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Simulations of transport in porous media

SCIENTIFIC COMPUTING LABORATORY

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Simulations of transport in porous media

1. Diffusion as continuous time random walk

2. Types of diffusion

3. Creation of the model porous structures

4. Diffusion in model porous structures

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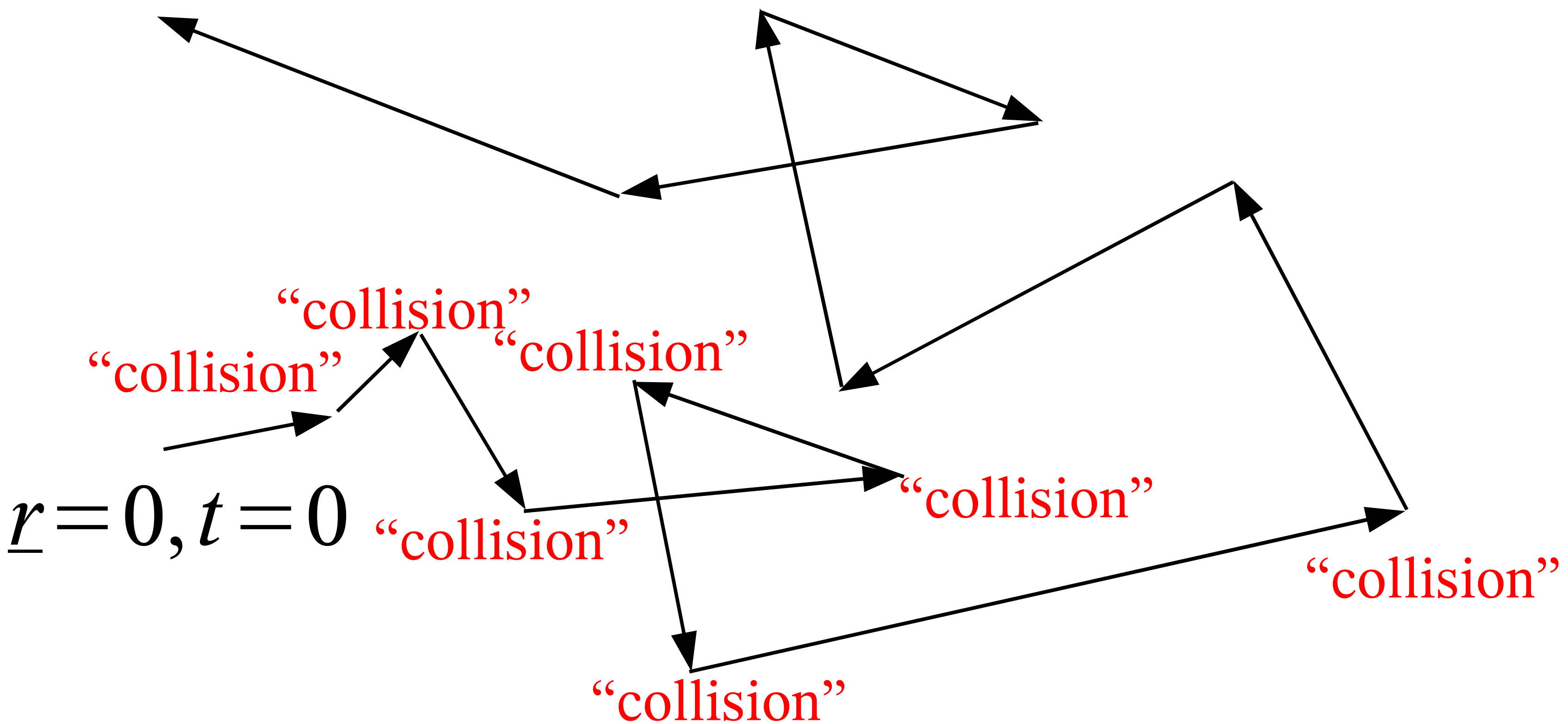
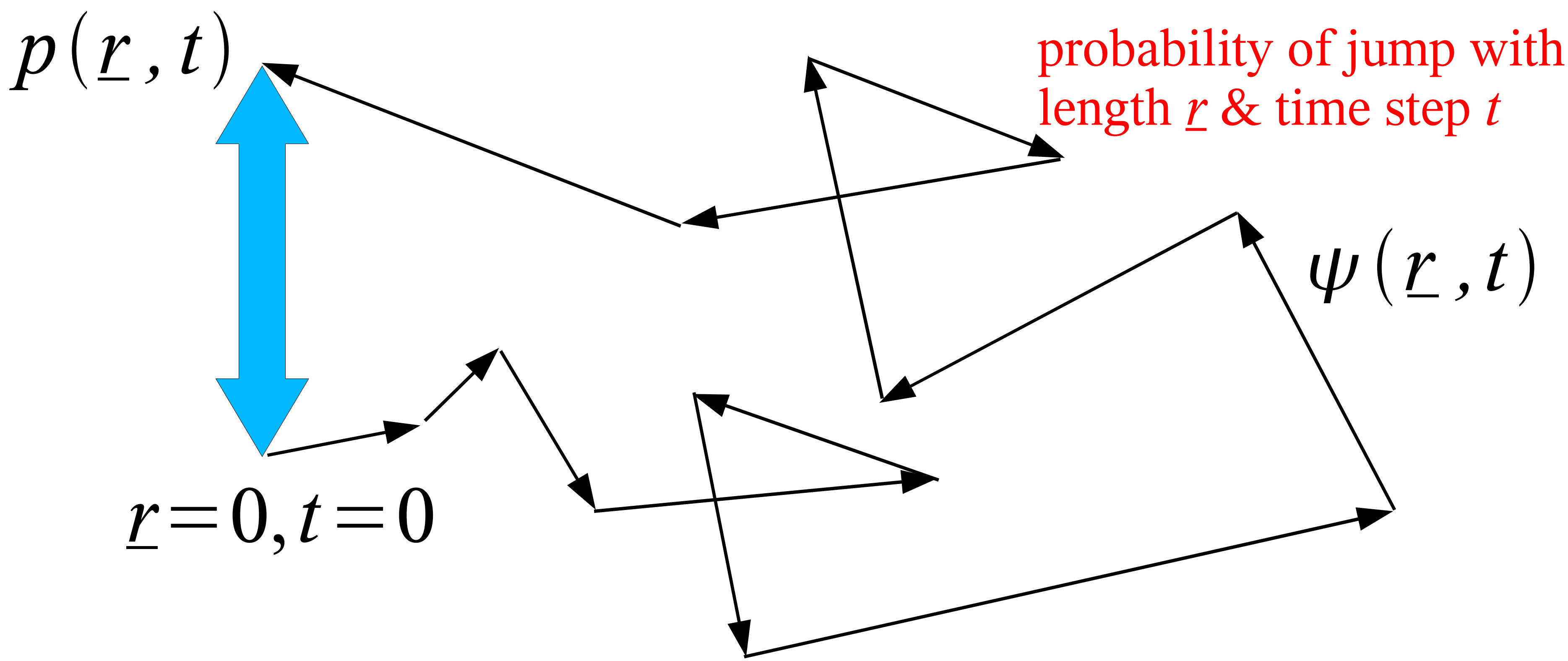
Diffusion as continuous time random walk



with: (1) another particle, **(2) porous structure walls,**
(3) crystal surface, (4) bubble surface, etc.

Diffusion as continuous time random walk

probability that particle is found at position $\underline{r}$ at time t



$$\langle r^2(t)\rangle = \int_{R_D} d\underline{r}\, r^2\, p(\underline{r},t)$$

mean square displacement

Diffusion as continuous time random walk

probability of previous position

$$\frac{\partial}{\partial t} p(\underline{r};t) = \int_{R_D} d\underline{r}' \int_0^{\infty} dt' \, K(\underline{r}-\underline{r}', t-t') \, p(\underline{r}', t')$$

kernel

What is form of kernel?

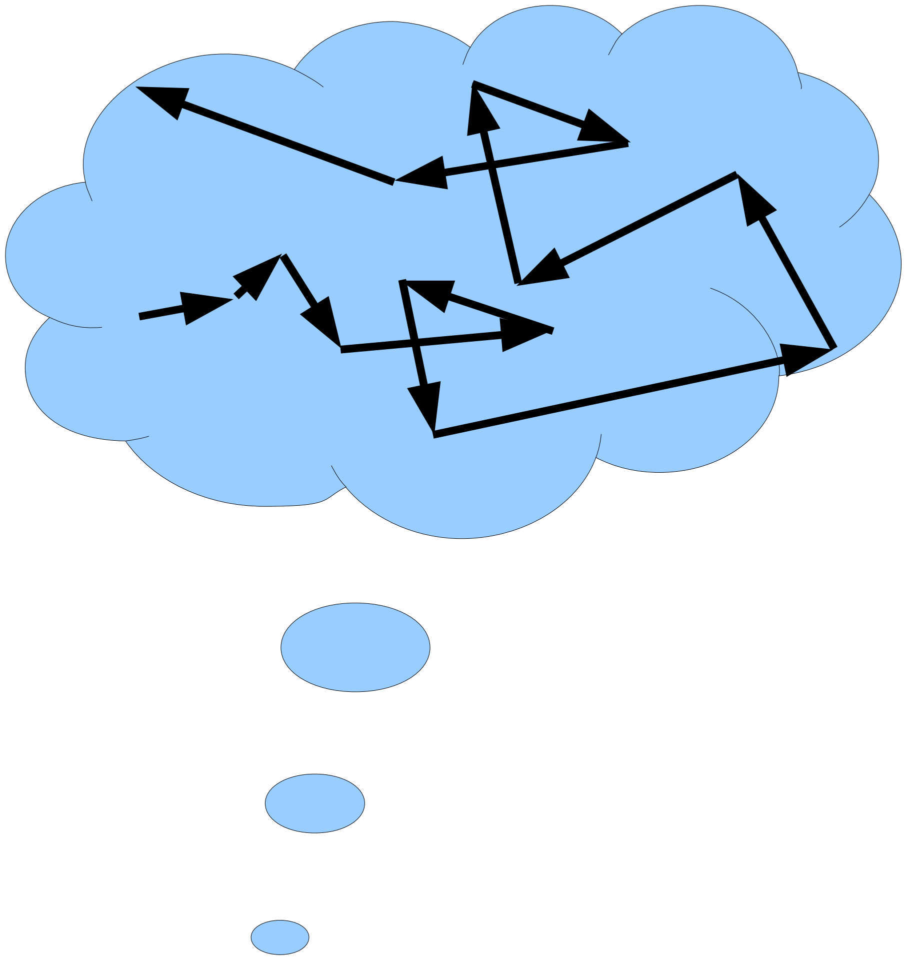
Diffusion as continuous time random walk

$$\frac{\partial}{\partial t} p(\underline{r};t) = \int_{R_D} d\underline{r}' \int_0^\infty dt' K(\underline{r}-\underline{r}', t-t') p(\underline{r}', t')$$

$$u p(\underline{k};u) - 1 = K(\underline{k};u) p(\underline{k};u)$$

Diffusion as continuous time random walk

$$p(\underline{r};t) = \left(\text{particle moves first time} \right) + \left(\text{particle already moved} \right)$$



Diffusion as continuous time random walk

probability of jump with length $\underline{r}$ and time step t

$$p(\underline{r};t)=\int_{R_D} dr' \int_t^{\infty} dt' \delta(\underline{r}-\underline{r}')\psi(r',t')$$

$$+\int_{R_D} dr' \int_0^{t} dt' p(t-t';\underline{r}-\underline{r}')\psi(r',t')$$

$$p(\underline{k};u)=\frac{1-\psi(u)}{u}+p(\underline{k};u)\psi(\underline{k},u)$$

