Introduction to diffusion in silicate melts

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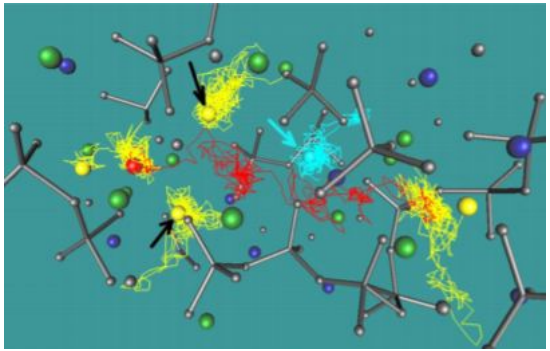
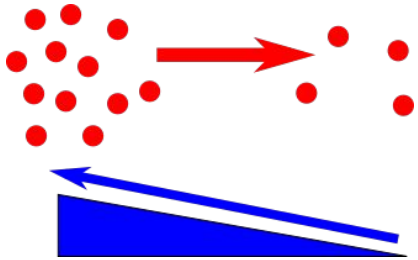
Sophie Schuller, CEA Marcoule

AGENDA

- Motivation: ubiquity of molecular diffusion, applications
- Kinetic origin of molecular diffusion and Fick's laws
- Origin and value of diffusivity coefficients in liquids and silicate melts
- Thermodynamic formalism of diffusion, phase separation
- Multicomponent diffusion in mixtures: couplings between species



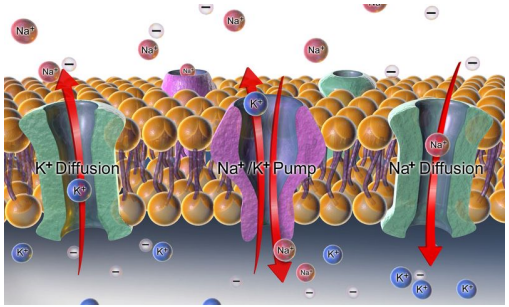
Introduction to molecular diffusion - Motivation



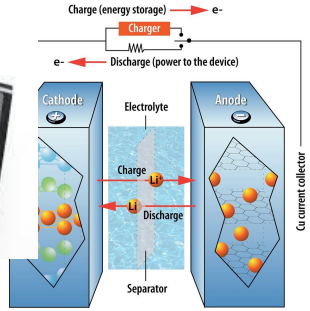
A first definition: flux of matter in the opposite direction of the concentration gradient

Smell

Cell biology



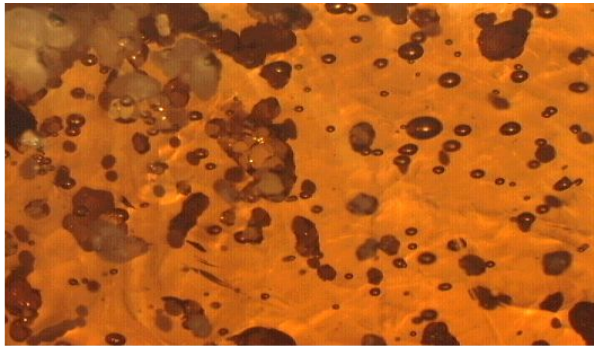
Li-ion batteries



https://live.staticflickr.com/4151/5029455937_5ff2964379_b.jpg

Consequences and applications of diffusion in silicate melts

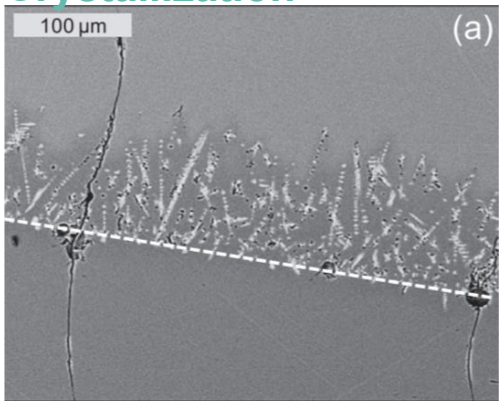
Glass melting



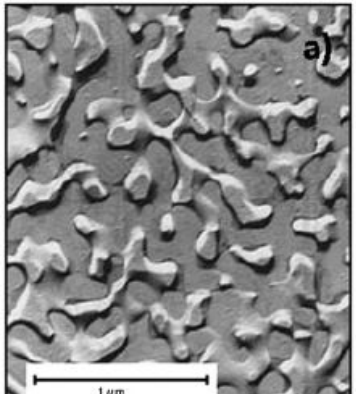
Refractory corrosion

Volatile diffusion & volcanic eruption

Crystallization



Phase separation

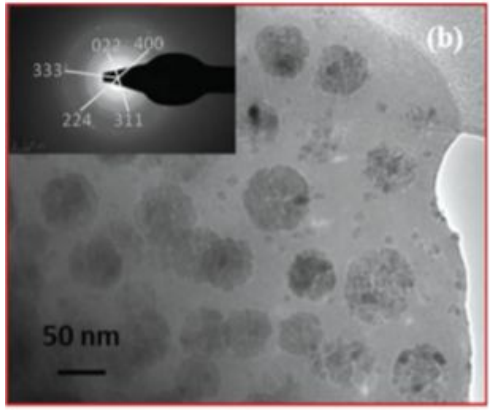


Pablo et al JNCS 2019.

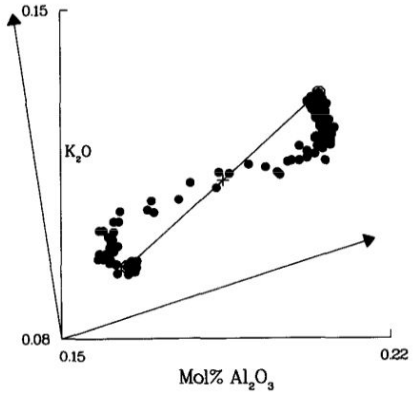
Typical scientific questions related to diffusion

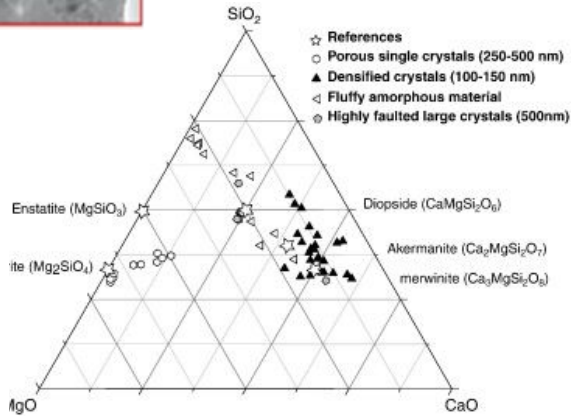
- How fast is diffusion-driven mass transport ? Prediction of relevant scales of mass transport
  - dissolution of refractories
  - crystal growth
  - …
- What is the chemical path of diffusion?

→ Prediction of concentration fields / profiles



Chenu, Sébastien, et al. "Tuneable nanostructuring of highly transparent zinc gallogermanate glasses and glass-ceramics." *Advanced Optical Materials* 2.4 (2014): 364-372.



