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Reaction-Diffusion in Inhomogeneous Fluids

Frank van Swol

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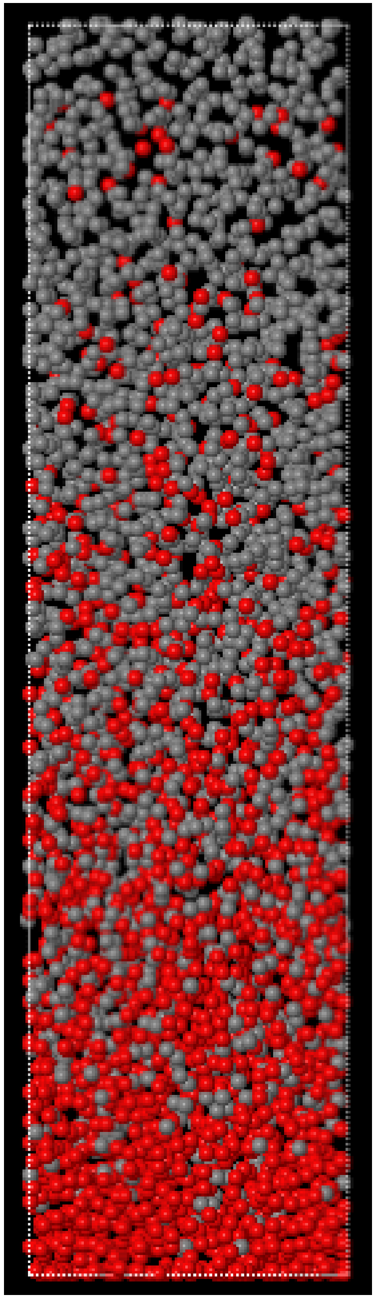
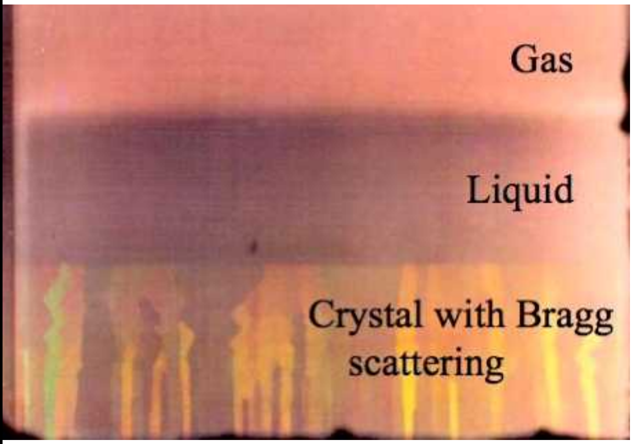
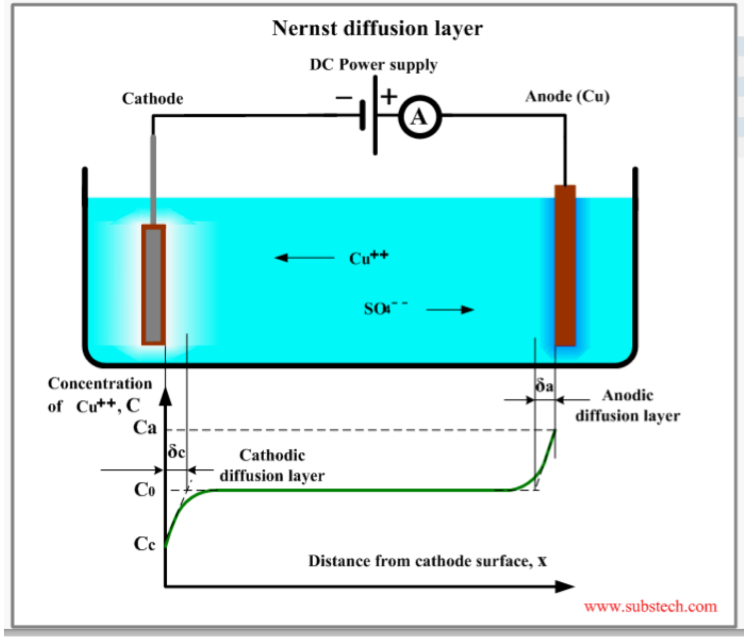
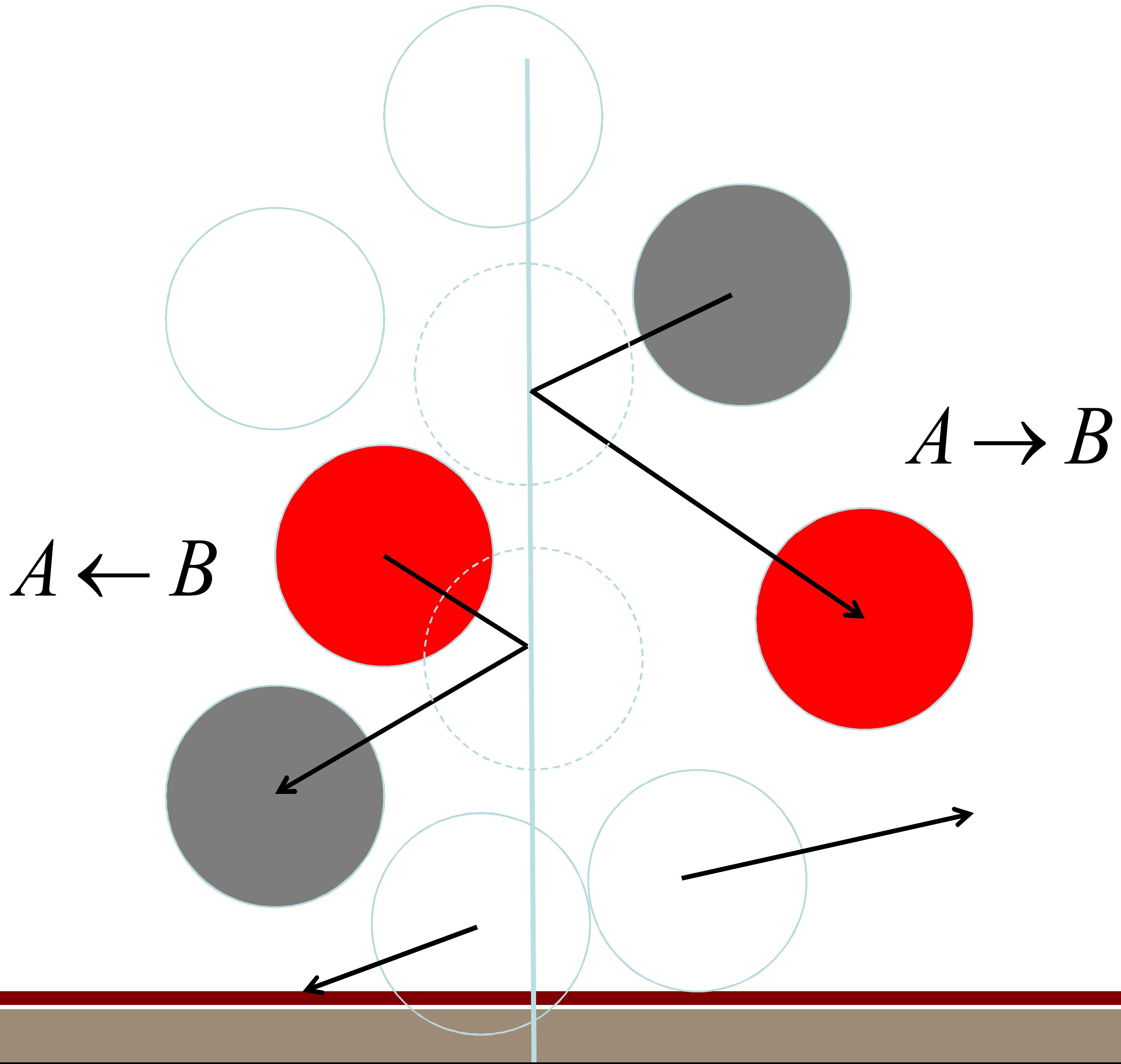





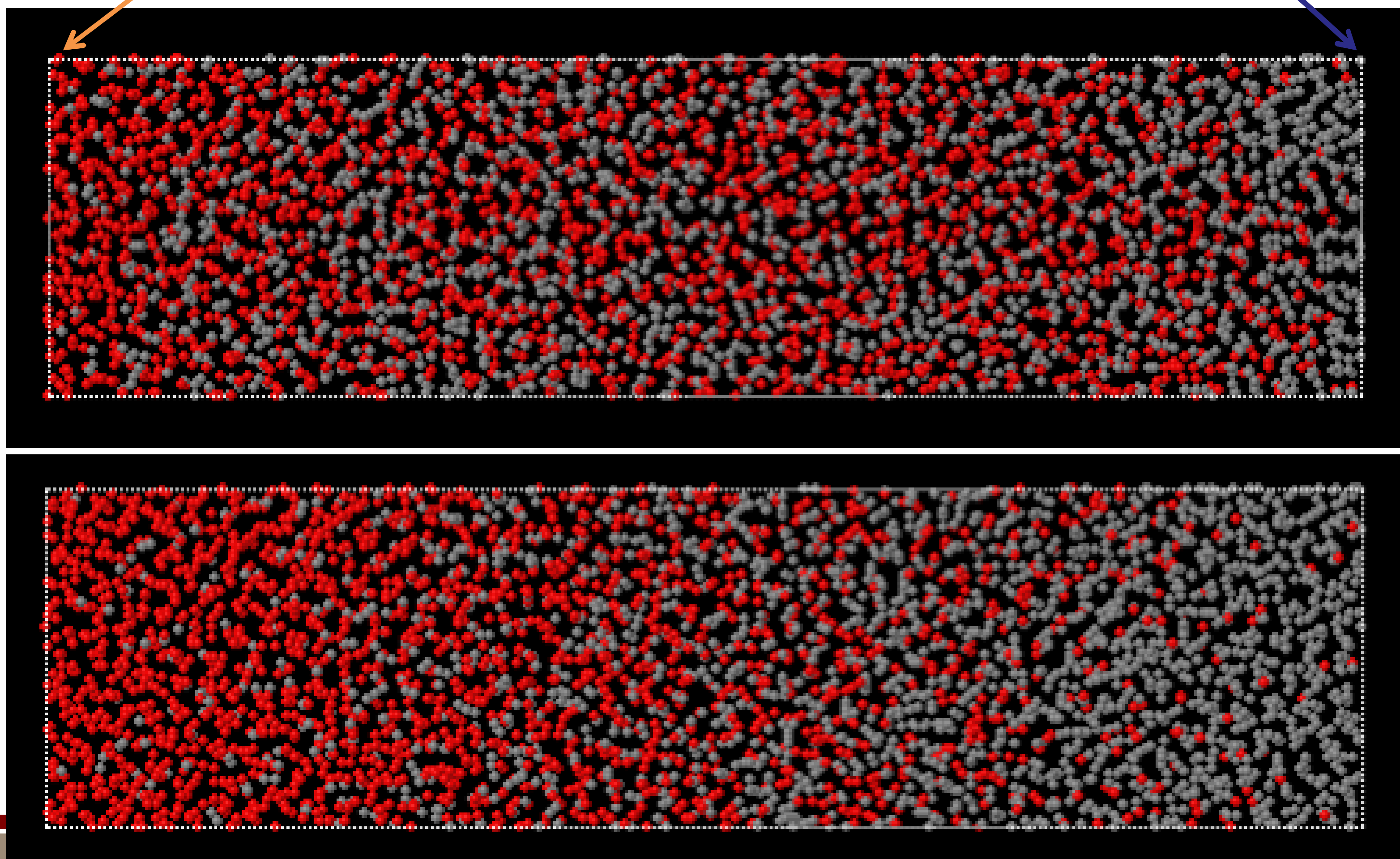
Reaction- (color) diffusion



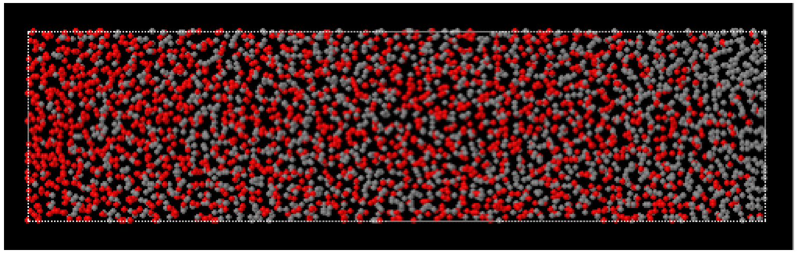
Reaction-color diffusion (PBC)

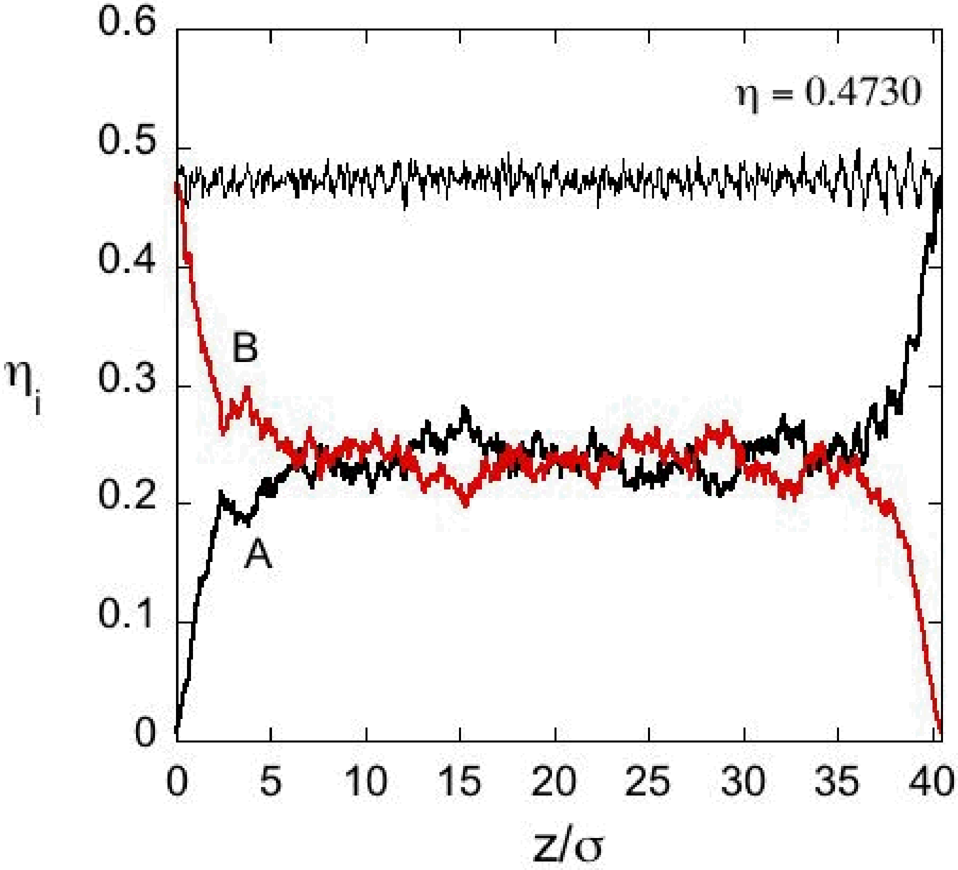
Transparent reflective & reactive boundary