Diffusion as continuous time random walk

$$u p(\underline{k};u) - 1 = K(\underline{k};u)\, p(\underline{k};u)$$

$$p(\underline{k};u) = \frac{1-\psi(u)}{u} + p(\underline{k};u)\,\psi(\underline{k},u)$$

$$K(\underline{k};u) = u\,\frac{\psi(\underline{k};u) - \psi(u)}{1-\psi(u)}$$

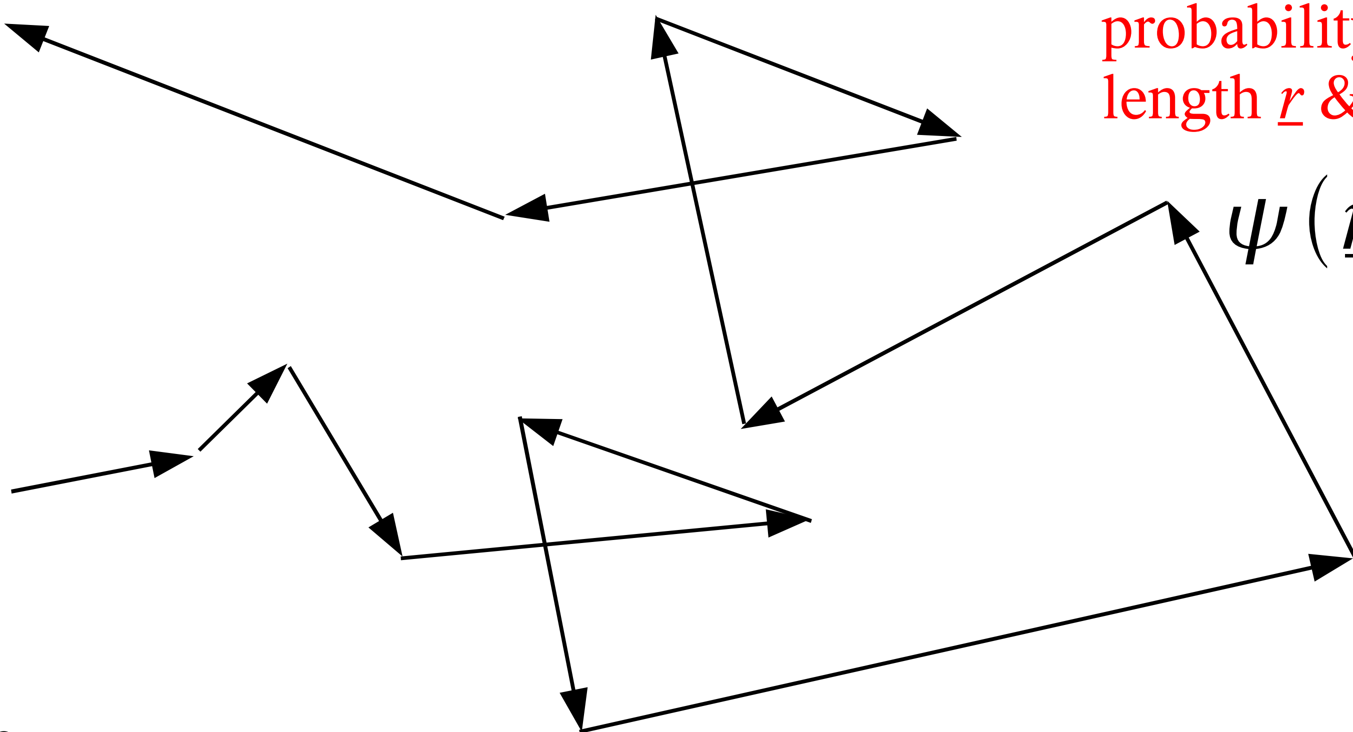
Diffusion as continuous time random walk

$$K(\underline{k};u) = u\frac{\psi(\underline{k};u) - \psi(u)}{1-\psi(u)}$$

assume decoupled
time and length

$$K(\underline{k};u) = (p(\underline{k}) - 1)\frac{u\psi(u)}{1-\psi(u)}$$

Diffusion as continuous time random walk



probability of jump with length $\underline{r}$ & time step t

$$\psi(\underline{r}, t)$$

$$\tau = \int_0^\infty dt\, t \int_{R_D} d\underline{r}\, \psi(\underline{r}, t)$$

waiting time

$$\sigma^2 = \int_0^\infty dt \int_{R_D} d\underline{r}\, r^2 \psi(\underline{r}, t)$$

space step

Diffusion as continuous time random walk

$$\tau = \int_0^\infty dt\, t \int_{R_D} d\underline{r}\, \psi(\underline{r}, t)$$

$$\sigma^2 = \int_0^\infty dt \int_{R_D} d\underline{r}\, r^2 \psi(\underline{r}, t)$$

$$t \to \infty, \quad k \to 0, \quad u \to 0$$

$$\tau < \infty, \sigma^2 < \infty \qquad \phi(u) = 1 - \tau u,\ p(k) = 1 - \frac{\sigma^2}{2} k^2$$

$$\tau = \infty, \sigma^2 < \infty \qquad \phi(u) = 1 - c_1 u^\alpha (0 < \alpha < 1),$$

$$p(k) = 1 - \frac{\sigma^2}{2} k^2$$

Diffusion as continuous time random walk

$$\tau < \infty , \sigma^2 < \infty \qquad \phi(u) = 1 - \tau u ,\; p(k) = 1 - \frac{\sigma^2}{2} k^2$$

$$u p(\underline{k};u) - 1 = \frac{\sigma^2}{2\tau} k^2 p(\underline{k};u)$$

normal diffusion

$$\frac{\partial}{\partial t} p(\underline{r};t) = \frac{\sigma^2}{2\tau} \frac{\partial^2}{\partial r^2} p(\underline{r},t')$$

$$\boxed{\tau = \infty} , \sigma^2 < \infty \qquad \phi(u) = 1 - c_1 u^\alpha (0 < \alpha < 1) ,$$

anomalous diffusion

$$p(k) = 1 - \frac{\sigma^2}{2} k^2$$

$$\frac{\partial}{\partial t} p(\underline{r};t) = \frac{\sigma^2}{2\tau} \boxed{\frac{\partial^\alpha}{\partial t^\alpha}} \frac{\partial^2}{\partial r^2} p(\underline{r},t')$$

Types of diffusion

$\tau < \infty , \sigma^2 < \infty$ **normal diffusion**

$$\langle r^2(t) \rangle = \int_{R_D} d\underline{r}\, r^2\, p(\underline{r}, t) = 6\mathrm{Dt}$$

$\boxed{\tau = \infty}, \sigma^2 < \infty$ **sub-diffusion**

$$\langle r^2(t) \rangle = \int_{R_D} d\underline{r}\, r^2\, p(\underline{r}, t) \sim t^{\alpha}, \quad 0 < \alpha < 1$$

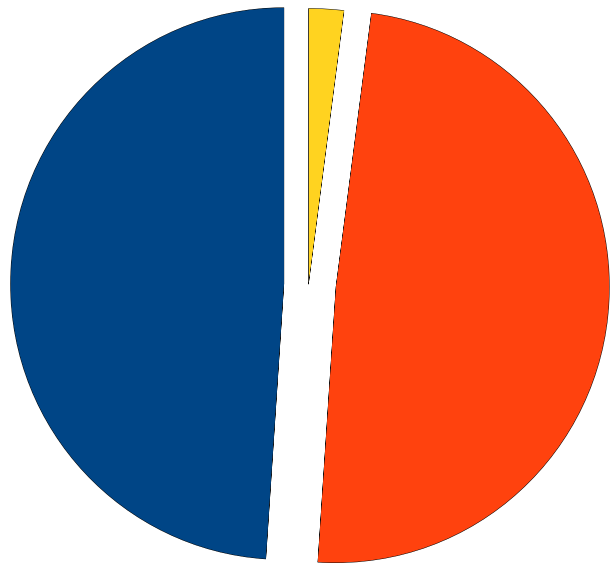
time and length have to be coupled **super-diffusion**

$$\langle r^2(t) \rangle = \int_{R_D} d\underline{r}\, r^2\, p(\underline{r}, t) \sim t^{\alpha}, \quad \alpha > 1$$

How frequent are different types of the diffusion?

sub-diffusion
(limiting case)

$\boxed{\tau = \infty}, \sigma^2 < \infty$

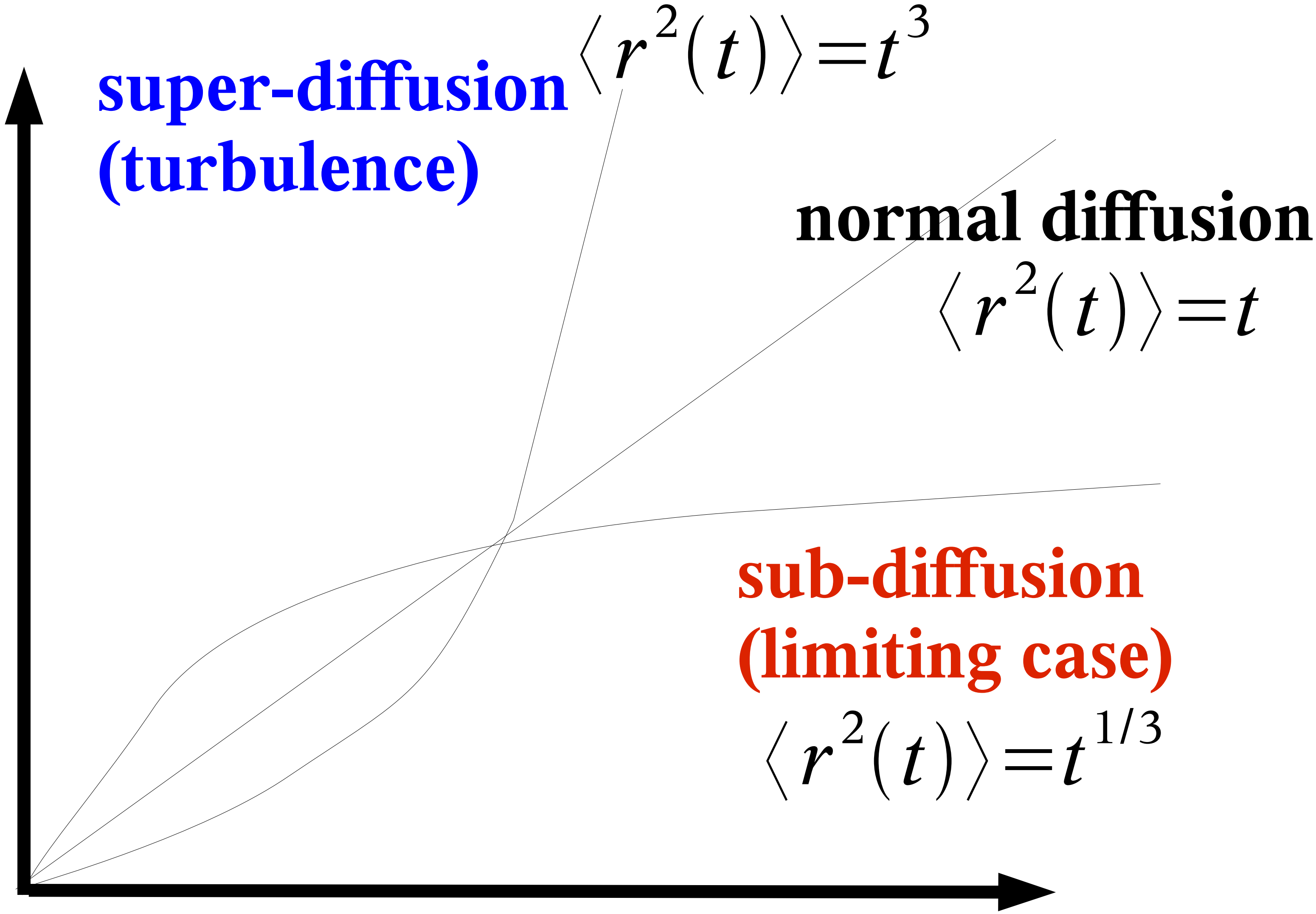


normal diffusion

$\tau < \infty, \sigma^2 < \infty$

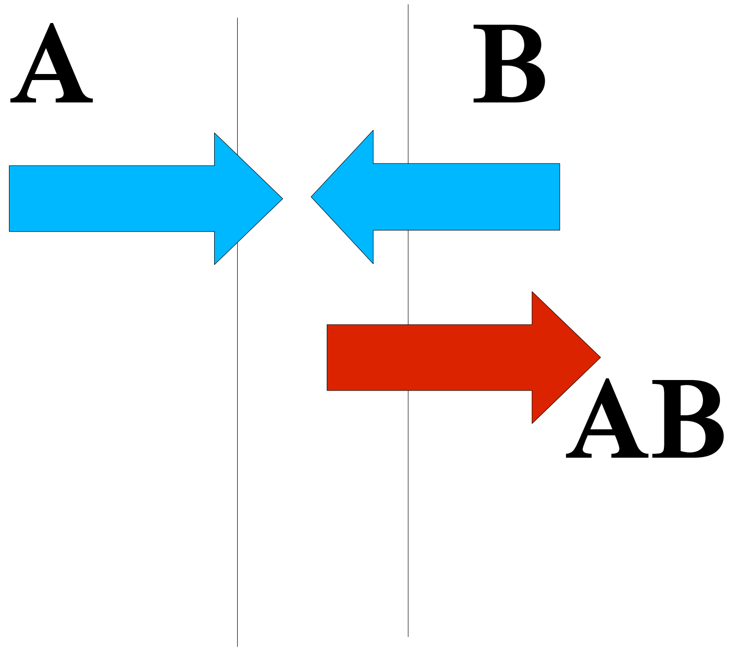
super-diffusion
(turbulence)