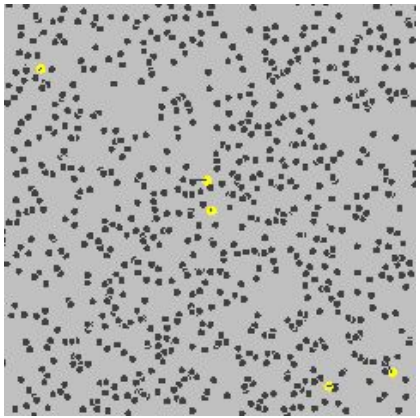


Kinetic origin of diffusion

Microscopic origin of diffusion: thermal fluctuations

Molecular diffusion at microscopic level = thermal motion of particles at finite temperature

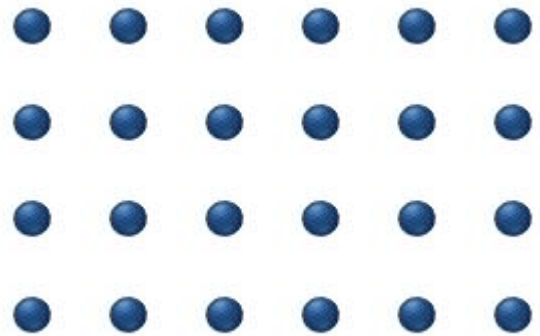
Disordered media (liquids, gases)



Ideal gas

$$v_{\mathrm{p}} = \sqrt{2 \cdot \frac{k_{\mathrm{B}} T}{m}},$$

Crystals

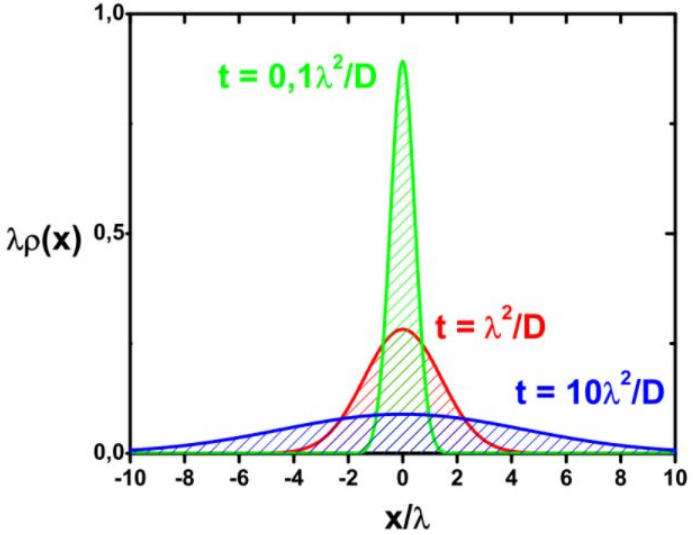


In this lecture: only silicate **liquids** (melts and metastable liquids)

https://en.wikipedia.org/wiki/Brownian_motion#/media/File:Brownianmotion5particles150frame.gif

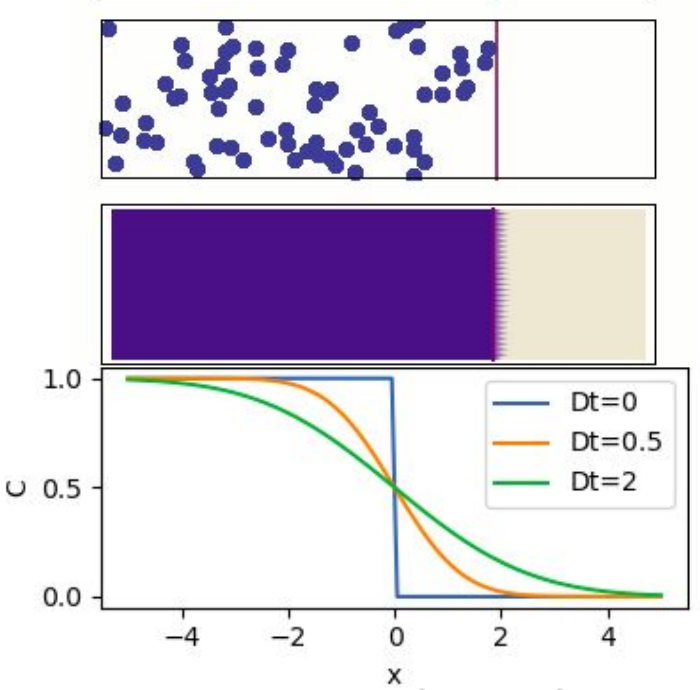
https://en.wikipedia.org/wiki/Thermal_fluctuations#/media/File:Chemical_surface_diffusion_slow.gif

Solutions of the diffusion equation



$$C(x, t = 0) = C_0 \delta(x)$$

$$C(x, t) = \frac{C_0}{2\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}}$$



$$n\,(x,t) = n_0\,\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right).$$

solutions can be r**escaled** using a rescaled coordinate $\frac{x}{\sqrt{Dt}}$

→ a way to check that transport is due to diffusion only

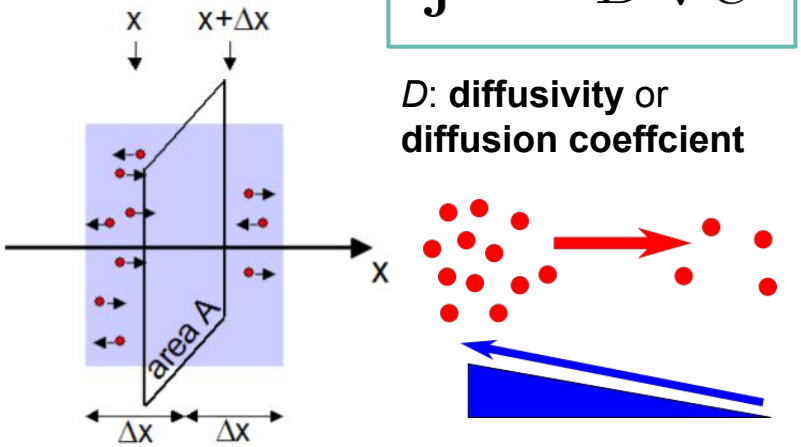
Fick's laws of diffusion

First law

Ingredients : random walk + mass conservation

$$J = -\frac{(\Delta x)^2}{2\tau}\frac{\left(C(x+\Delta x)-C(x)\right)}{\Delta x} = -D\frac{\partial C(x)}{\partial x}$$

$$\mathbf{j} = -D\nabla C$$

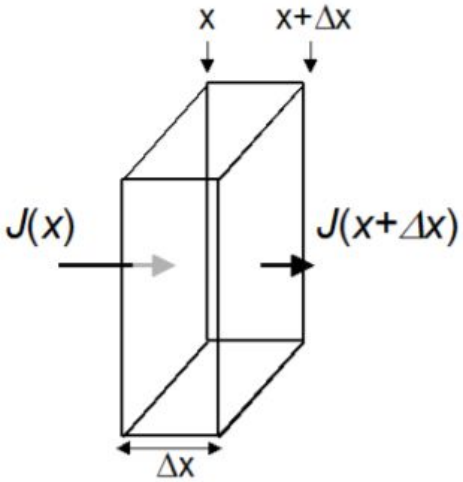


D: **diffusivity** or **diffusion coeffcient**

https://www.doitpoms.ac.uk/tlplib/diffusion/fick1_derivation.php
http://web.mit.edu/biophysics/sbio/PDFs/L15_notes.pdf

Second law

Ingredients : mass conservation



$$\frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C)$$

$$\frac{\partial C}{\partial t} = D\Delta C$$

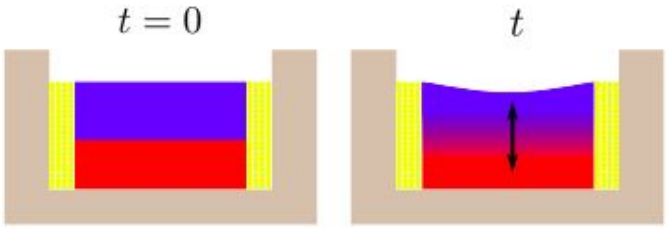
Fick 1855

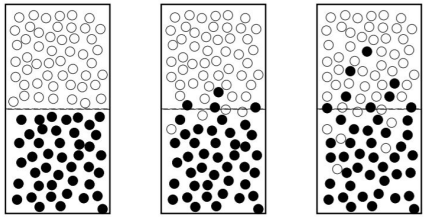
https://en.wikipedia.org/wiki/Fick%27s_laws_of_diffusion

Zhang, Youxue. "Diffusion in minerals and melts: theoretical background." *Reviews in mineralogy and geochemistry* 72.1 (2010): 5-59.

