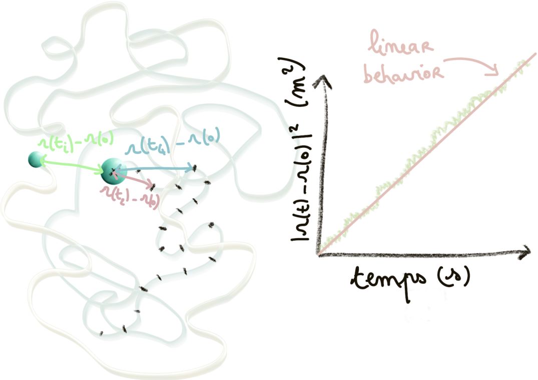
Sur la diffusion anormale des ions : Effet d'un champ électrique

Marie Landeiro Dos Reis, Sébastien Touzain & Abdallah El Hamidi,
Laboratoire LaSIE, La Rochelle Université

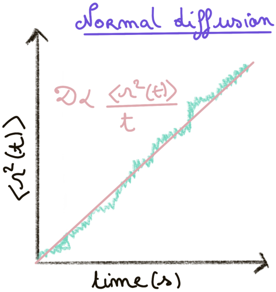
Normal diffusion / anomalous diffusion

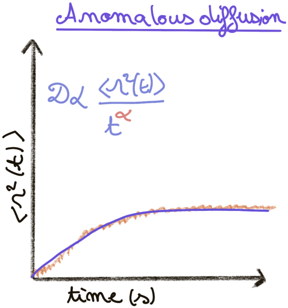
- **At the microscopic scale :** particule displacements are due to thermal agitation and interactions with neighboring molecules/particles (collisions, repulsion, attraction). Without external driving force : random.



Normal diffusion (Louis Bachelier (1900) and Einstein (1905)) : $< r^2(t) > \propto Dt$

Normal diffusion / anomalous diffusion





Normal diffusion :

$$< r^2(t) > \propto Dt \quad (1)$$

Anomalous diffusion :

$$< r^\beta(t) > \propto Dt^\alpha \quad (2)$$

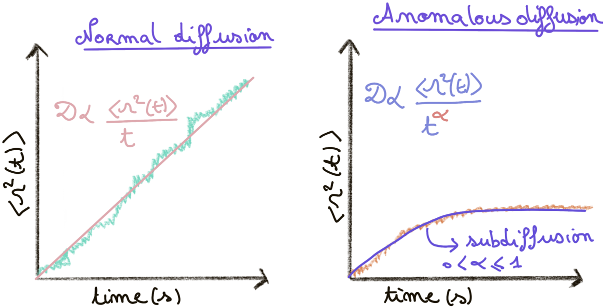
Eq. 2 established by fractional derivative approach.
1 2 3

1. L. Bachelier, Theory of speculation in the random character of stock market prices, MIT Press, Cambridge, Mass. Blattberg 1018, 17 (1900).

2. A. Einstein et al., On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat, Annalen der physik 17, 208 (1905)

3. R. Metzler, J.-H. Jeon, A. G. Cherstvy, and E. Barkai, Anomalous diffusion models and their properties : non-stationarity, non-ergodicity, and ageing at the centenary of single particle tracking, Physical Chemistry Chemical Physics 16, 24128 (2014)

Normal diffusion / anomalous diffusion



Normal diffusion :

$$< r^2(t) > \propto Dt \quad (3)$$

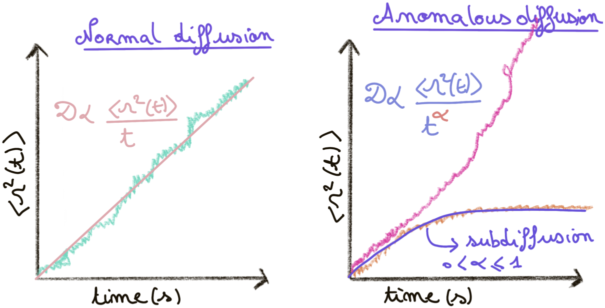
Anomalous diffusion :

$$< r^\beta(t) > \propto Dt^\alpha \quad (4)$$

Eq. 4 established by fractional derivative approach. [4] [5] [6]