$A \rightarrow B$ $A \leftarrow B$

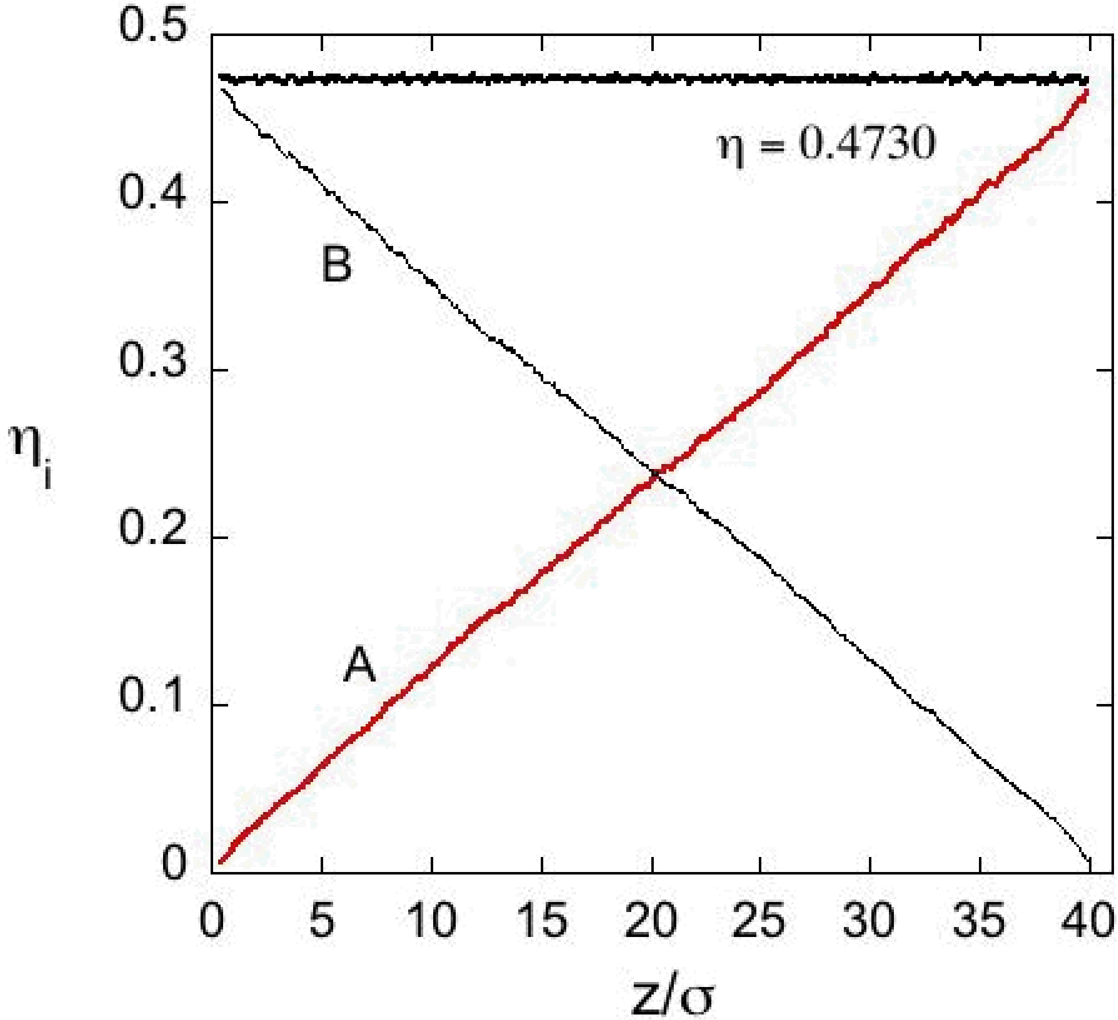


Transients





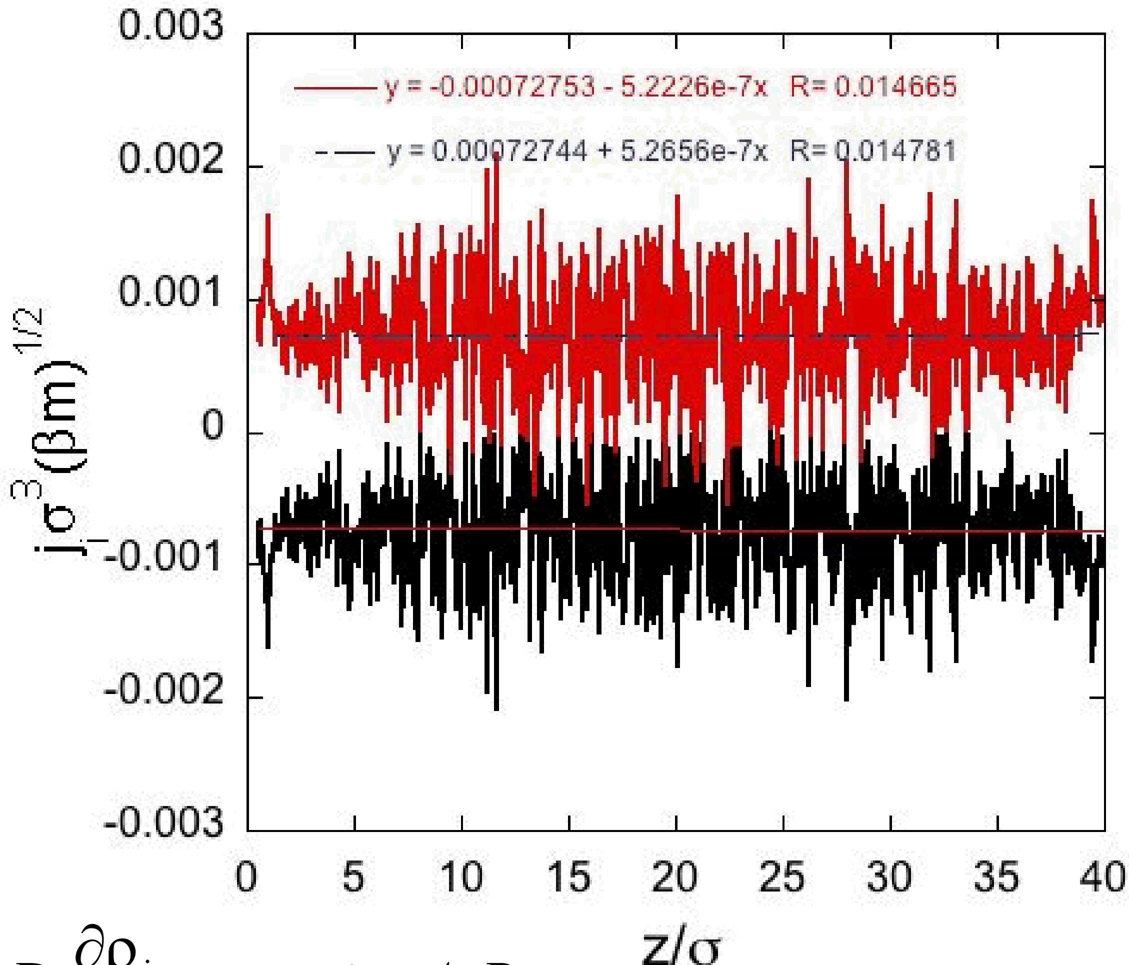
Steady-State

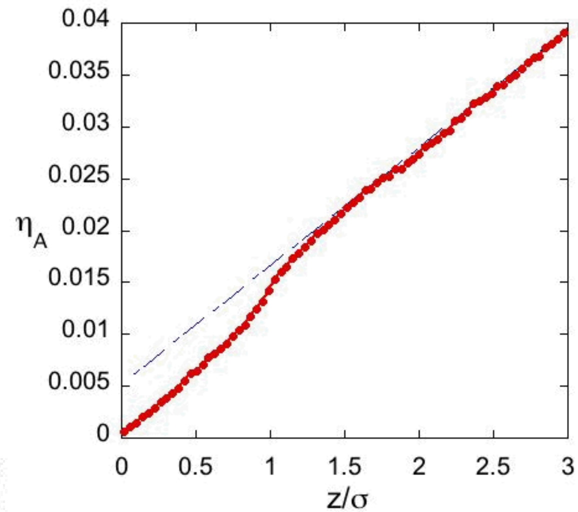


Adolph Fick 1855

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

Color fluxes





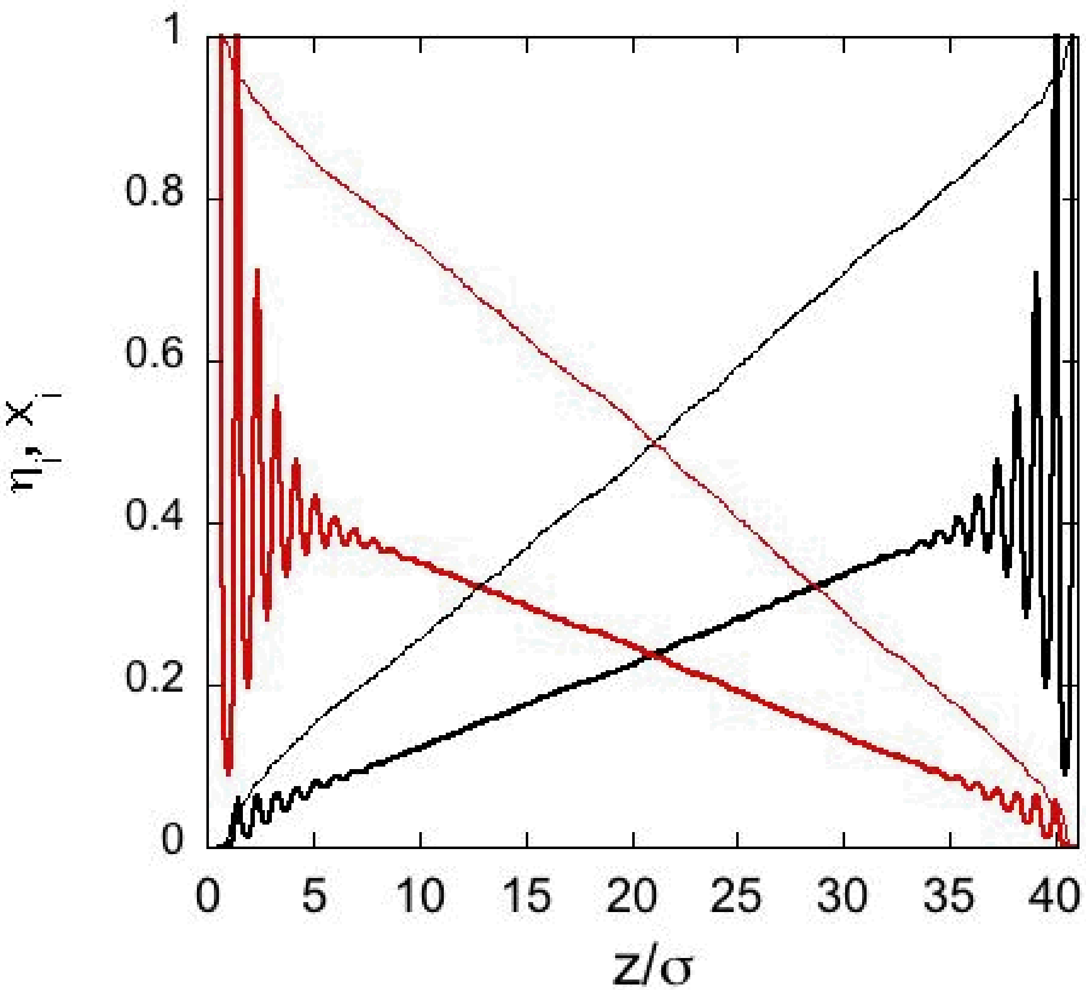
$$j_i = -D_i \frac{\partial \rho_i}{\partial x} \qquad i = A, B$$

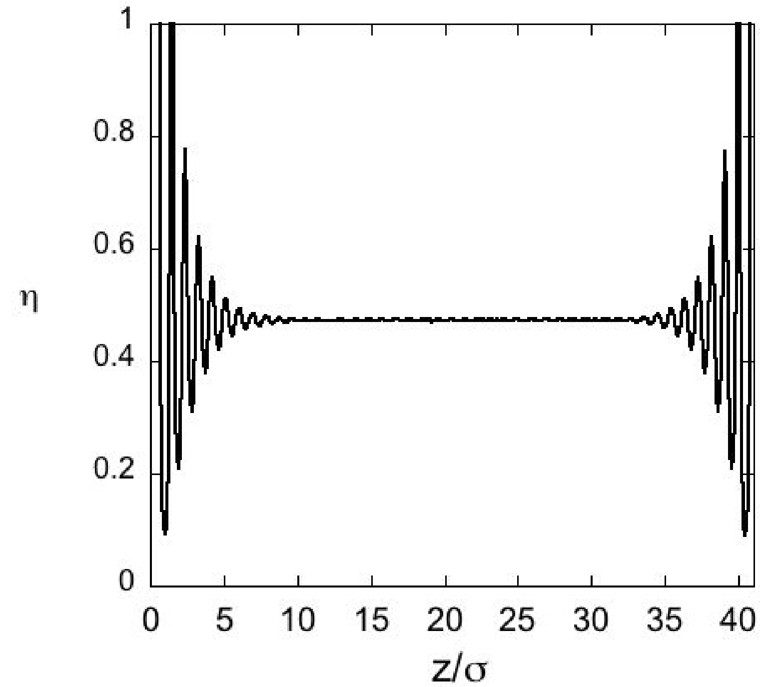
$$D_i = D_s = 0.0339 \sqrt{\mathrm{kT}\sigma^2 / m}$$

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

Inhomogeneous Hard Sphere Fluid

reactive boundary = hard wall



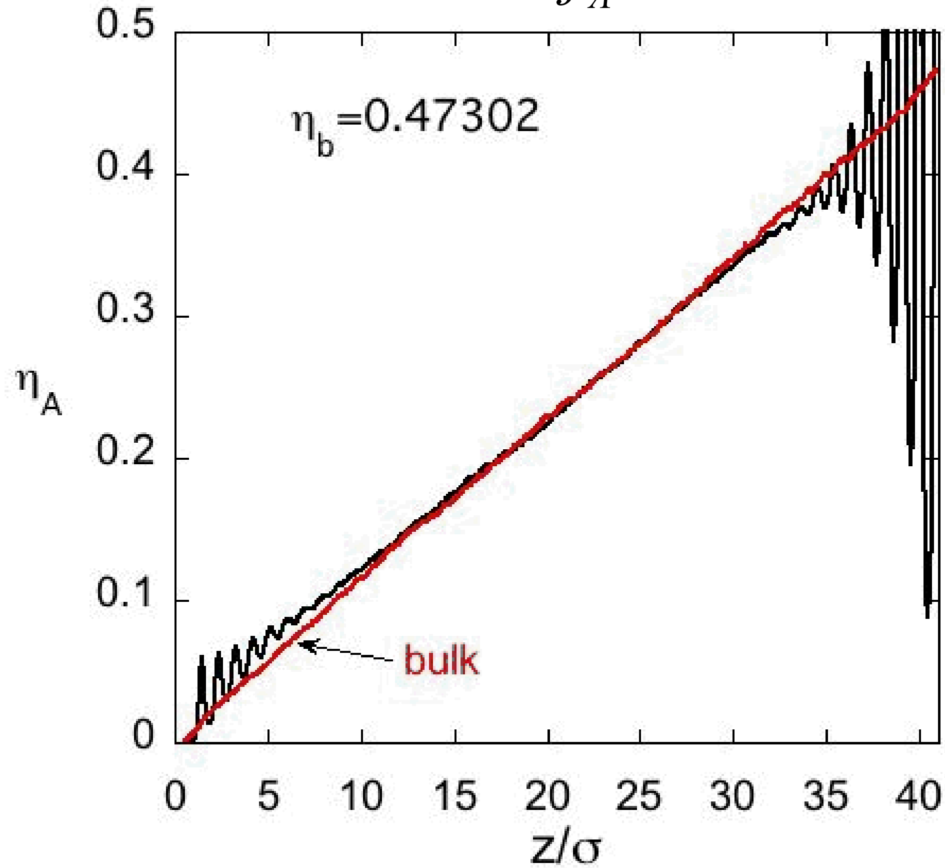


$$j_i = -D\,\frac{\partial \rho_i}{\partial x} \qquad ?$$

Comparing fluxes

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

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



What to do?

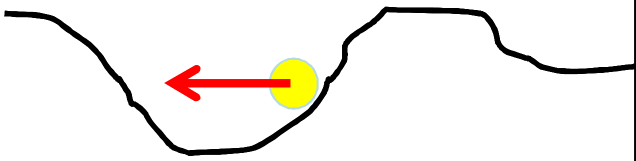
$$j_i = -D \frac{\partial \rho_i}{\partial x}$$

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

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

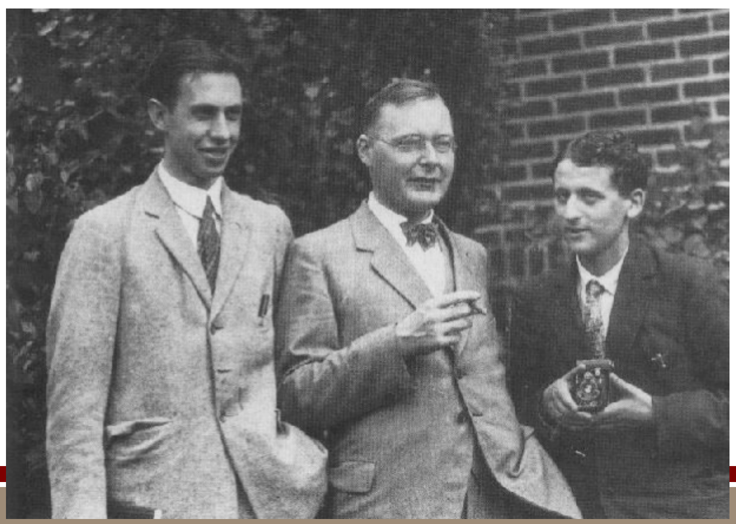
2) Smoluchowski equation

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



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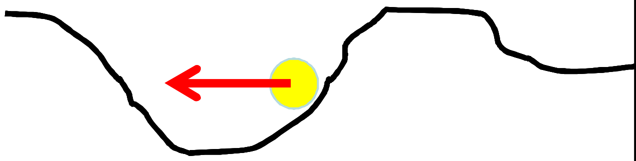
tracting the force K(z) om the SS profiles

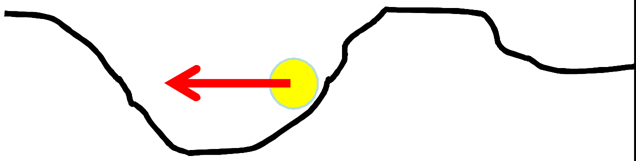


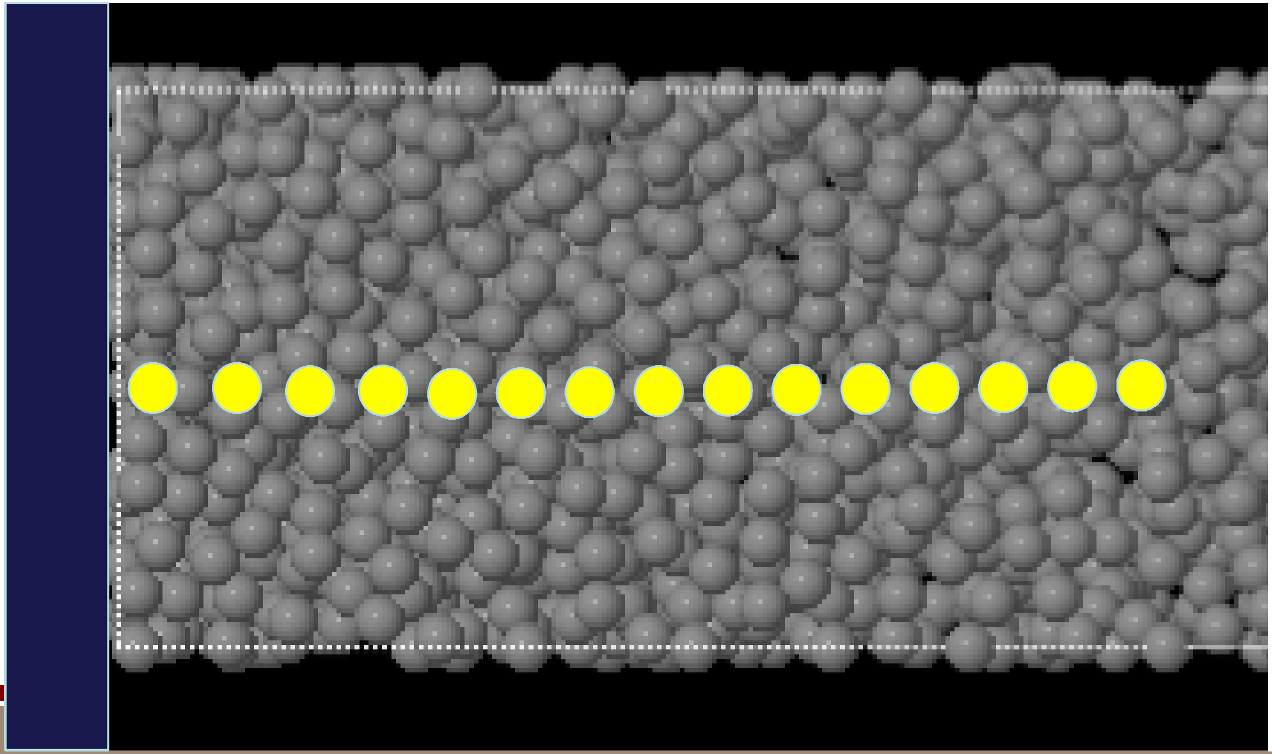
$$j_i = -D\frac{\partial \rho_i}{\partial z} - D\frac{K(z)\rho_i}{kT}; \qquad i = A, B$$

$$\downarrow$$

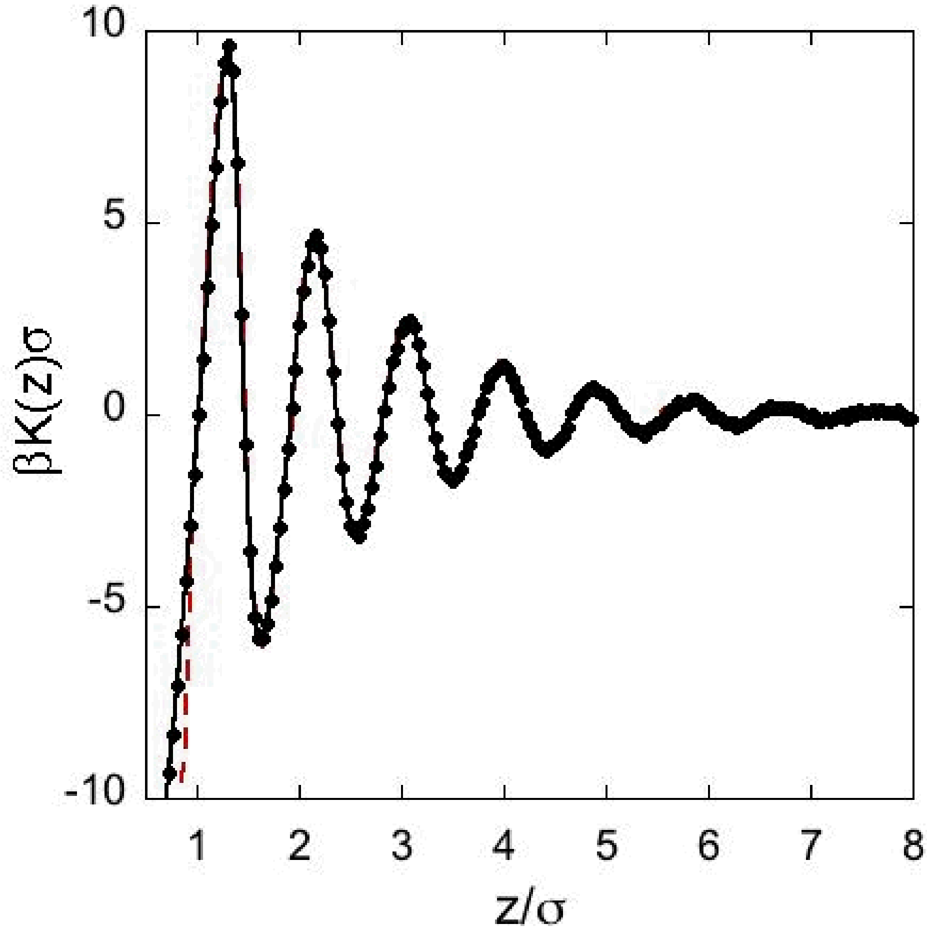
$$\frac{K(z)}{kT} = \frac{j_i}{D\rho_i} + \frac{\partial ln \rho_i}{\partial z}; \qquad i = A, B$$

Alternatively: measure K(z) directly





K(z) = Solvation Force



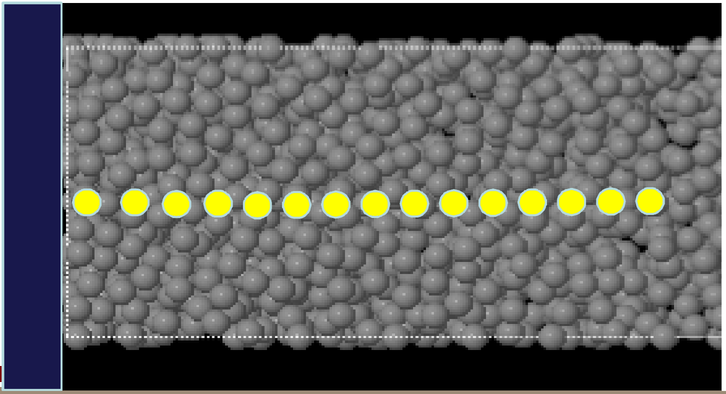
9.5 Potential Distribution Theorem (hard walls)

Pure fluid, at equilibrium:

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

From which it follows that

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

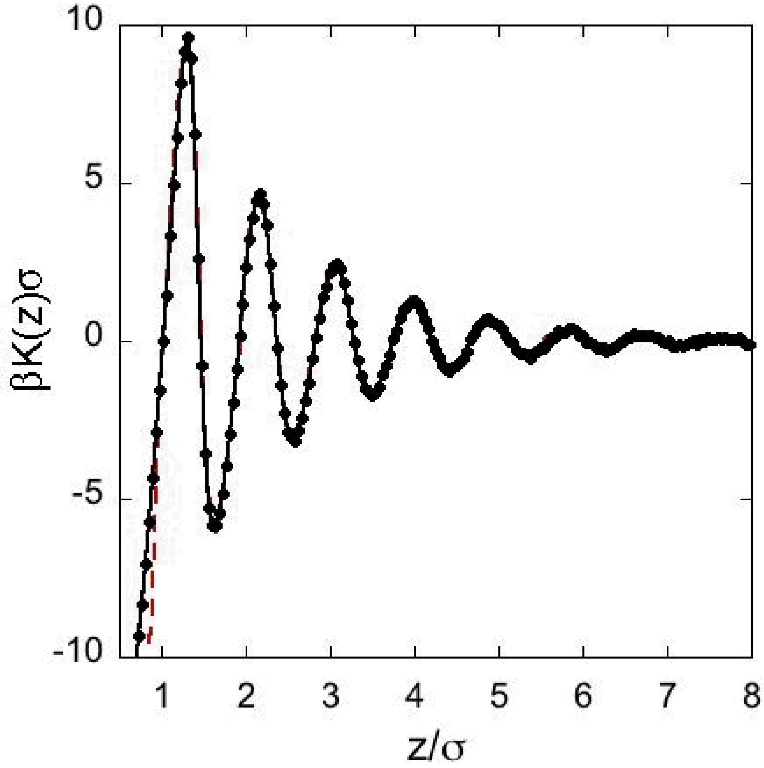


K(z) from three routes

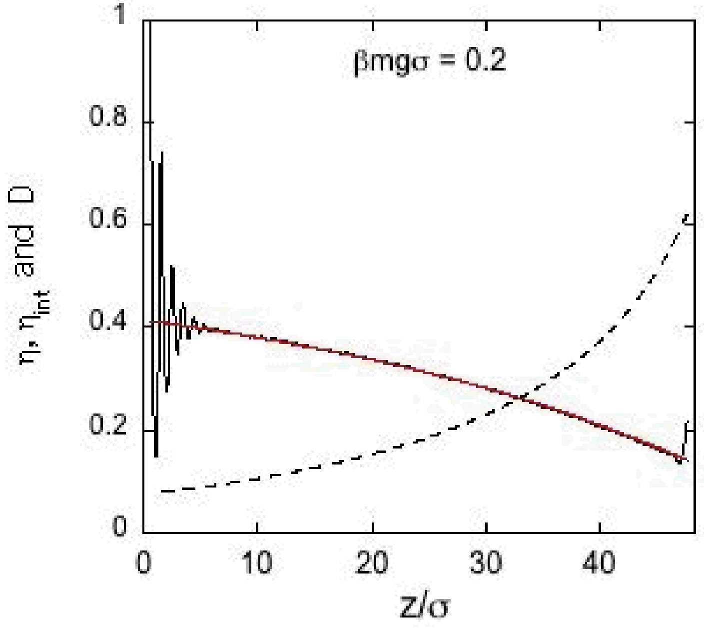
1. Force measurement
2. PDT
3. Fluxes and Profiles

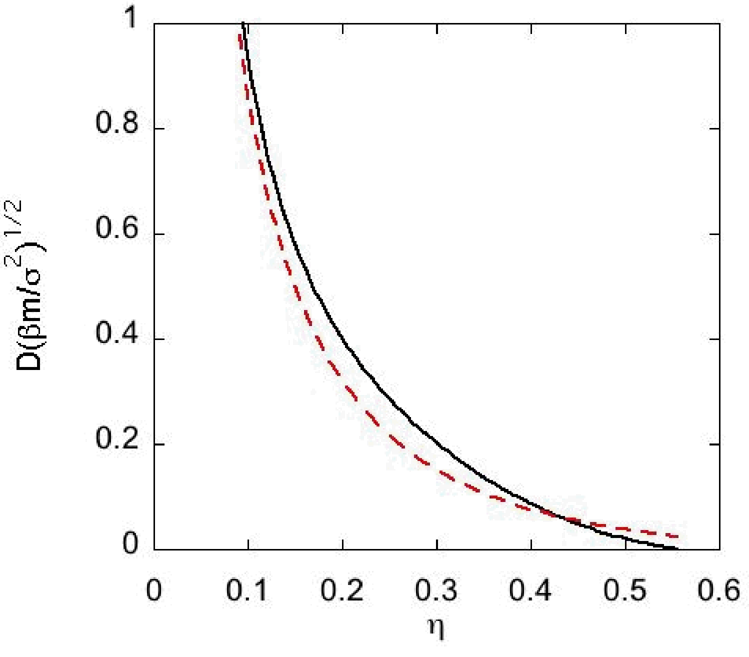
Note, route 3 assumed:

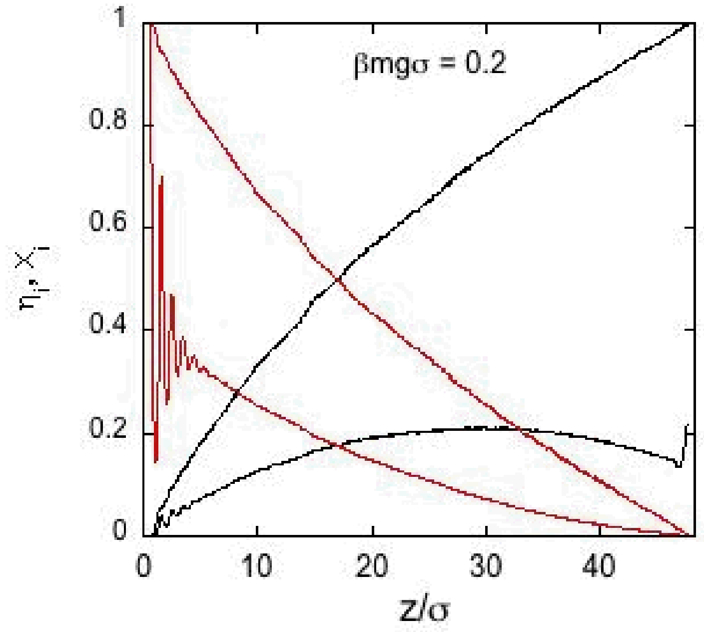
$D = \text{constant} = D(\rho_b)$



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

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

$$= ln\rho_i(z) + \beta\tilde{\mu}^{ex}(z) + V_{ext}(z) \tag{54}$$

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

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

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

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

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

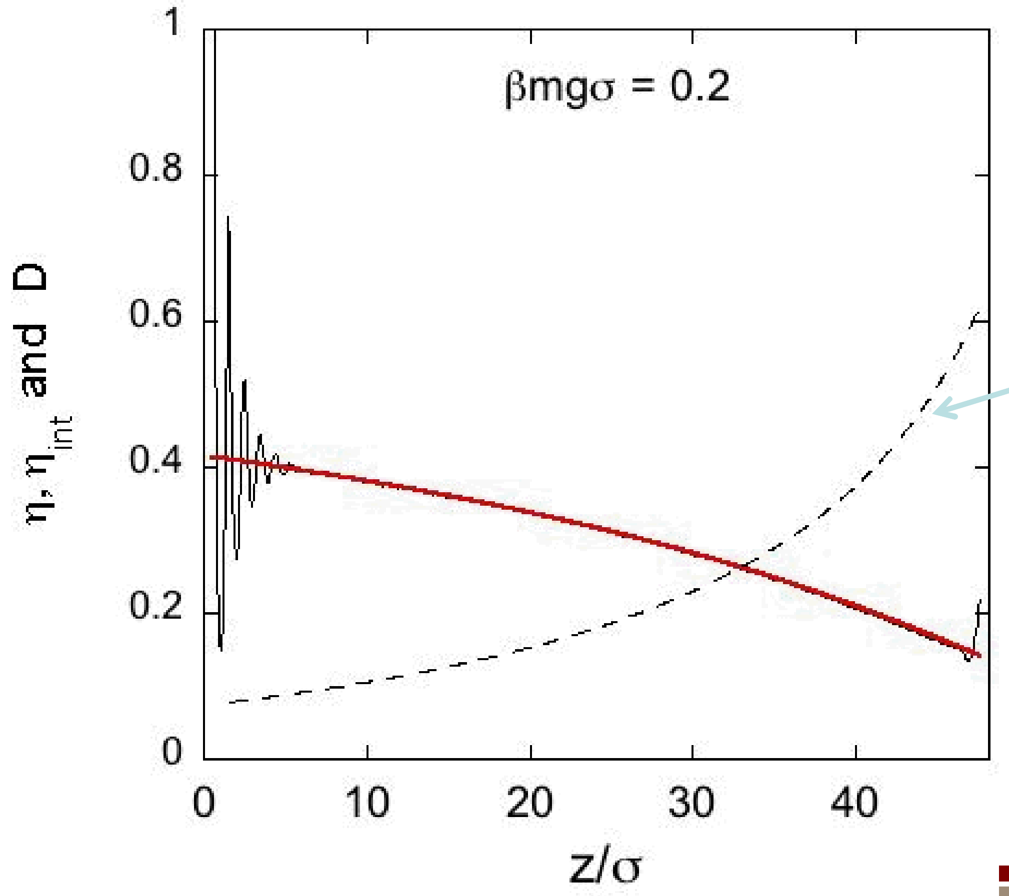
$$\begin{aligned}\mu_{int}(z) &\equiv \mu - V_{ext}(z) \\ &= \mu - mg(z - z_0); \qquad gravity\end{aligned}$$

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

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

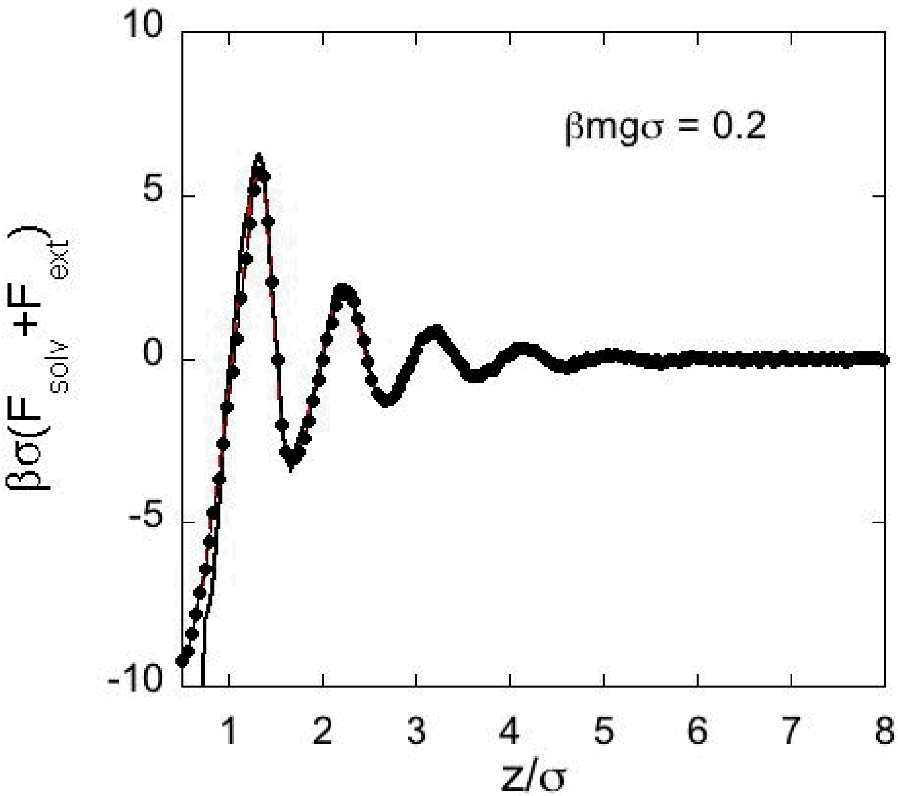
The intrinsic density profile

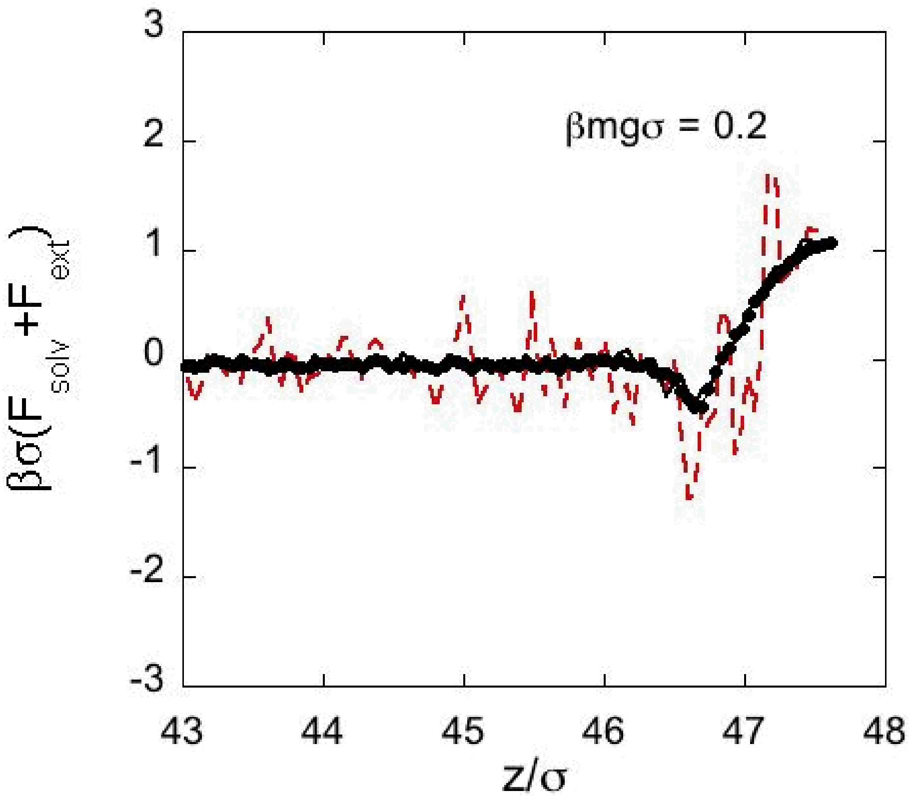
$$\mu_{\text{int}}(z) = \mu(z_0) - mg(z - z_0)$$



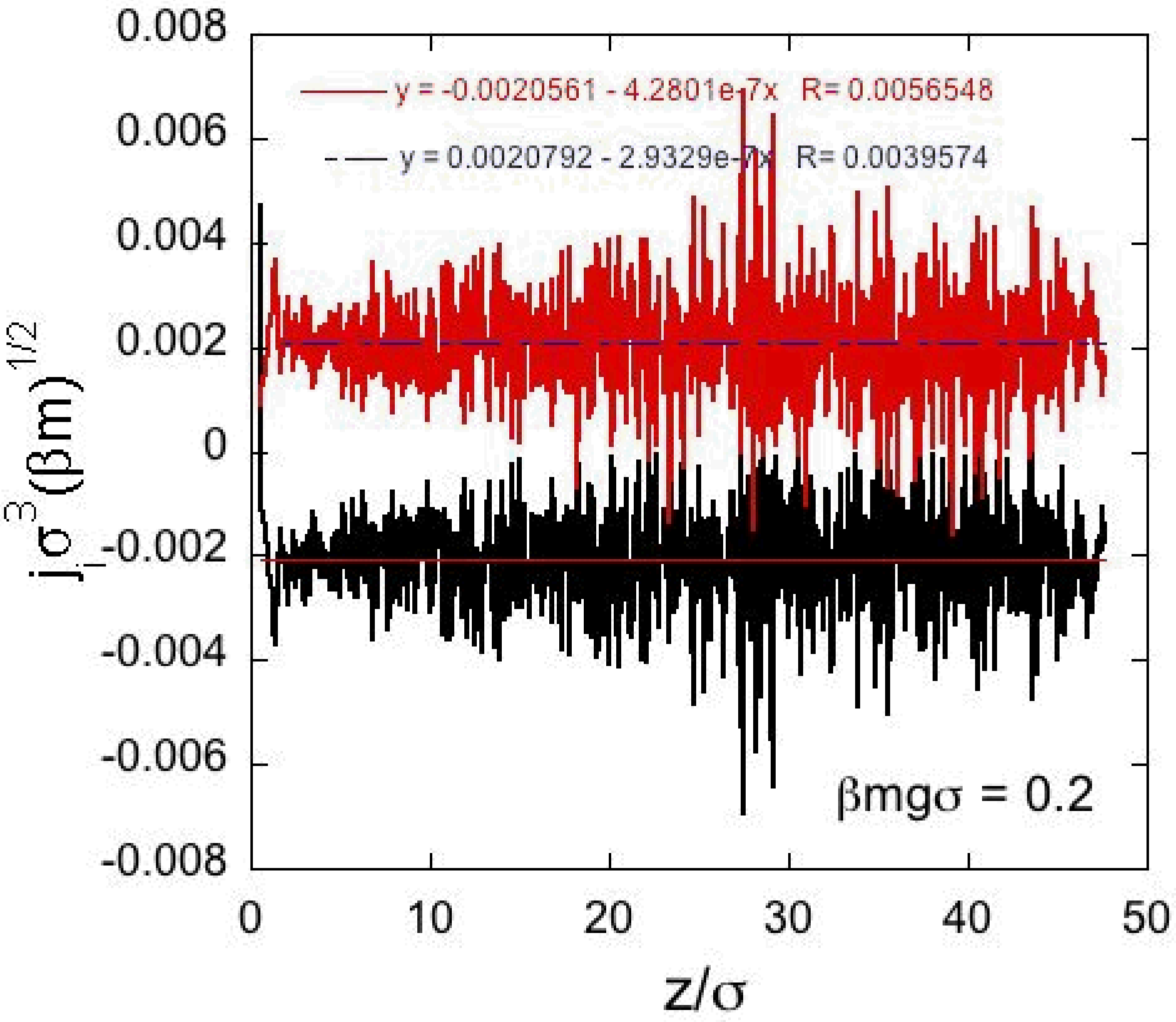
$$D = D[\mu_{\text{int}}(z)]$$

Checking K(z) in gravity





Checking the fluxes, j_A & j_B



Concusion

For inhomogeneous fluids use

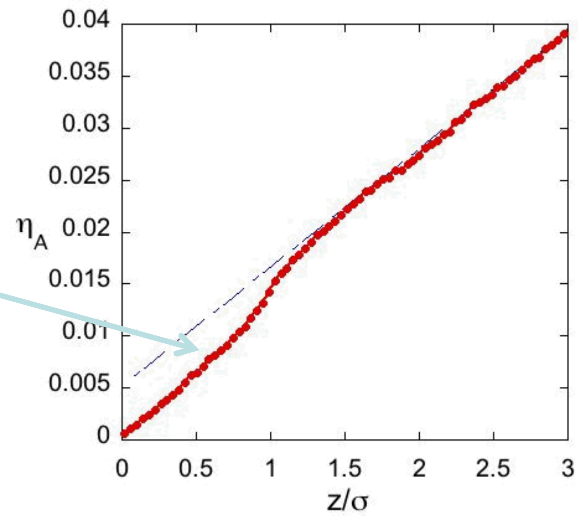
$$D(z) = D[\mu_{int}(z)]$$

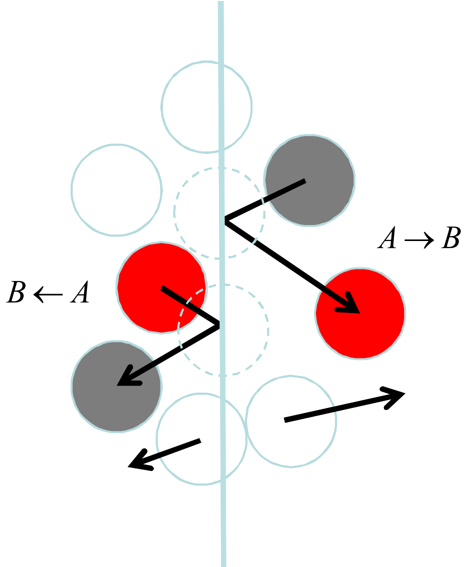
and combine with the solvation force.

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

Question

What is this?