$\langle r^2(t) \rangle = t^3$



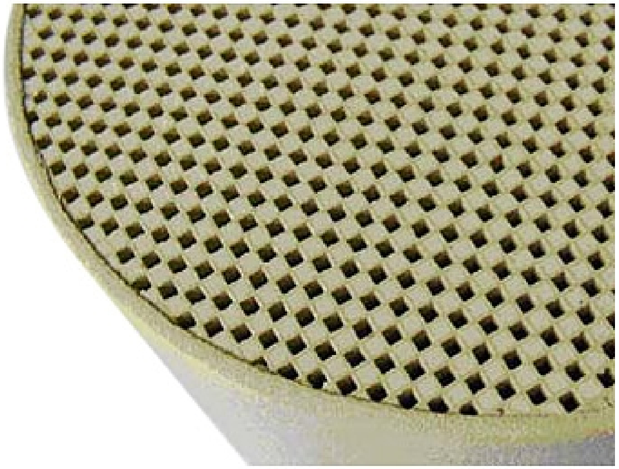
super-diffusion
(turbulence)
$\langle r^2(t) \rangle = t^3$
normal diffusion
$\langle r^2(t) \rangle = t$
sub-diffusion
(limiting case)
$\langle r^2(t) \rangle = t^{1/3}$

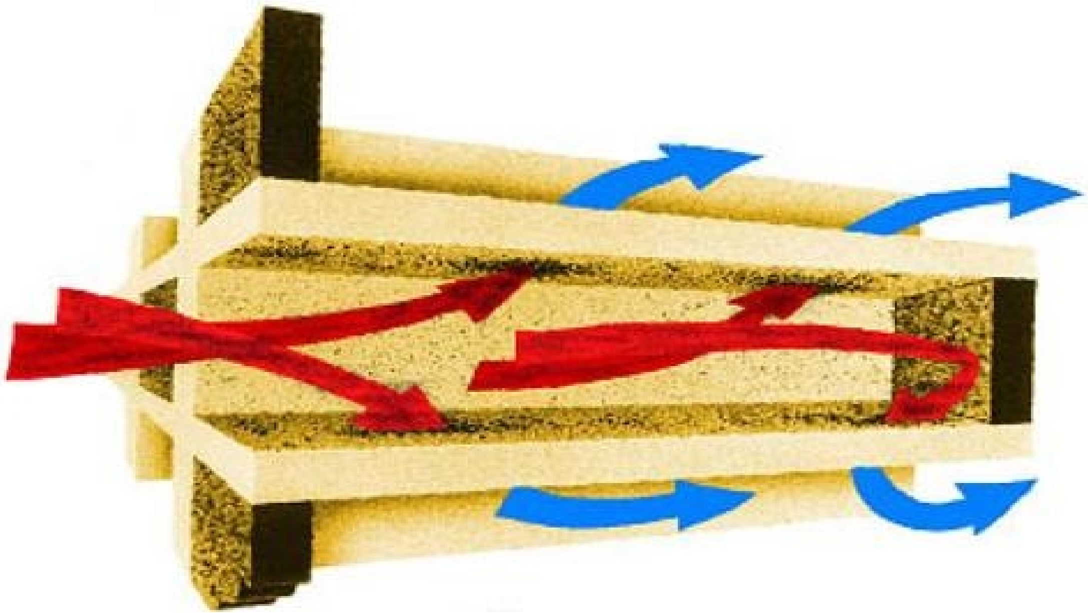
Some applications:

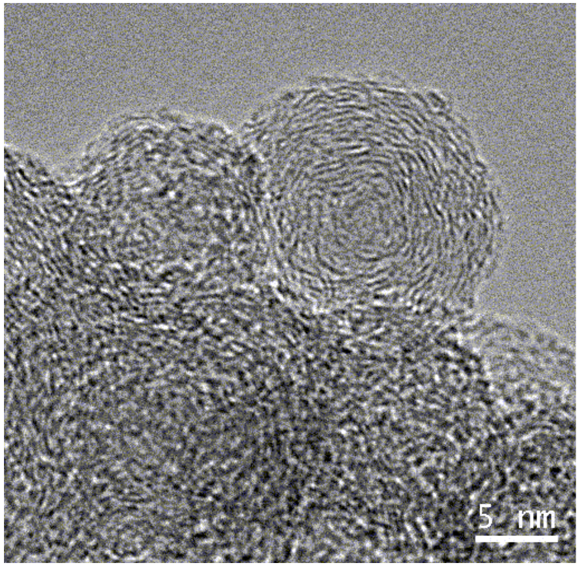


selective membranes

Some applications:







Creation of the model porous structures

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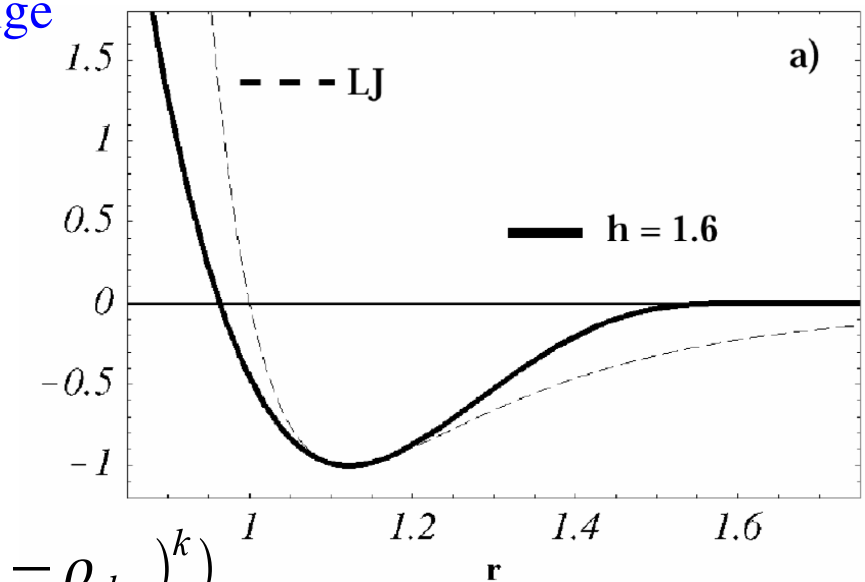
Total energy in the system is expressed as sum of two contributions:

$$E_{tot}=\sum_i\left(\sum_j \Phi(r_{ij})+F(\rho_i)\right)$$

$$\Phi(r)=\phi_0 r_0^{-6}\left(3(r-r_{cut})^4-4(r_{cut}-r_{min})(r_{cut}-r)^3\right),\ r\leqslant r_{cut}$$

$$\Phi(r)=0,\ r>r_{cut}$$

binary contribution - short range attractive potential (SHRAT)



$$r_{min}=2^{1/6},\ r_{cut}=1.6,\ w_0=\frac{105}{16\pi r_{cut}^3},\ \rho_{des}=1$$

$$F(\rho_i)=\phi_0\sum_{k=2,4,\ldots} r_0^{3k}F_k\left((\rho_i-\rho_{des})^k-(w(0)-\rho_{des})^k\right)$$

many-body contribution embedding functional

$$\rho_i=\sum_j w(r_{ij})$$

$$w(r)=w_0\left(1+3\frac{r}{r_{cut}}\right)\left(1-\frac{r}{r_{cut}}\right)^3$$

Lucy's weight function

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http://www.fisica.uniud.it/~ercolessi/md/

Molecular dynamics method: Basics

$$\dot{\mathbf{r}}_i=\mathbf{v}_i$$
$$\dot{\mathbf{v}}_i=-\nabla_{\mathbf{i}}V(\mathbf{r}_1,..,\mathbf{r}_N)$$

molecules, atoms

$$V(\mathbf{r}_1,\mathbf{r}_{2,...},\mathbf{r}_N)=\sum_i\sum_{j>i}\phi(|\mathbf{r}_i-\mathbf{r}_j|)$$

$$\Phi(r)=\phi_0 r_0^{-6}(3(r-r_{cut})^4-4(r_{cut}-r_{min})(r_{cut}-r)^3),\ r\leqslant r_{cut}$$
$$\Phi(r)=0,\ r>r_{cut}$$

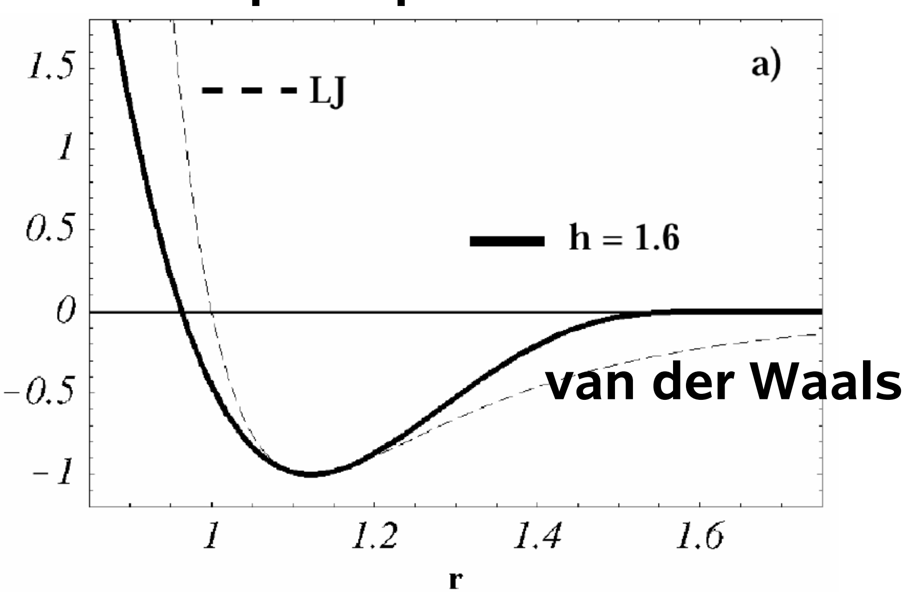
metals, semiconductors

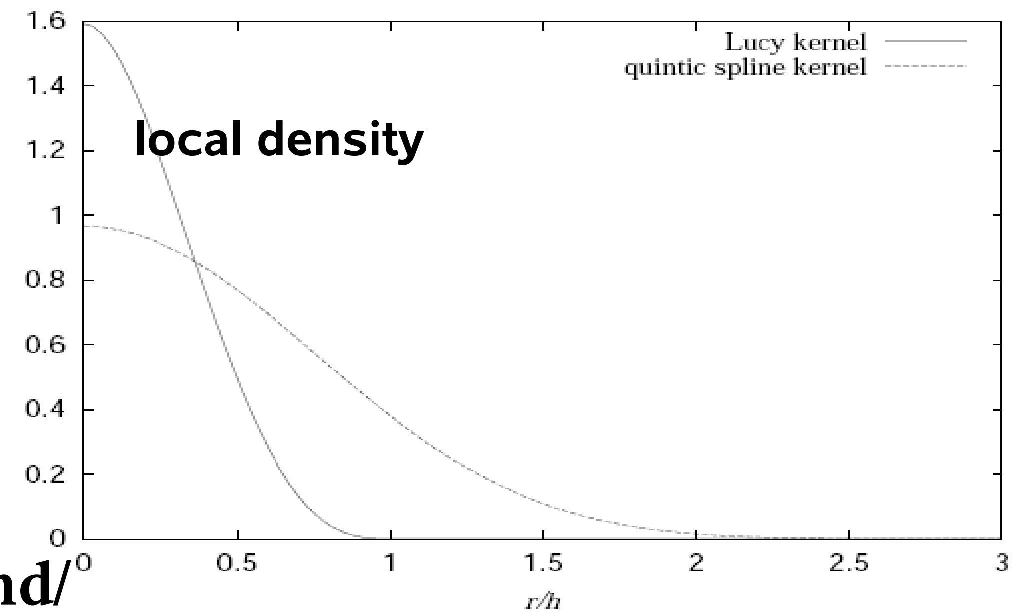
$$V(\mathbf{r}_1,\mathbf{r}_{2,...},\mathbf{r}_N)=\sum_i\left(\sum_{j>i}\phi(|\mathbf{r}_i-\mathbf{r}_j|)+\Theta(\rho_i)\right)$$

$$\Theta(\rho_i)=\phi_0\sum_{k=2,4,\ldots}r_0^3 k F_k((\rho_i-\rho_{des})^k-(w(0)-\rho_{des})^k)$$

$$\rho_i=\sum_j w(r_{ij})$$
$$w(r)=w_0(1+3\frac{r}{r_{cut}})(1-\frac{r}{r_{cut}})^3$$

Paulie principle





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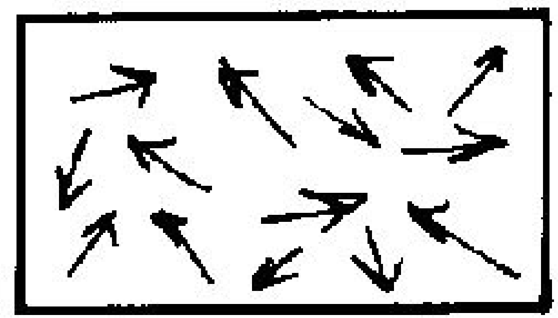
Molecular dynamics method: What can we get out of it?



$$V(t)=\sum_i \sum_{j>i} \phi(|\mathbf{r}_i(t)-\mathbf{r}_j(t)|)$$ **potential energy**

$$K(t)=\frac{1}{2}\sum_i m_i [v_i(t)]^2$$ **kinetic energy**

$$E(t)=K(t)+V(t)$$ **total energy**

$$K(t)=\frac{3}{2} N k_B T(t)$$ **temperature from kinetic energy**

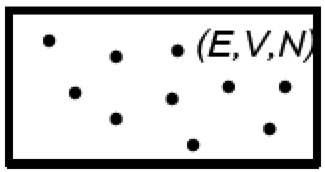
$$PV = N k_B T - \frac{1}{3}\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \rangle$$ **pressure**

http://www.fisica.uniud.it/~ercolessi/md/

Molecular dynamics method: How to keep temperature constant?