Measuring experimental values of diffusion coefficients

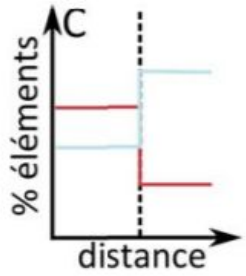
From concentration profiles in diffusion experiments

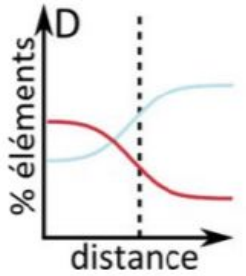




- **Self-diffusion:** no gradient of species concentration. Can be a gradient of *isotope* concentration.
- **Tracer diffusion**: (very) small concentration and gradient of minor element. Diffusion-couple experiment, but very small difference between endmembers.
- **Chemical diffusion**: concentration gradient of major elements (and minor elements if any).
  - Binary diffusion: specific case of chemical diffusion, where the initial gradient is only for 2 species.

Zhang, Youxue. "Diffusion in minerals and melts: theoretical background." *Reviews in mineralogy and geochemistry* 72.1 (2010): 5-59.





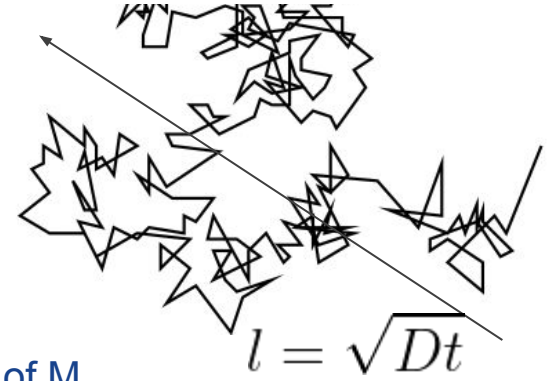
Measuring experimental values of diffusion coefficients

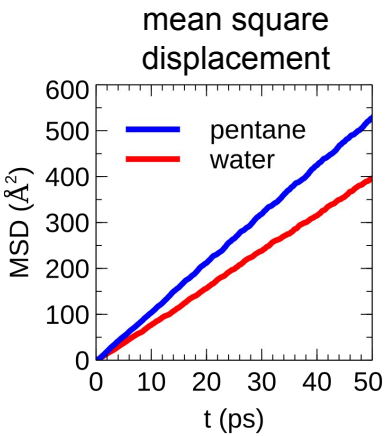
Propagation of individual particles

Molecular dynamics (lecture of M. Salanne):

access to individual trajectories

$$D_i = \lim_{t\to\infty} \frac{1}{6t} \langle |\delta \mathbf{r}_a(t)|^2 \rangle$$





NMR technique: PFG with propagation (lecture of M. Deschamps) Rollet, A. L., Sarou-Kanian, V., & Bessada, C. (2009). Measuring self-diffusion coefficients up to 1500 K: a powerful tool to investigate the dynamics and the local structure of inorganic melts. *Inorganic chemistry*, *48*(23), 10972-10975.

Bullerjahn, Jakob Tómas, Sören von Bülow, and Gerhard Hummer. "Optimal estimates of self-diffusion coefficients from molecular dynamics simulations." *The Journal of Chemical Physics* 153.2 (2020): 024116.

Einstein relations

$$D_i = M_i k T \gamma_i$$ mobility $$M_i = v/F$$

The diffusion of different kinds of species can be investigated through different physical quantities.

Charged particles: Nerst-Einstein relation (lecture of Mohammed Malki) → network **modifiers**

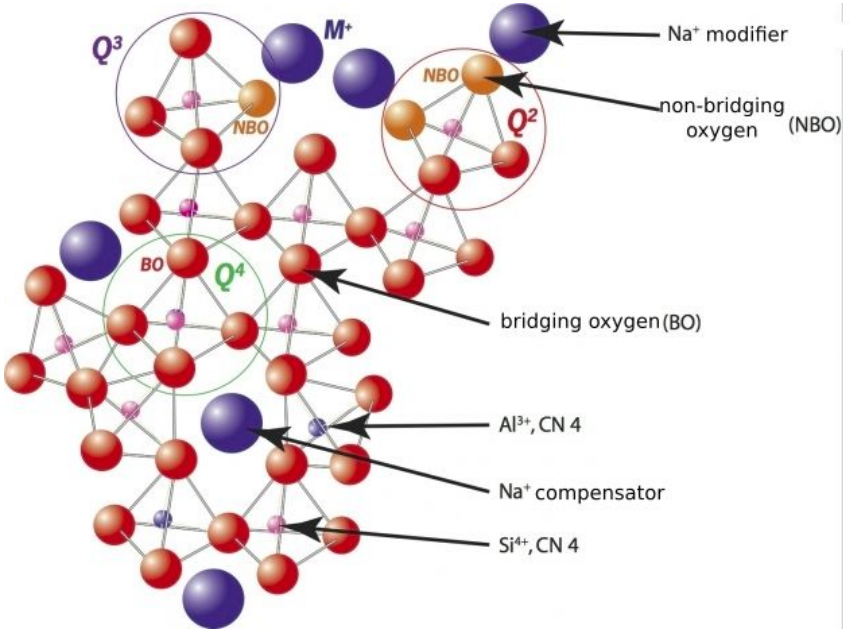
$$D = \frac{\mu_q k T}{q}$$ *q:* charge of ions

Viscous liquids: Stokes-Einstein and Eyring relation (lecture of Daniel Neuville) → network **formers**

$$D = \frac{k_B T}{6\pi\eta r}. \qquad D = \frac{kT}{2\eta r}$$

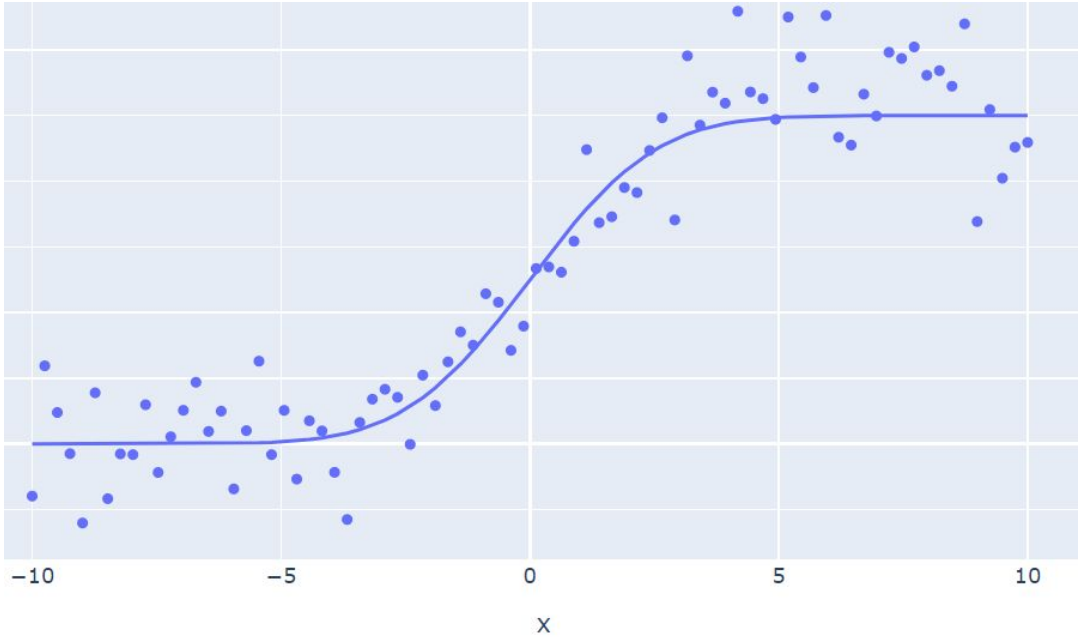
η: viscosity

r: radius of particle or bond length



from USTV website
D. Neuville

Fitting experimental diffusion profiles



Fit known parametric laws through noisy experimental points.

$$n\left(x,t\right)=n_0\,\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right).$$

Subject of practical session today

Importance of :