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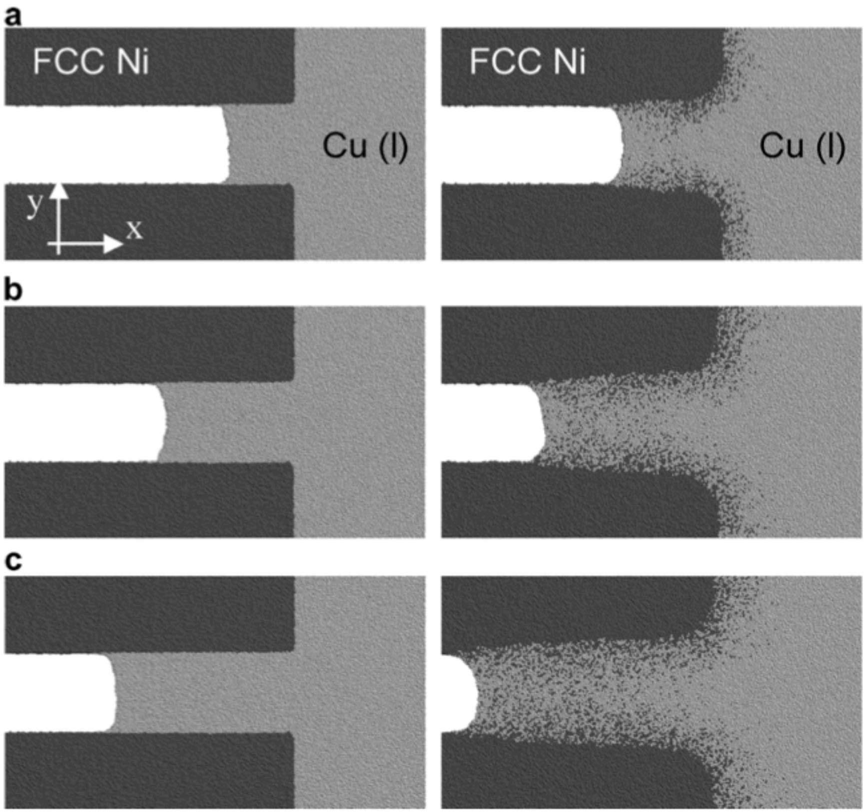


Fig. 1. Snapshots from MD simulations of liquid Cu infiltration into a Ni channel at $T = 1750$ K; Cu(Ni) atoms are rendered as light(dark) spheres. Results are shown for the non-dissolutive (left) and the dissolutive (right) simulations at varying simulation times: (a) $t = 400$ ps, (b) $t = 900$ ps and (c) $t = 1400$ ps.

Liquid-Cu infiltration

Washburn eqn

$$L^2 = \frac{h\gamma_{LV}\cos\theta}{3\eta}t$$

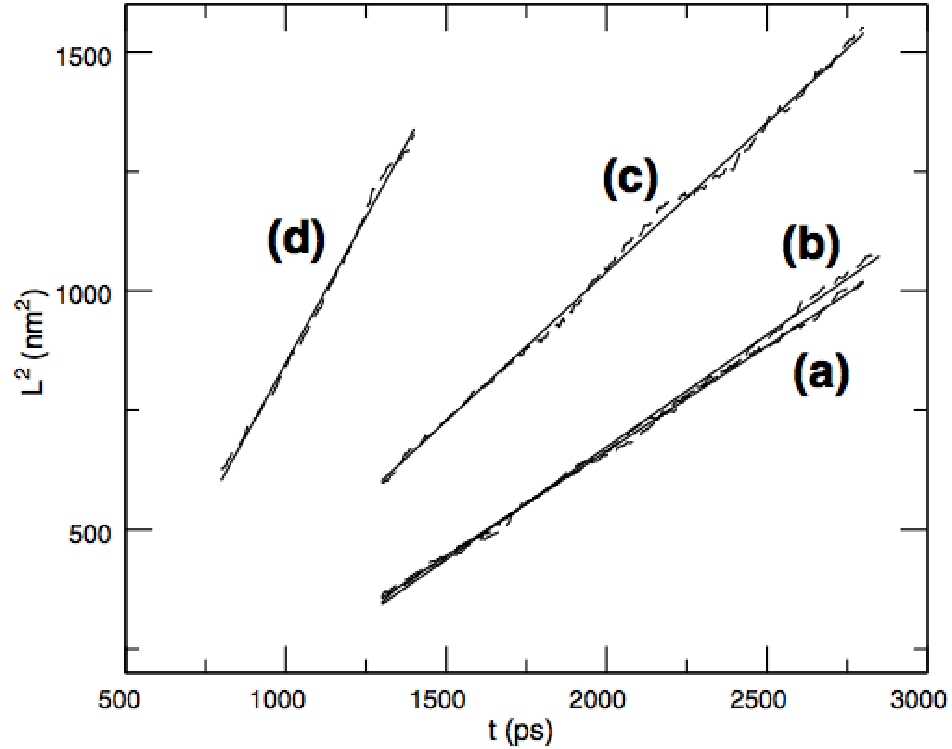
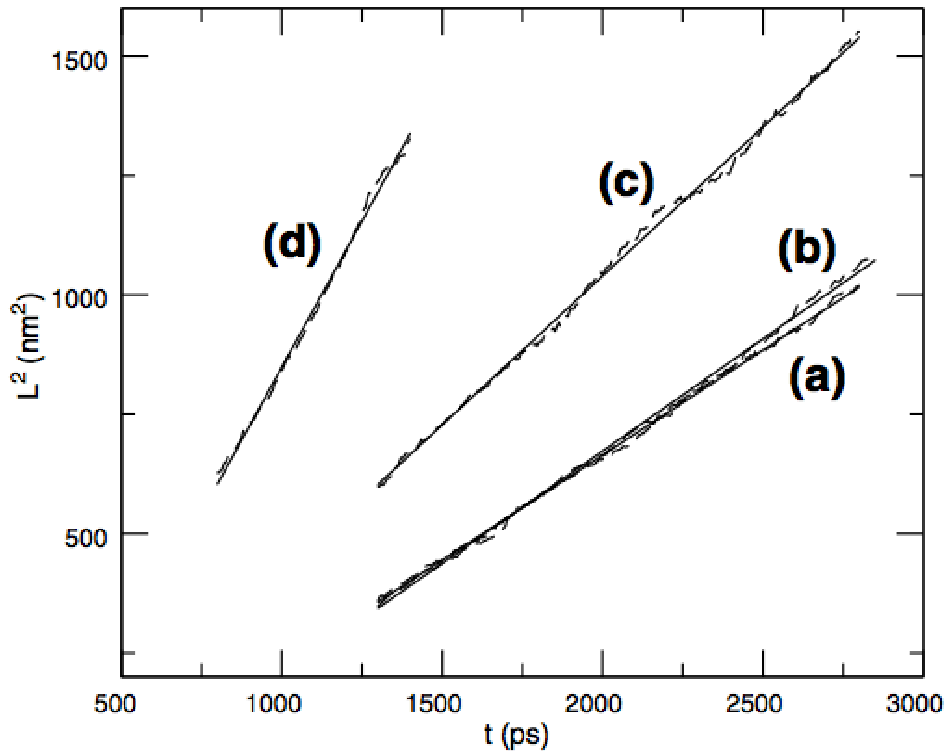


Fig. 6. Penetration length squared vs. time for $T = 1500$ K (lower curves) and $T = 1750$ K (upper curves); (a) and (c) show results for ND cases, while (b) and (d) are for D cases. Broken curves show simulation data, while solid lines are fits.

Liquid-Cu infiltration

Washburn eqn

$$L^2 = \frac{h\gamma_{LV}\cos\theta}{3\eta}t$$



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Liquid-Cu infiltration

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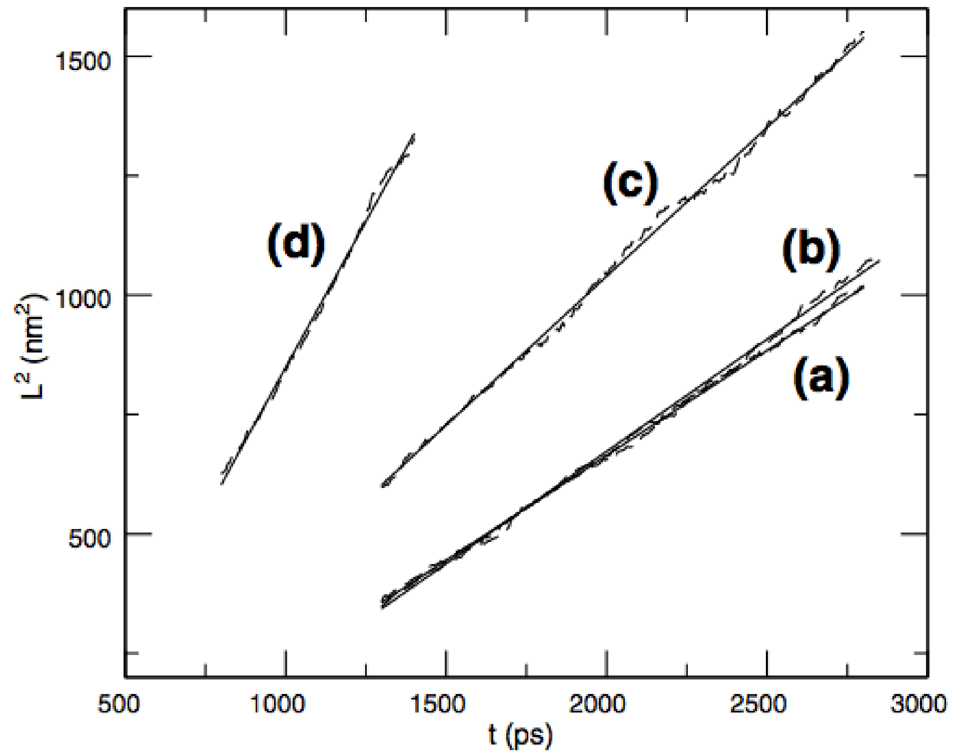

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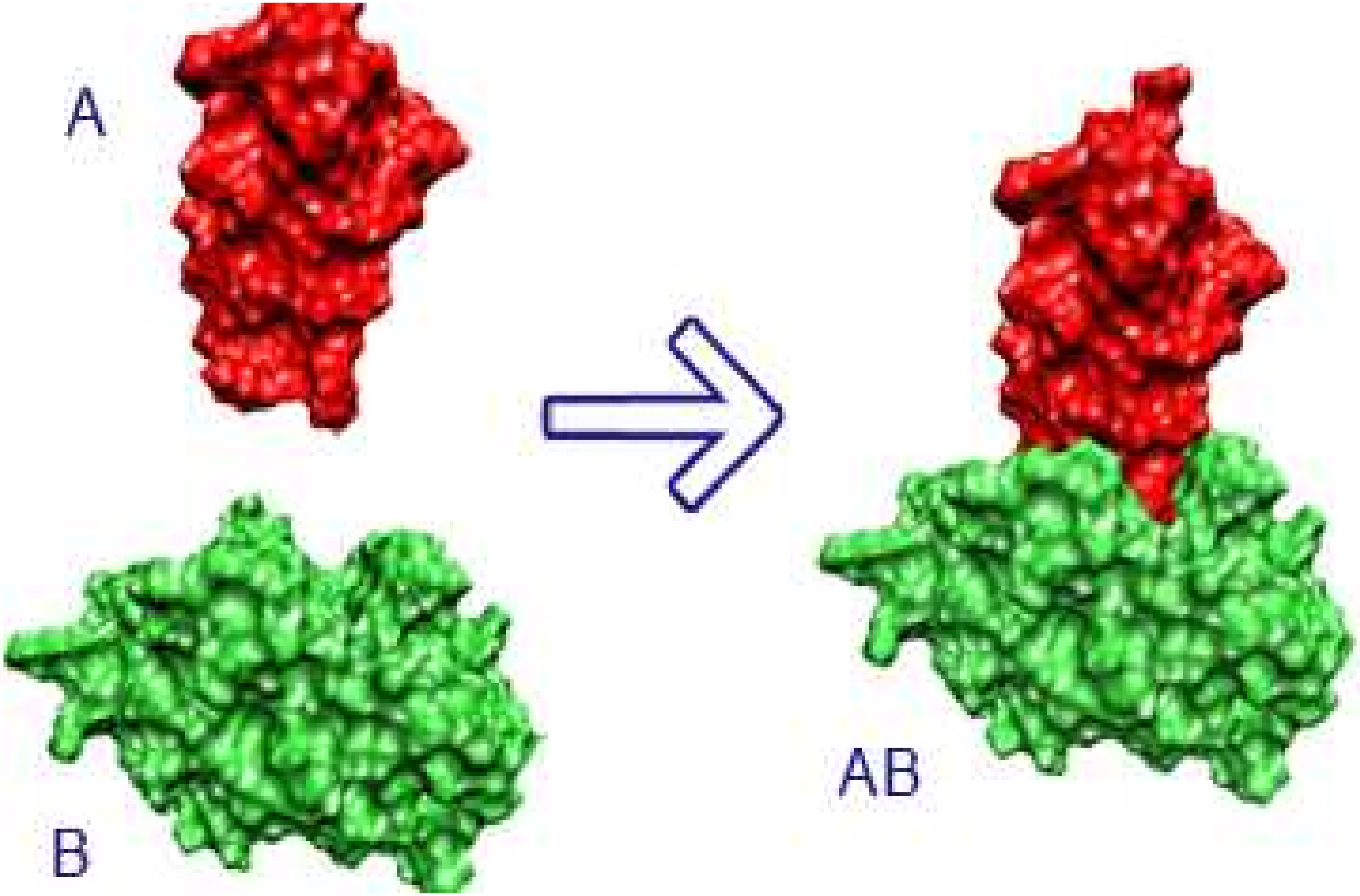
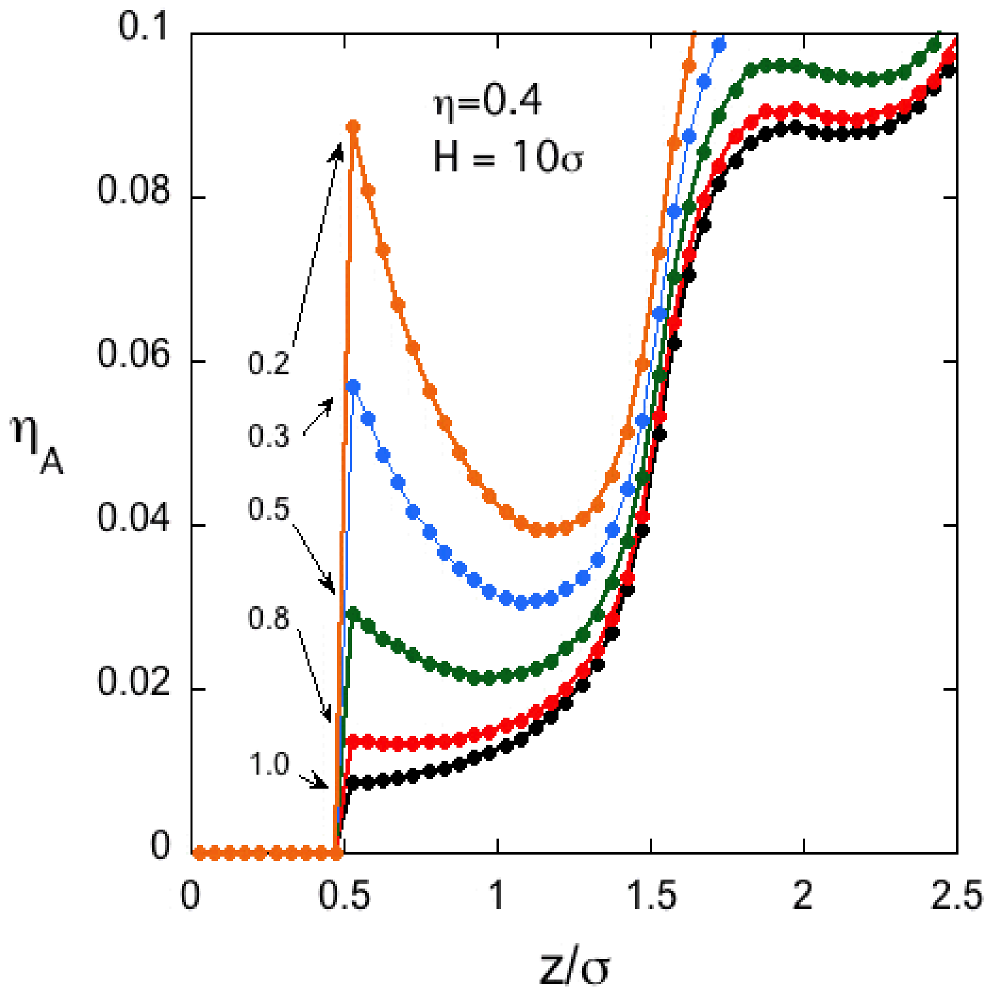
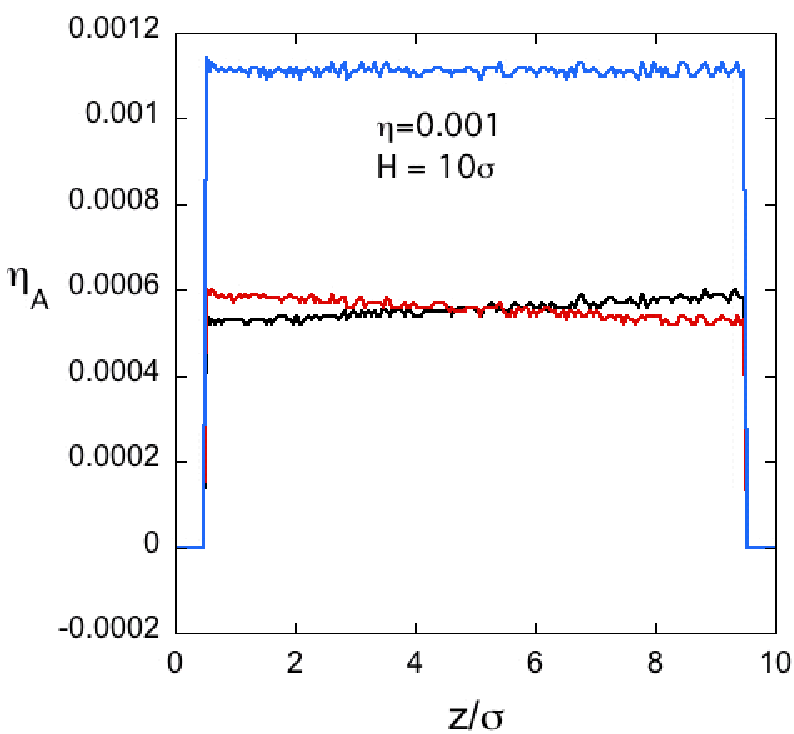
Docking Proteins