- *Microcanonical ensemble*

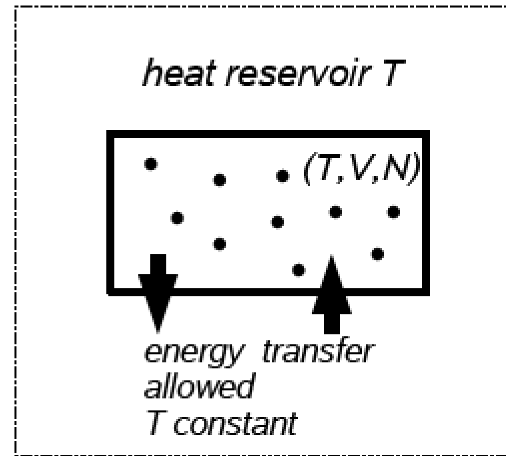
isolated system



energy transfer not allowed
E constant

$$f(\Gamma) = \delta(H(\Gamma) - E)$$

- *Canonical ensemble*



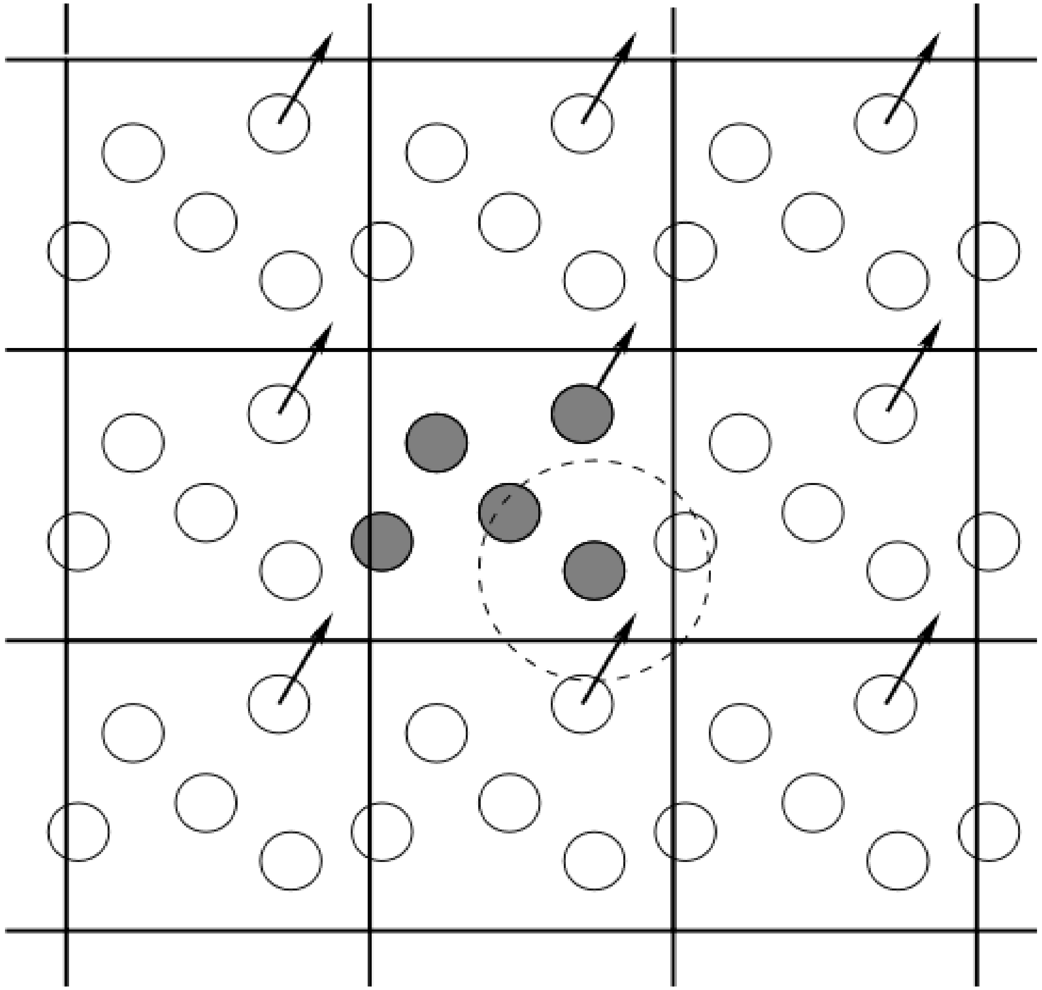
$$f(\Gamma) = exp(-H(\Gamma)/k_B T)$$

$$\hat{\mathbf{v}}_i\left(t+\frac{\Delta t}{2}\right) = S\,\mathbf{v}_i\left(t+\frac{\Delta t}{2}\right)$$

$$S = \left[\frac{\frac{3}{2} N k_B T}{\sum_i \frac{m_i}{2}\left[\mathbf{v}_i\left(t+\frac{\Delta t}{2}\right)\right]^2}\right]^{1/2}$$

http://www.fisica.uniud.it/~ercolessi/md/

Molecular dynamics method: How to simulate bulk material?



periodic boundary conditions

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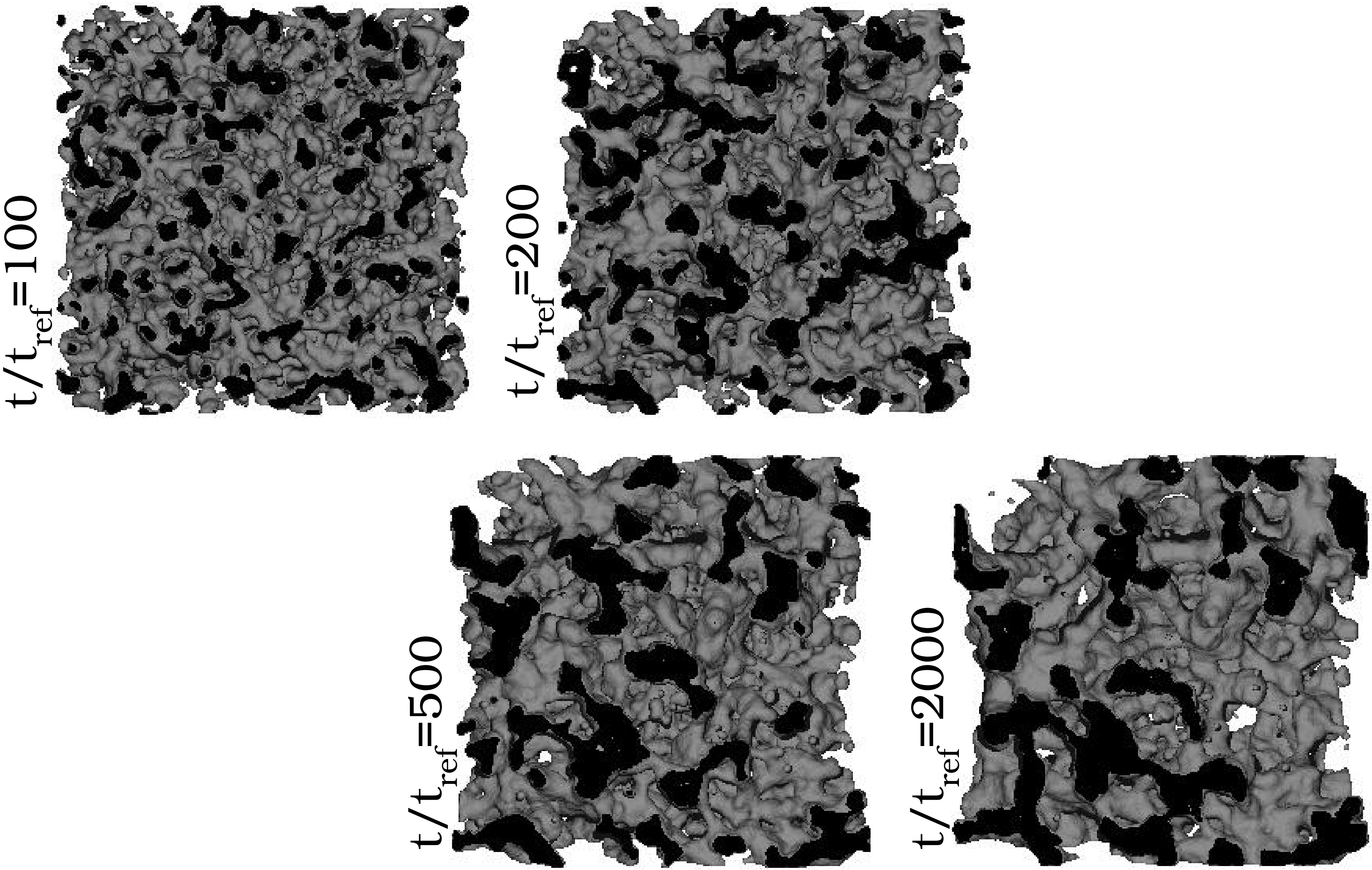

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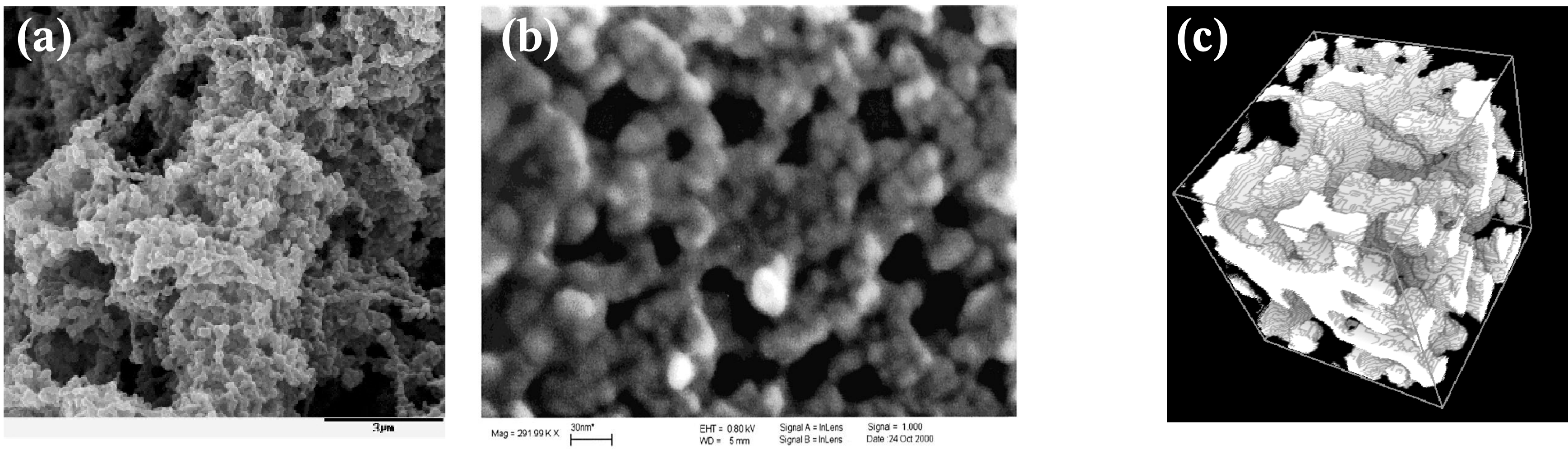

(a) U.Mähr, H. Purnama, E. Kempin, R. Schomäcker, and K.-H. Reichert, J. Membr. Sci., **171** (2000), 285.
(b) M. Meyer, A. Fischer, and H. Hoffman, J. Phys. Chem. B, **106** (2002) 1528.
(c) http://ciks.cbt.nist.gov/~garbocz/paper75/paper75.html

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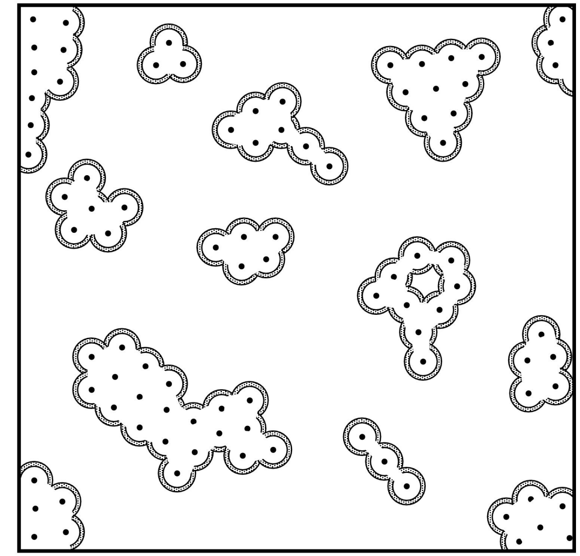
Monte Carlo integration:

volume - points from a random sample are counted, if they are within certain radius around the particles (r): $V/V_0=N_{within}/N_{tot}$.