4. L. Bachelier, Theory of speculation in the random character of stock market prices, MIT Press, Cambridge, Mass. Blattberg 1018, 17 (1900).
5. A. Einstein et al., On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat, Annalen der physik 17, 208 (1905)
6. R. Metzler, J.-H. Jeon, A. G. Cherstvy, and E. Barkai, Anomalous diffusion models and their properties : non-stationarity, non-ergodicity, and ageing at the centenary of single particle tracking, Physical Chemistry Chemical Physics 16, 24128 (2014)

Normal diffusion / anomalous diffusion



Normal diffusion :

$$< r^2(t) > \propto Dt \quad (5)$$

Anomalous diffusion :

$$< r^\beta(t) > \propto Dt^\alpha \quad (6)$$

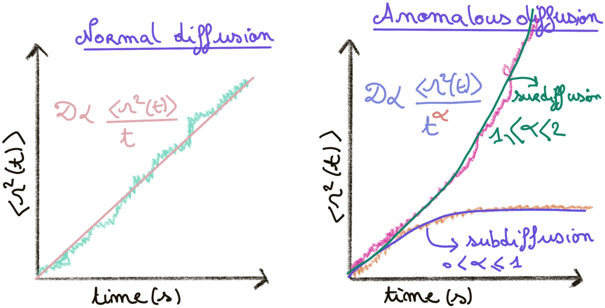
Eq. 6 established by fractional derivative approach.
7 8 9

7. L. Bachelier, Theory of speculation in the random character of stock market prices, MIT Press, Cambridge, Mass. Blattberg 1018, 17 (1900).

8. A. Einstein et al., On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat, Annalen der physik 17, 208 (1905)

9. R. Metzler, J.-H. Jeon, A. G. Cherstvy, and E. Barkai, Anomalous diffusion models and their properties : non-stationarity, non-ergodicity, and ageing at the centenary of single particle tracking, Physical Chemistry Chemical Physics 16, 24128 (2014)

Normal diffusion / anomalous diffusion



Normal diffusion :

$$< r^2(t) > \propto Dt \quad (7)$$

Anomalous diffusion :

$$< r^\beta(t) > \propto Dt^\alpha \quad (8)$$

Eq. 8 established by fractional derivative approach.
[10] [11] [12]

---

10. L. Bachelier, Theory of speculation in the random character of stock market prices, MIT Press, Cambridge, Mass. Blattberg 1018, 17 (1900).

11. A. Einstein et al., On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat, Annalen der physik 17, 208 (1905)

12. R. Metzler, J.-H. Jeon, A. G. Cherstvy, and E. Barkai, Anomalous diffusion models and their properties : non-stationarity, non-ergodicity, and ageing at the centenary of single particle tracking, Physical Chemistry Chemical Physics 16, 24128 (2014)

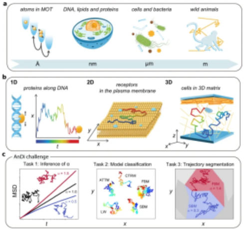
Observation of anomalous diffusion ?

Cite this: Phys. Chem. Chem. Phys., 2011, 13, 1800–1812
www.rsc.org/pccp
PAPER

Single particle tracking in systems showing anomalous diffusion: the role of weak ergodicity breaking

Stas Burov,[a] Jae-Hyung Jeon,[b] Ralf Metzler[a,b] and Eli Barkai[a,c]

Received 20th September 2010, Accepted 16th November 2010
DOI: 10.1039/c0cp01879a



G. Muñoz-Gil *et al.* Nat. Com. (2021)

12 February 2001
PHYSICS LETTERS A
ELSEVIER
Physics Letters A 280 (2001) 97–103
www.elsevier.nl/locate/pla

Anomalous diffusion near structural-glass transformations

V.B. Kokshenev[a,*], N.S. Sullivan[b]
[a] Departamento de Física, Universidade Federal de Minas Gerais, Caixa Postal 702, 30161-970 Belo Horizonte, Minas Gerais, Brazil
[b] Physics Department, University of Florida, P.O. Box 118400, Gainesville, FL 32611-8400, USA

Received 5 December 2000; accepted 7 December 2000
Communicated by A. Lagendijk

Biophysical Journal Volume 73 August 1997 1073–1080

Single-Molecule Microscopy on Model Membranes Reveals Anomalous Diffusion

G. J. Schütz, H. Schindler, and Th. Schmidt
Institute for Biophysics, University of Linz, 4040 Linz, Austria

IOP Publishing — Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter 23 (2011) 485005 (5pp)