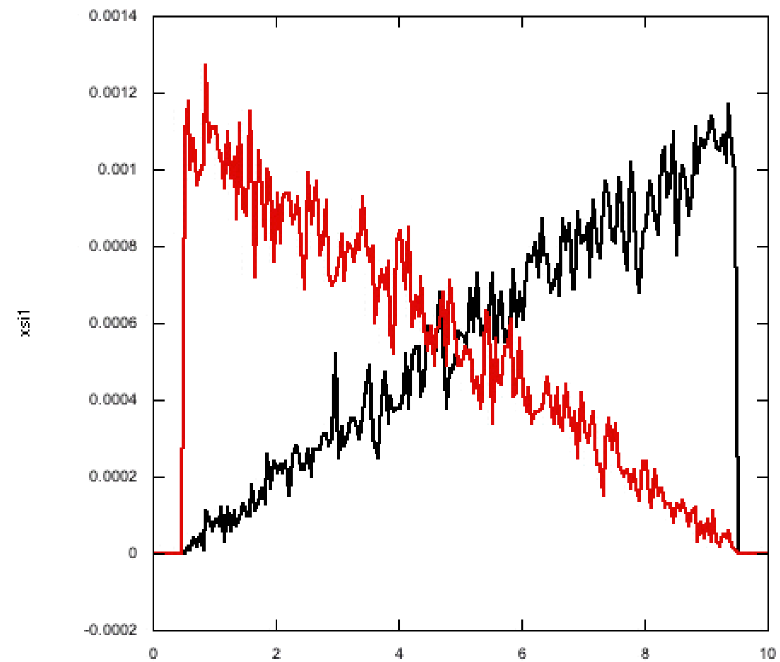
Contact densities



Very low density gas

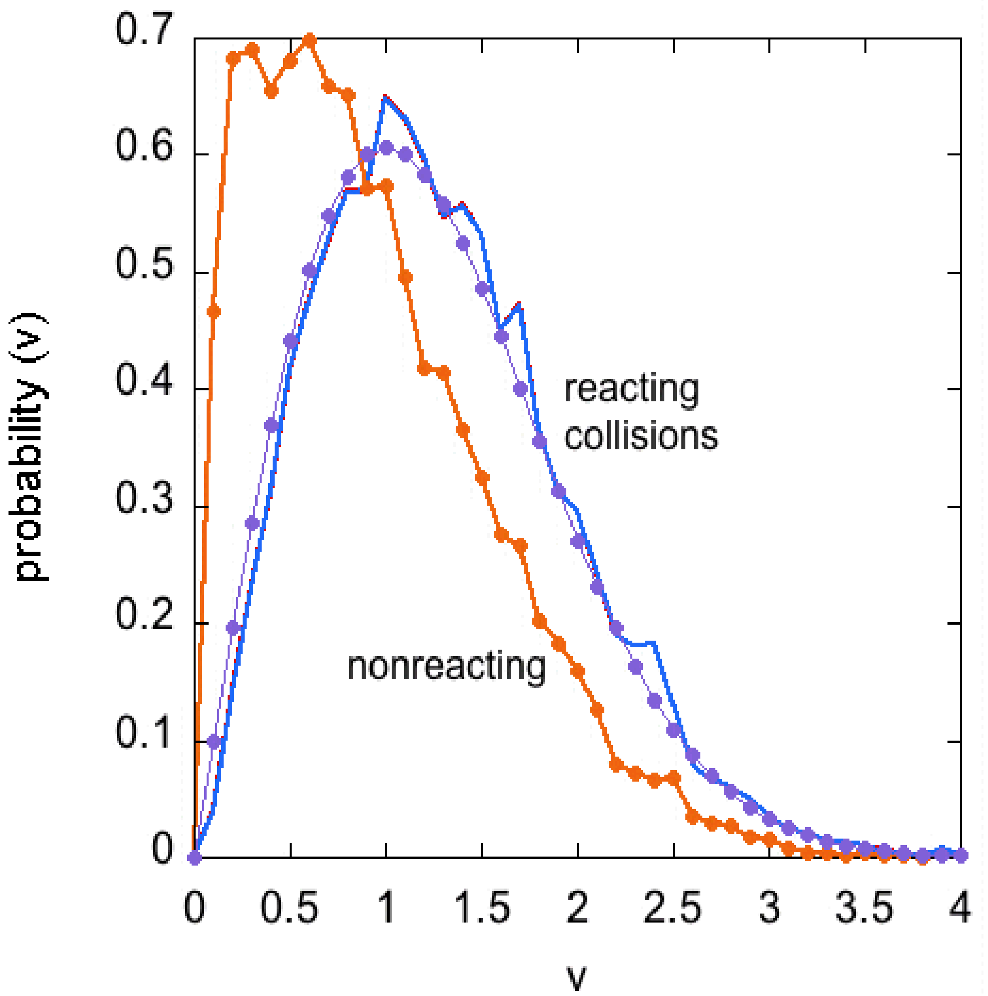


Molecular dynamics

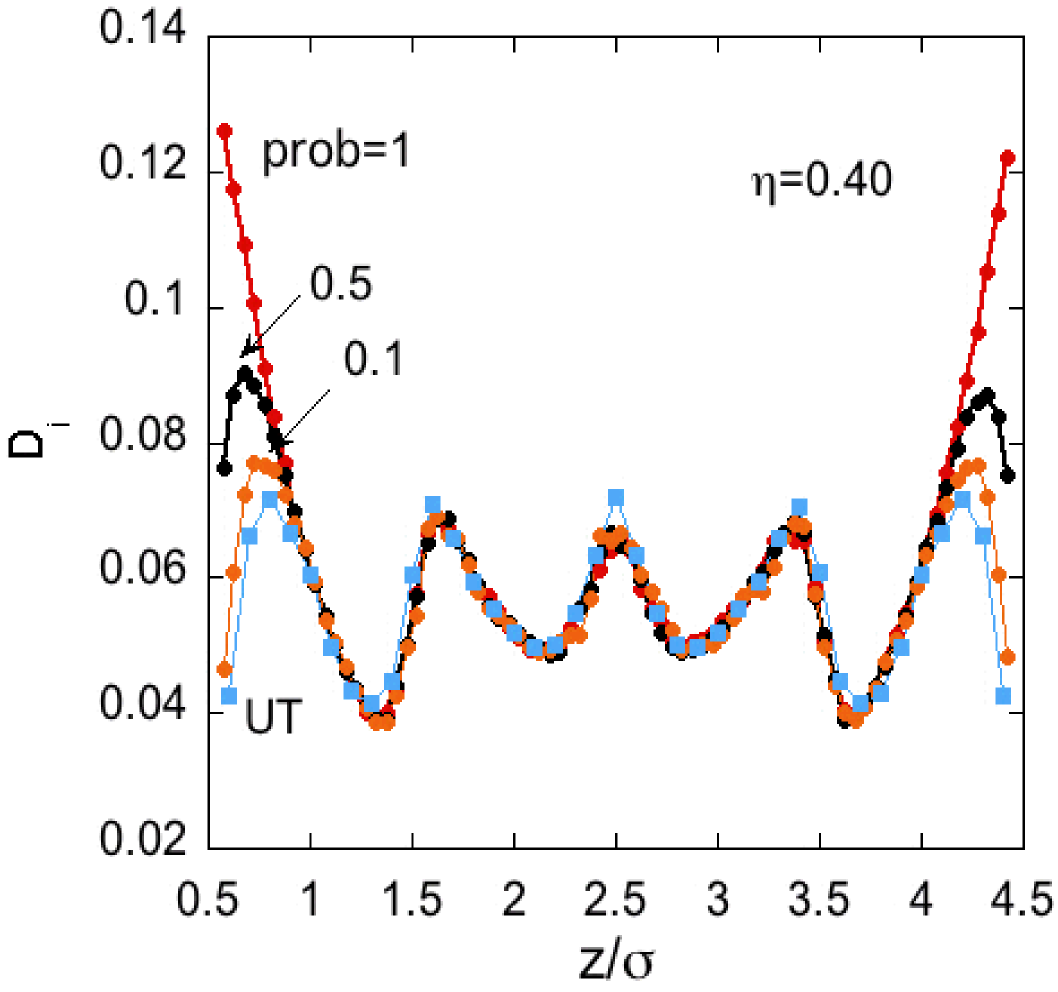


Brownian Dynamics

Velocity distributions



Narrow Slit Pores



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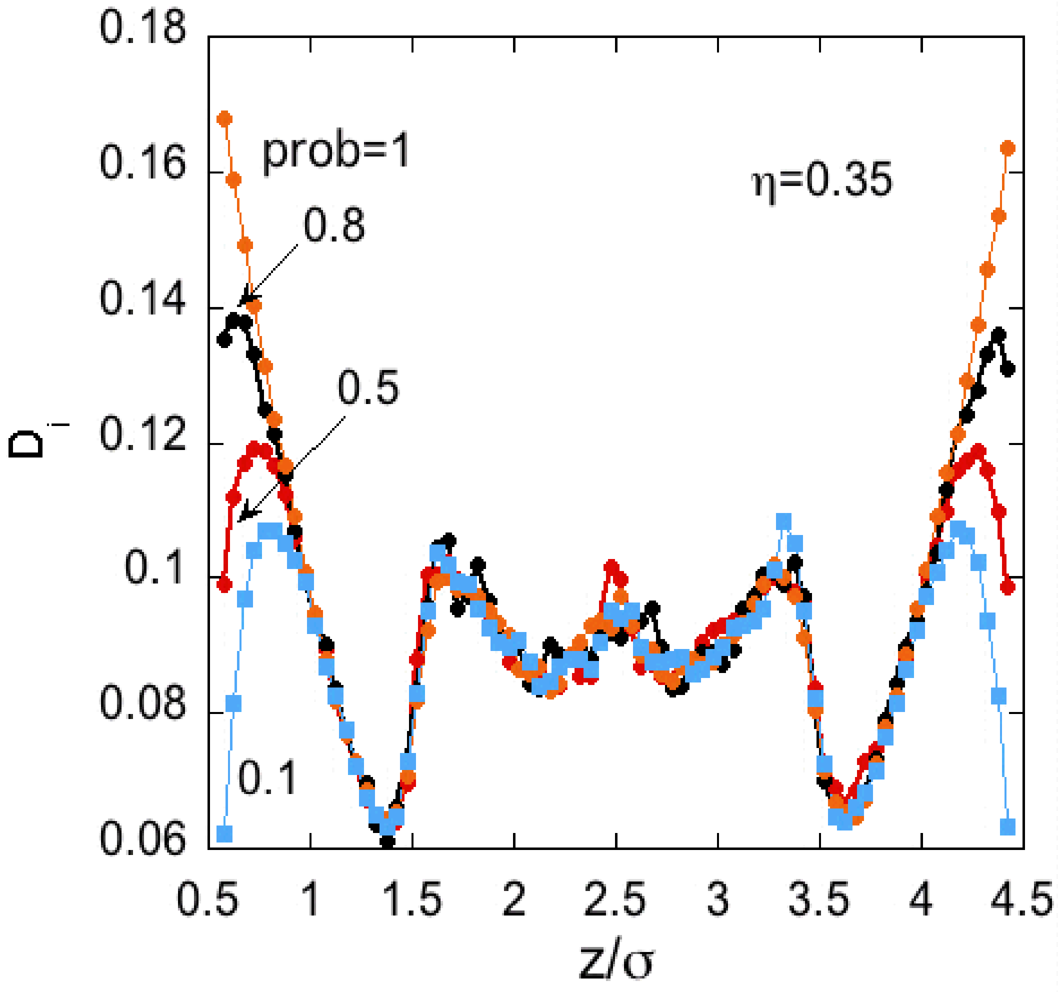

PRL 100, 145901 (2008) PHYSICAL REVIEW LETTERS week ending 11 APRIL 2008

Layering and Position-Dependent Diffusive Dynamics of Confined Fluids

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We study the diffusive dynamics of a hard-sphere fluid confined between parallel smooth hard walls. The position-dependent diffusion coefficient normal to the walls is larger in regions of high local packing density. High density regions also have the largest available volume, consistent with the fast local diffusivity. Indeed, local and global diffusivities as a function of the Widom insertion probability approximately collapse onto a master curve. Parallel and average normal diffusivities are strongly coupled at high densities and deviate from bulk fluid behavior.

quote

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We use a recently proposed propagator-based formalism to estimate the position-dependent diffusion coefficients self-consistently from simulation trajectory data [6]. For diffusion, the propagator (or Green's function) $G(z,\Delta t|z',0)$ for single-particle displacements along the coordinate z normal to the confining walls is assumed to satisfy the Smoluchowski diffusion equation,

$$\frac{\partial G}{\partial t} = \frac{\partial}{\partial z}\left\{D_{\perp}(z)e^{-\beta F(z)}\frac{\partial}{\partial z}\left[e^{\beta F(z)}G\right]\right\}, \qquad (1)$$

with $\beta = 1/k_B T$, k_B Boltzmann's constant, and T the

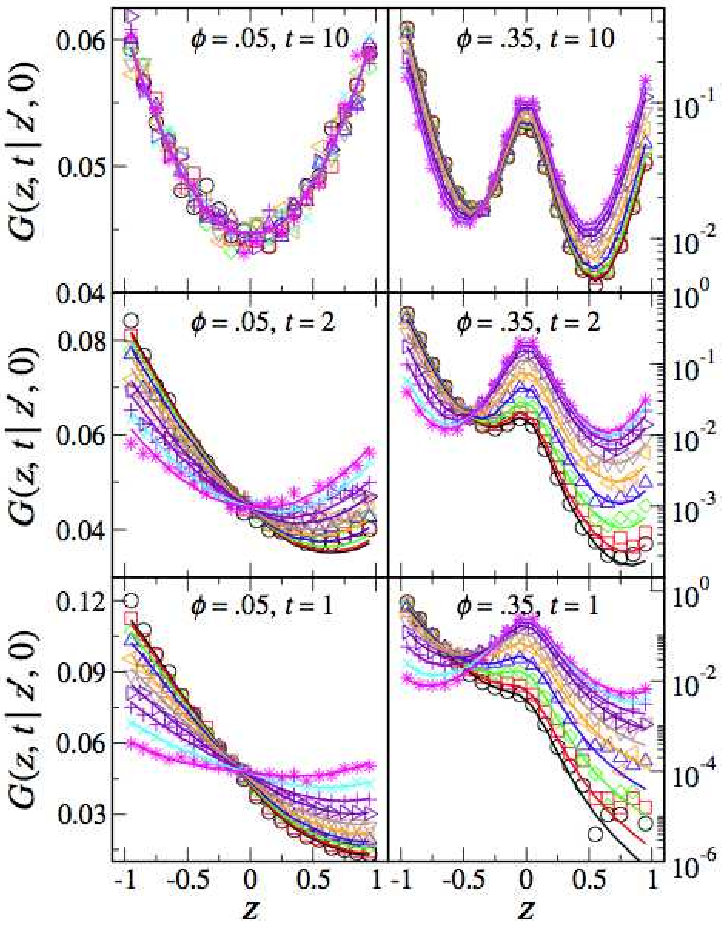
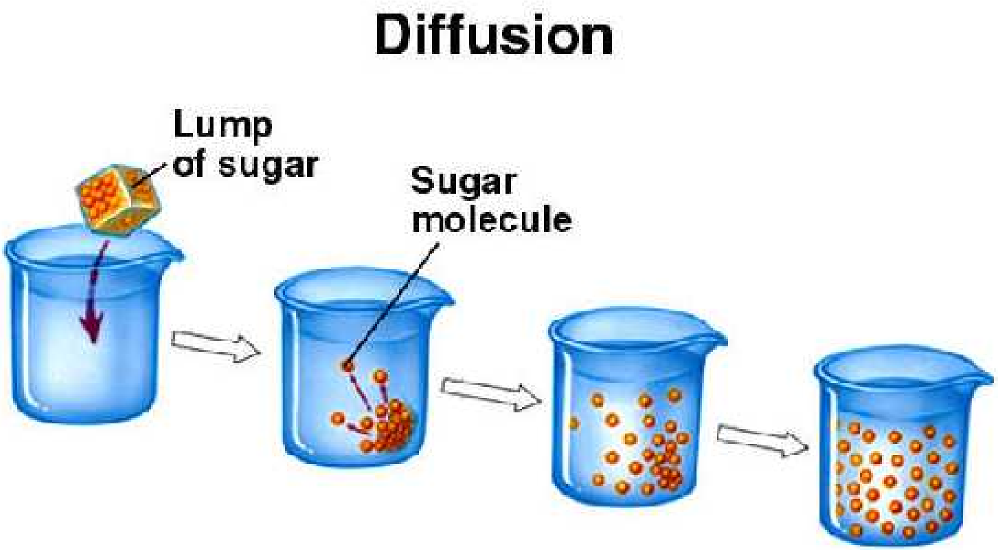


FIG. 1 (color online). The conditional probability $G(z, t|z', 0)$ of observing a particle at a position z at time t if it started at z' at $t = 0$. Results are shown for pore size $H = 3$, packing fractions $\phi = 0.05$ (left) and 0.35 (right), and times $t = 1$, 2, and 10 (bottom to top). The observation time $t = 1$ is used to obtain parameters of the diffusion model Eq. (1) (lines). Simulation results for $G(z, t|z', 0)$ for different z' are shown as symbols, where z' varies from -0.05 to -0.95 (symbol ∘ to *) in intervals of 0.1. (For reference, mean collision frequencies for the bulk hard-sphere fluid are approximately 852 and 7369 for $\phi = 0.05$ and 0.35, respectively.)



Oil &
water

Equilibrium DFT: Grand Canonical Ensemble

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$$\beta\Omega[\rho] = \sum_i^l \left[(1 - \sum_k^{lspe} \rho_i^k) \ln(1 - \sum_k^{lspe} \rho_i^k) + \sum_k^{lspe} \left(\rho_i^k \ln \rho_i^k + \rho_i^k \beta V_i^k - \rho_i^k \beta \mu_i^k + \frac{\beta}{2} \sum_m^{Ne} \sum_n^{lspe} \epsilon_{d(i,m)}^{kn} \rho_i^k \rho_{I(i,m)}^n \right) \right]$$

Take the partial of the grand potential with respect to the site densities gives a set of equations which will all be zero at equilibrium.

$$\frac{\partial(\beta\Omega[\rho])}{\partial \rho_i^k} = \ln \rho_i^k - \ln(1 - \sum_k^{lspe} \rho_i^k) + \beta V_i^k - \beta \mu_i^k + \beta \sum_m^{Ne} \sum_n^{lspe} \epsilon_{d(i,m)}^{kn} \rho_{I(i,m)}^n$$

The equations can be rearranged in the following form Suitable for a picard iteration solution method.

$$\rho_i^k = \frac{(1 - \Sigma_{m \neq k}^{lspe} \rho_i^m) \exp(C_t)}{1 + \exp(C_t)}$$

$$C_t = \beta \mu_i^k - \beta V_i^k - \beta \sum_m^{Ne} \sum_n^{lspe} \epsilon_{d(i,m)}^{kn} \rho_{I(i,m)}^n$$

Equilibrium Density Functional Theory (DFT):
Grand Canonical Ensemble

$$\Omega[\rho] = \mathcal{F}[\rho] + \int d\mathbf{r}\, \rho(\mathbf{r})(V_{\text{ext}}(\mathbf{r}) - \mu),$$

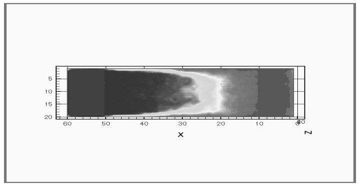
$$\beta\mathcal{F}_{\text{id}}[\rho] = \int d\mathbf{r}\, \rho(\mathbf{r}) \left(\ln(\Lambda^3 \rho(\mathbf{r})) - 1\right),$$

$$\beta\mathcal{F}_{ex}[\{\rho_i\}] = \int d^3r'\, \Phi(\{n_\alpha(\mathbf{r}')\})$$

Example: Non equilibrium DFT (on a lattice)

Use diffusive equations to determine site flux of material

$$\frac{d\rho_i^k}{dt} = -\nabla J_i^k \quad \text{where} \quad J_i^k = -\sum_n^{lspe} D_i^{kn} \rho_i^n \nabla \mu_i^n$$



These equations can be combined to give

$$\frac{d\rho_i^k}{dt} = \sum_n^{lspe} D_i^{kn} \left(\rho_i^n \nabla^2 \mu_i^n + \nabla \rho_i^n \nabla \mu_i^n \right)$$

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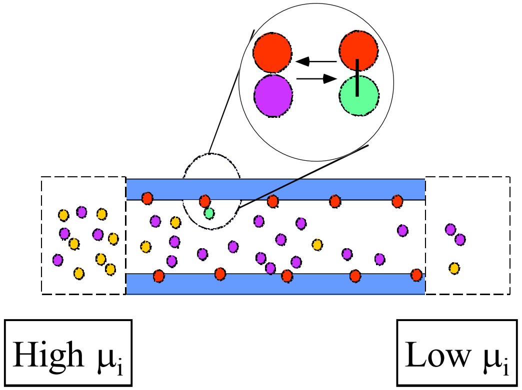
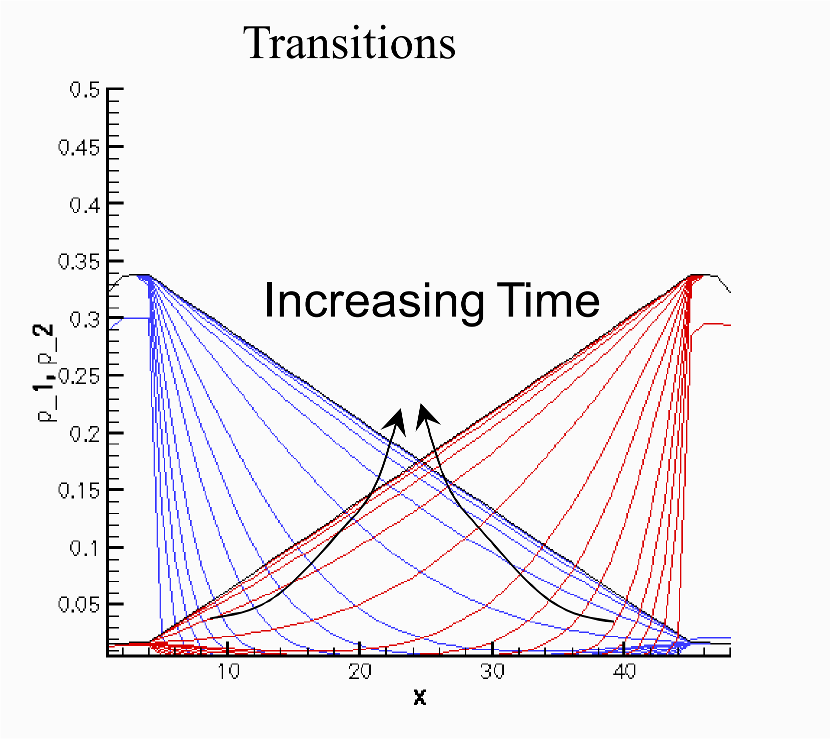
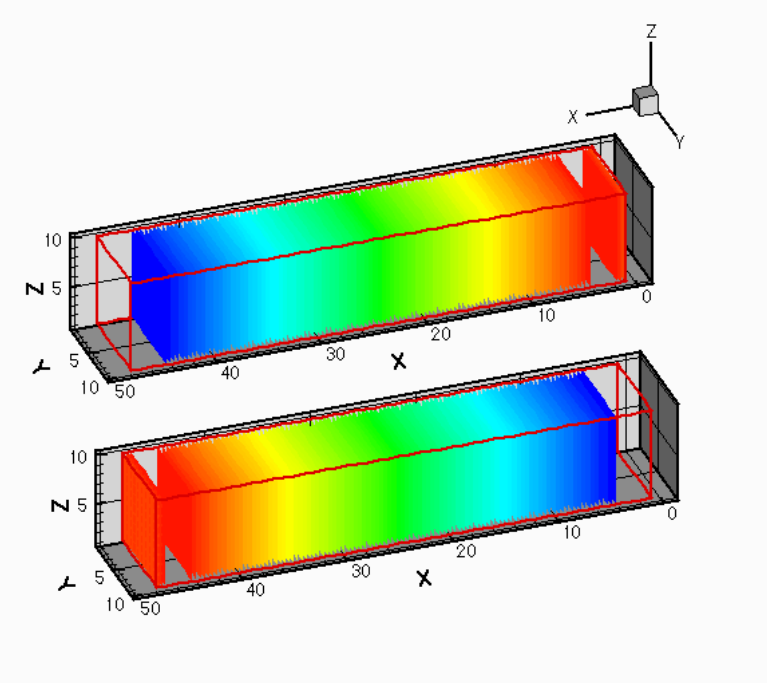
$$\left(\rho_i^k\right)^{t+} = \left(\rho_i^k\right)^{t-} + \sum_n^{lspe} (\Delta t) D_i^{kn} \left(\rho_i^n \nabla^2 \mu_i^n + \nabla \rho_i^n \nabla \mu_i^n \right)$$



