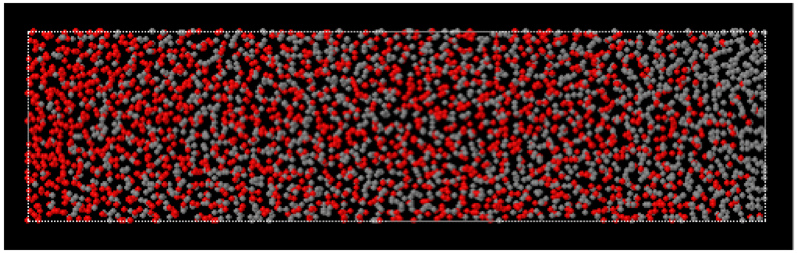
Transparent reflective & reactive boundary

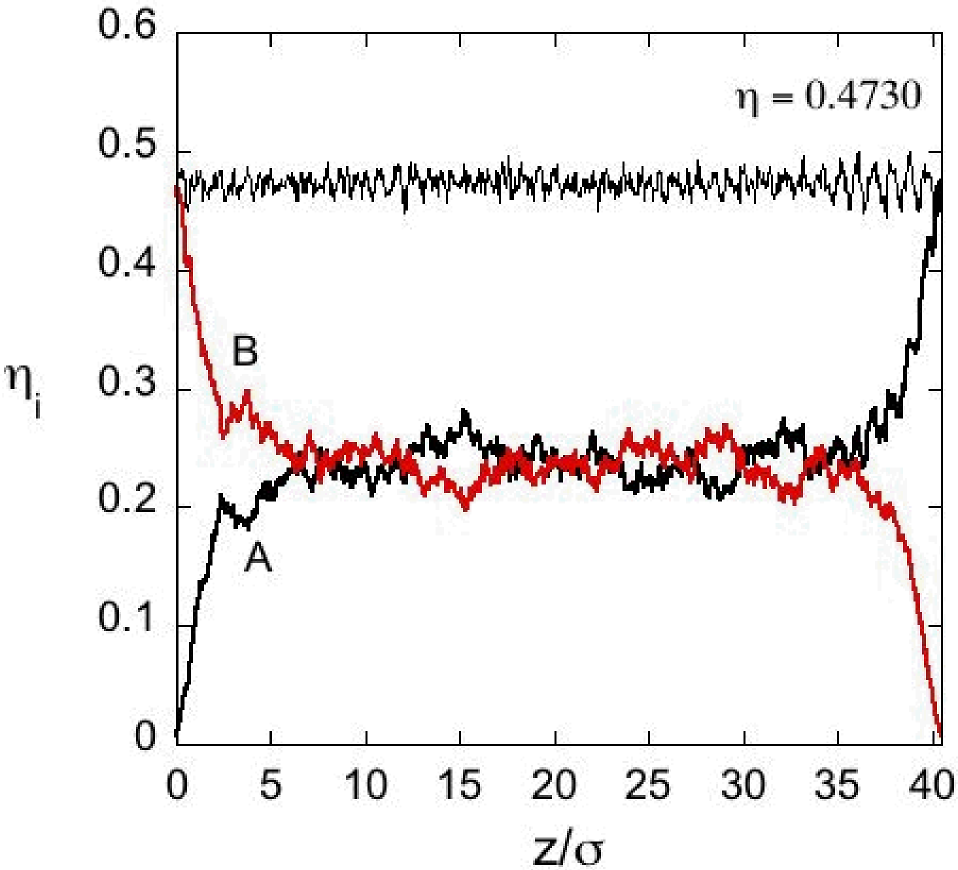
$A \rightarrow B$

$A \leftarrow B$

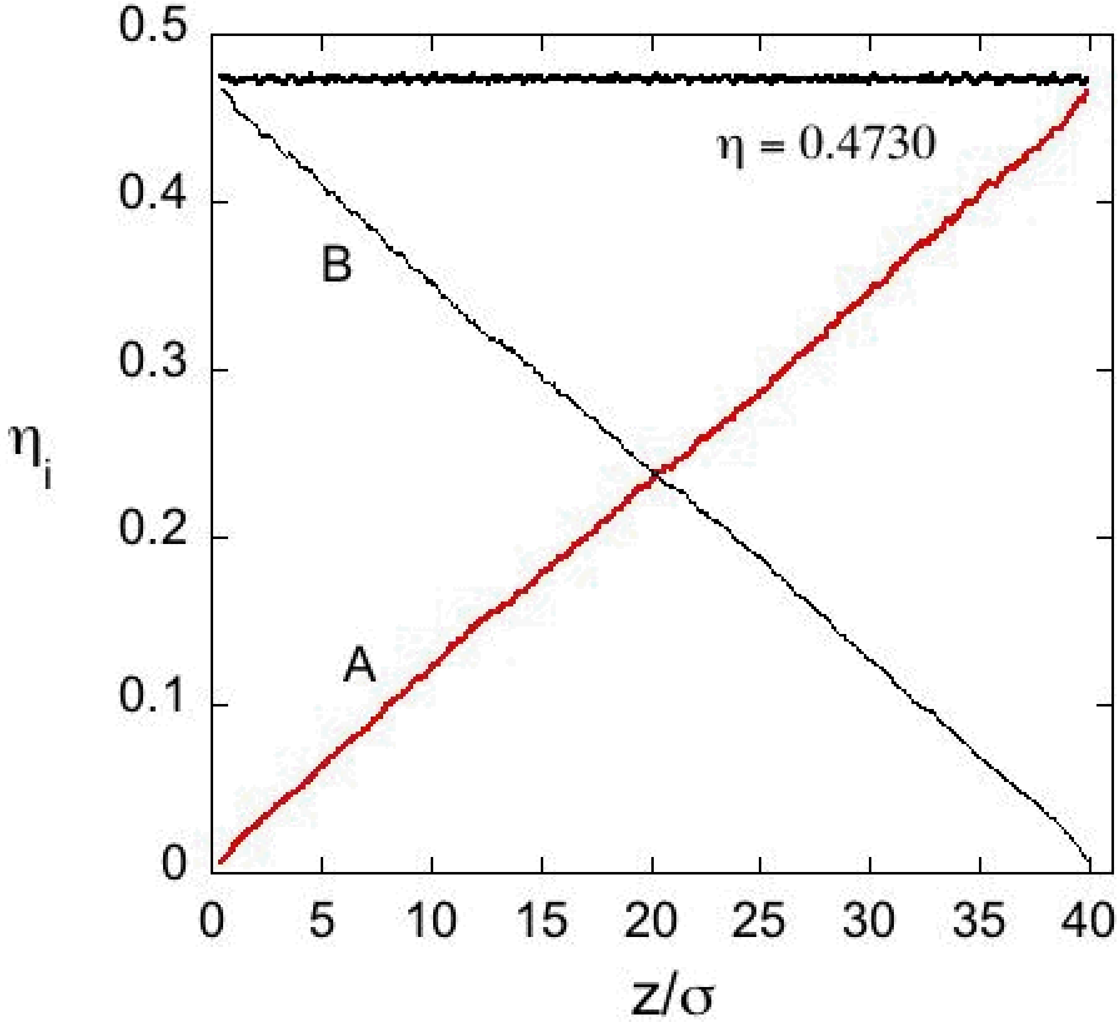


Transients





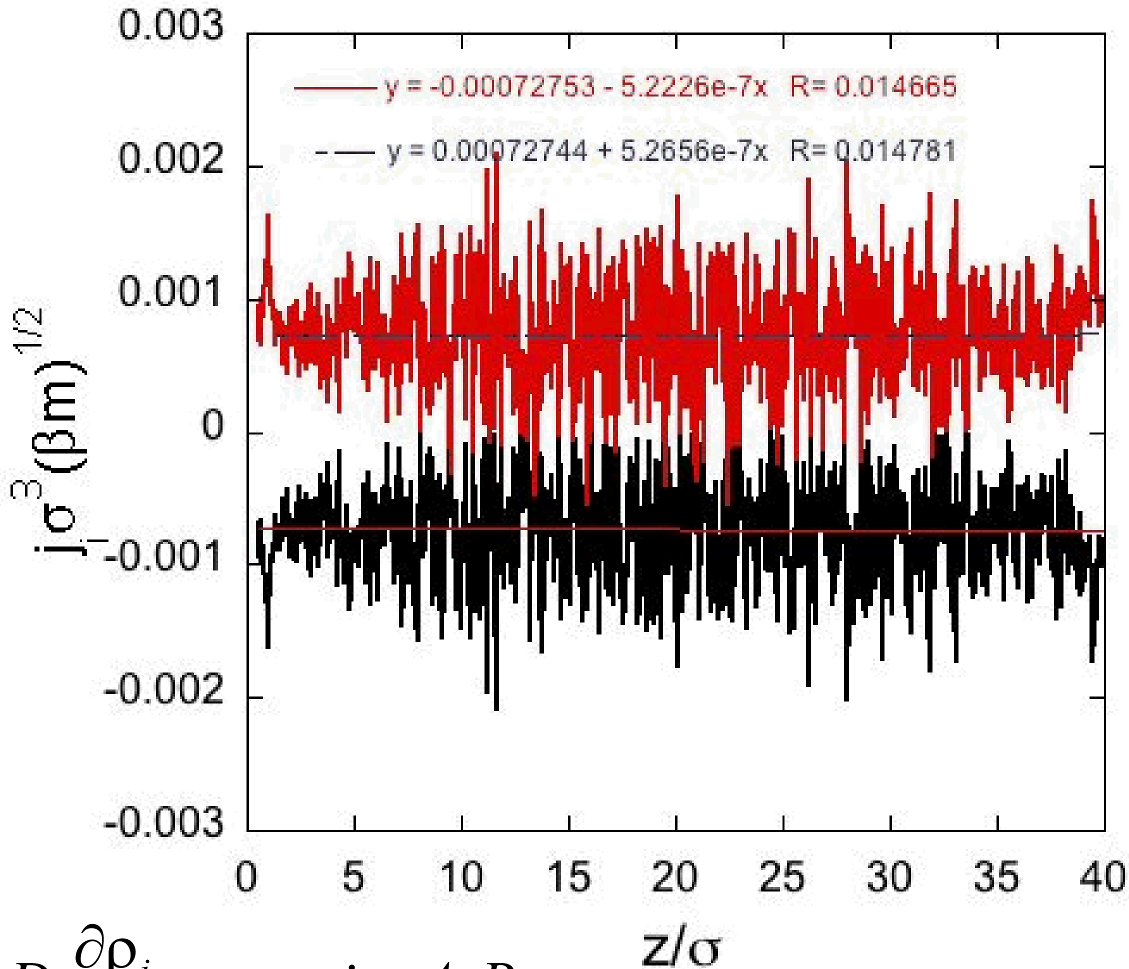
Steady-State

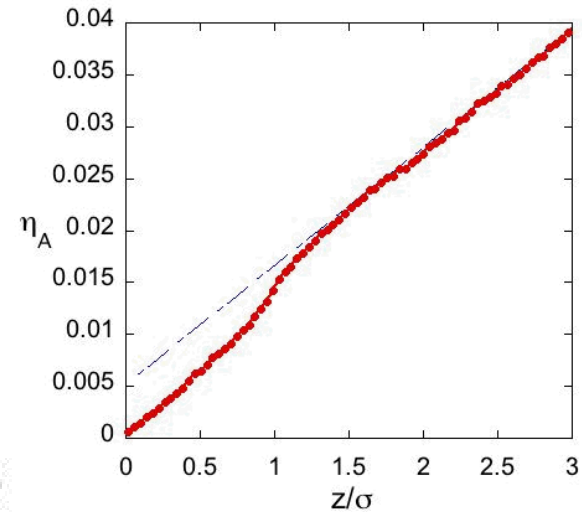