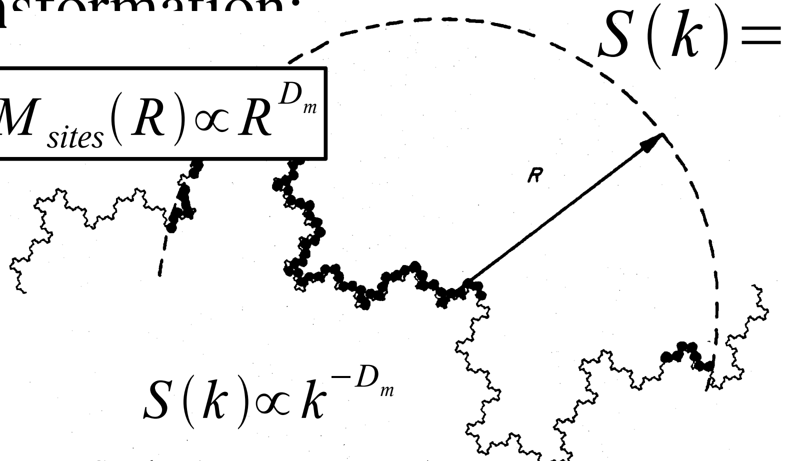
surface is calculated as numerical differential of volume over radius: $\partial V(r)/\partial r$.



Structre factor and fractal dimension:

structure factor S(k) is related to the *pair distribution function*, *g(r)*, by the Fourier transformation:

$$S(k)=1+4\pi n\int_0^\infty (g(r)-1)r^2\frac{\sin(kr)}{kr}dr$$



$$M_{sites}(R)\propto R^{D_m}$$

$$S(k)\propto k^{-D_m}$$

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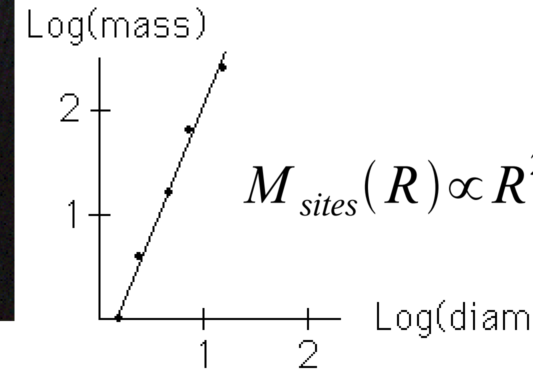
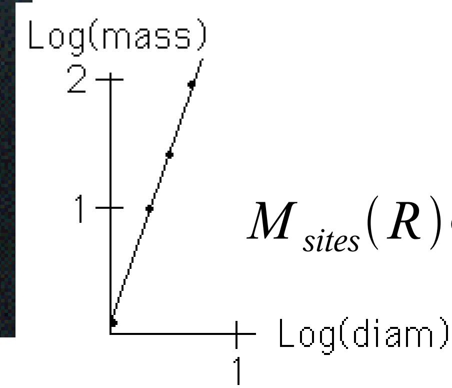


$$M_{sites}(R) \propto R^{2.5}$$



$$M_{sites}(R) \propto R^{3}$$

http://classes.yale.edu/fractals/FracAndDim/BoxDim/PowerLaw/PowerLaw.html

Mass and surface fractals:

$$M_{sites}(R) \propto R^{D_m}$$

$$M_{\substack{sites\,on\,the\\surface}}(R) \propto R^{D_s}$$

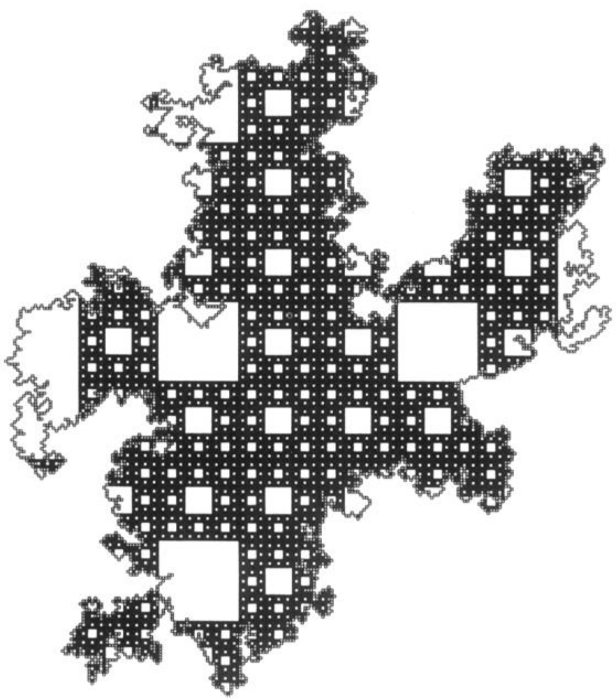
for small r!

$$g(r) \propto r^{D_m - 3}$$

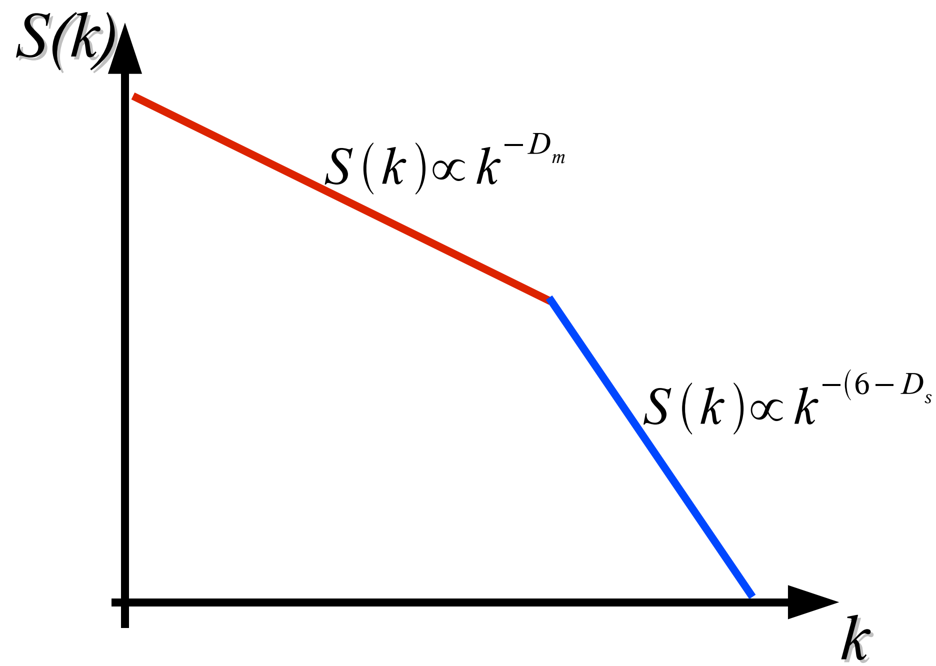
$$g(r) \propto 1 - r^{3 - D_s}$$

$$S(k) \propto k^{-D_m}$$

$$S(k) \propto k^{-(6 - D_s)}$$



in reality structures are fractal only on a certain range of scales:



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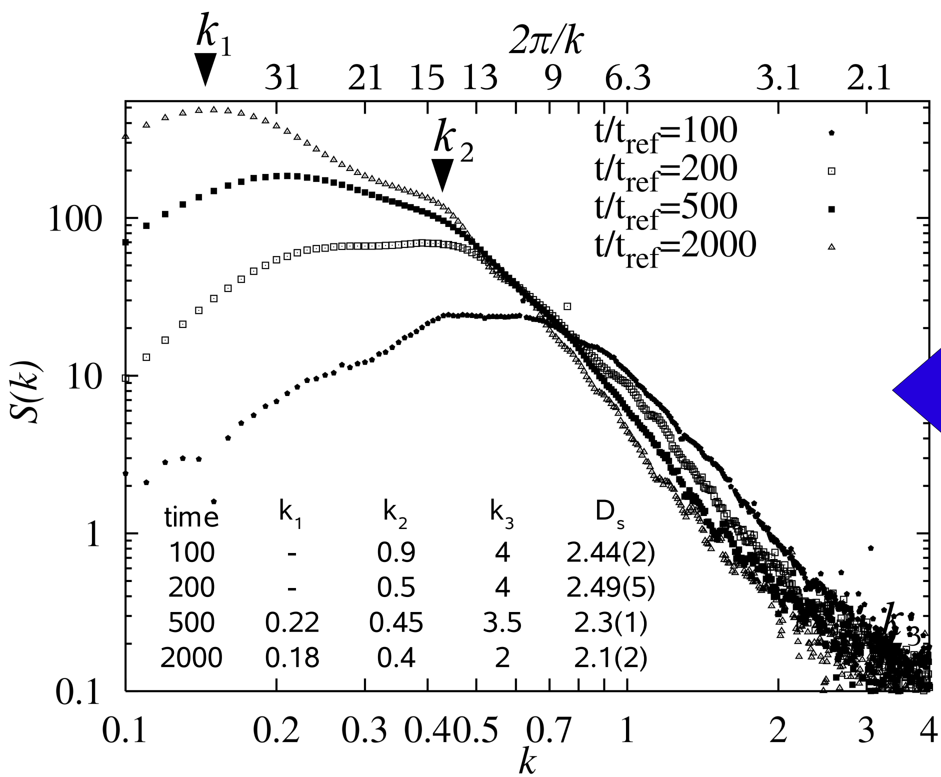
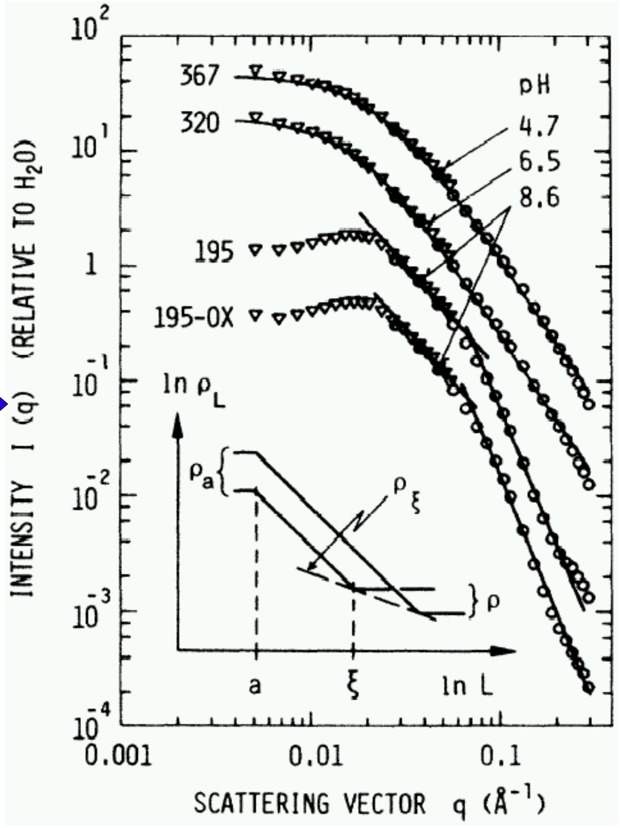
GEAM (F_2=1, F_k=0 k>2), n=0.25, T=0.01