Anomalous diffusion and memory effects on the impedance spectroscopy for finite-length situations

L R Evangelista[1], E K Lenzi[1], G Barbero[2] and J R Macdonald[3]
[1] Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, Paraná, Brazil
[2] Dipartimento di Fisica del Politecnico, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[3] Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599, USA

PHYSICAL REVIEW E **90**, 063012 (2014)

Anomalous transport and chaotic advection in homogeneous porous media

D. R. Lester*
Mathematics, Informatics and Statistics, CSIRO, PO Box 56, Highett, Victoria 3190, Australia and School of Civil, Environmental and Chemical Engineering, Royal Melbourne Institute of Technology, Melbourne, Victoria 3001, Australia
G. Metcalfe
Materials Science and Engineering, CSIRO, PO Box 56, Highett, Victoria 3190, Australia
M. G. Trefry
Land and Water, CSIRO, Private Bag 5, Wembley, Western Australia 6913, Australia and School of Earth and Environment, The University of Western Australia, 35 Stirling Highway, Crawley, Western Australia 6009, Australia
(Received 10 August 2014; published 19 December 2014)

PHYSICAL REVIEW E **79**, 041402 (2009)

Anomalous diffusion in ferrofluids

Alenka Mertelj,[1] Luka Cmok,[1] and Martin Čopič[1,2]
[1]*J. Stefan Institute, Jamova 39, SI-1001 Ljubljana, Slovenia*
[2]*Department of Physics, University of Ljubljana, SI-1000 Ljubljana, Slovenia*
(Received 10 November 2008; revised manuscript received 30 January 2009; published 8 April 2009)

accepted for publication in Physical Review Letters, January 8th, 2009

The Nernst–Einstein equation for an anomalous diffusion at short spatial scales

D.N. Gerasimov
National Research University, Moscow Power Engineering Institute, 111250, Krasnokazarmennaya, 14, Moscow, Russian Federation

$$\frac{D}{\mu} = \frac{kT}{q} \longrightarrow \frac{D_\alpha}{\mu^\alpha} = \frac{kT}{q} E^{\alpha-1} A_\alpha x^{1-\alpha}$$

Anomalous diffusion mediated by atom deposition into a porous substrate.

Pascal Brault,[1,*] Christophe Josserand,[2,3] Jean-Marc Bauchire,[1] Amaël Caillard,[1,4] Christine Charles,[4] and Rod W. Boswell[4]
[1]*Groupe de Recherches sur l'Energétique des Milieux Ionisés, UMR6606 CNRS-Université d'Orléans BP 6744, 45067 Orléans Cedex 2, France*
[2]*Institut Jean Le Rond d'Alembert, UMR 7190 CNRS-Paris VI Case 162, UPMC, 4 place Jussieu, 75252 Paris Cedex 05, France*
[3]*Kavli Institute for Theoretical Physics, University of California, Santa Barbara, CA 93106,USA*
[4]*Space Plasma, Power, and Propulsion group (SP3), Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia*

Experimental evidences of anomalous diffusion

Ionic diffusion in electrochemical cell ? Small scale, distance between electrodes : mm

Observations : Anomalous diffusion behavior

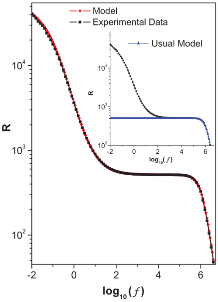


FIG. 1. (Color online) Real part of the electrical impedance of the cell versus the frequency of the applied voltage $f = \omega/2\pi$. The inset compares the behavior of the usual model with the experimental data of the real part of the impedance.

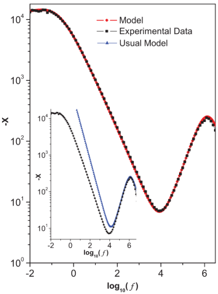


FIG. 2. (Color online) Imaginary part of the electrical impedance of the cell versus the frequency of the applied voltage $f = \omega/2\pi$. The inset compares the behavior of the usual model with the experimental data of the imaginary part of the impedance.