Adolph Fick 1855

$$j_i = -D_i \frac{\partial \rho_i}{\partial x}$$

Color fluxes





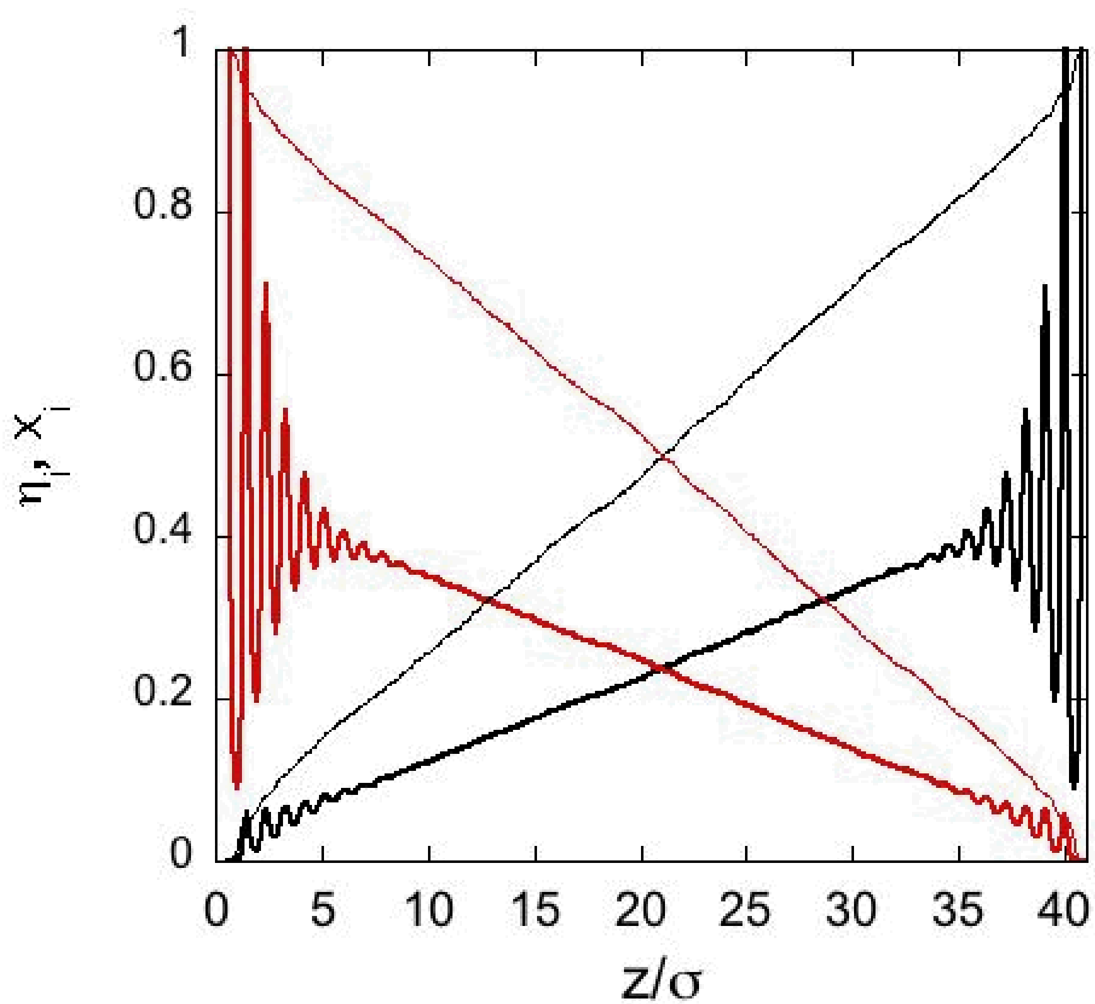
$$j_i = -D_i \frac{\partial \rho_i}{\partial x} \qquad i = A, B$$

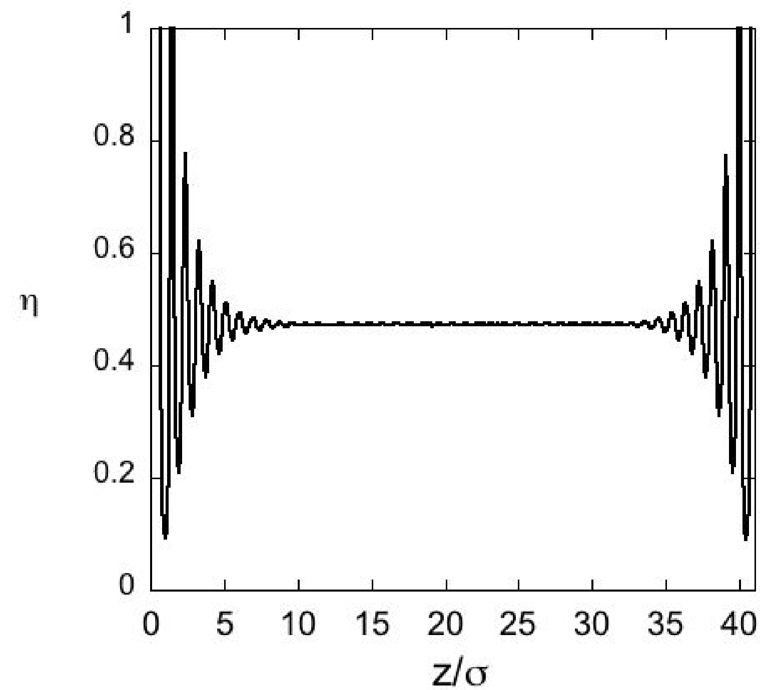
$$D_i = D_s = 0.0339\sqrt{\mathrm{kT}\sigma^2/m}$$