Example: Non equilibrium DFT (on a lattice)





Colloids: Confocal Microscopy

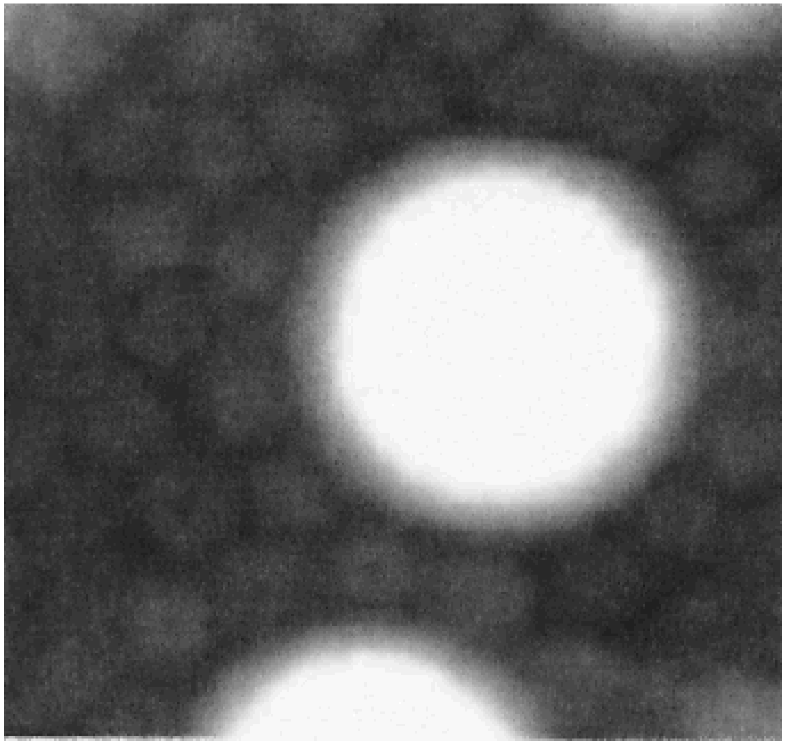
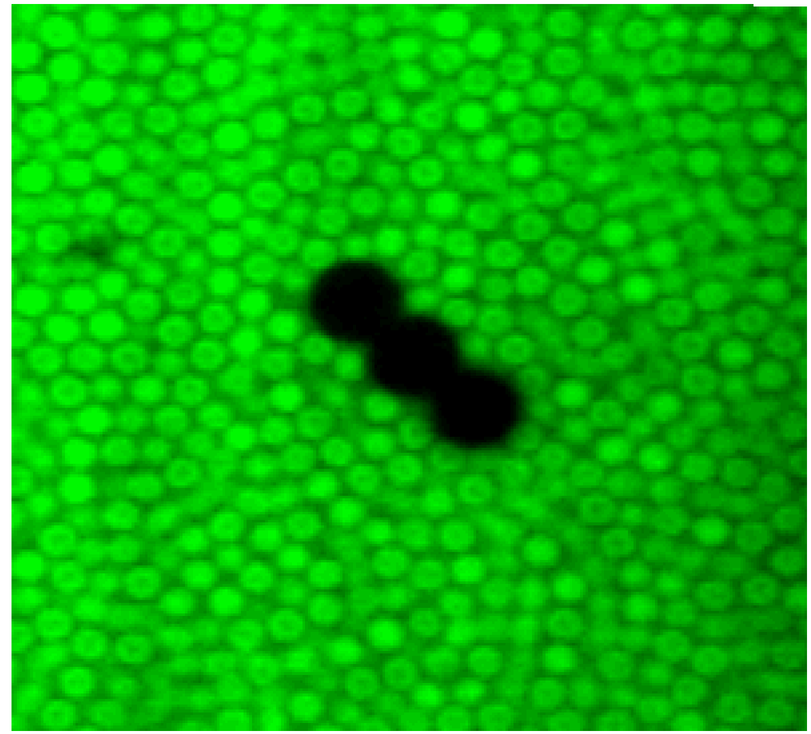
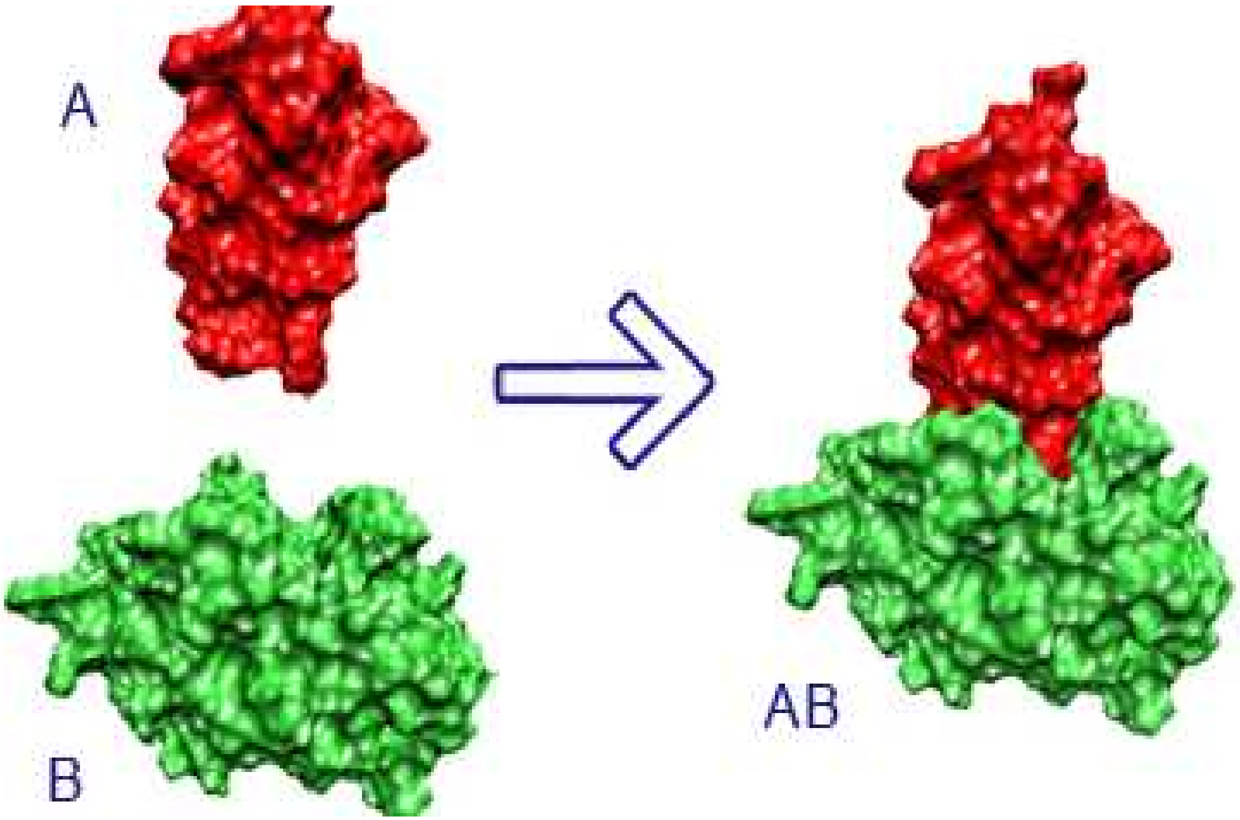


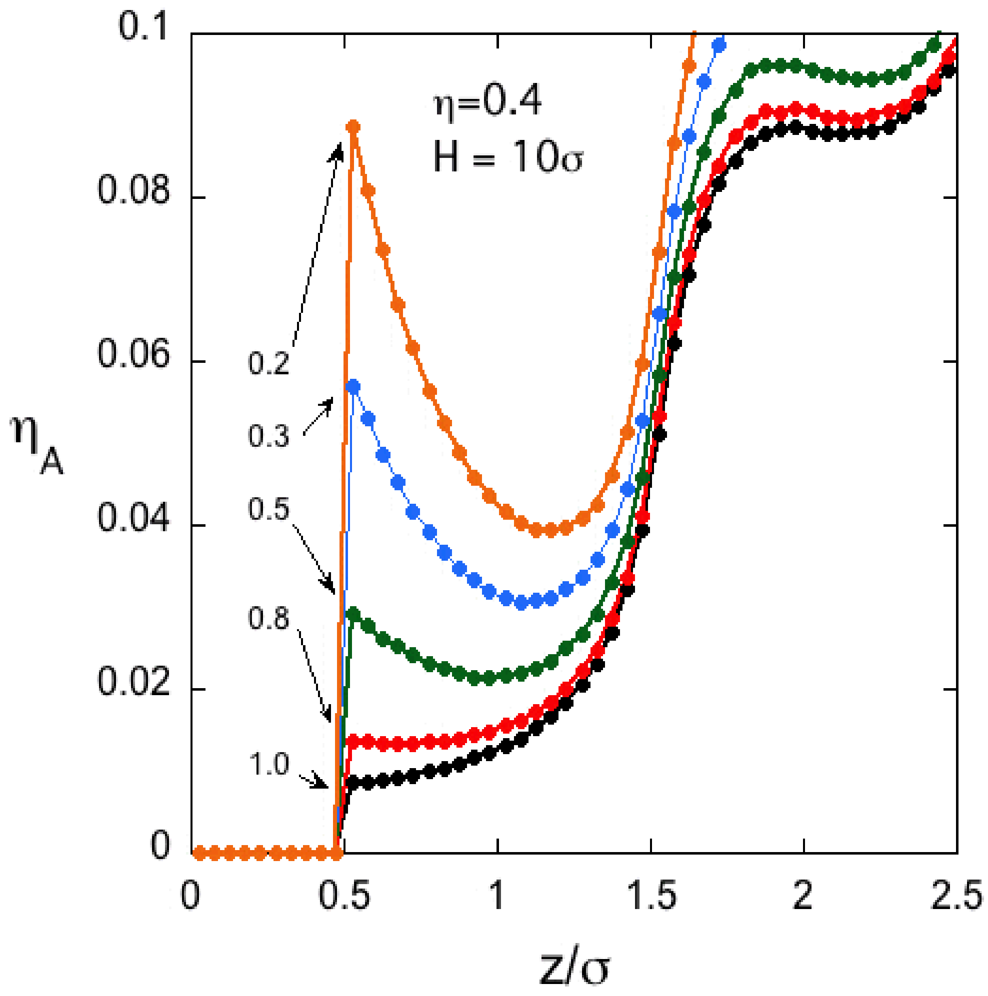
Fig. 5. Confocal microscope image of a pair of 2.1-μm-diameter spheres surrounded by 0.5-μm-diameter spheres. The pronounced layering of the smaller spheres gives rise to the depletion repulsion. The volume fractions of the larger and the smaller spheres are 0.24 and 0.28, respectively.