- spatial resolution and number of points
- experimental noise

Values of diffusivity coefficients in silicate melts

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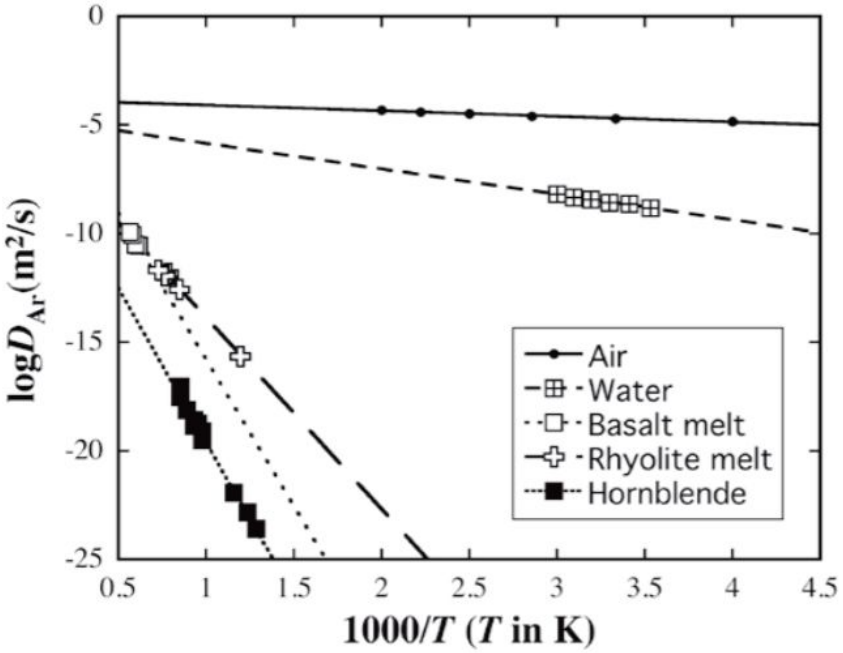
Values of diffusion coefficients in silicate glasses and melts

Diffusion coefficients have low values in silicate melts compared to less viscous fluids.



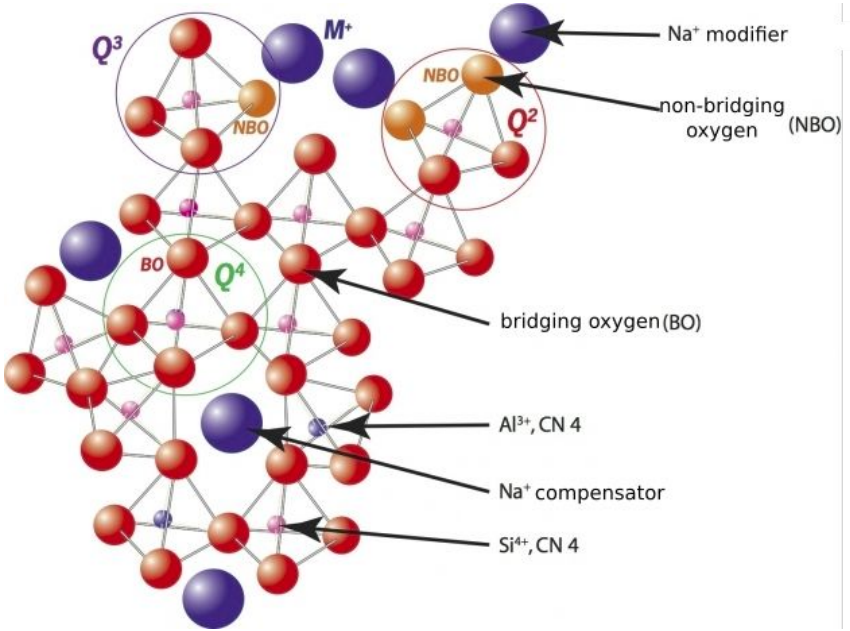
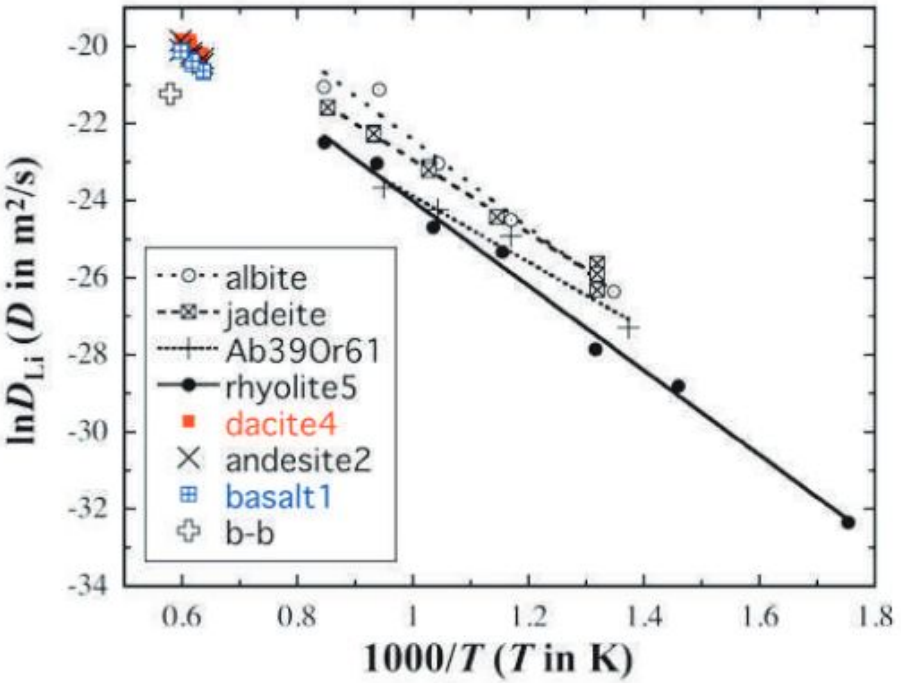


Figure 2. Ar diffusion data in air (gas) (calculated using relations in Cussler 1997), water (liquid) (Wise and Houghton 1966), basalt melt (Nowak et al. 2004), rhyolite melt (Behrens and Zhang 2001) and the mineral hornblende (Harrison 1981).

Values of diffusivities in silicate melts - influence of temperature



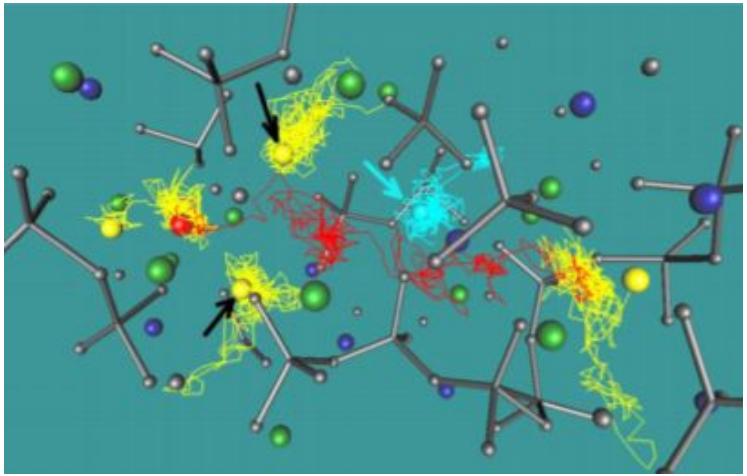
Self-diffusion of lithium in various silicate melts

Zhang, Y., Ni, H., & Chen, Y. (2010). Diffusion data in silicate melts. *Reviews in Mineralogy and Geochemistry*, *72*(1), 311-408.