$$R_{A\to B} = \frac{\rho_A}{\rho_A + \rho_B} p_{kin} = 0.000729$$

Inhomogeneous Hard Sphere Fluid

reactive boundary = hard wall



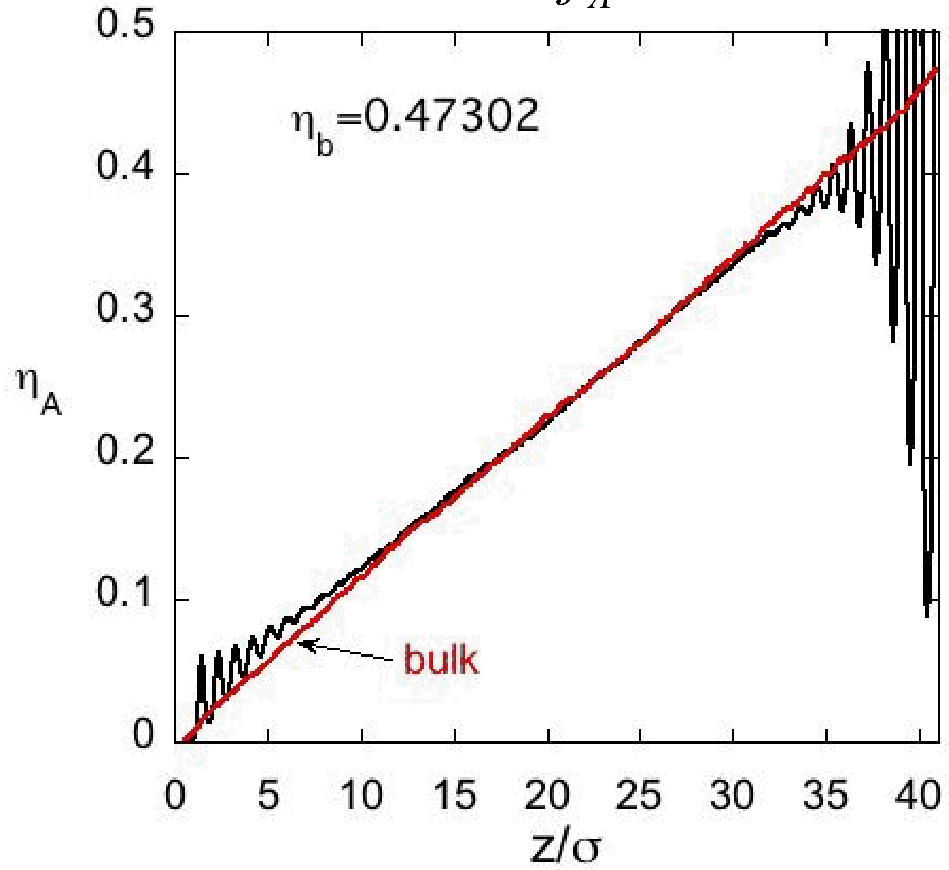


$$j_i = -D \frac{\partial \rho_i}{\partial x} \quad ?$$

Comparing fluxes

$$j_A = 0.669\ 10^{-3}$$ inhomogeneous

$$j_A = 0.937\ 10^{-3}$$ bulk



What to do?

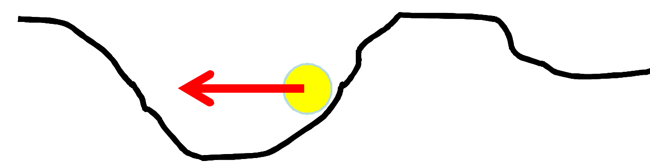
$$j_i = -D \frac{\partial \rho_i}{\partial x}$$

- Consider $D_i = D_i[\rho_i(z)]$?
- Consider a different equation?

1) $$j_i = -D \rho_i \frac{\partial \mu_i}{\partial x}$$

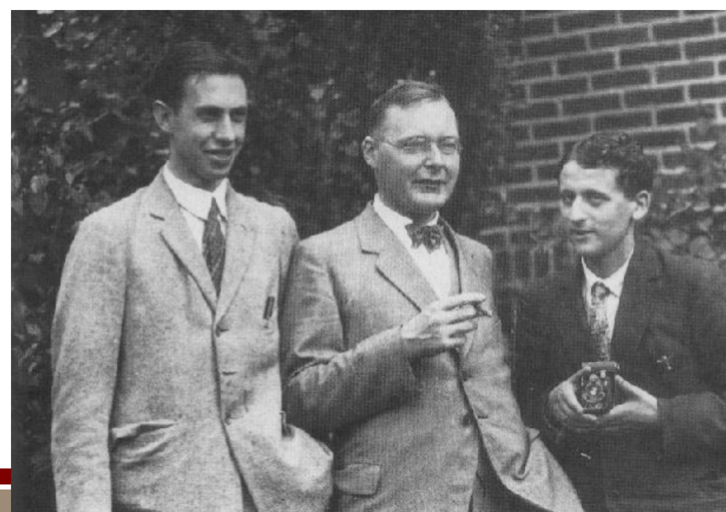
2) Smoluchowski equation

v. Smoluchowski (1906)
Kramers(1940)-Klein(1922)

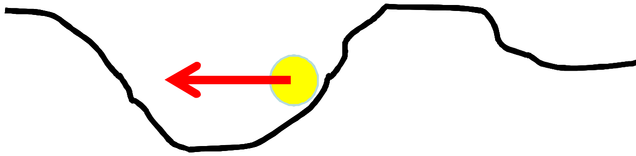


$$j_i = -D\frac{\partial \rho_i}{\partial z} - D\frac{K(z)\rho_i}{kT}; \qquad i = A, B$$

Chemical kinetics and diffusion approach: *the history of the Klein-Kramers equation, S. Zambelli, Archive for History of Exact Sciences, 64, 395 (2010)*
Brownian Motion: *Fluctuations, Dynamics, and Applications*
Robert M. Mazo



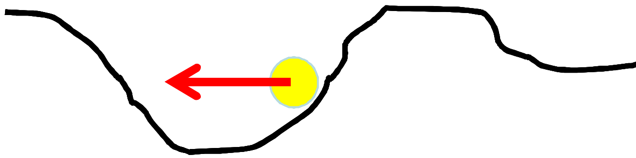
tracting the force K(z)
om the SS profiles

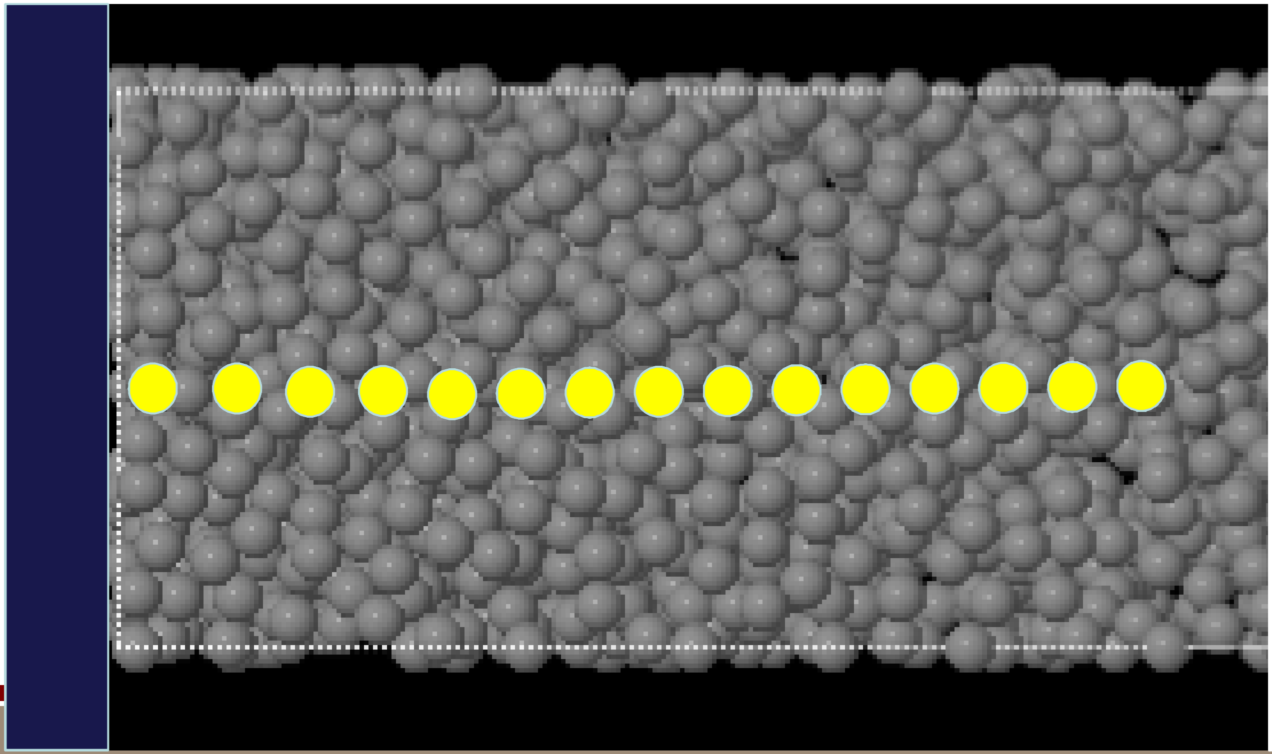


$$j_i = -D\frac{\partial \rho_i}{\partial z} - D\frac{K(z)\rho_i}{kT}; \qquad i = A, B$$