D_S=2.4

R. Vacher et al., Phys. Rev. B, **37** (1988), 6500.

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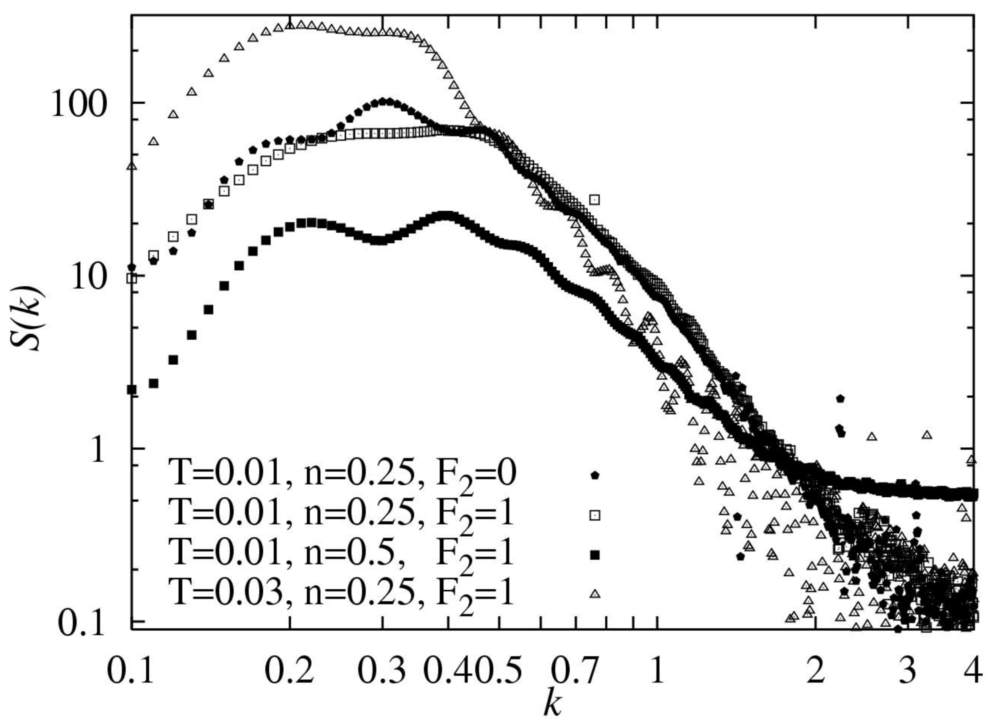
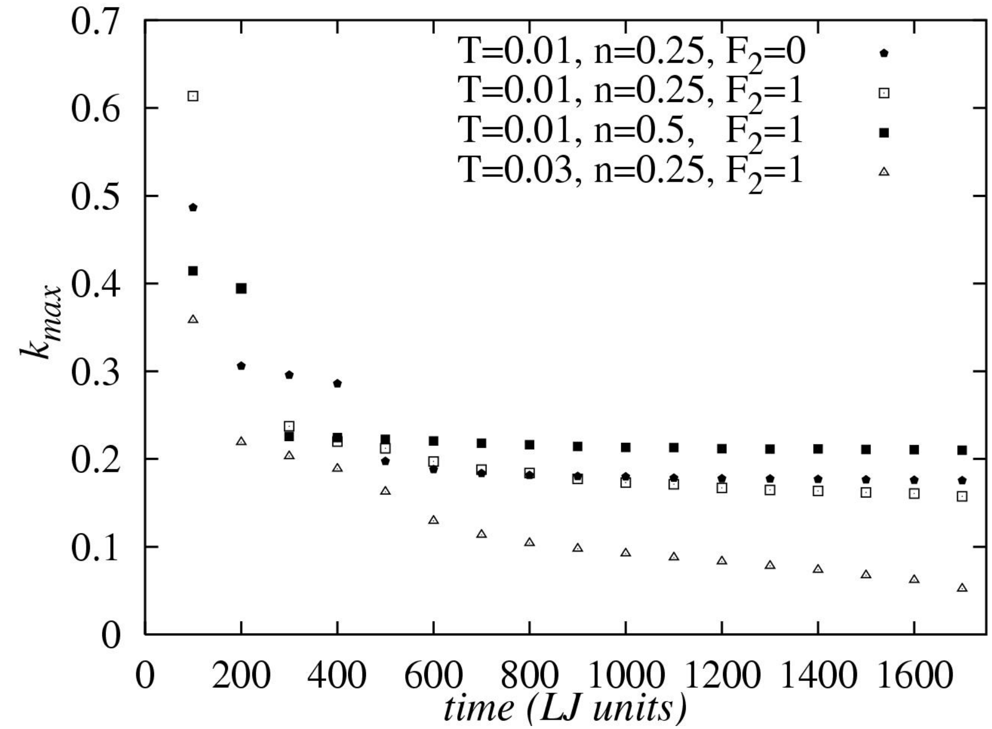
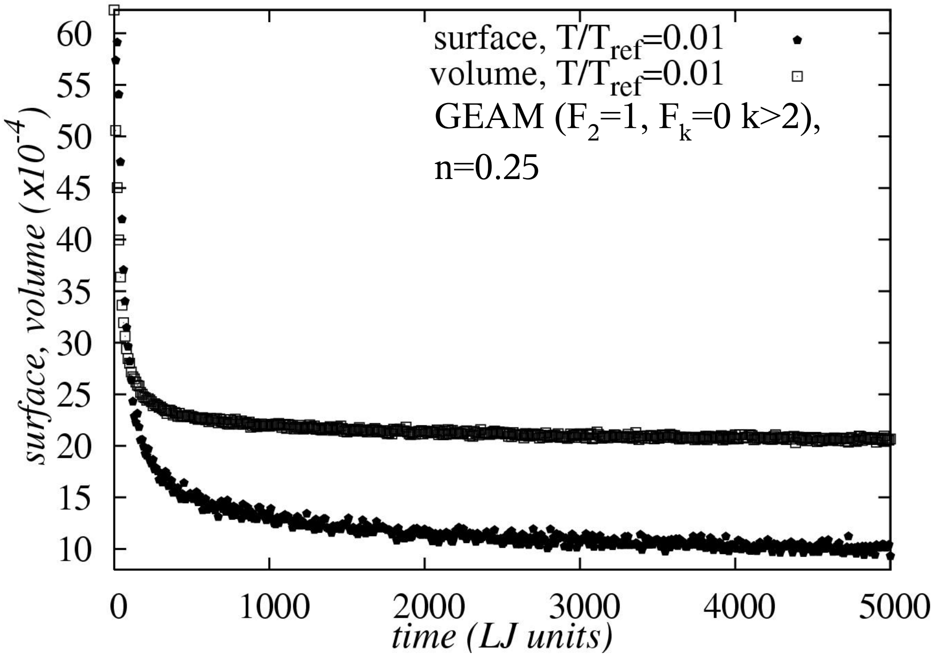
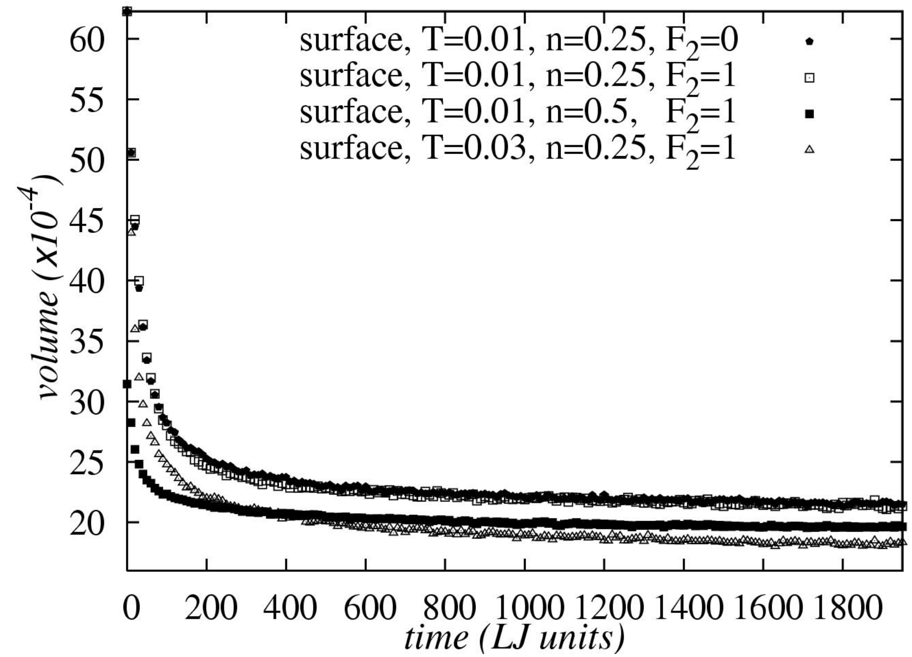




T	n	F_2	D
0.01	0.25	0	D_m=2.5(2)
0.01	0.25	1	D_s=2.7(4)
0.01	0.5	1	D_s=2.5(2)
0.03	0.25	1	D_s=2.2(2)

Volume and surface:

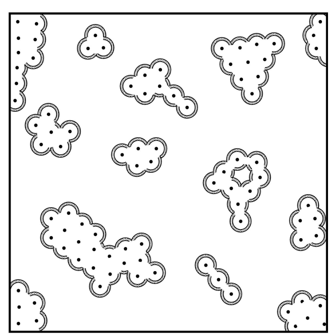




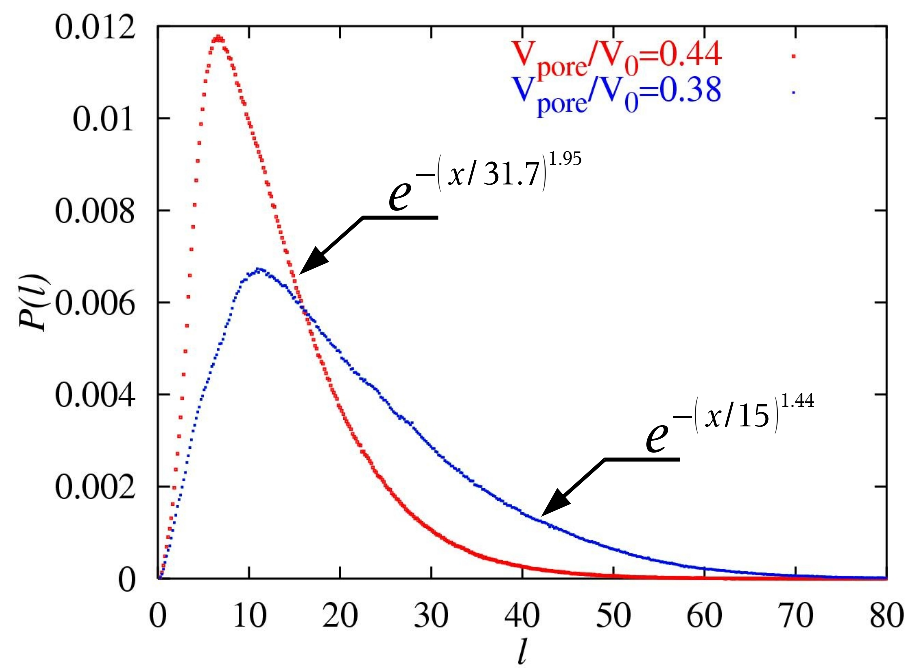
Monte Carlo integration:

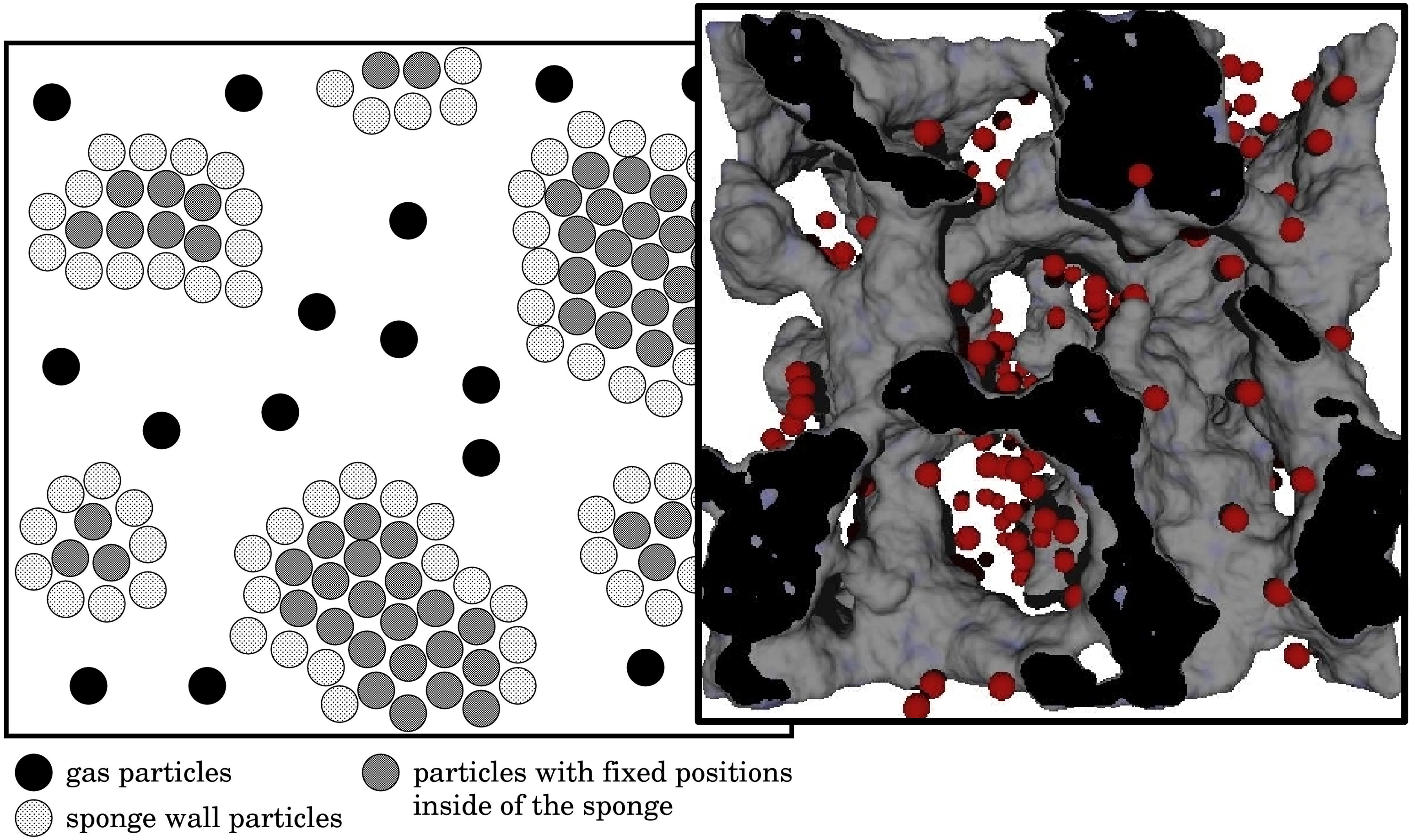
volume - $V/V_0=N/N_{tot}$,

surface - $\partial V(r)/\partial r$.