Origin of diffusion : thermal fluctuations
→ Temperature-activated process

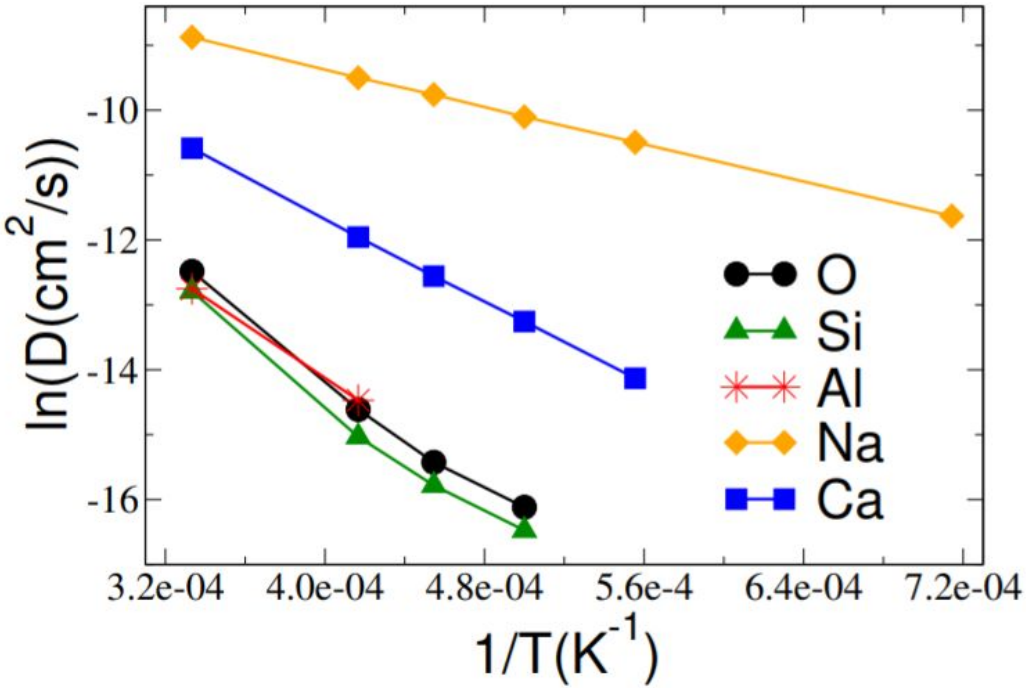
Arrhenian behaviour of trace diffusivities

$$D = D_0 e^{\frac{-E_a}{RT}}$$



Tilocca, Antonio. *The Journal of chemical physics* 133.1 (2010): 014701.

Values of diffusivities in silicate melts - influence of temperature



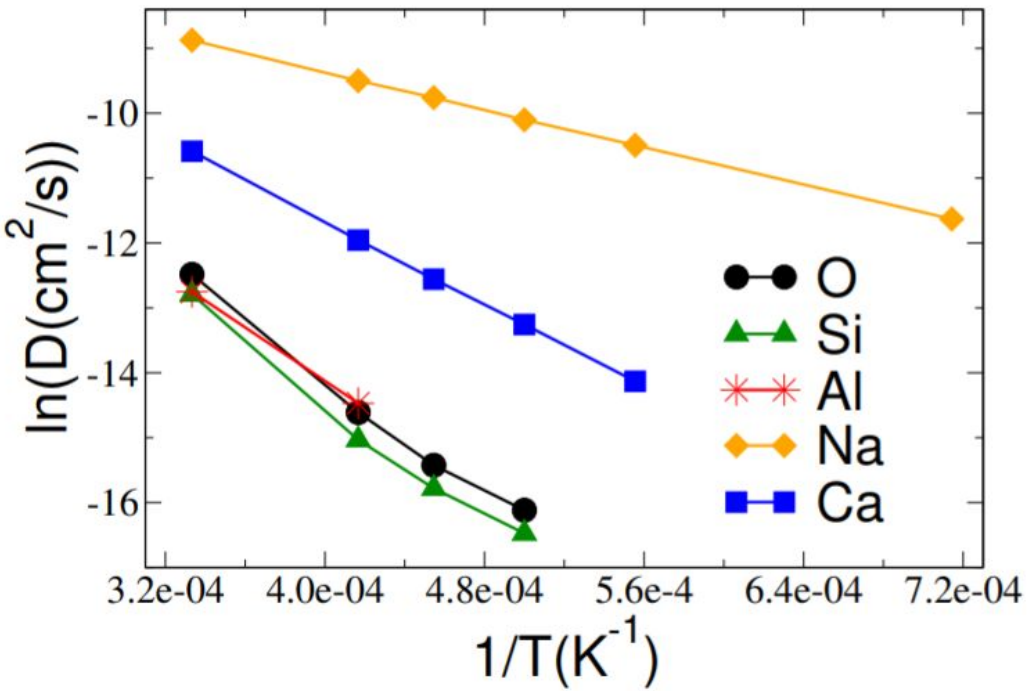
Serva, Alessandra, et al. "Structural and dynamic properties of soda–lime–silica in the liquid phase." *The Journal of Chemical Physics* 153.21 (2020): 214505.

Activation energy related to chemical bonds

Larger for network formers (covalent bonds) than for network modifiers (more ionic bonds).

Activation energy :
~ 100 kJ/mol for alkali species
~ 300 - 400 kJ/mol for network formers

Values of diffusivities in silicate melts - influence of species



D depends on **strength** and **number** of chemical bonds (i.e. on silicate structure)

D(network modifiers) > D(network formers)

D(monovalent alkali ions) > D(divalent alkali-earth ions)

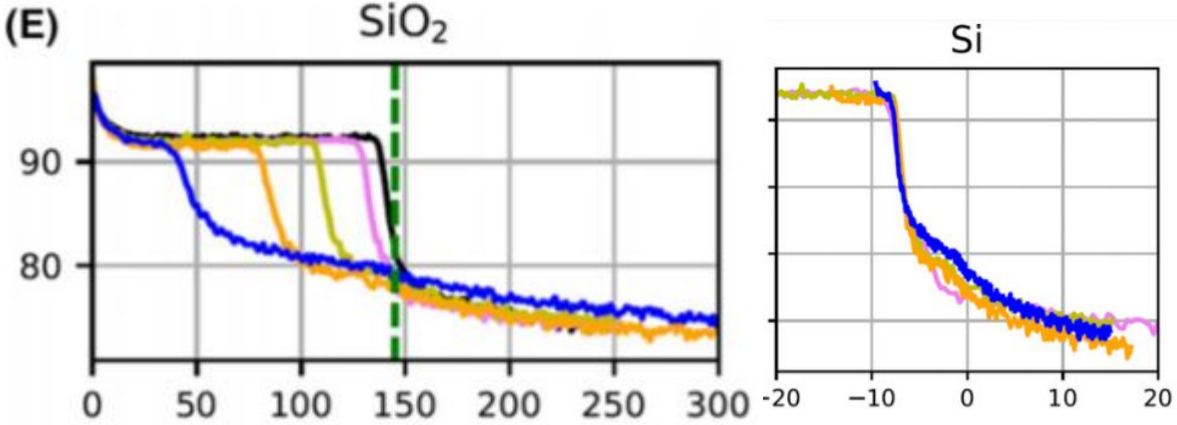
Serva, Alessandra, et al. "Structural and dynamic properties of soda–lime–silica in the liquid phase." *The Journal of Chemical Physics* 153.21 (2020): 214505.

Non-linear diffusion equation

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C)$$

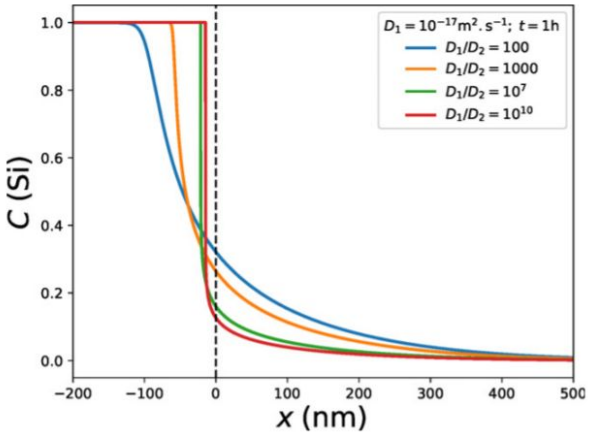
D often considered constant, but sometimes this approximation cannot be used

silica thin film	soda-lime glass
smaller D	larger D



Fonné, Jean-Thomas, et al. "Aluminum-enhanced alkali diffusion from float glass to PVD-sputtered silica thin films." *Journal of the American Ceramic Society* 101.4 (2018): 1516-1525.