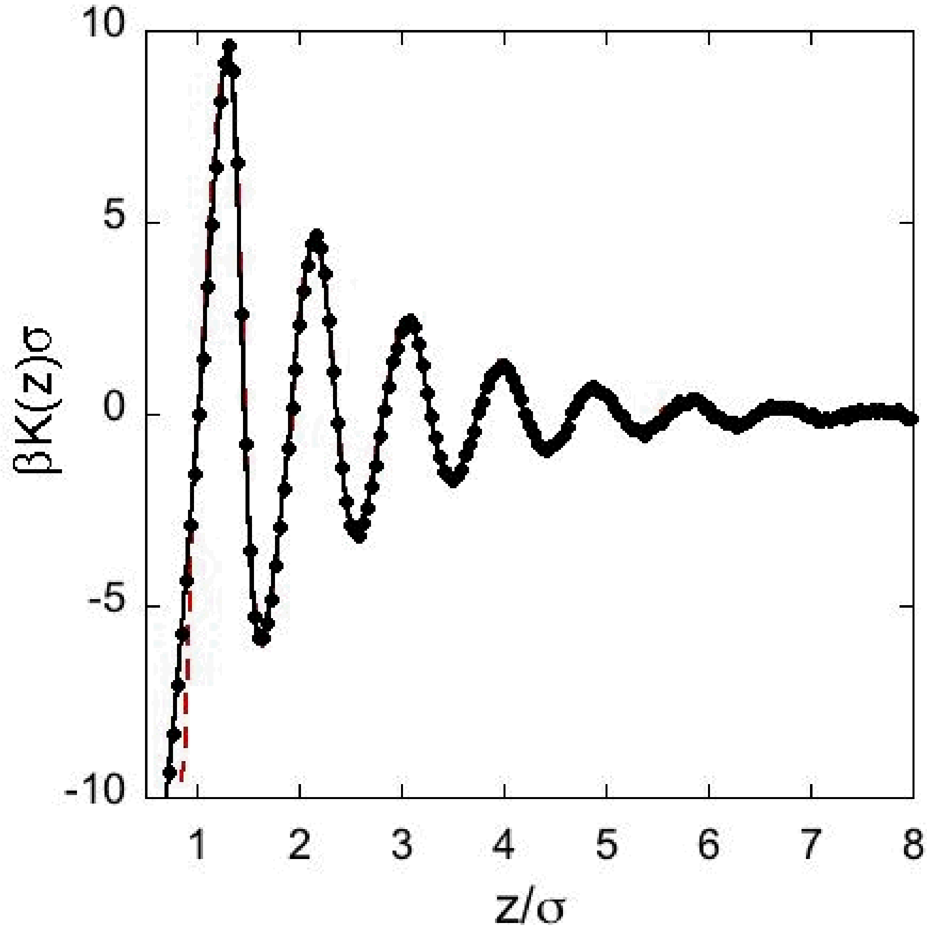
$$\frac{K(z)}{kT} = \frac{j_i}{D\rho_i} + \frac{\partial ln\rho_i}{\partial z}; \qquad i = A, B$$

Alternatively:
measure K(z) directly





K(z) = Solvation Force



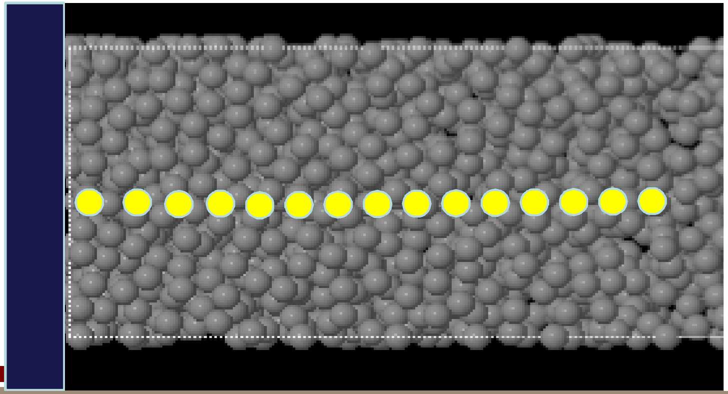
9.5 Potential Distribution Theorem (hard walls)

Pure fluid, at equilibrium:

$$\begin{aligned}\beta\mu &= ln\rho(z) - ln < e^{-\beta U_\iota(z)} > \ ; \ 0 < z < L_z \\ &\equiv ln\rho(z) + \beta\tilde{\mu}^{ex}(z)\end{aligned}$$

From which it follows that

$$\frac{K(z)}{kT} = \frac{\partial ln\rho}{\partial z} = \frac{\partial\beta\tilde{\mu}^{ex}(z)}{\partial z}$$

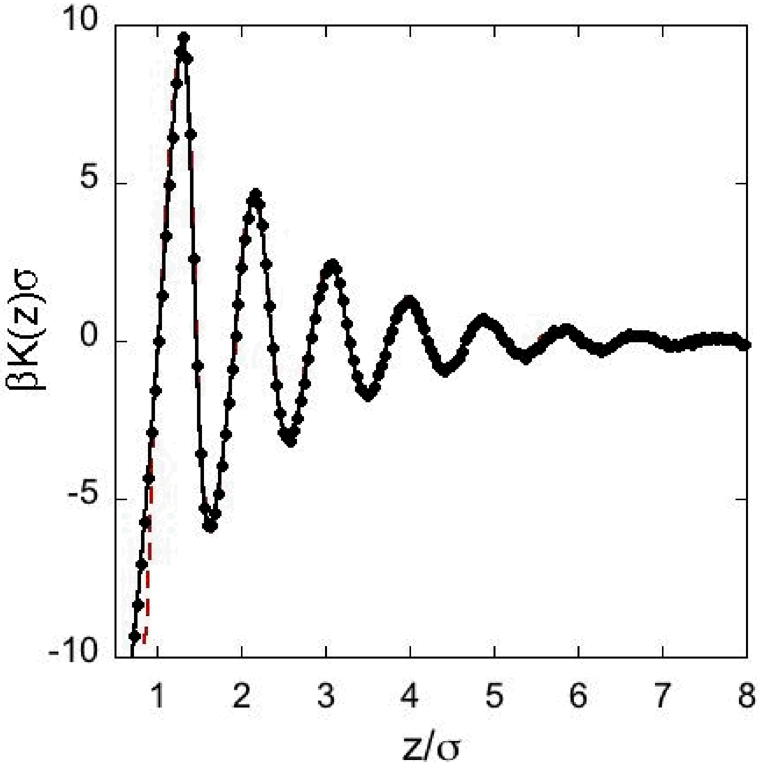


K(z) from three routes

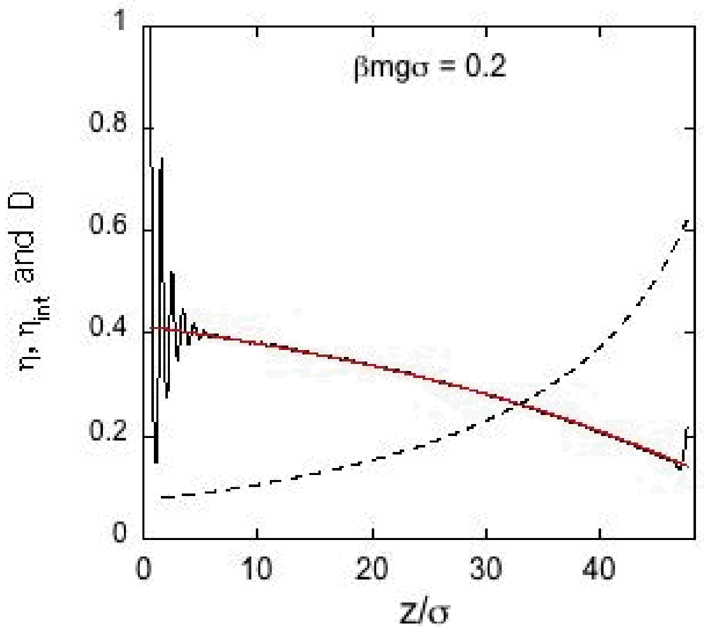
1. Force measurement
2. PDT
3. Fluxes and Profiles

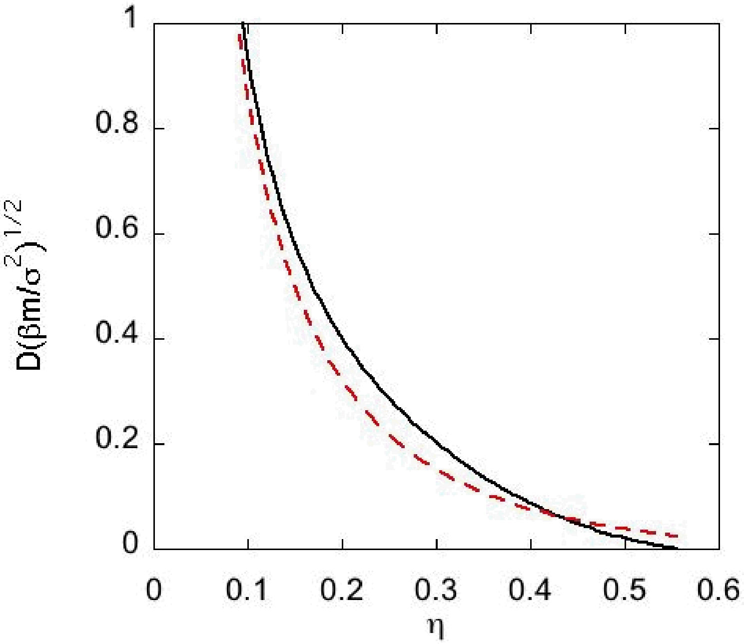
Note, route 3 assumed:

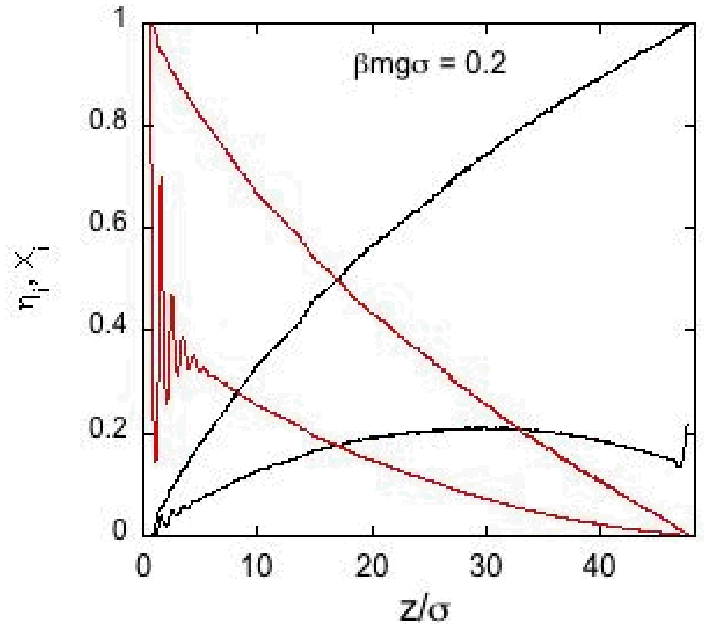
$D = \text{constant} = D(\rho_b)$



Inhomogeneous Hard Sphere Fluid in gravity







9.6 Color Diffusion in a Slowly-Varying External Field: an alternate derivation

Color mixture, at "pure" equilibrium, and at "color" steady-state

$$\beta\mu_i(z) = ln\rho_i(z) - ln < e^{-\beta U_{t,i}(z)} > + V_{ext}(z) \quad ; \; i = A, B \tag{53}$$
$$= ln\rho_i(z) + \beta\tilde{\mu}^{ex}(z) + V_{ext}(z) \tag{54}$$

$$\beta\mu_i(z) = ln x_i(z) + \beta\mu; \qquad x_i \equiv \rho_i(z)/\rho(z) \tag{55}$$

$$j_i = -D_i(z)\rho_i \frac{\partial \beta\mu_i}{\partial z} \tag{56}$$
$$= -D_i(z)\frac{\partial \rho_i}{\partial z} - D_i\rho_i \frac{\partial ln\rho}{\partial z} \tag{57}$$

given that the total local density, ρ, is also a function of z. Note that if ρ is a constant, this equation reduces to the simplest form of Fick's first law

$$-\frac{j_i}{D(z)\rho_i(z)} = \frac{\partial ln\rho_i(z)}{\partial z} - \frac{\partial ln\rho(z)}{\partial z} \quad ; i = A, B \tag{58}$$

Finding D(z)

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9.7 The intrinsic chemical potential: pure fluid in gravity

$$\begin{aligned} \beta\mu &= ln\rho(z) - ln < e^{-\beta U_i(z)} > + V_{ext}(z) \\ &= \underbrace{ln\rho_i(z) + \beta\tilde{\mu}^{ex}(z)}_{\mu_{int}(z)} + V_{ext}(z) \end{aligned}$$

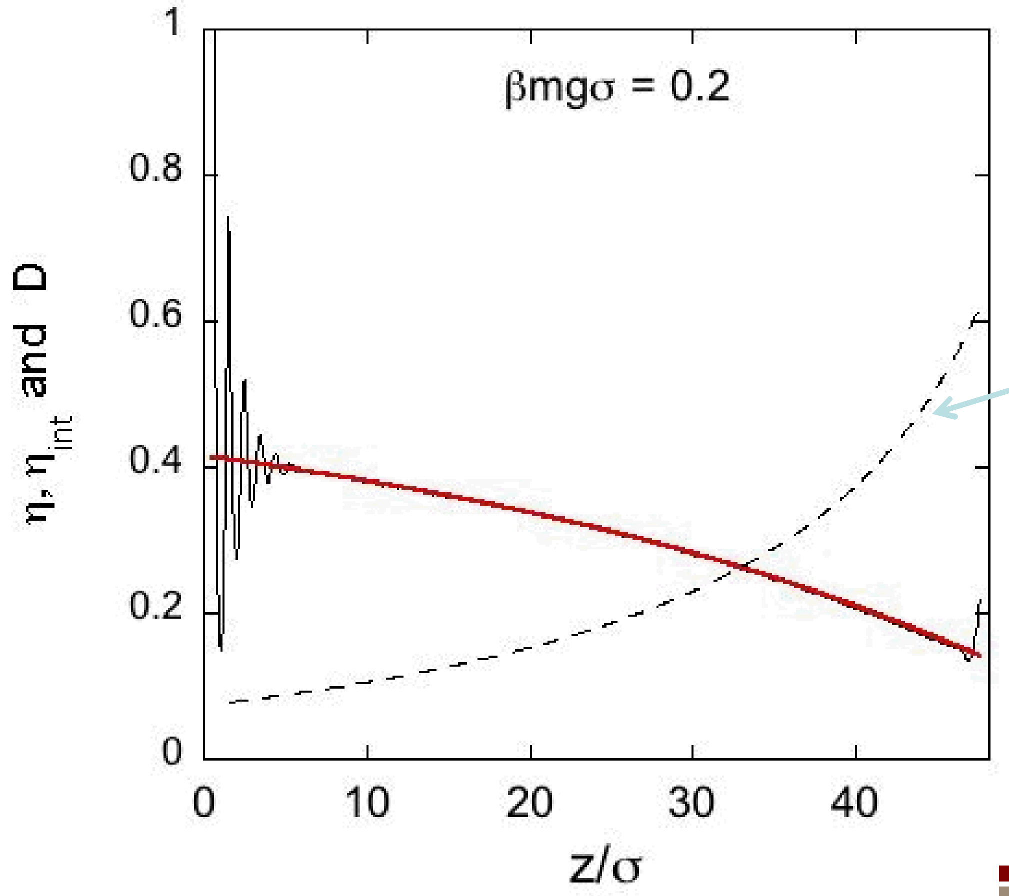
$$\begin{aligned} \mu_{int}(z) &\equiv \mu - V_{ext}(z) \\ &= \mu - mg(z - z_0); \qquad \textit{gravity} \end{aligned}$$