distribution of free flight paths

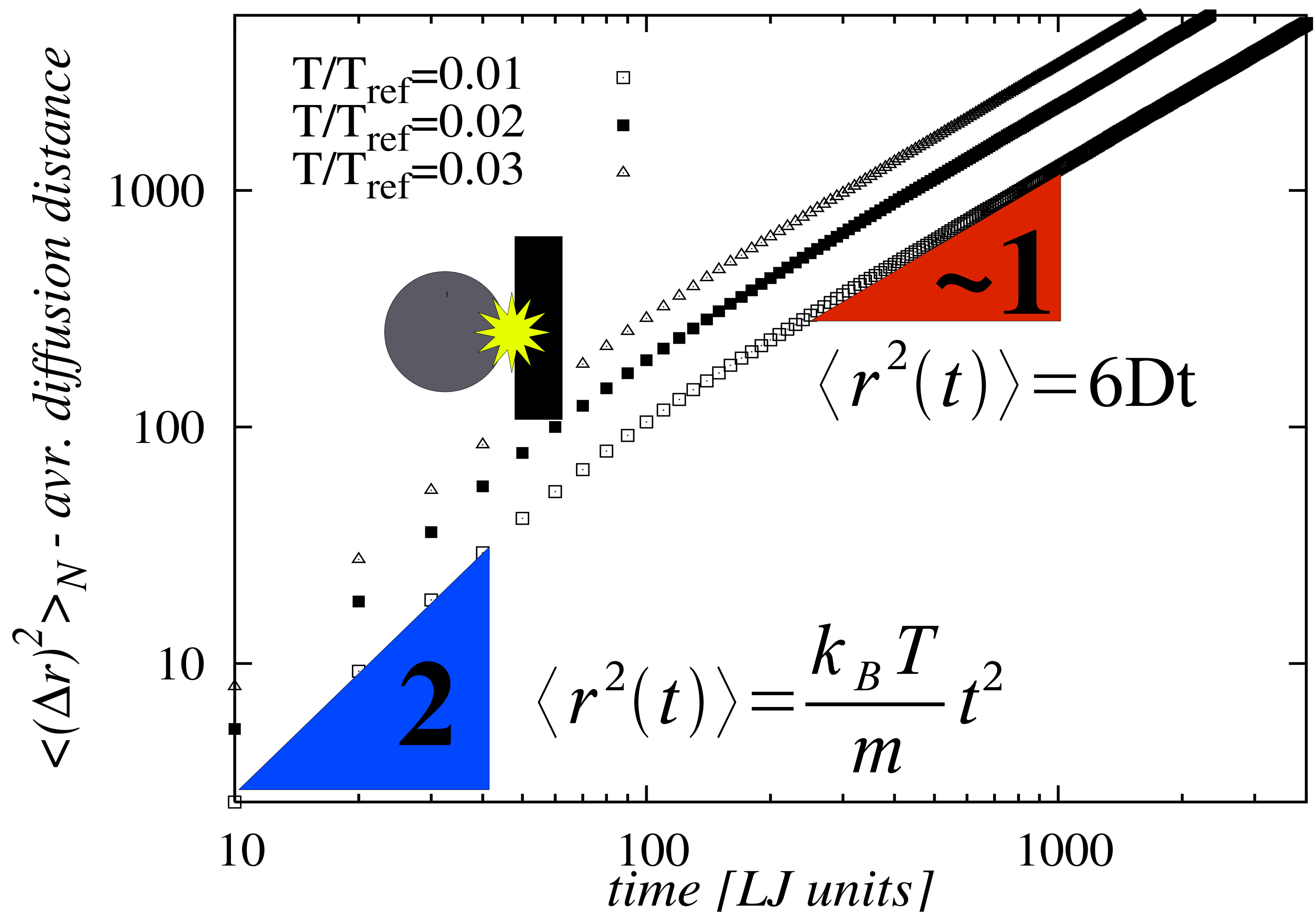


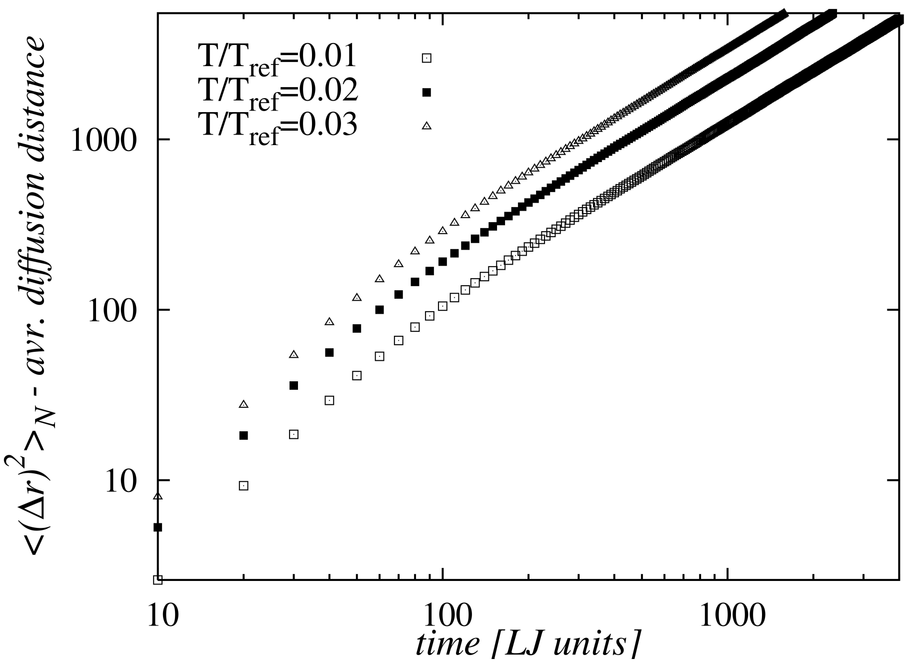


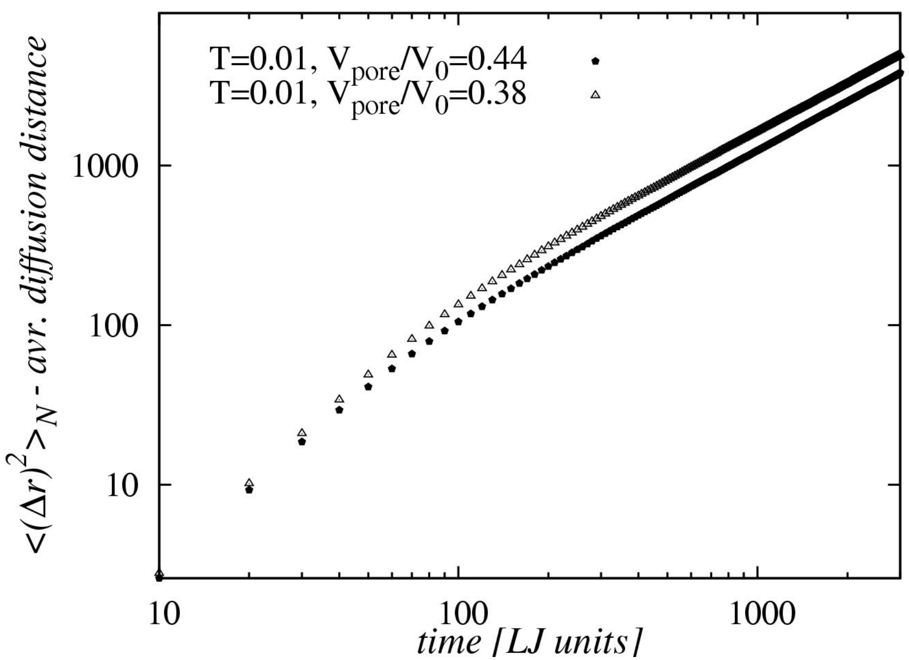
- gas particles do not interact
- gas-wall interaction SHREP » $\Phi(r)=\phi r_0^{-4}(r-r_{cut})^4, r\le r_{cut}$
- thermostat acts only on wall particles!

$\Phi(r)=0,\ r>r_{cut}$ (repulsive)

Knudsen self-diffusion (small densities):