$$D_{\mathrm{Si}} = D_0 \exp(-\beta C_{\mathrm{Si}})$$



Asymmetric concentration profile

Thermodynamic origin of diffusion

Thermodynamic formalism of molecular diffusion

Velocity induced by the gradient of a potential

$$J_i = C_i M_i \frac{\partial \mu_i}{\partial x}$$

$$D_i = C_i M_i \frac{\partial \mu_i}{\partial C_i}$$

μ: chemical potential

Ideal solutions

$$\mu_i = \mu_{i,0} + kT \log C_i \gamma_i$$

$$D_i = kT M_i \gamma_i$$

γ: activity coefficient (1 for ideal solution)

Application: phase separation

Gibbs free energy

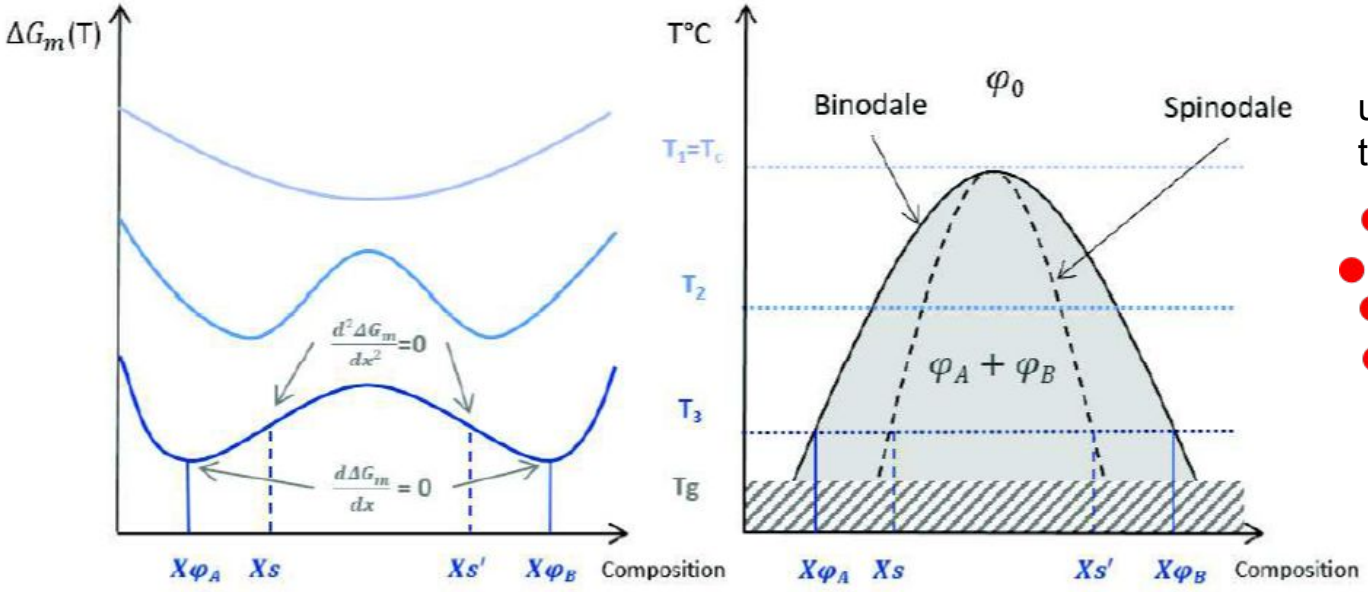
$$\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T + \sum_i \mu_i\,\mathrm{d}N_i$$

$$D_i = C_i M_i \frac{\partial \mu_i}{\partial C_i}$$

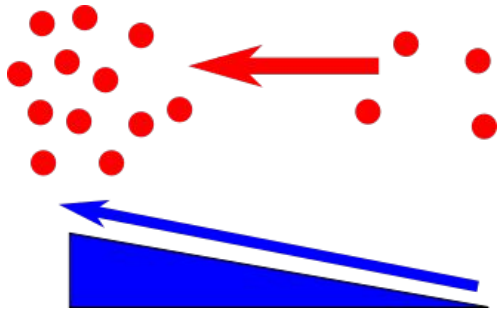
$$D_i = \frac{C_i M_i}{V}\frac{\partial^2 G}{\partial^2 C_i}$$

> 0 for convex G

< 0 for concave G



uphill diffusion: flux goes “up” the gradient



Application: phase separation

Gibbs free energy

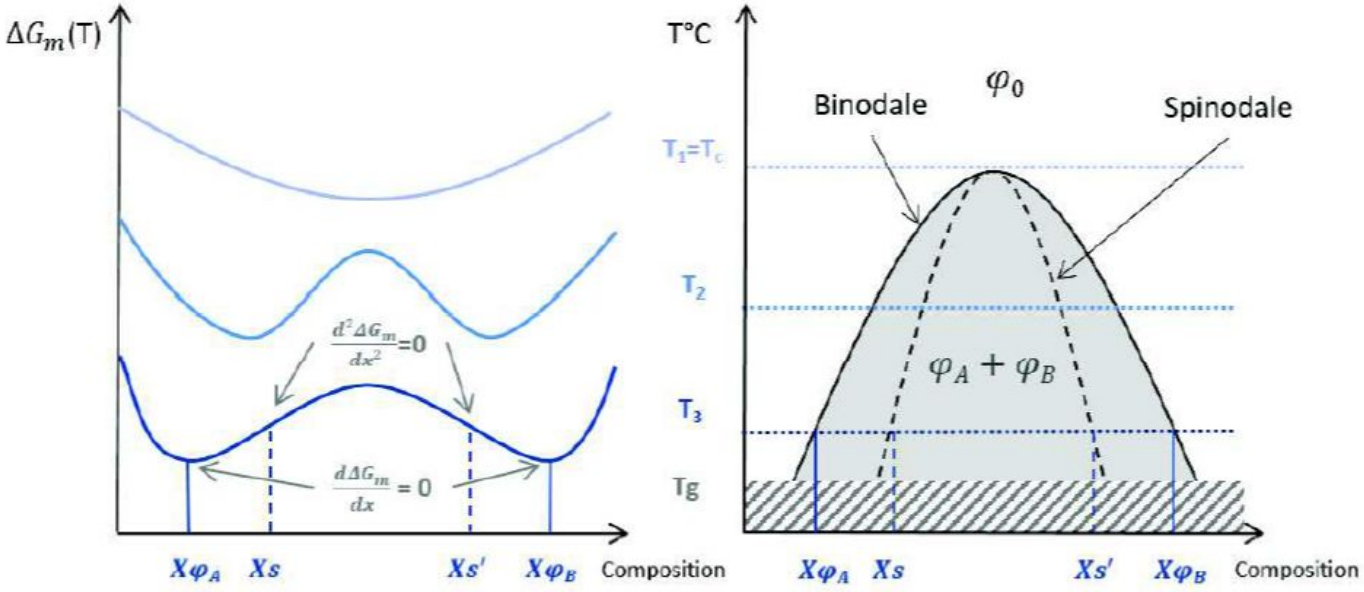
$$dG = V\,dp - S\,dT + \sum_i \mu_i\,dN_i$$