This determines the "state" of the local fluid. Now approximate

$$D = D[\mu_{int}(z)]$$

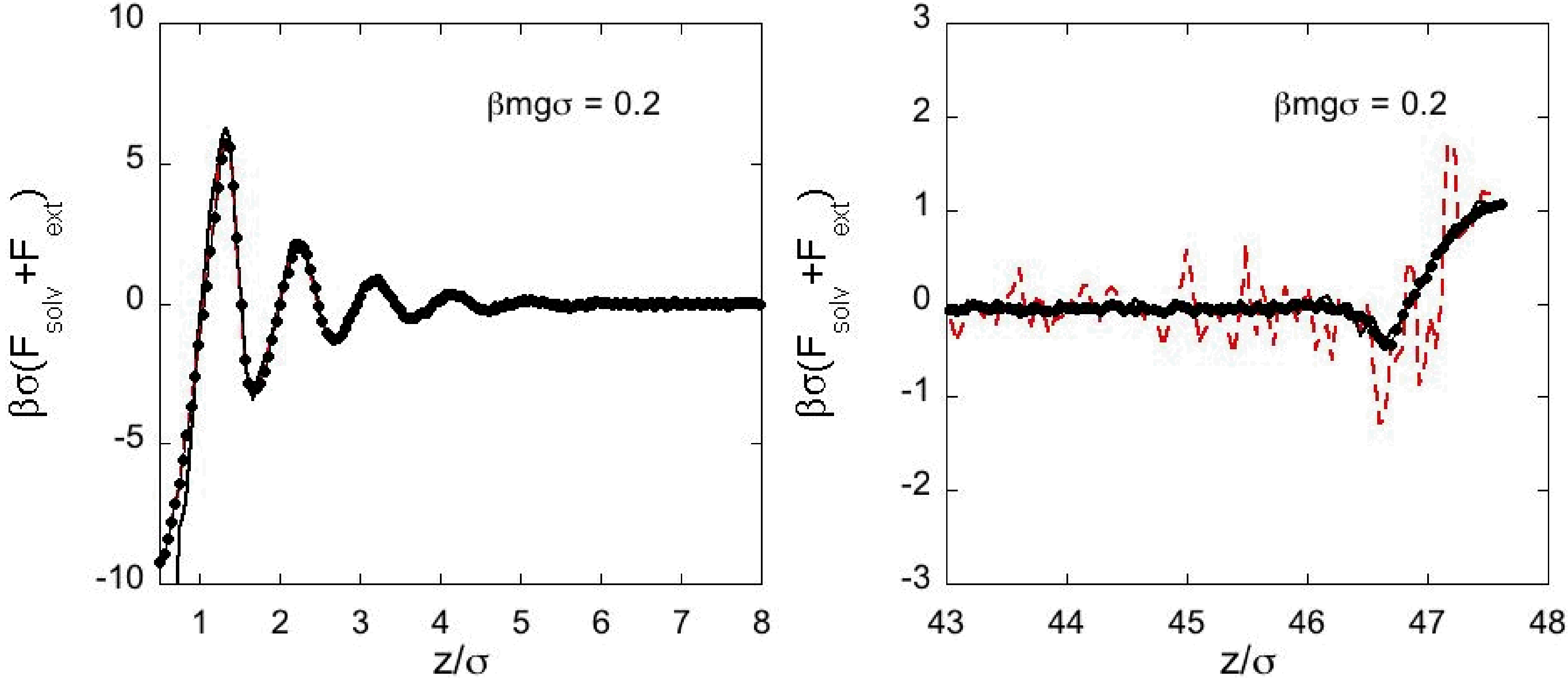
The intrinsic density profile

$$\mu_{\text{int}}(z) = \mu(z_0) - mg(z - z_0)$$

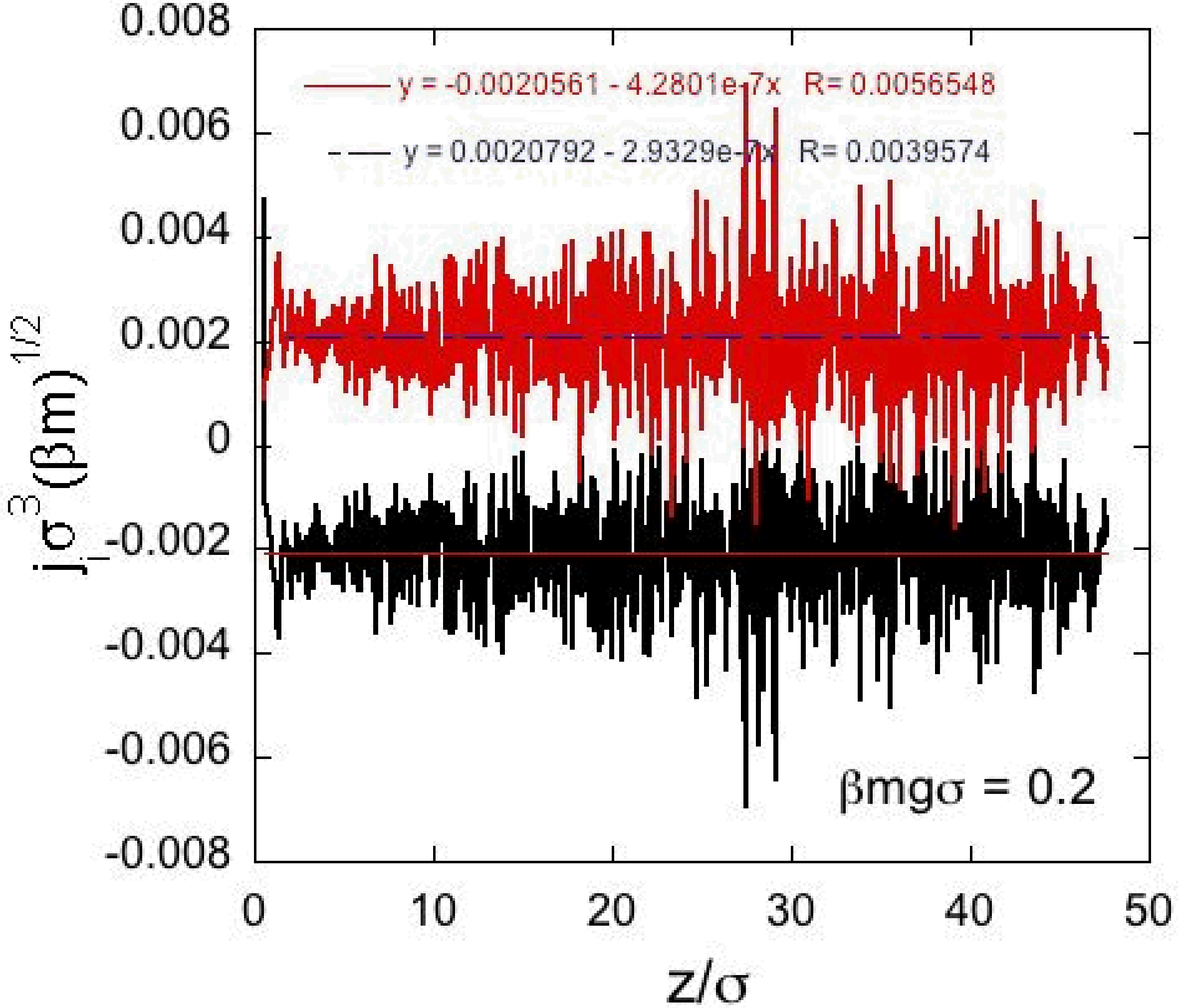


$$D = D\left[\mu_{\text{int}}(z)\right]$$

Checking K(z) in gravity



Checking the fluxes, j_A & j_B



Concusion

For inhomogeneous fluids use

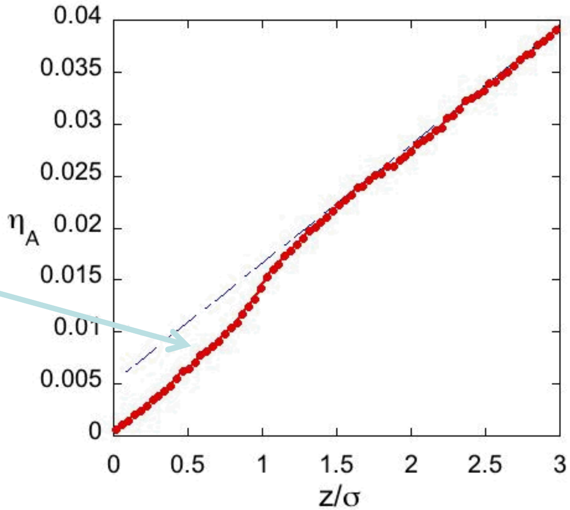
$$D(z) = D[\mu_{int}(z)]$$

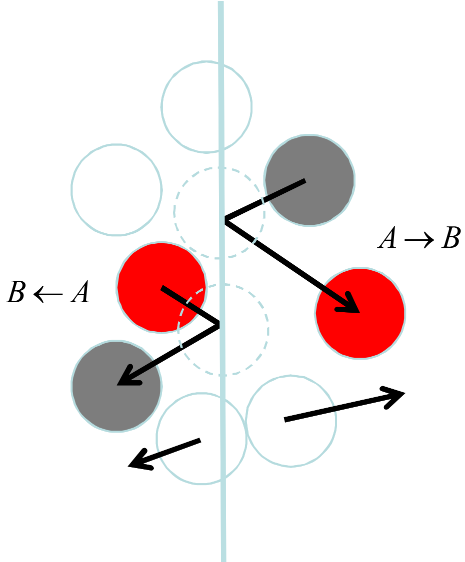
and combine with the solvation force.

This also works in the presence of slowly-varying fields (e.g., gravity)

Question

What is this?





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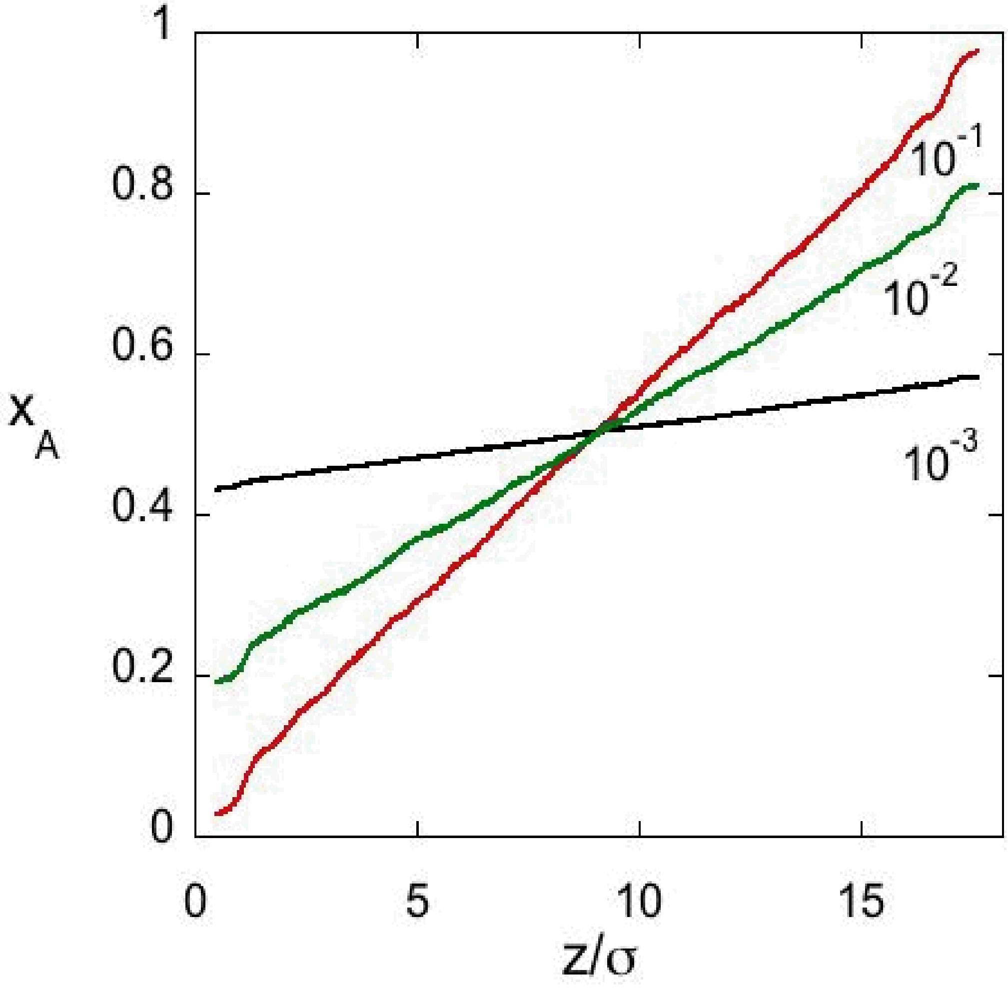
The effect of Reaction Probabilities