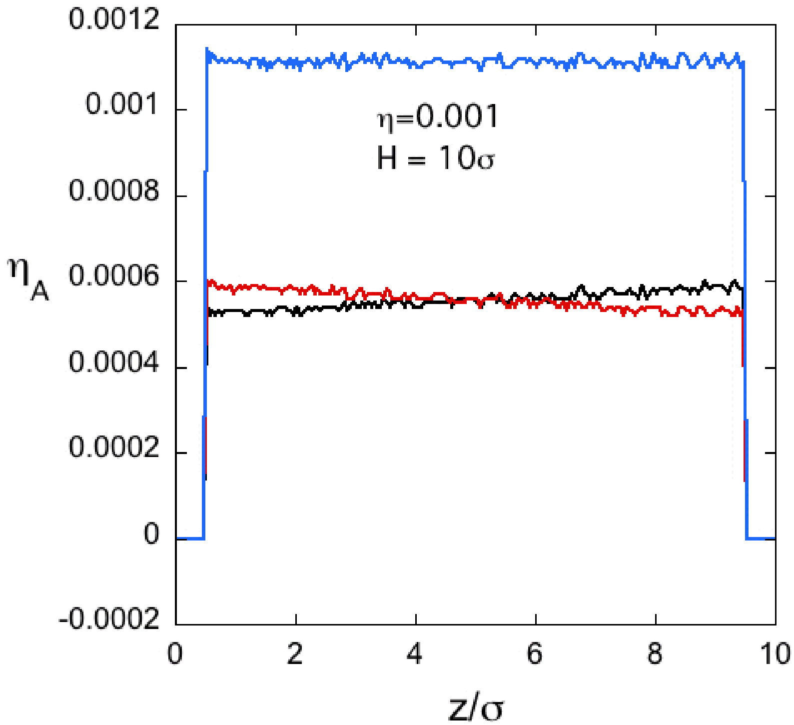
Docking Proteins



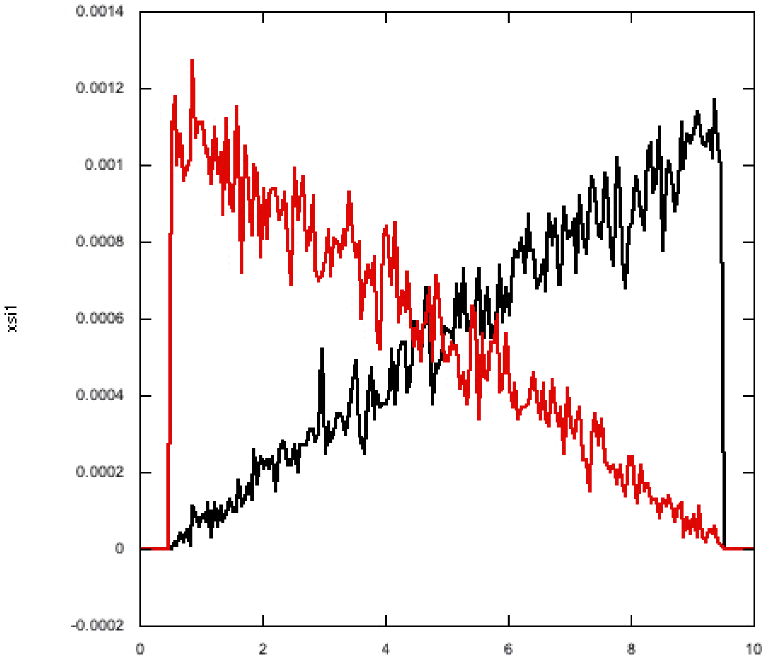
Contact densities



Very low density gas

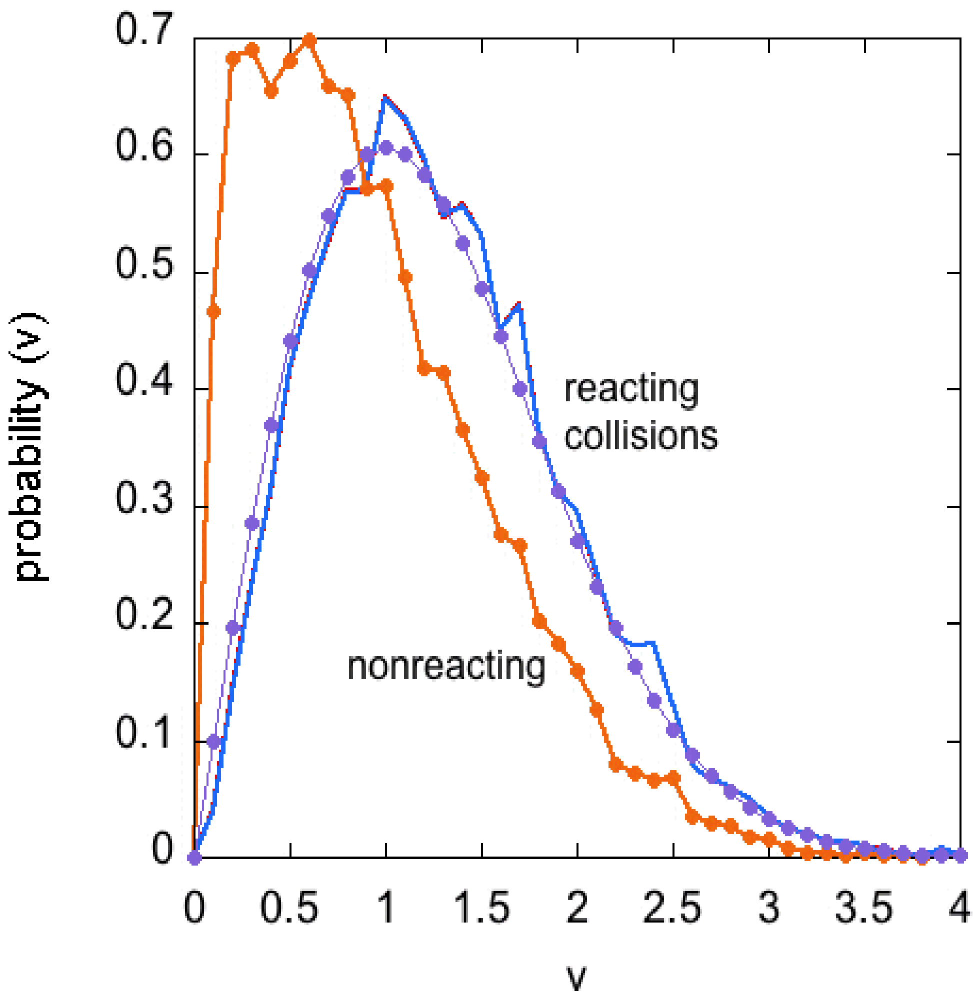


Molecular dynamics

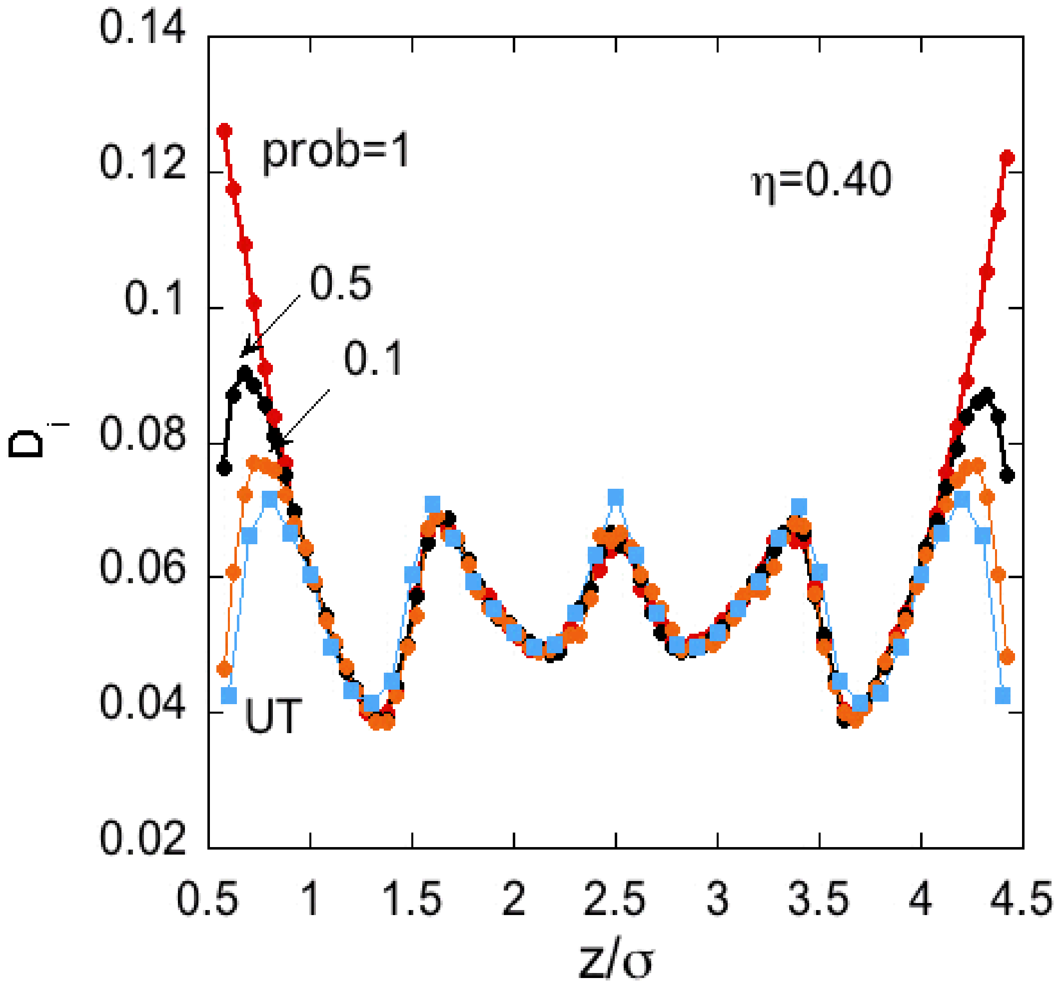


Brownian Dynamics

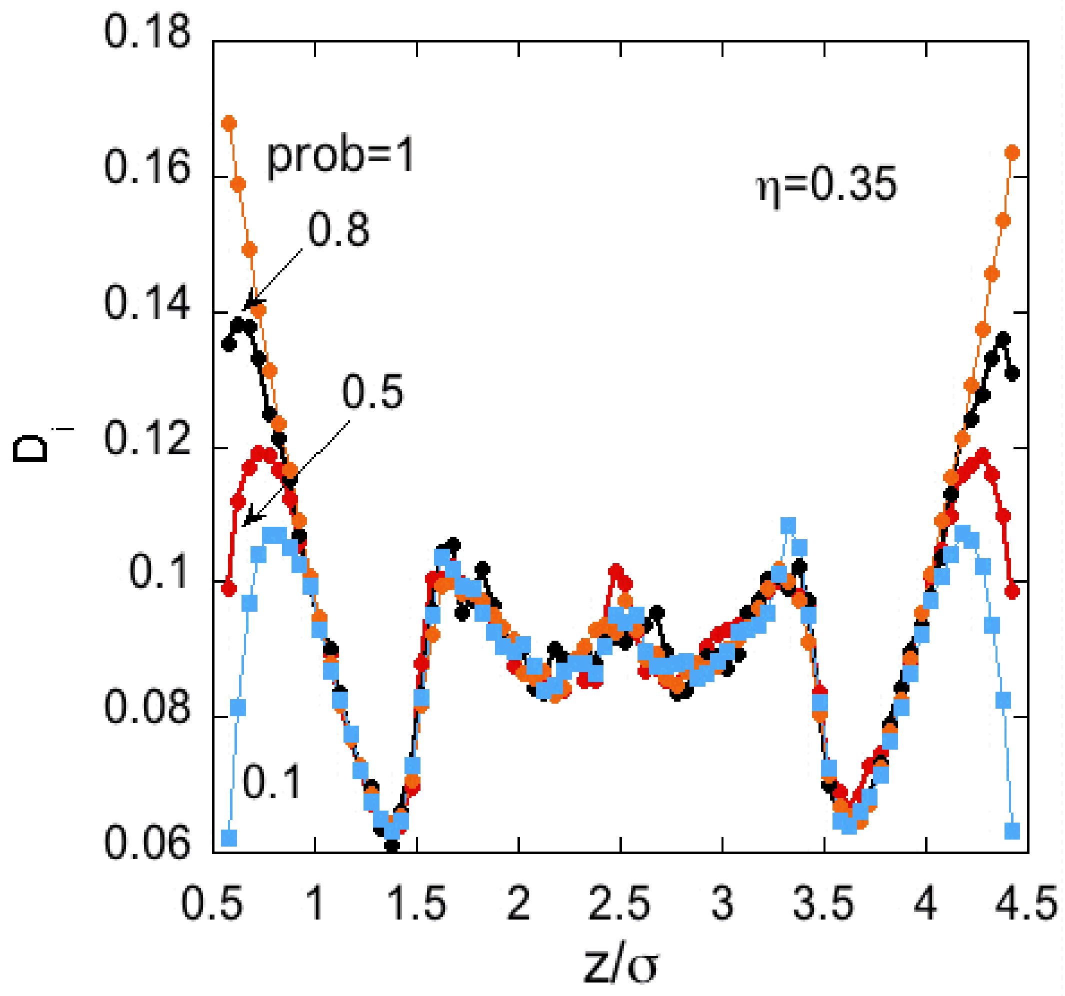
Velocity distributions



Narrow Slit Pores



Narrow Slit Pores



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PRL 100, 145901 (2008) PHYSICAL REVIEW LETTERS week ending 11 APRIL 2008

Layering and Position-Dependent Diffusive Dynamics of Confined Fluids

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(Received 4 January 2008; published 11 April 2008)

We study the diffusive dynamics of a hard-sphere fluid confined between parallel smooth hard walls. The position-dependent diffusion coefficient normal to the walls is larger in regions of high local packing density. High density regions also have the largest available volume, consistent with the fast local diffusivity. Indeed, local and global diffusivities as a function of the Widom insertion probability approximately collapse onto a master curve. Parallel and average normal diffusivities are strongly coupled at high densities and deviate from bulk fluid behavior.

Quote:

We use a recently proposed propagator-based formalism to estimate the position-dependent diffusion coefficients self-consistently from simulation trajectory data [6]. For diffusion, the propagator (or Green's function) $G(z, \Delta t|z', 0)$ for single-particle displacements along the coordinate z normal to the confining walls is assumed to satisfy the Smoluchowski diffusion equation,

$$\frac{\partial G}{\partial t} = \frac{\partial}{\partial z}\left\{D_{\perp}(z)e^{-\beta F(z)}\frac{\partial}{\partial z}[e^{\beta F(z)}G]\right\}, \quad (1)$$

with $\beta = 1/k_B T$, k_B Boltzmann's constant, and T the

Propagator profiles

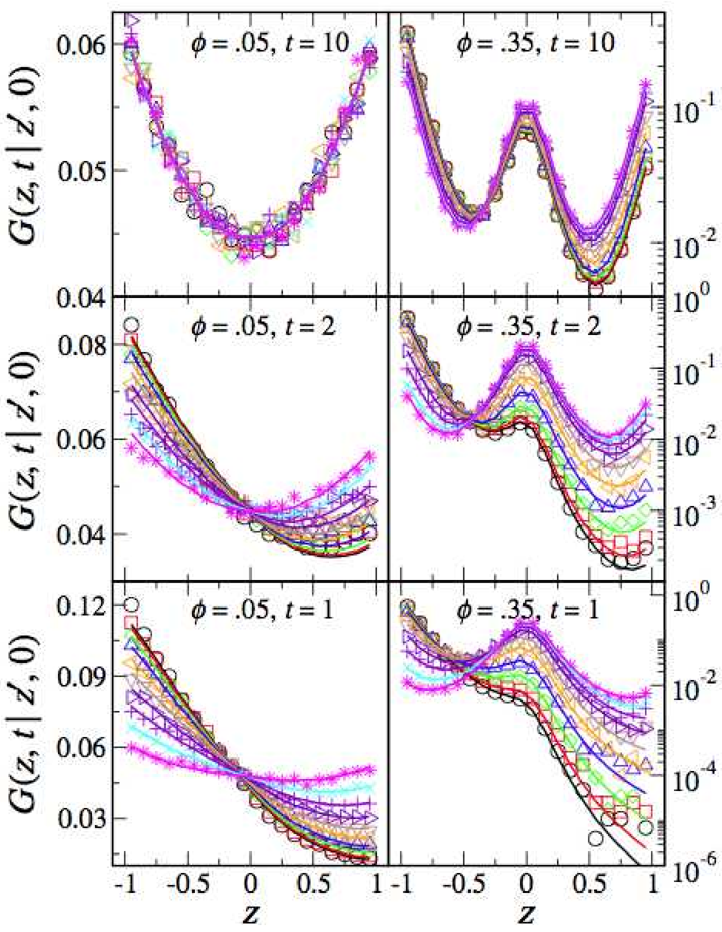
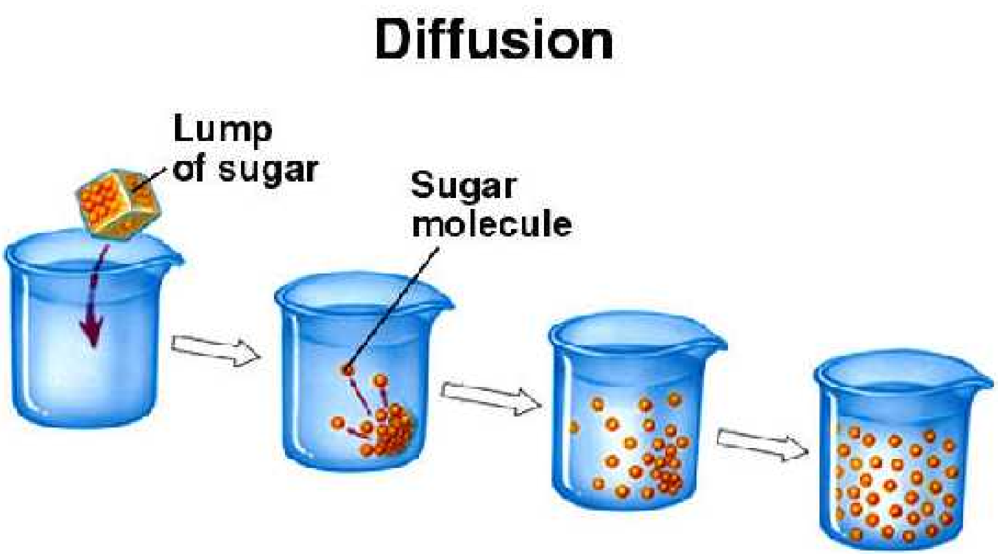


FIG. 1 (color online). The conditional probability $G(z, t|z', 0)$ of observing a particle at a position z at time t if it started at z' at $t = 0$. Results are shown for pore size $H = 3$, packing fractions $\phi = 0.05$ (left) and 0.35 (right), and times $t = 1$, 2, and 10 (bottom to top). The observation time $t = 1$ is used to obtain parameters of the diffusion model Eq. (1) (lines). Simulation results for $G(z, t|z', 0)$ for different z' are shown as symbols, where z' varies from -0.05 to -0.95 (symbol ∘ to *) in intervals of 0.1. (For reference, mean collision frequencies for the bulk hard-sphere fluid are approximately 852 and 7369 for $\phi = 0.05$ and 0.35, respectively.)



Oil &
water

Equilibrium DFT: Grand Canonical Ensemble

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$$\beta\Omega[\rho] = \sum_i^l \left[(1 - \sum_k^{lspe} \rho_i^k) \ln(1 - \sum_k^{lspe} \rho_i^k) + \sum_k^{lspe} \left(\rho_i^k \ln \rho_i^k + \rho_i^k \beta V_i^k - \rho_i^k \beta \mu_i^k + \frac{\beta}{2} \sum_m^{Ne} \sum_n^{lspe} \epsilon_{d(i,m)}^{kn} \rho_i^k \rho_{I(i,m)}^n \right) \right]$$

Take the partial of the grand potential with respect to the site densities gives a set of equations which will all be zero at equilibrium.

$$\frac{\partial(\beta\Omega[\rho])}{\partial \rho_i^k} = \ln \rho_i^k - \ln(1 - \sum_k^{lspe} \rho_i^k) + \beta V_i^k - \beta \mu_i^k + \beta \sum_m^{Ne} \sum_n^{lspe} \epsilon_{d(i,m)}^{kn} \rho_{I(i,m)}^n$$

The equations can be rearranged in the following form
Suitable for a picard iteration solution method.

$$\rho_i^k = \frac{(1 - \Sigma_{m \neq k}^{lspe} \rho_i^m) \exp(C_t)}{1 + \exp(C_t)}$$

$$C_t = \beta \mu_i^k - \beta V_i^k - \beta \sum_m^{Ne} \sum_n^{lspe} \epsilon_{d(i,m)}^{kn} \rho_{I(i,m)}^n$$

Equilibrium Density Functional Theory (DFT):

Grand Canonical Ensemble

$$\Omega[\rho] = \mathcal{F}[\rho] + \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r})(V_{\mathrm{ext}}(\mathbf{r}) - \mu),$$

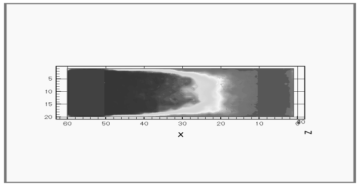
$$\beta\mathcal{F}_{\mathrm{id}}[\rho] = \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r}) \left(\ln(\Lambda^3 \rho(\mathbf{r})) - 1\right),$$

$$\beta\mathcal{F}_{ex}[\{\rho_i\}] = \int \mathrm{d}^3 r'\, \Phi(\{n_\alpha(\mathbf{r}')\})$$

Example: Non equilibrium DFT (on a lattice)

Use diffusive equations to determine site flux of material

$$\frac{d\rho_i^k}{dt} = -\nabla J_i^k \quad \text{where} \quad J_i^k = -\sum_n^{lspe} D_i^{kn} \rho_i^n \nabla \mu_i^n$$



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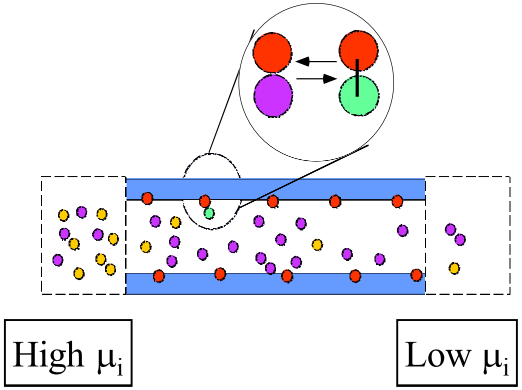
$$\frac{d\rho_i^k}{dt} = \sum_n^{lspe} D_i^{kn} \left(\rho_i^n \nabla^2 \mu_i^n + \nabla \rho_i^n \nabla \mu_i^n\right)$$

A forward time step solution method uses

$$\left(\rho_i^k\right)^{t+} = \left(\rho_i^k\right)^{t-} + \sum_n^{lspe} (\Delta t) D_i^{kn} \left(\rho_i^n \nabla^2 \mu_i^n + \nabla \rho_i^n \nabla \mu_i^n\right)$$



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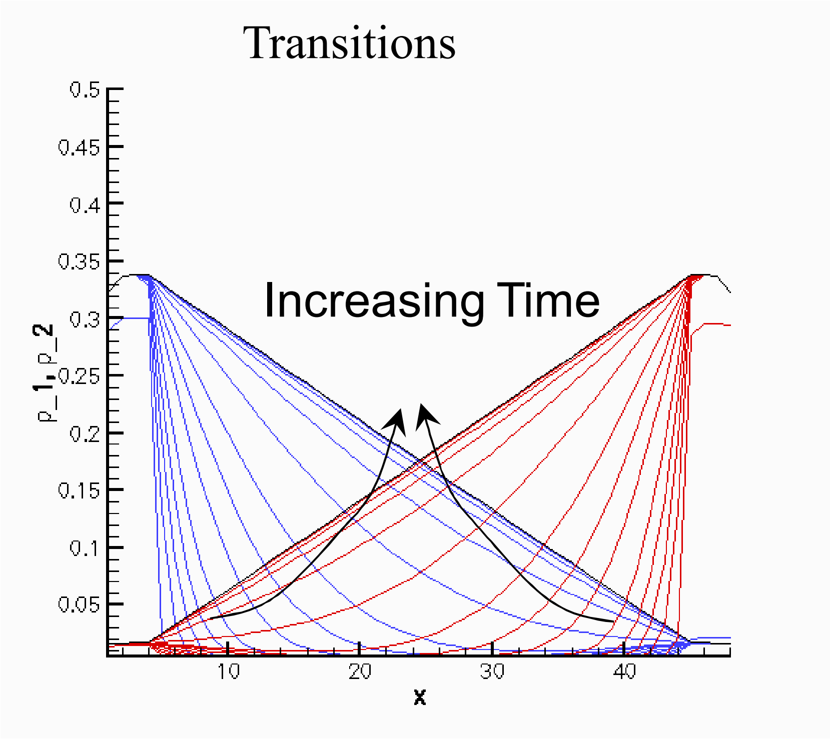
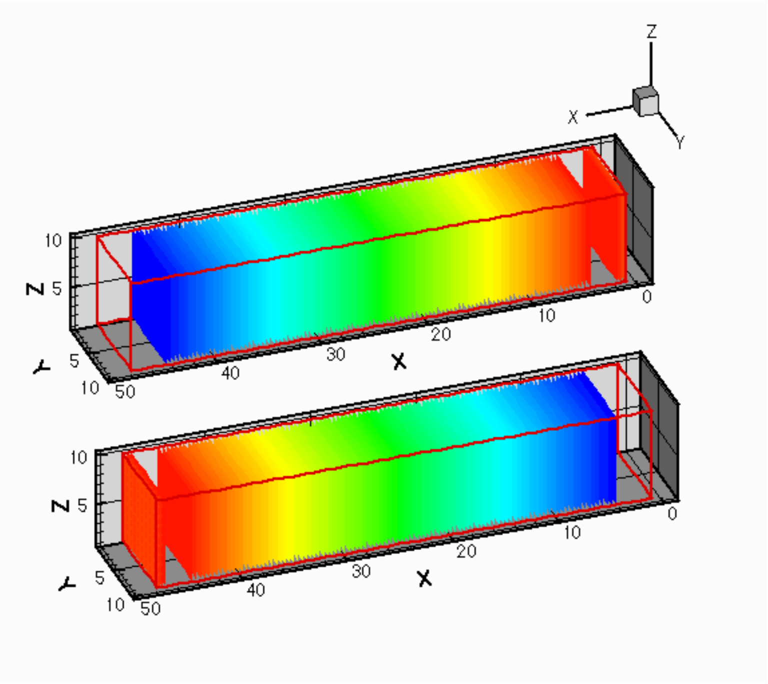