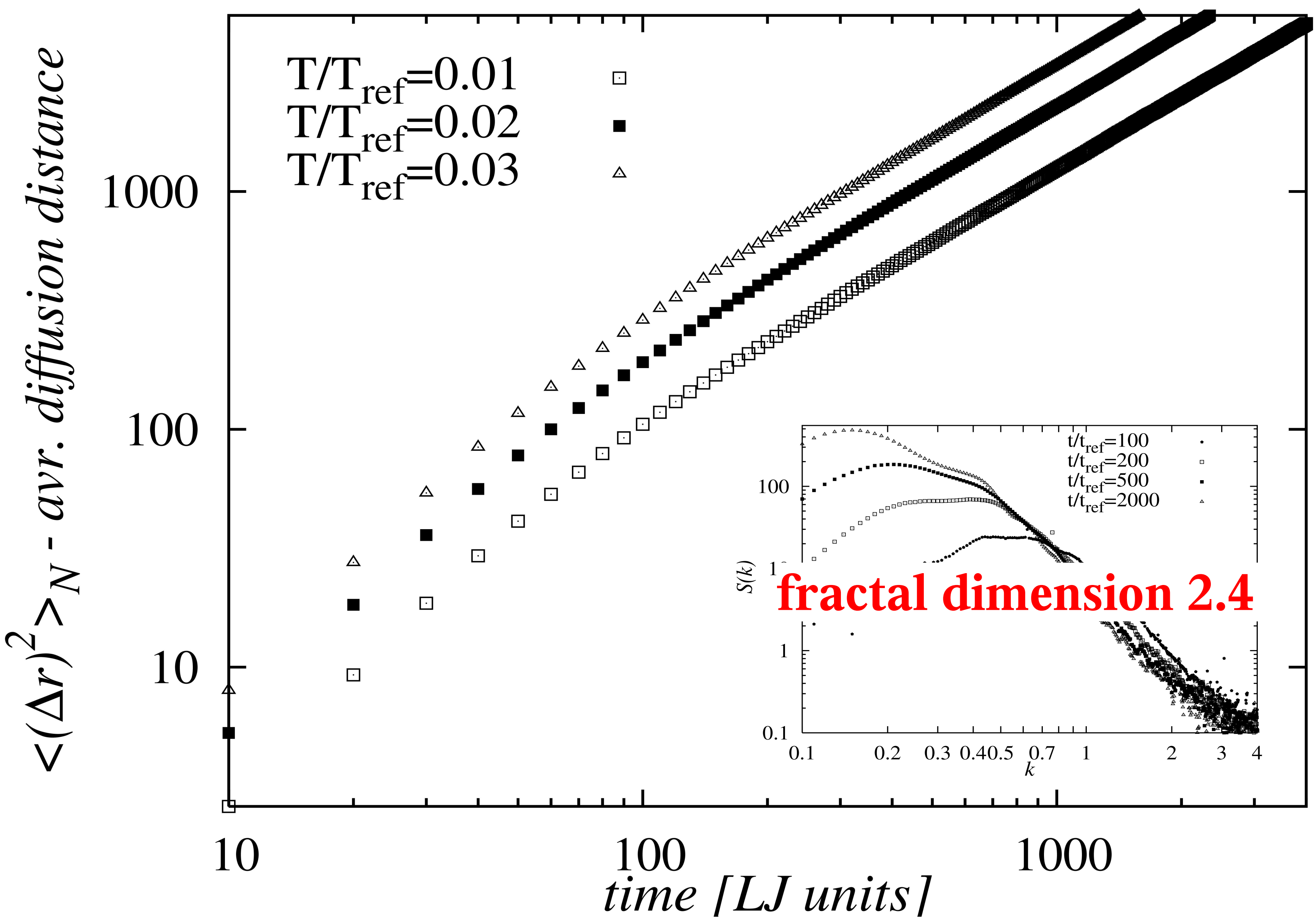


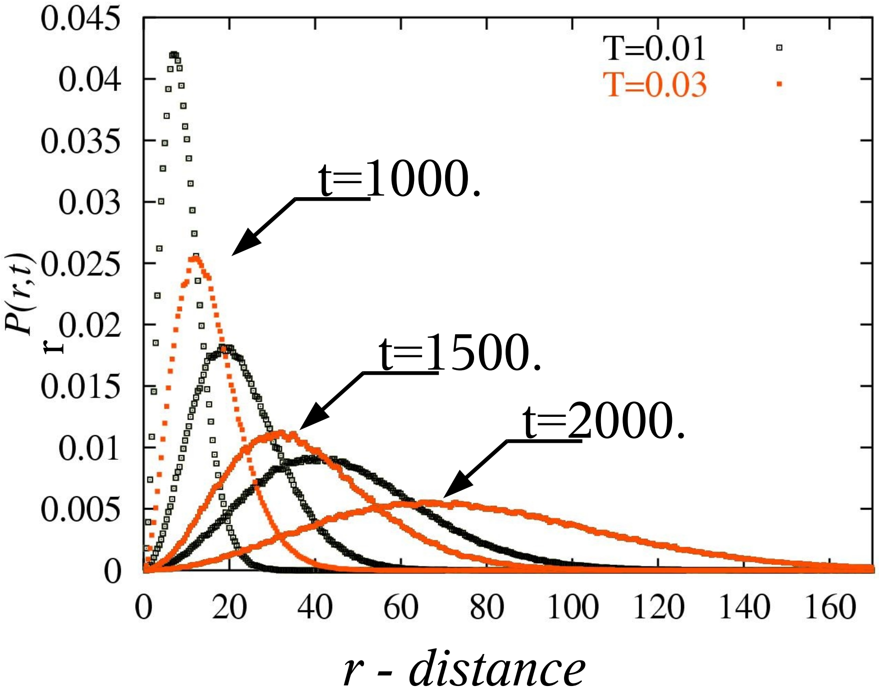


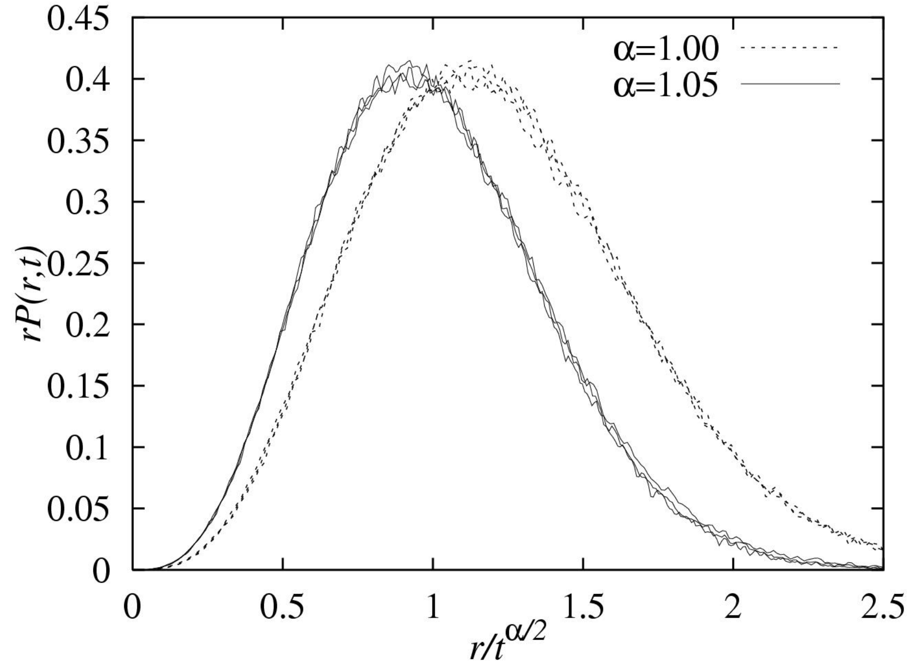
$$\langle r^2(t) \rangle \approx D t^{\alpha} \quad \text{for } t/t_{free} >> 1 \quad \Rightarrow$$

T	V_{pore}/V_0	D	α
0.01	0.445	1.18(1)	1.008(1)
0.02	0.445	1.52(2)	1.019(2)
0.03	0.445	2.19(4)	1.055(2)
0.01	0.378	1.41(2)	0.976(2)
0.02	0.378	3.42(6)	1.058(2)
0.03	0.378	3.50(3)	1.02(1)

Knudsen self-diffusion (small densities):





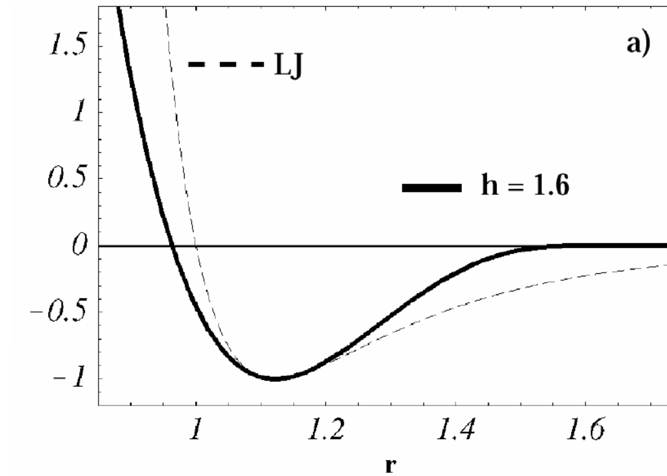


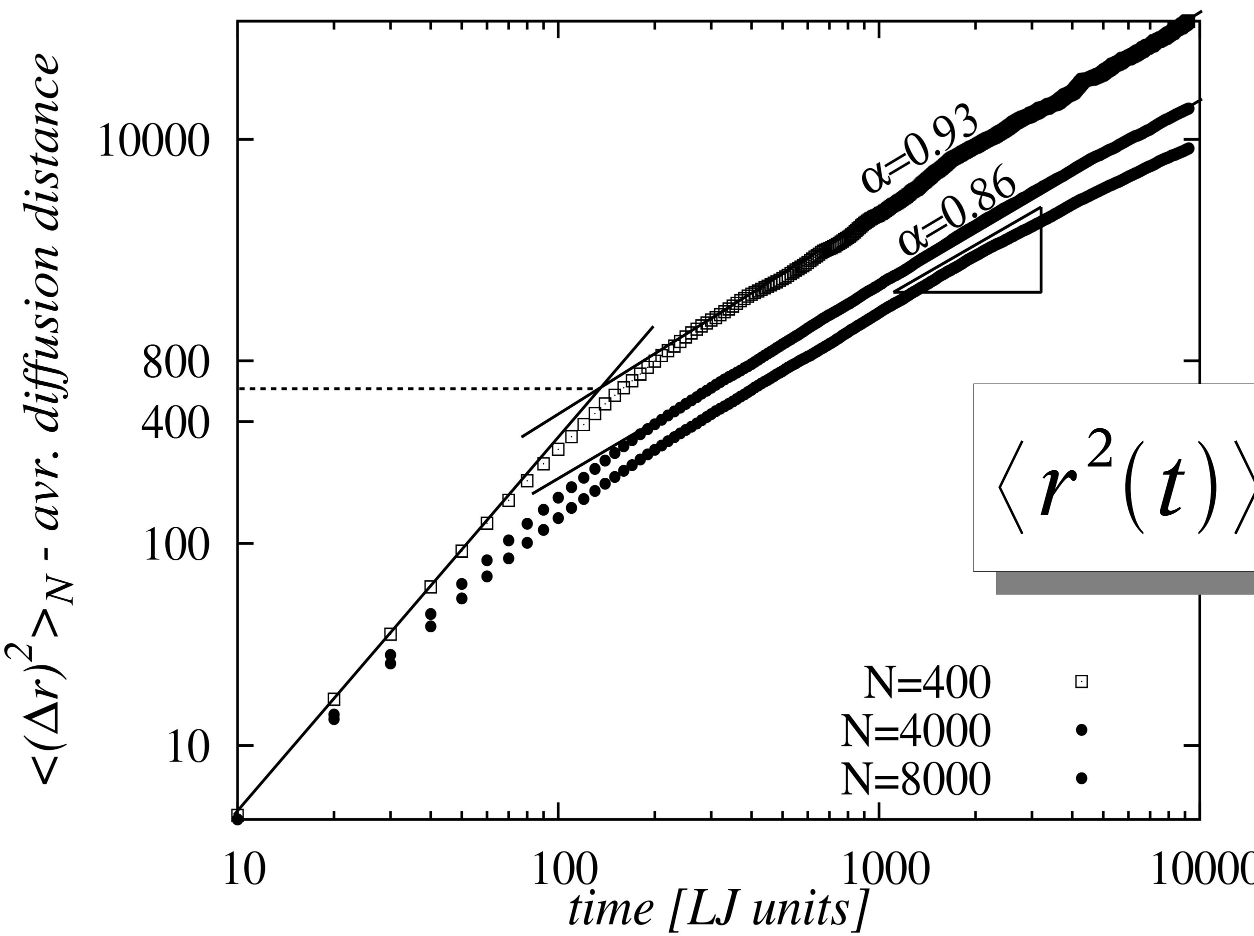
P(r,t) - probability that random walker has displaced to distance r after time t

$$P(r,t)=C_{1t}^{-3\alpha/2}\, e^{\frac{r^2}{2Dt^{\alpha}}}$$

- gas-gas interaction SHRAT (attractive)

- gas-wall interaction SHREP

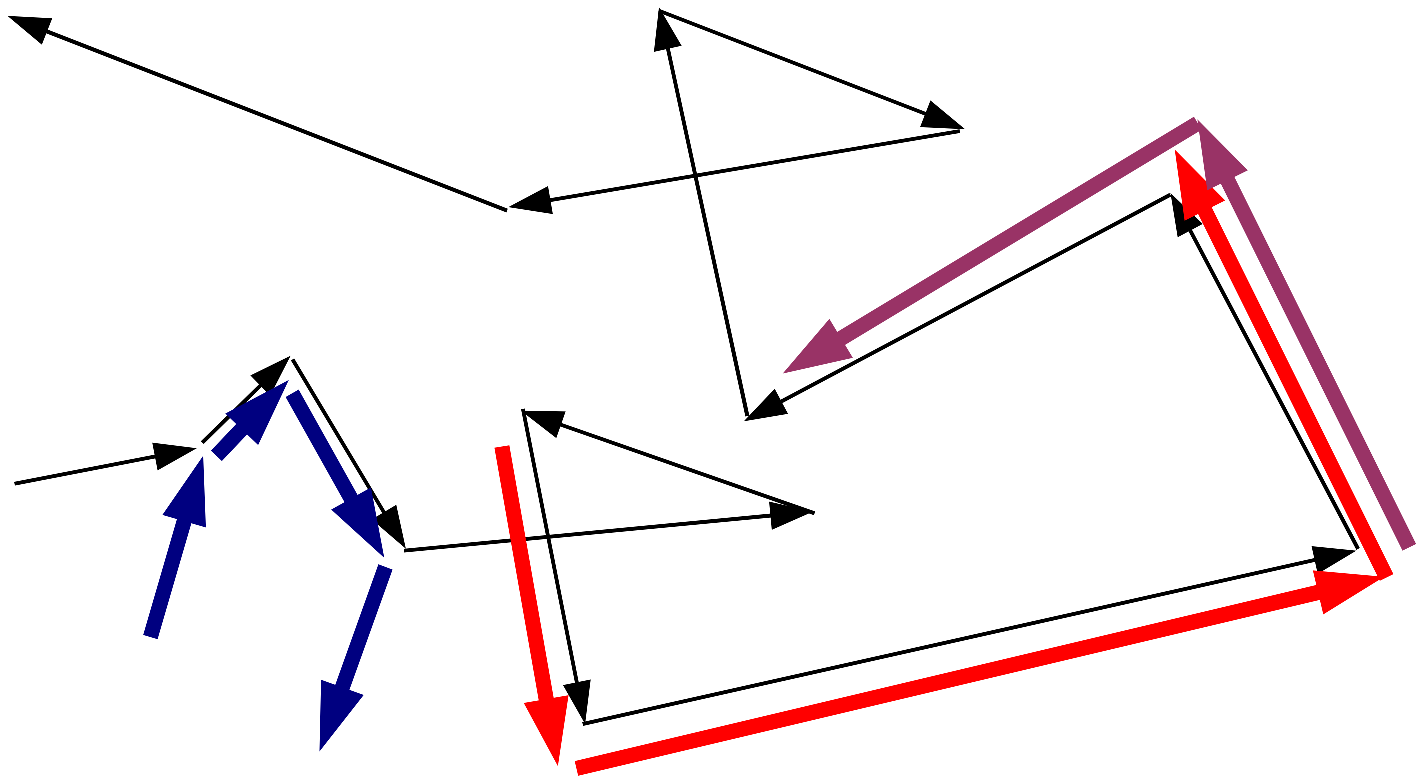




$$\langle r^2(t)\rangle \sim t^{\alpha}, \quad 0<\alpha<1$$

sub-diffusion

particles group → mass increases/ speed decreases



$\boxed{\tau = \infty}, \sigma^2 < \infty$

as result we have sub-diffusion