13

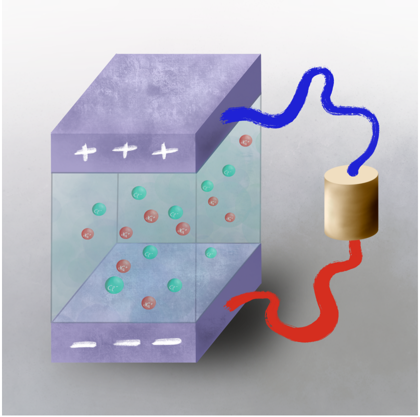
Experimental conditions :

- Impedance spectroscopy : Milli-Q water, frequency from $10^{-}2$Hz to 5MHz, AC = 20mV, resitivity ρ=18.2MΩcm, pH = 6.1
- electrods : circular surface at 1 mm from each other, area 3.14 cm^2
- Potassium chloride solution

Necessity to use a fractionnal derivative approch

13. Lenzi *et al.* Phys. Rev. E 84, 041128 (2011)

Ionic diffusion



- Origin of anomalous diffusion ? Mechanisms at the atomic scale ?
- How does **ionic concentration** affect diffusion in saline solution ?
- How does **electric field** influence diffusion in saline solution ?

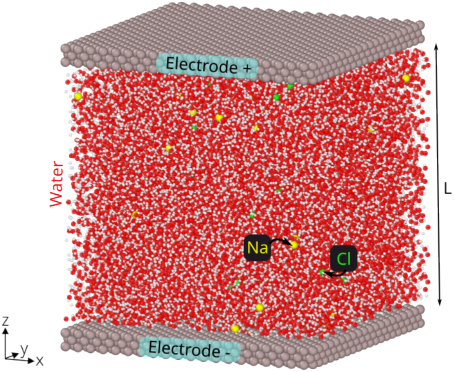
$\Rightarrow$ **Model system : Water + NaCl**

Ionic diffusion under electric field ?

System : Nanometric electrochemical cell

Molecular dynamics simulations were conducted using the Large-scale Atomic/Molecular Massively Parallel Simulator (**LAMMPS**)[1]

The atomic visualization was performed using **OVITO**[2]



L (Å)	d_x (Å)	d_y (Å)	d_z (Å)
90	79	79	95

- L : inter-electrode distance
- d_x, d_y, d_z : cell dimensions in x, y, z

n_{H_2O}	n_M
18218	4800

- n_{H_2O} : number of water molecules
- n_M : number of atoms in the electrodes

1. Thomson *et al.*, Comput. Phys. Comm. 271, 108171 (2022)
2. Stukowski *et al.* Model. Simul. Mater. Sci. Eng. 18, 015012 (2009)

Atomic scale simulations : Molecular Dynamic

Total energy :

$$E = \sum_i \frac{\boldsymbol{p}_i^2}{2m_i} + V(\boldsymbol{r_1}, \boldsymbol{r_2}, .., \boldsymbol{r_N}) \tag{9}$$

Canonical ensemble : 2nd Newton law + thermostat

$$\frac{d\mathbf{v}_i(t)}{dt} = -\frac{1}{m_i}\nabla V(\mathbf{r}(t)) - \zeta(t)\mathbf{v}_i(t) \tag{10}$$

where

$$\frac{d\zeta(t)}{dt} = \frac{1}{Q}\left(\sum_{i=1}^{N} m_i \mathbf{v}_i^2(t) - gNk_B T\right) \tag{11}$$

$\mathbf{v}_i(t)$ velocity of atom i

$\zeta(t)$ friction term, Q effective mass, g degree of freedom

La Rochelle Université

Molecular Dynamics : Interatomic potential

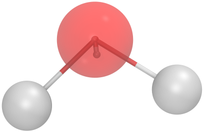
The interatomic potential used is a combination of Coulombic interactions and a simple Lennard-Jones (LJ) potential :

$$V_{ij}(r_{ij}) = \sum_i \sum_j \frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \quad (12)$$

- A rigid water model based on TIP4P/2005 [1]
- Parameters for Na^+ and Cl^- ions were derived from the CHARMM-27 force field [2].
- The long-range Coulombic interactions were accounted for using the FFT-based particle-particle/particle-mesh (PPPM) method in LAMMPS [3] .

Table – LJ pair potential parameters used in this study [**?**, **?**].