Colloids: Confocal Microscopy

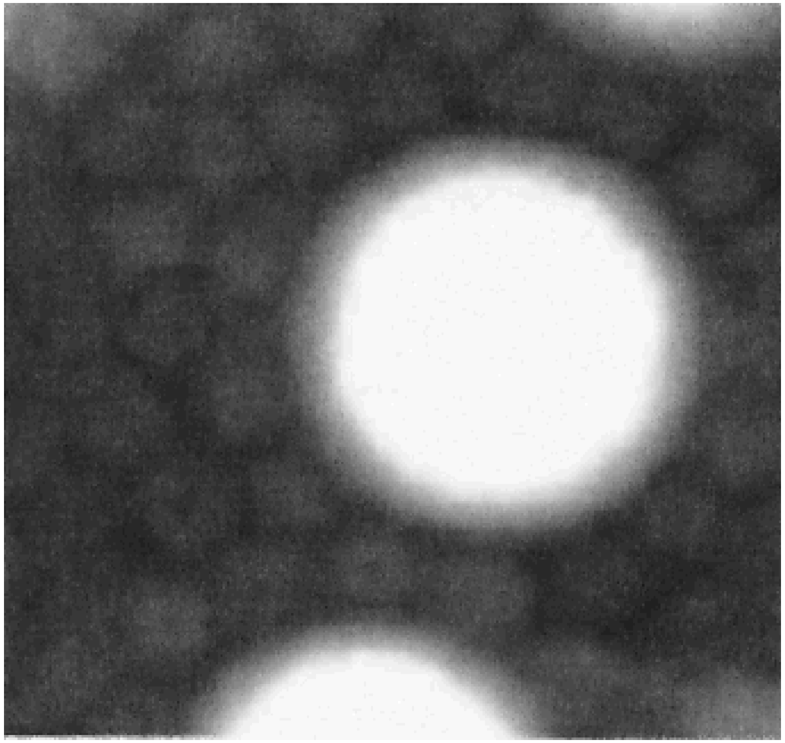
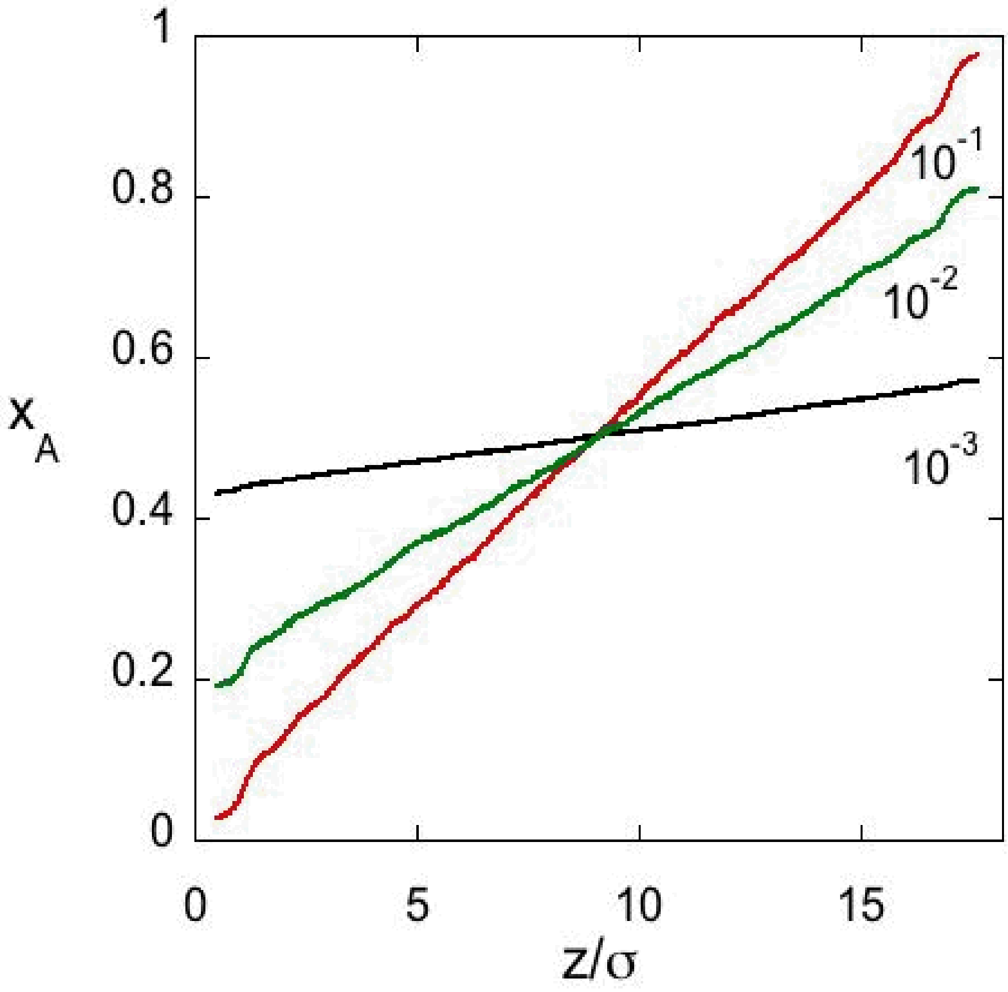
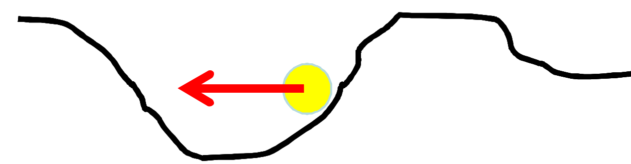


Fig. 5. Confocal microscope image of a pair of 2.1-μm-diameter spheres surrounded by 0.5-μm-diameter spheres. The pronounced layering of the smaller spheres gives rise to the depletion repulsion. The volume fractions of the larger and the smaller spheres are 0.24 and 0.28, respectively.

The effect of Reaction Probabilities

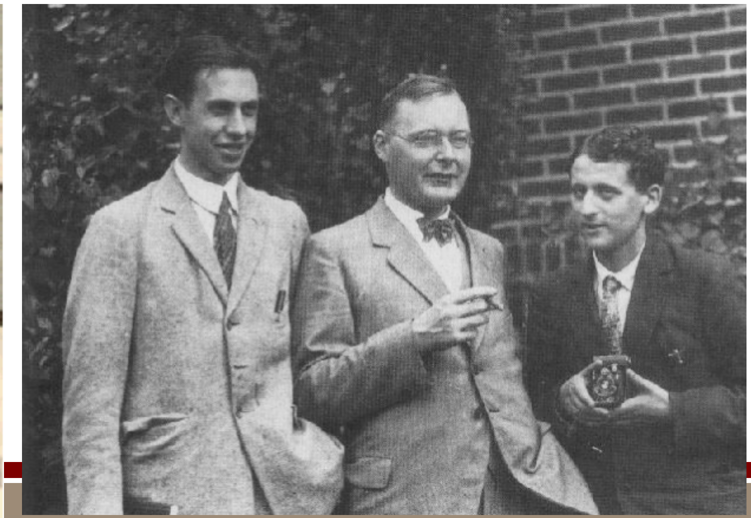


v. Smoluchowski (1906)
Kramers(1940)-Klein(1922)

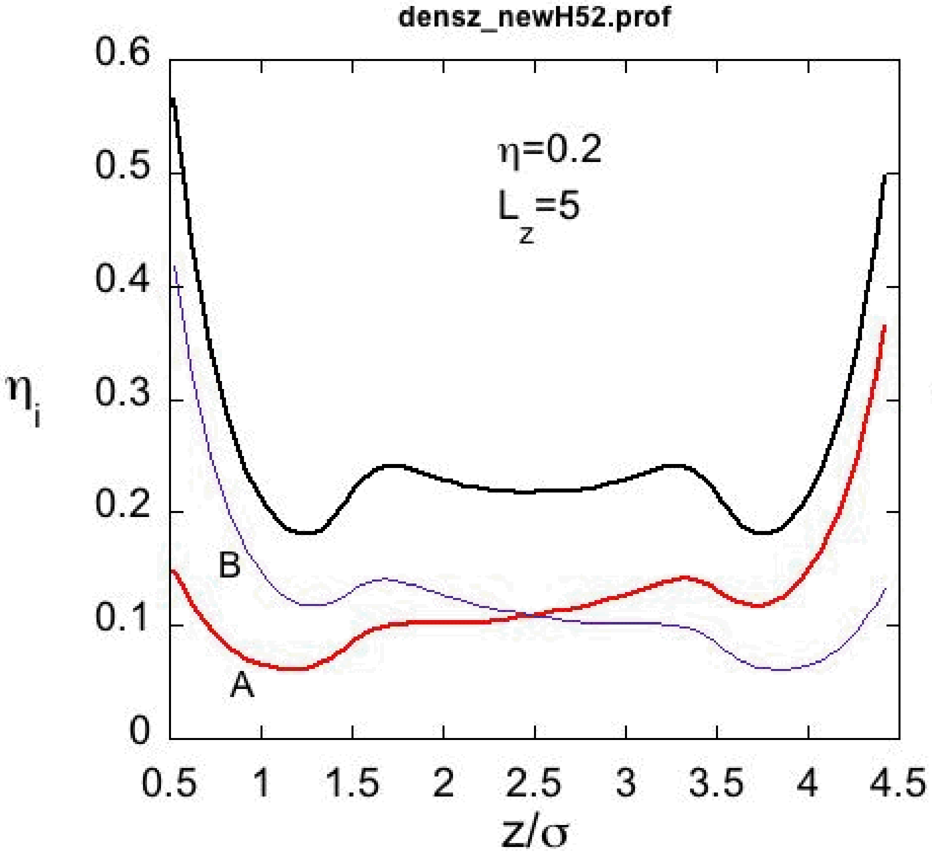


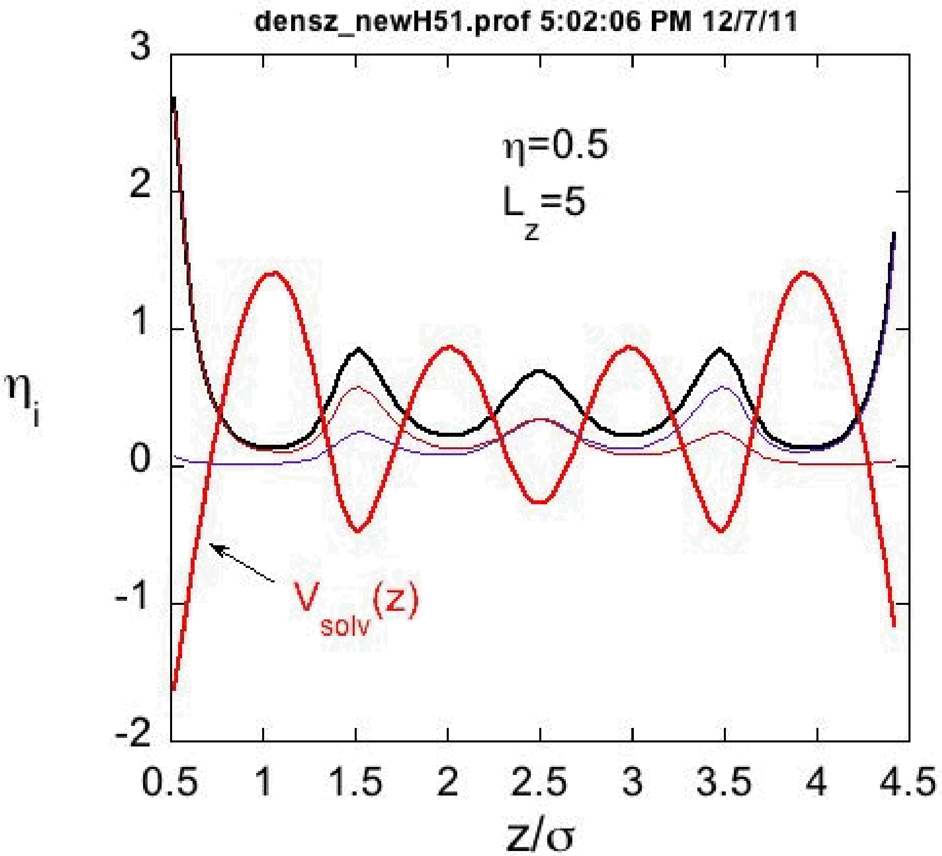
$$j_i = -D\frac{\partial \rho_i}{\partial z} - D\frac{K(z)\rho_i}{kT}; \qquad i = A, B$$

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

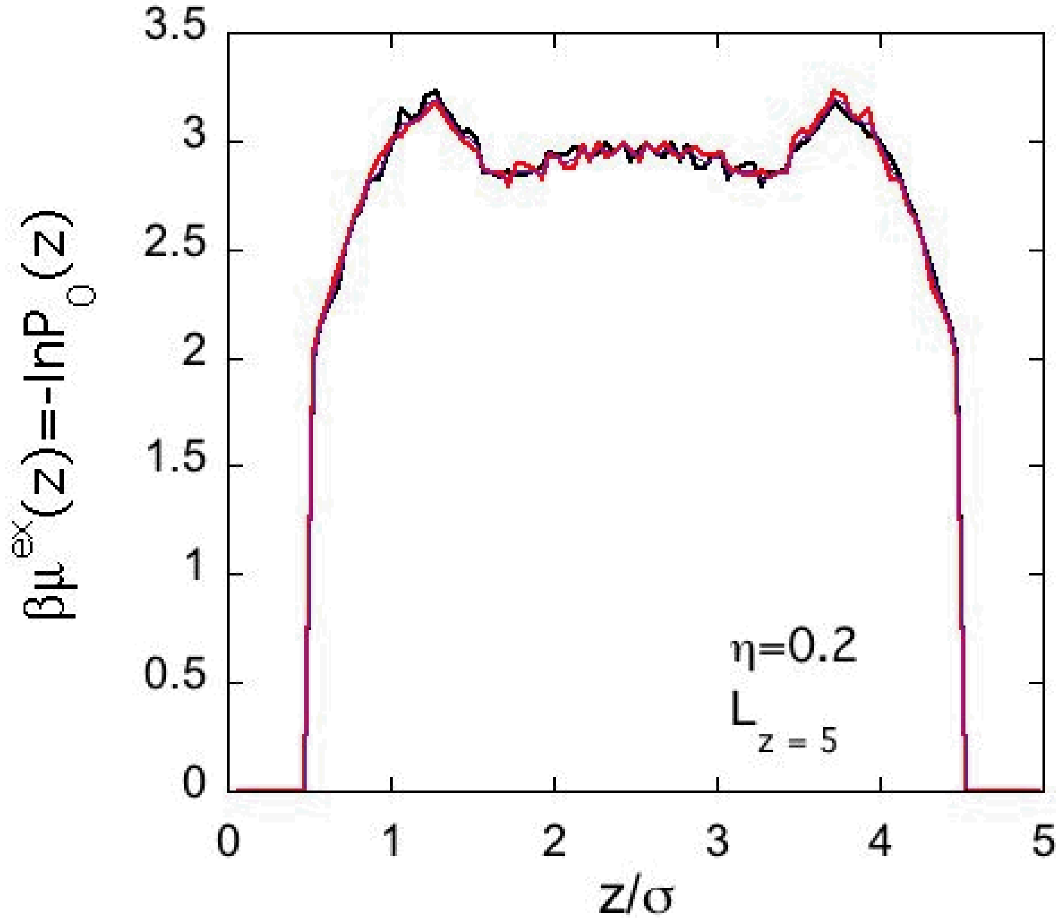


profiles


densz_newH52.prof
η=0.2
L
z
=5
B
A
η
i
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
z/σ


densz_newH51.prof 5:02:06 PM 12/7/11
η=0.5
L
z
=5
V
solv
(z)
η
i
3
2
1
0
-1
-2
0.5
1
1.5
2
2.5
3
3.5
4
4.5
z/σ

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

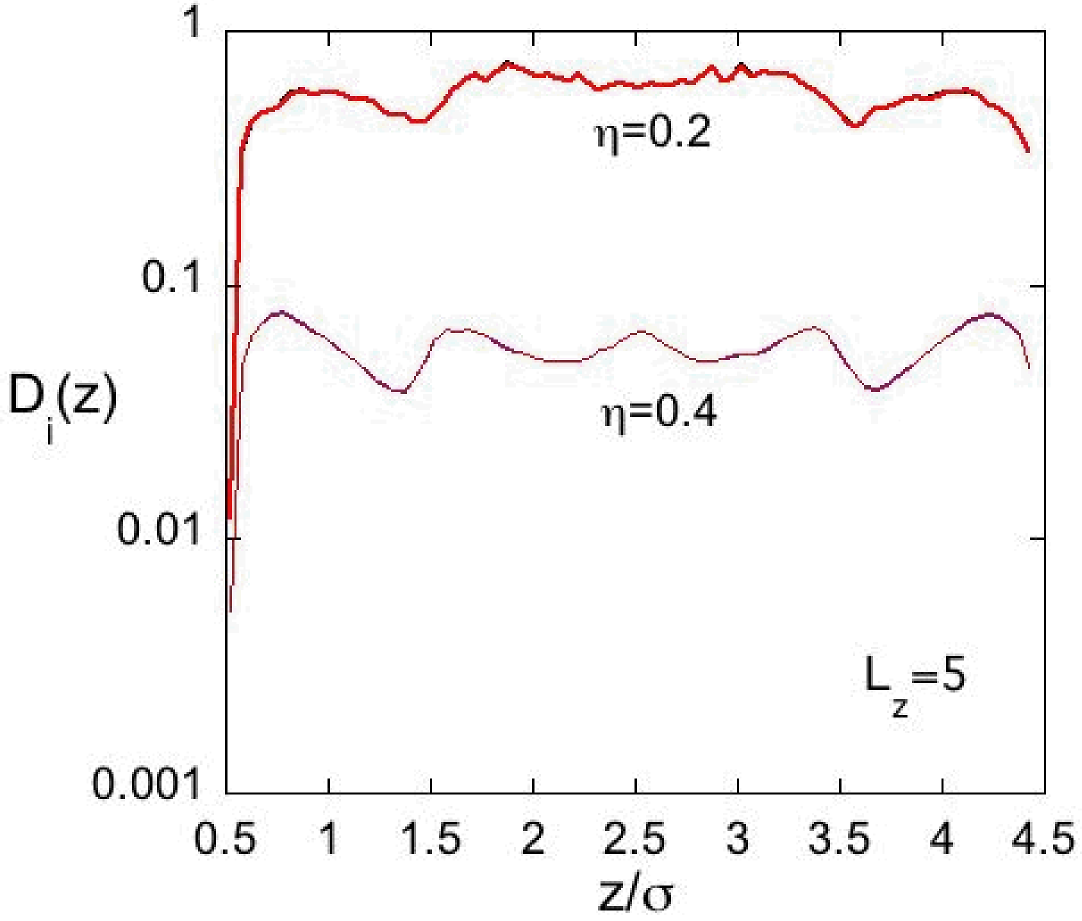


$$D(z) = -j_i \left[\rho_i \left(\frac{K(z)}{kT} + \frac{\partial \ln \rho_i}{\partial z} \right) \right]^{-1} ; i = A, B$$

Ideal gas:

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

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



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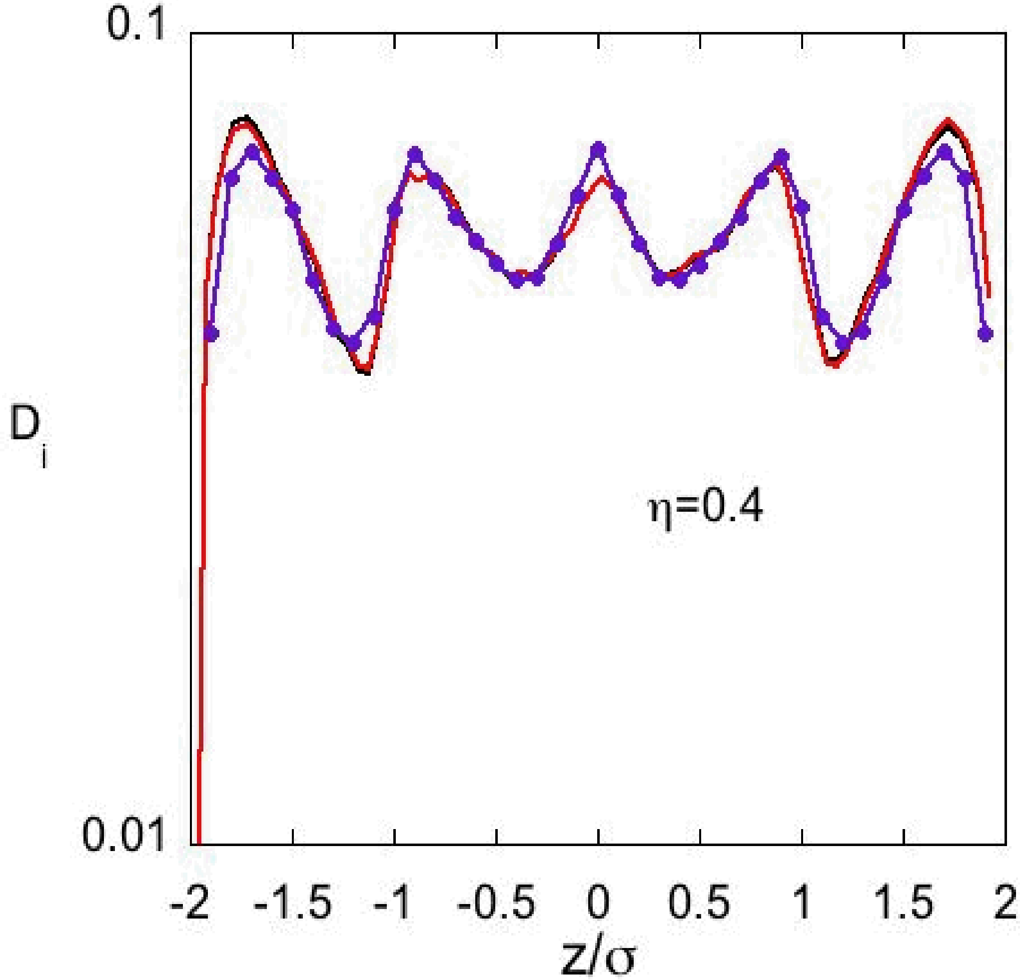

$\beta\mu^{ex}(z)$ in gravity