v. Smoluchowski (1906)
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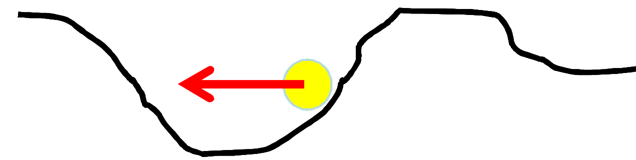
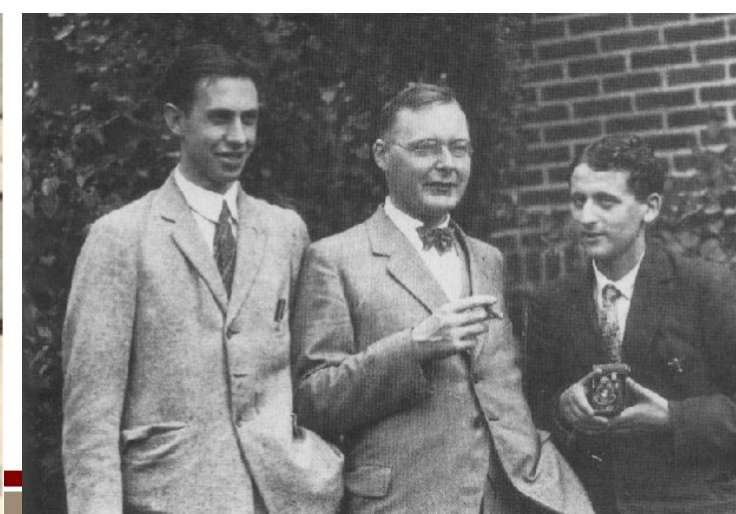
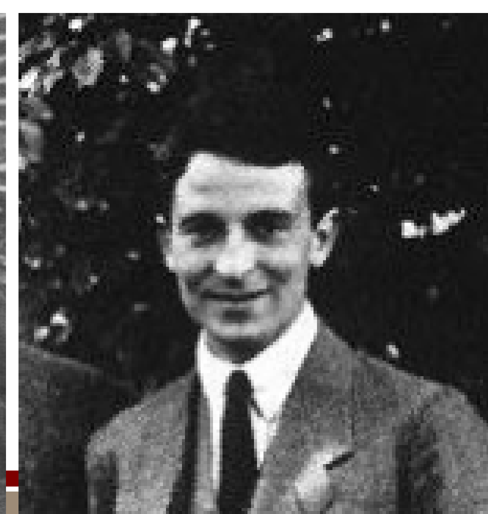


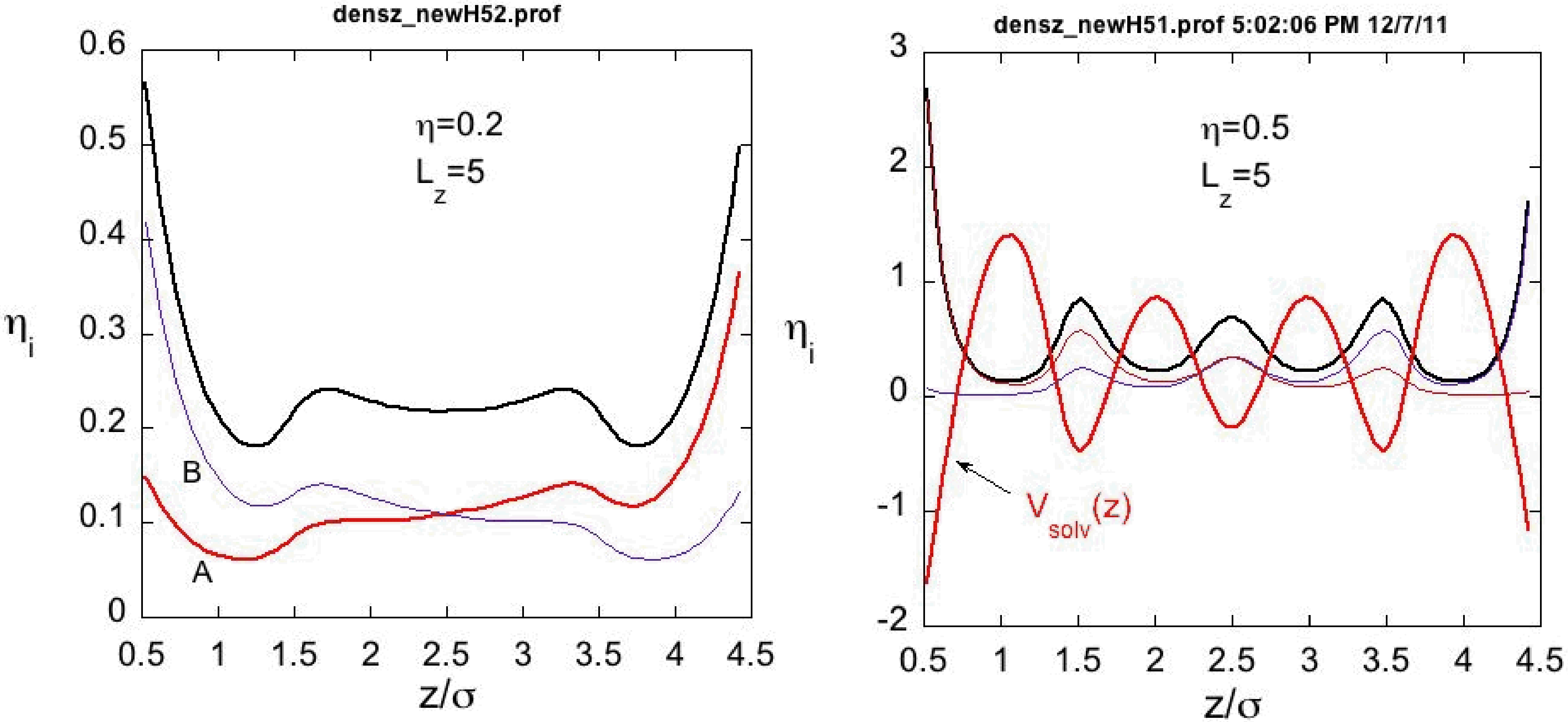
$$j_i = -D\frac{\partial \rho_i}{\partial z} - D\frac{K(z)\rho_i}{kT}; \qquad i = A, B$$

$$\frac{\partial P(x, x_0, t)}{\partial t} = D\frac{\partial^2 P(x, x_0, t)}{\partial^2 x^2} - \frac{\partial}{\partial x}\left[\frac{F(x)}{\xi} P(x, x_0, t)\right]$$