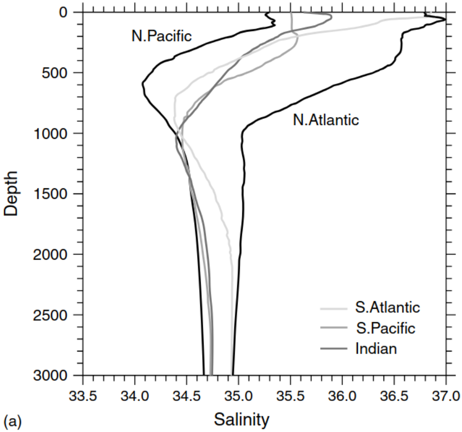
	σ_{ij} (Å)	ε_{ij} (kcal/mol)
O-O	0.185199	3.1589
Na-Na	0.04690	2.4299
Cl-Cl	0.1500	4.04470
M-M	11.697	2.574
O - M	0.4	2.86645



1. Abascal *et al.*, J. Chem. Phys. (2005)
2. Mackerell *et al.*, Biopolymers (2000)
3. Thomson *et al.*, Comput. Phys. Comm. 271, 108171 (2022)

Choice of salinity and electric field

Salinity : How many ions Na^+ and Cl^- in the system ?



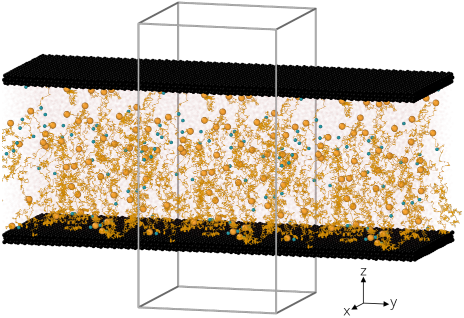
(a) Figure from : Talley (2002)

- Salinity : between 5 and 40 g/kg of water (Baltic sea - Red sea)
- $n_{Cl^-} = n_{Na^+}$
- For $n_{H_2O} = 18218$: $25 < n_{Cl^-} < 200$
- Electric field : between 1×10^5 V/m ($q^M \approx 0.001e$) and 1×10^7 V/m ($q^M \approx 0.05e$).

Diffusion measurement (canonical, NVT), T = 300K

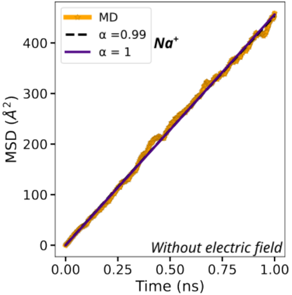
1) Water equilibration at 300K
2) All system equilibration
3) Mean Squared Displacement (MSD) :

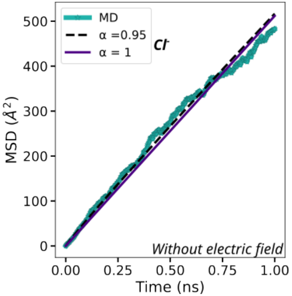
$$< r_{ion}^2(t) >= \frac{1}{N_{ion}} \sum_{i=1}^{N_{ion}} |r_i(t) - r_i(0)|^2 \quad (13)$$



- N_{ion} : number of ions in the solution
- $r_i(t)$: ion position at time t

MSD without electric field at T = 300K





Mean Squared Displacement (MSD) :

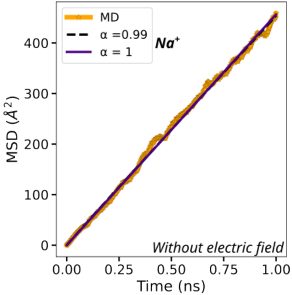
$$< r_{ion}^2(t) >= \frac{1}{N_{ion}} \sum_{i=1}^{N_{ion}} |r_i(t) - r_i(0)|^2 \qquad (14)$$

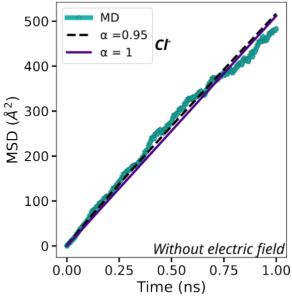
- N_{ion} : number of ions in the solution
- $r_i(t)$: ion position at time t

$$< \hat{r}_{ion}^2(t) >= \frac{6D_{ion}}{\Gamma(1+\alpha)} t^{\alpha} \qquad (15)$$