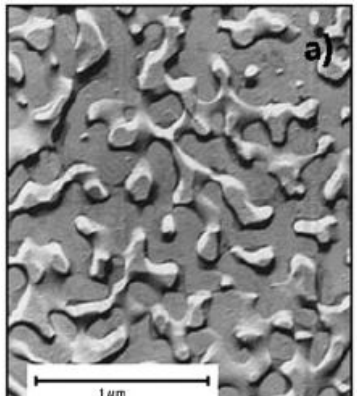
$$D_i = C_i M_i \frac{\partial \mu_i}{\partial C_i}$$

$$D_i = \frac{C_i M_i}{V} \frac{\partial^2 G}{\partial^2 C_i}$$

> 0 for convex G

< 0 for concave G





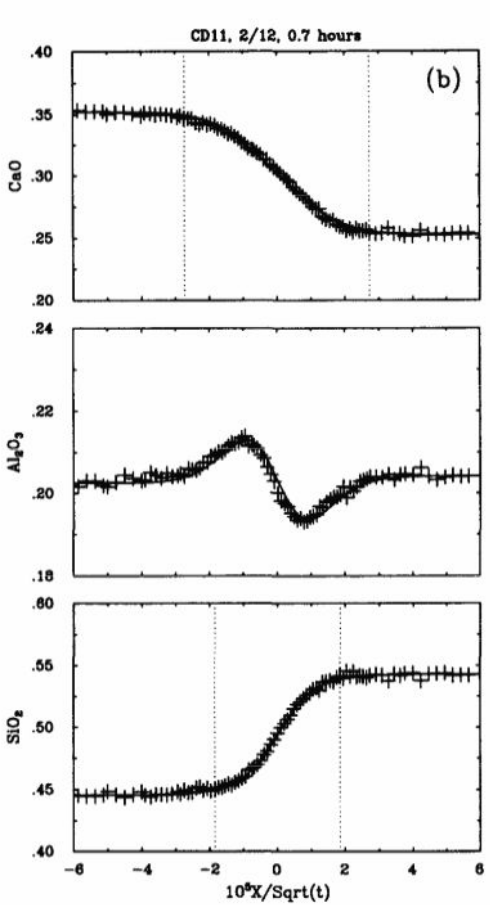
Multicomponent diffusion

Multicomponent diffusion

Diff Couple	$D(SiO_2)$ ($\mu m^2/s$)
Si–Ti	19.5 ± 2.8
Si–Al	15.7 ± 1.5
Si–Mg	30.0 ± 1.7
Si–Ca	28.7 ± 2.8
Si–Na	44.2 ± 4.0
Si–K	102.9 ± 19.5
Ti–Mg	
Mg–Ca	
Ca–Na	
An diss	

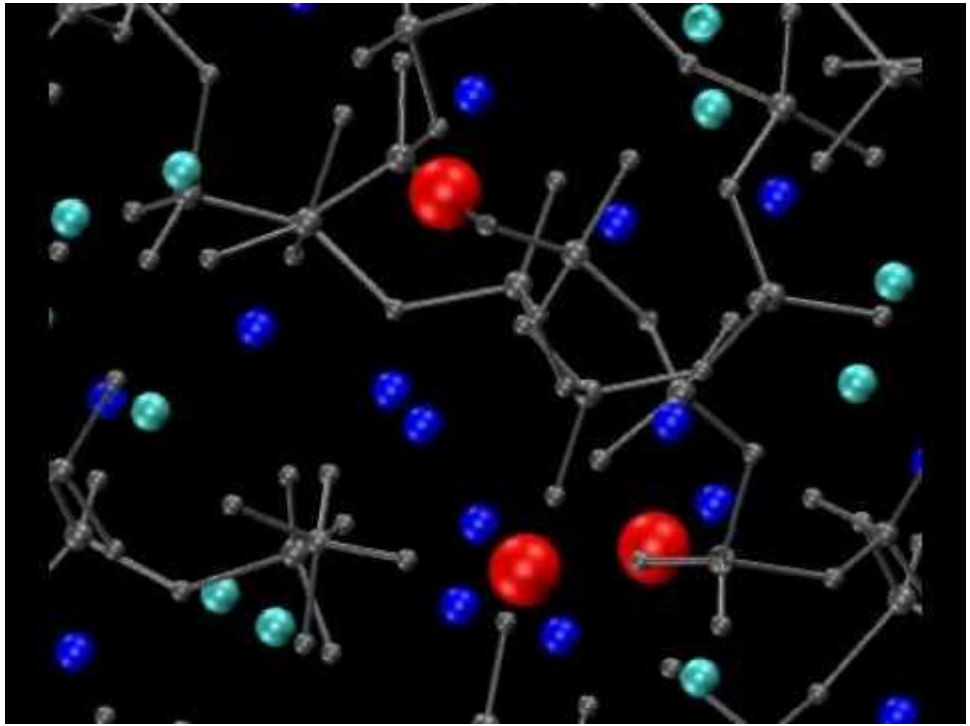
chemical diffusion: D value depends strongly on endmember

Guo, Chenghuan, and Youxue Zhang. "Multicomponent diffusion in silicate melts: SiO2–TiO2–Al2O3–MgO–CaO–Na2O–K2O System." *Geochimica et Cosmochimica Acta* 195 (2016): 126-141.



uphill diffusion

Liang, Yan, Frank M. Richter, and E. Bruce Watson. *Geochimica et Cosmochimica Acta* 60.24 (1996): 5021-5035.



https://www.youtube.com/watch?v=S0UIMspT4jw

Tilocca, Antonio. *The Journal of chemical physics* 133.1 (2010): 014701.

Generalization of the diffusion equation to multicomponent diffusion

Flux of one species down its own concentration gradient

$$\mathbf{j} = -D\nabla C$$

Flux of one species down the concentration gradient **of all species**

$$\mathbf{j}_i(\mathbf{x}) = -\sum_k D_{ik}\nabla C_k(\mathbf{x})$$

Example of soda-lime glass

$$\mathbf{j}_{Na}(\mathbf{x}) = -D_{NaNa}\nabla C_{Na}(\mathbf{x}) - D_{NaCa}\nabla C_{Ca}(\mathbf{x}) - D_{NaSi}\nabla C_{Si}(\mathbf{x})$$

$$\mathbf{j}_{Ca}(\mathbf{x}) = -D_{CaNa}\nabla C_{Na}(\mathbf{x}) - D_{CaCa}\nabla C_{Ca}(\mathbf{x}) - D_{CaSi}\nabla C_{Si}(\mathbf{x})$$

$$\mathbf{j}_{Si}(\mathbf{x}) = \dots$$

Diffusion matrix

$$\mathbf{j}_i(\mathbf{x}) = -\sum_k D_{ik} \nabla C_k(\mathbf{x})$$

$$\frac{\partial C_i}{\partial t} = \sum_k D_{ik} \Delta C_k(\mathbf{x})$$

$$\frac{\partial \mathbf{C}}{\partial t} = \mathbf{D} \Delta \mathbf{C}(\mathbf{x})$$

$$\frac{\partial}{\partial t} \begin{pmatrix} C_{\mathrm{Na}} \\ C_{\mathrm{Ca}} \\ C_{\mathrm{Al}} \\ C_{\mathrm{Si}} \end{pmatrix} = \begin{pmatrix} D_{\mathrm{Na,Na}} & D_{\mathrm{Na,Ca}} & D_{\mathrm{Na,Al}} & D_{\mathrm{Na,Si}} \\ D_{\mathrm{Ca,Na}} & D_{\mathrm{Ca,Ca}} & D_{\mathrm{Ca,Al}} & D_{\mathrm{Ca,Si}} \\ D_{\mathrm{Al,Na}} & D_{\mathrm{Al,Ca}} & D_{\mathrm{Al,Al}} & D_{\mathrm{Al,Si}} \\ D_{\mathrm{Si,Na}} & D_{\mathrm{Si,Ca}} & D_{\mathrm{Si,Al}} & D_{\mathrm{Si,Si}} \end{pmatrix} \Delta \begin{pmatrix} C_{\mathrm{Na}} \\ C_{\mathrm{Ca}} \\ C_{\mathrm{Al}} \\ C_{\mathrm{Si}} \end{pmatrix}$$

Characteristic of the diffusion matrix: eigenvalues and eigenvectors

Let us define

$$\mathbf{D} = \mathbf{P}\mathbf{L}\mathbf{P}^{-1},$$

with

$$\mathbf{L} = \begin{pmatrix} \lambda_1 & \dots & \dots \\ \vdots & \ddots & \dots \\ \vdots & \vdots & \lambda_{n-1} \end{pmatrix}$$

the diagonal matrix of **eigenvalues** λ_i, and $\mathbf{P} = (\mathbf{v}_1, \dots, \mathbf{v}_{n-1})$ is the block matrix of the **eigenvectors** $\mathbf{v}_i$: $\mathbf{L}\mathbf{v}_i = \lambda_i \mathbf{v}_i$