profiles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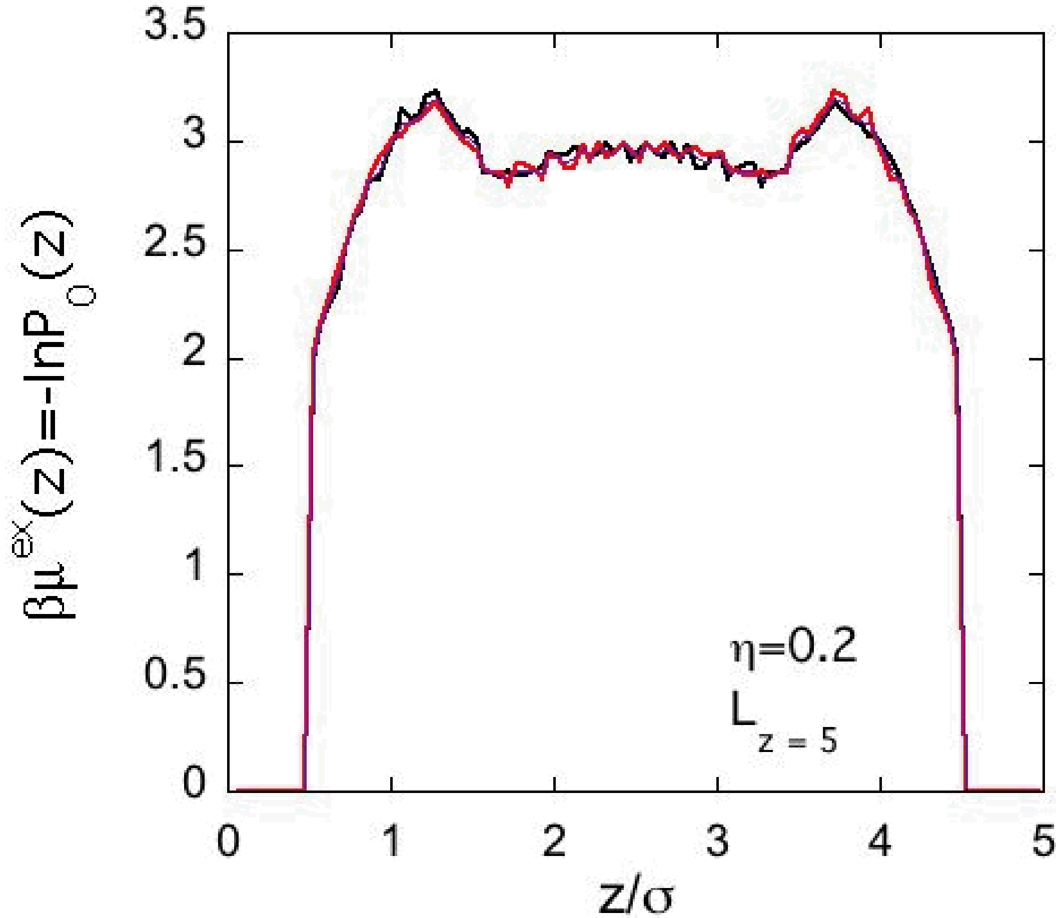
η=0.2
L_z=5
B
A
η_i
z/σ
0.6
0.5
0.4
0.3
0.2
0.1
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
densz_newH51.prof 5:02:06 PM 12/7/11
η=0.5
L_z=5
V_solv(z)
η_i
z/σ
3
2
1
0
-1
-2
0.5
1
1.5
2
2.5
3
3.5
4
4.5

$\beta\mu^{ex}(z)$

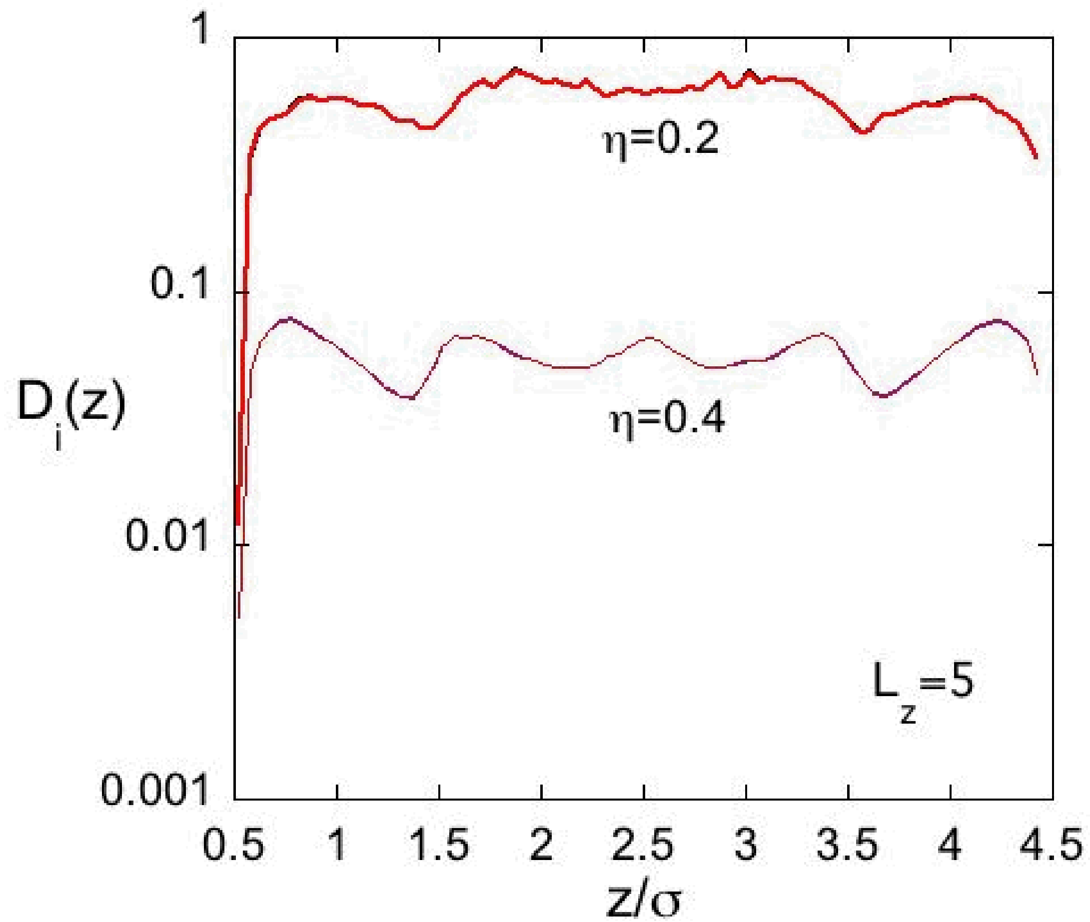


$$D(z) = -j_i\left[\rho_i\left(\frac{K(z)}{kT} + \frac{\partial \ln \rho_i}{\partial z}\right)\right]^{-1}; i = A, B$$

Ideal gas:

$$D(z) = -j_i\left[\left(\frac{\partial \rho_i}{\partial z}\right)\right]^{-1}; i = A, B$$

$$D(z) = \text{constant}$$

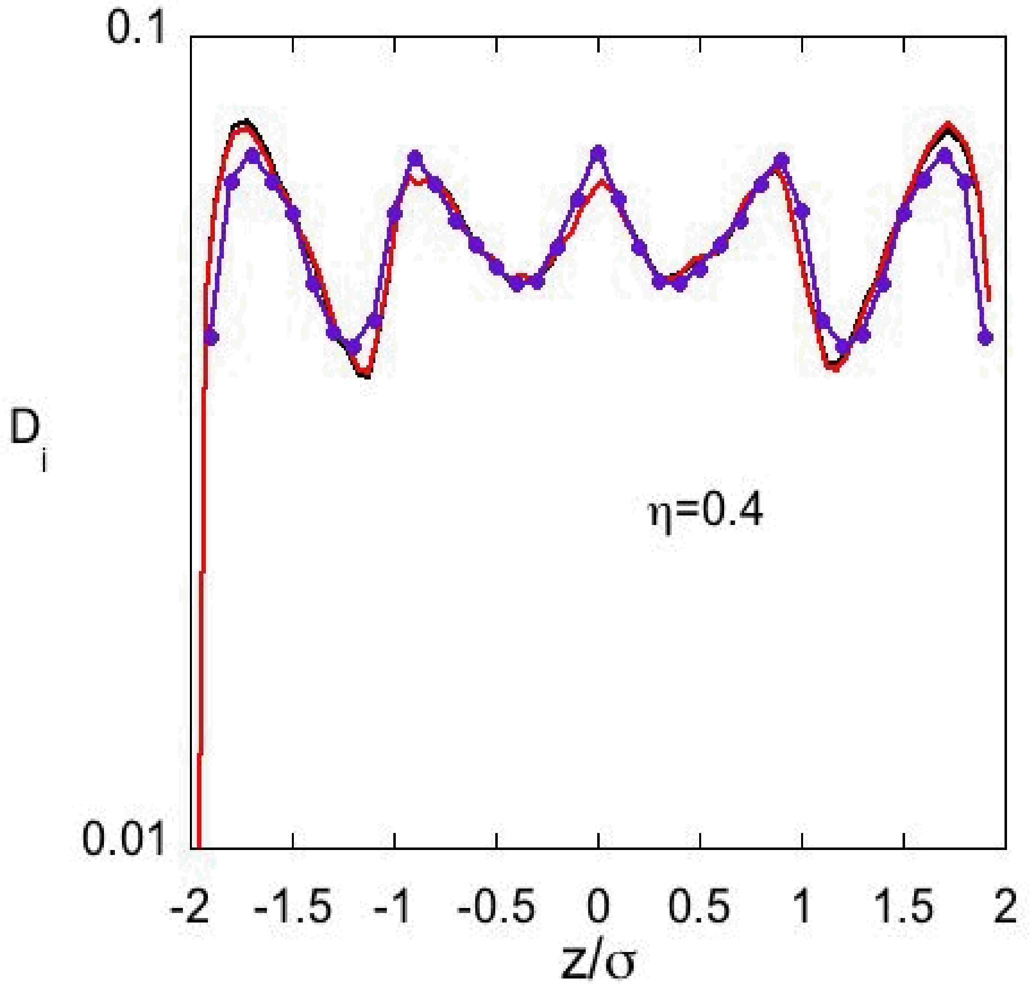


$$D(z) = -j_i\left[\rho_i\left(\frac{K(z)}{kT} + \frac{\partial \ln \rho_i}{\partial z}\right)\right]^{-1};i = A, B$$

Ideal gas:

$$D(z) = -j_i\left[\left(\frac{\partial \rho_i}{\partial z}\right)\right.$$

$$D(z) = \text{constant}$$



$\beta\mu^{ex}(z)$ in gravity