- D_{ion} : diffusion coefficient
- α : fractionnal coefficient

MSD without electric field at T = 300K



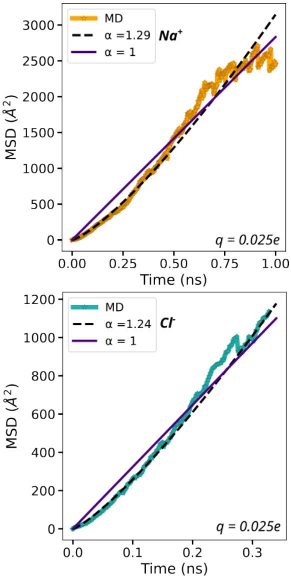


- Na^+ and Cl^- ions
  $\rightarrow$ **quasi-Brownian motion, $\alpha \simeq 1$**

- D_{Na^+} between **0.7 and 0.9x10^{-9}m^2/s**
  Experimental value : **$\simeq$1x10^{-9} m^2/s**
- D_{Cl^-} between **0.8 and 1.1x10^{-9} m^2/s**
  Experimental value : **$\simeq$2x10^{-9} m^2/s** [a]

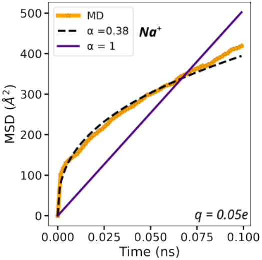
a. Mills, J. ACS (1955) ; Mills, J. Chem. Phys. (1957) ; Wang *et al.* J ACS (1953), Passiniemi J Sol. Chem. (1983)

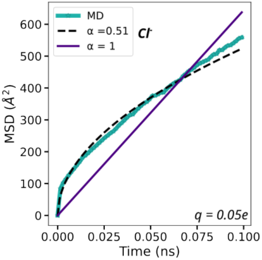
MSD with electric field at T = 300K



- Nonlinear time dependence
  $\rightarrow$ **anomalous diffusion** $\alpha \neq 1$
- Diffusion is slightly accelerated ($\alpha > 1$)
  $\rightarrow$ Surdiffusion regime
- At the end of the simulations :
  all ions become fixed on the electrodes

MSD with electric field at T = 300K



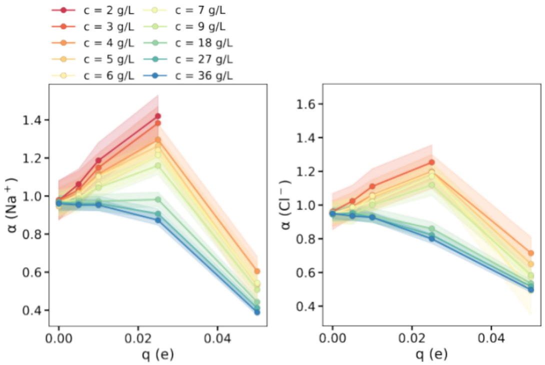


- Nonlinear time dependence
  $\rightarrow$ **anomalous diffusion** $\alpha \neq 1$
- Diffusion is slightly slowdown ($\alpha < 1$)
  $\rightarrow$ Subdiffusion regime

Remarques

- Without electric field : $\alpha \simeq 1$
  MSD follow normal diffusion
  (Bachelier, Einstein)
- With electrical field : $\alpha \neq 1$
  Anomalous diffusion $\rightarrow$
  Sub/Surdiffusion regime ?
  Depend on electric field level

Effect of concentration and q on the fractionnal exponent α



- **Without electric field** : *normal* ionic diffusion $\rightarrow \alpha \simeq 1$
- **Under electric field** : *anomalous* ionic diffusion
  - **Superdiffusion** regime at low concentration for q < 0.05e $\rightarrow 2 > \alpha > 1$
  - **Subdiffusion** for salt concentration above 20 g/L :
    due to higher effect of Coulombic interaction between ions ?
  - **Subdiffusion/balistic** regime at q $= 0.5$e ? $\rightarrow \alpha \simeq 0.5$

Effective activiy coefficient : Confrontration between MD simulations, Extend Debye Hückel Model and experiments.