With $\tilde{\mathbf{C}} = \mathbf{P}^{-1}\mathbf{C}$ and $\Delta\tilde{\mathbf{C}} = \mathbf{P}^{-1}\Delta\mathbf{C}$,

$$\frac{\partial \tilde{\mathbf{C}}}{\partial t} = \mathbf{L}\nabla^2\tilde{\mathbf{C}}$$

$$\tilde{C}_i(x,t) = \Delta\tilde{C}_i \operatorname{erf}\left(\frac{x}{\sqrt{2\lambda_i t}}\right).$$

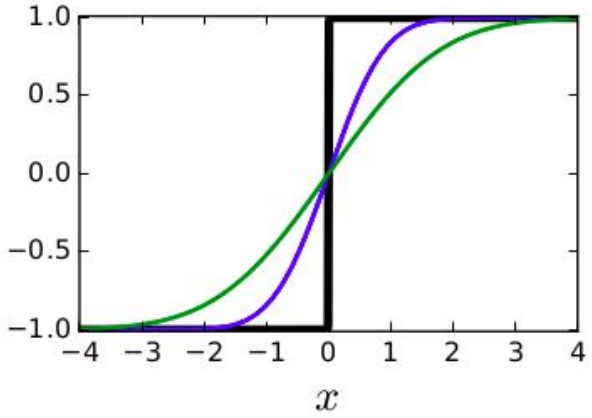
Characteristic of the diffusion matrix: eigenvalues and eigenvectors

$$\mathbf{D} = \mathbf{P}\mathbf{L}\mathbf{P}^{-1},$$

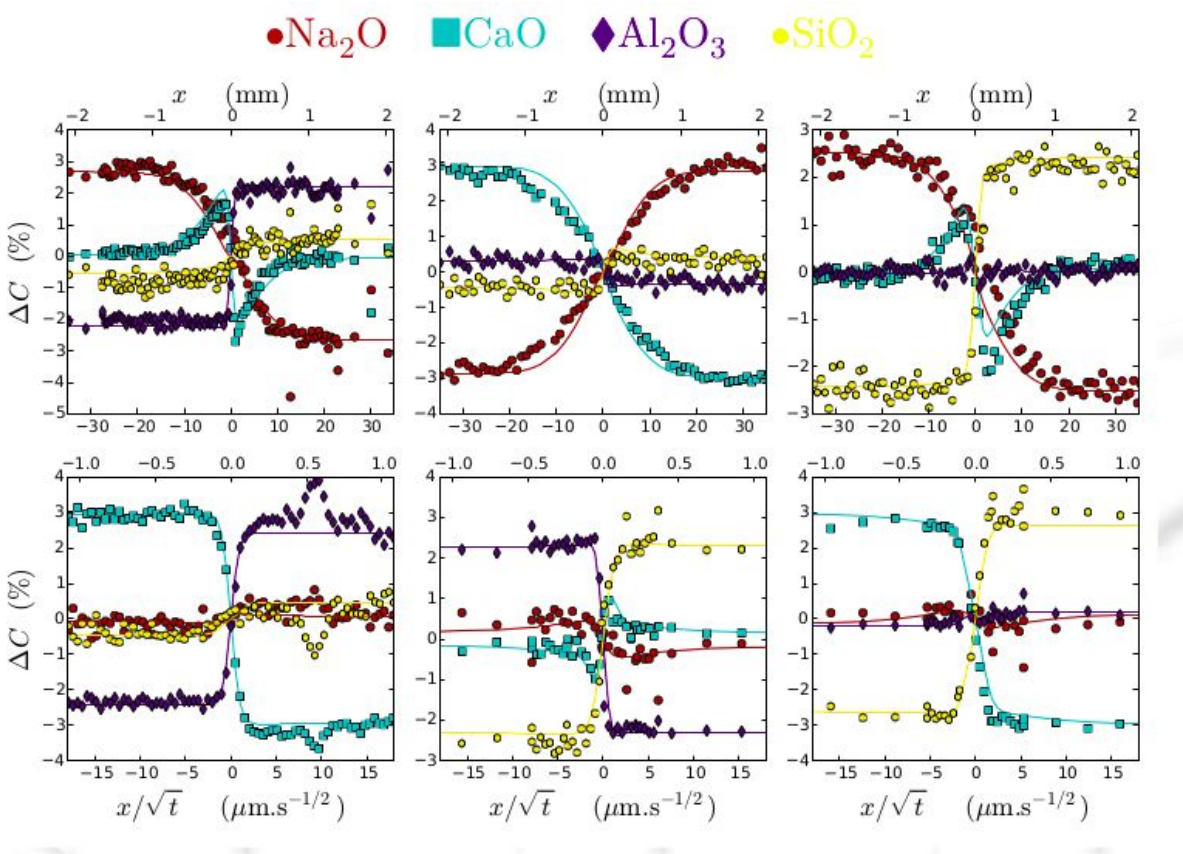
With $\tilde{\mathbf{C}} = \mathbf{P}^{-1}\mathbf{C}$ and $\tilde{\Delta\mathbf{C}} = \mathbf{P}^{-1}\Delta\mathbf{C}$,

$$\frac{\partial \tilde{\mathbf{C}}}{\partial t} = \mathbf{L}\nabla^2\tilde{\mathbf{C}}$$

$$\tilde{C}_i(x,t) = \tilde{\Delta C}_i \operatorname{erf}\left(\frac{x}{\sqrt{2\lambda_i t}}\right).$$



Example: multicomponent diffusion in a quaternary system

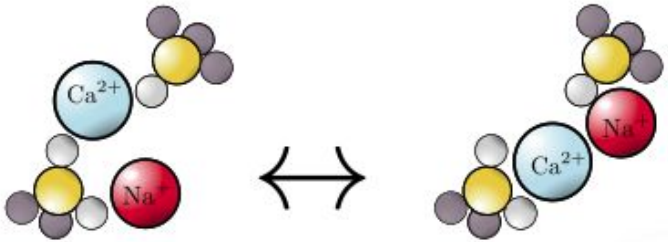


Claireaux, Corinne, et al. "Atomic mobility in calcium and sodium aluminosilicate melts at 1200 C." *Geochimica et Cosmochimica Acta* 192 (2016): 235-247.

Dominant eigenvector

$$\Delta \begin{pmatrix} C_{Na_2O} \\ C_{CaO} \\ C_{Al_2O_3} \\ C_{SiO_2} \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \\ 0 \\ 0 \end{pmatrix}$$

$$\frac{1}{2}Ca^{2+} \leftrightarrow Na^{+}$$

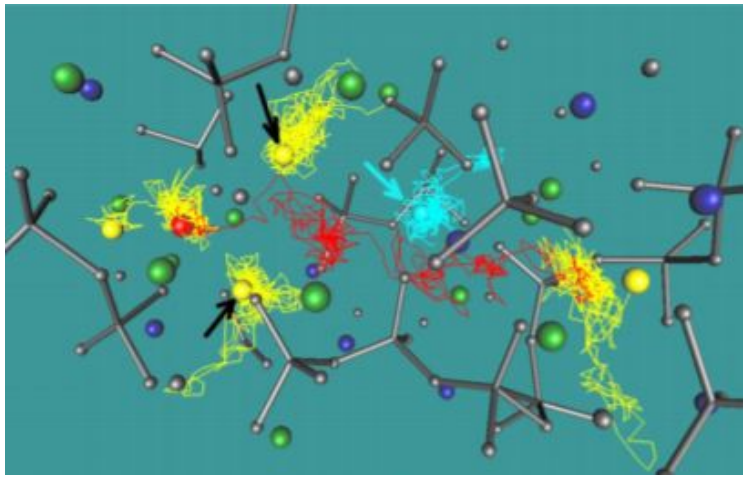


Claireaux, Corinne, et al. "Atomic mobility in calcium and sodium aluminosilicate melts at 1200 C." *Geochimica et Cosmochimica Acta* 192 (2016): 235-247.

Other eigenvectors:
involve network formers,
smaller diffusivity value

Conclusions

Diffusion is a microscopic phenomenon, with macroscopic consequences (corrosion of refractories for example).



The complex structure of silicate melts has strong consequences about diffusion:

- D(network formers) << D(modifiers)
- Strong multicomponent effects (couplings)

Diffusion is a thermally activated phenomenon.