From MD simulation

The effective activity coefficient γ :

$$\gamma \propto \frac{N_{ion} - N_{pairs}}{N_{ion}} \tag{16}$$

Chemical model : Extend Debye Hückel (EDH) model

$$-\log_{10}\gamma = \frac{A_m |q_{Na^+} q_{Cl^-}| I_m^{1/2}}{1 + B_m a_i I_m^{1/2}} \tag{17}$$

with A_m and B_m two coefficient and I_m the ionic strengh :

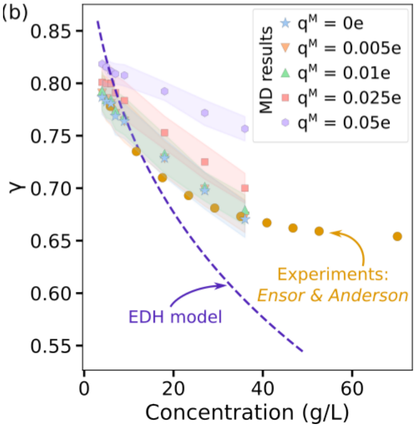
$$A_m = \left(\frac{2\pi N_a}{1000}\right)^{1/2} \times \frac{e^3}{2.3026(k_B T \epsilon_r)^{3/2}}, B_m = \left(\frac{8\pi N_a}{1000}\right)^{1/2} \times \frac{e}{(k_B T \epsilon_r)^{1/2}} \tag{18}$$

and

$$I_m = \frac{1}{2}\frac{c}{m_{NaCl}}\left(v_{Na^+} + v_{Cl^-}\right) \tag{19}$$

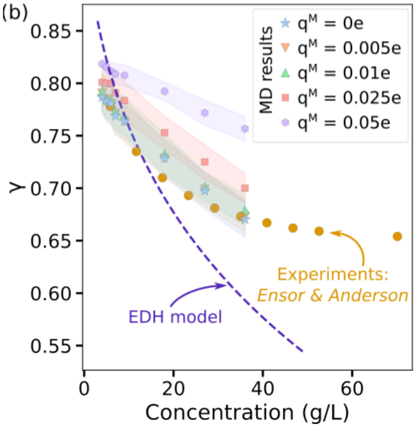
Effective activiy coefficient : Confrontration between MD simulations, Extend Debye Hückel Model and experiments.

- EDH model underestimate γ at high concentrations : cannot capture ion–ion interactions, particularly salt effects and short-range correlations.
- Higher concentration = more quasi neutral ion pairs = less impact of q
- explain why the deviation of α from 1 indicative of anomalous diffusion tends to diminish as the ion concentration increases

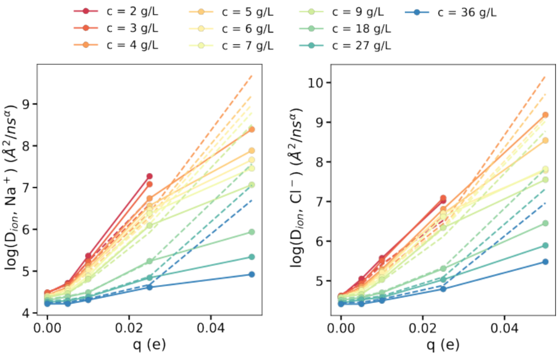


Effective activiy coefficient : Confrontration between MD simulations, Extend Debye Hückel Model and experiments.

- stronger electric field = higher γ.
- electric field counteract the attractive Coulomb interactions.



Effect of concentration and q on D_{ion}



- Decrease of ionic diffusion coefficient with salt concentration due to Coulombic interaction
- Same order of magnitude than experiments ($4 < \log(D) < 5$, D being in Å^2/ns) (Mills, Wang, Passiniemi)
- Increase of diffusion concentration with electric field
- Comparison with Nernst Einstein equation : $D = \mu \frac{RT}{F}$?

Conclusion & perspectives

Conclusion :

- Anomalous diffusion behavior appears from the application of an electric field :
  $q = 0e \Leftrightarrow \alpha \simeq 1$, normal diffusion.
- At low concentrations, superdiffusion phenomenon ($\alpha > 1$), which diminishes as the concentration increases, eventually leading to subdiffusion ($\alpha < 1$) explain by the formation of neutral pairs
- D_{ion} increases with the applied electric charge. Electric field biases diffusion and promotes migration in a preferred direction.
- Higher the ion concentration in the solution, the lower D_{ion}. Competition between the driving force pushing the ions toward the electrodes and the Coulombic interactions between ions.

Perspectives :

- **Origin of the anomalous diffusion** :
  Non ergodicity due to boundary conditions ? To do : simulations in a 3D periodic system
- Poisson Nernst Planck model ?
- Impedance experiments ?