MODELING OF MELTS AND GLASSES BY MD SIMULATION: AN INTRODUCTION

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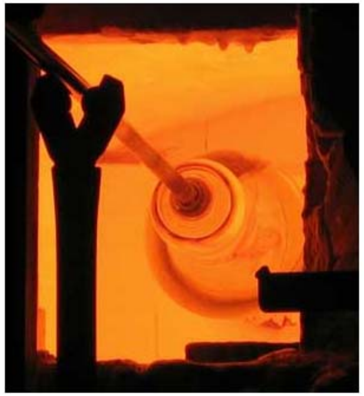
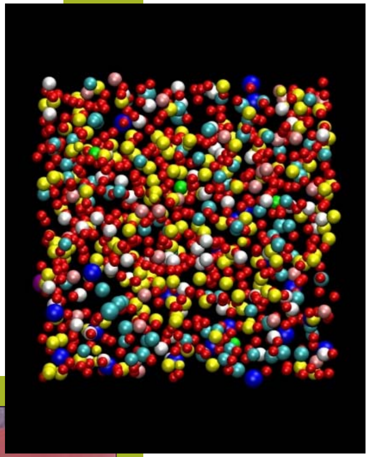
Le verre



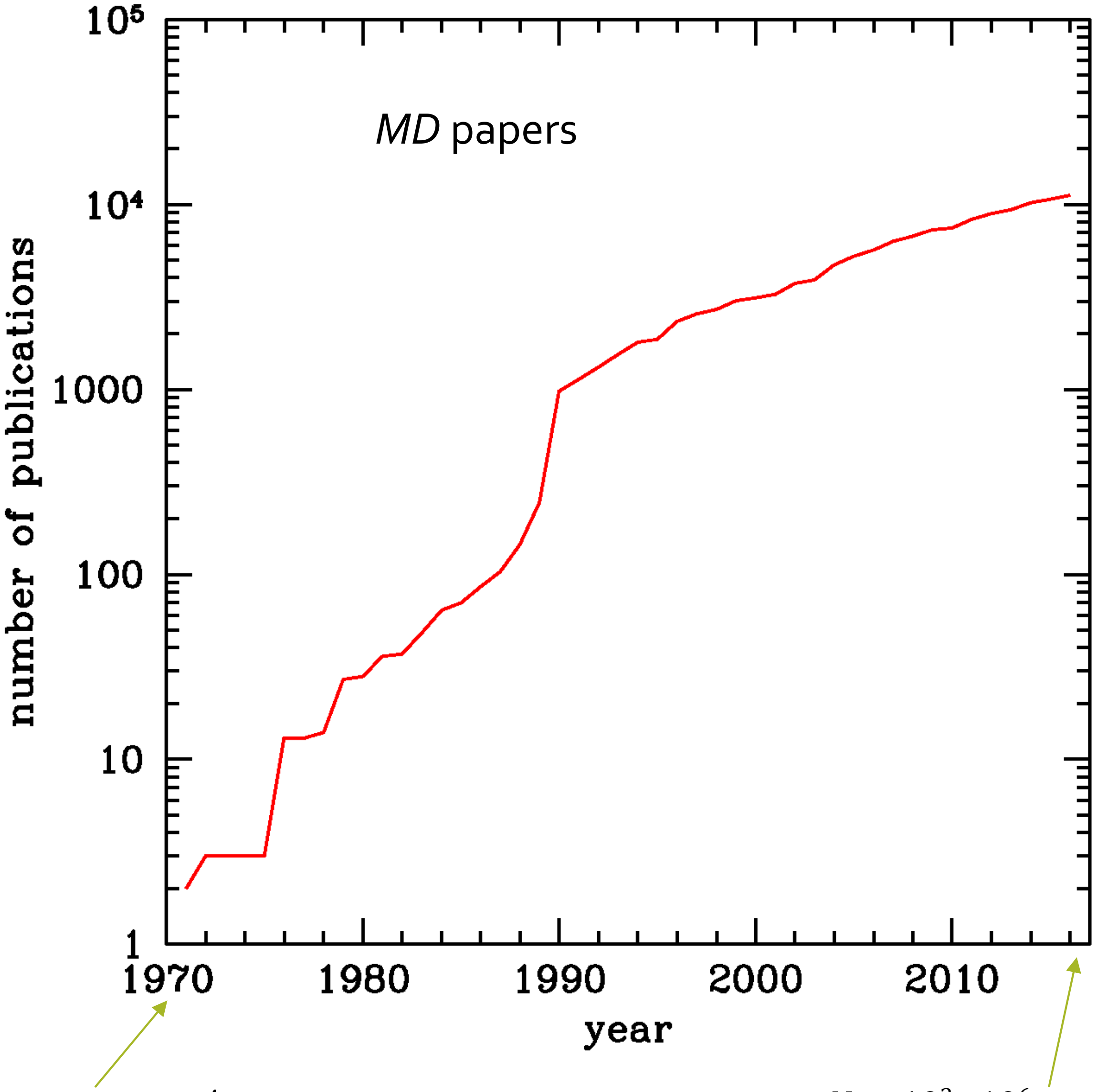


Obsidienne

Basalte de dorsale océanique

A brief history of MD simulations

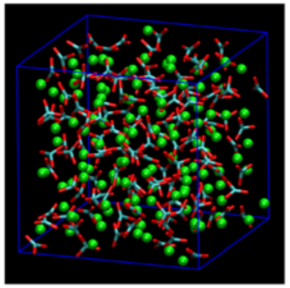
Milestone	
1946	***Genesis of the Monte Carlo method (Von Neumann et al. at Los Alamos)***
1953	***Seminal paper by Metropolis, Rosenbluth^2 and Teller***: *« EOS calculations by fast computing machines »*
1956	***B.J.Alder and T.E. Wainwright made the first presentation of a MD simulation***
1964	***A. Rahman publishes the first MD simulation with a continuous potential***
1967	***L. Verlet proposes the leap-frog algorithm***
1972	***The first MD simulation of water by F.H. Stillinger and A. Rahman***
1976	***The first MD simulation of silica (glass) by Woodcock, Angell and Cheeseman***
1985	***R. Car and M. Parrinello combine MD and density-functional theory***
....	
....	
Present	*available on the web*: CHARMM, AMBER, DLPOLY, GROMACS, LAMMPS, TINKER, VASP, CP2K, SIESTA,..



$N \sim 100, trun \sim 10^4$ $MD\ steps$

$N = 10^3 \sim 10^6, trun \sim 10^8$ $MD\ steps$

General schema for MD simulation



N= 10^3-10^6 atoms in a cubic box with periodic boundary conditions

Classical Force field

$U_{pot}=\Sigma u_{ij} + \Sigma u_{ijk} + \ldots$

or

Ab initio calculation with DFT + pseudopotentials

Molecular Dynamics

$m_i a_i = \Sigma F_{ij}$

integration time step ~ 10^{-15}s

atomic trajectories (10^7~10^8 steps with *classical* MD and only 10^4 ~10^5 with AIMD)

ergodic principle

time averaging for equilibrium properties

$\langle A \rangle = (1/N)\, \Sigma A_i$ for N steps

Thermo. Properties

N,V,E → <T>, <P>

N,P,T → <V>

-EOS

-structure (pair distribution functions,..)

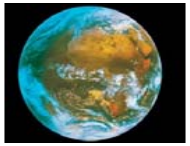
-transport coefficients (viscosity, ..)

-phase equilibria (L-S, L-L, L-V)

Validation step:

comparison with experimental data

e.g. EOS, structure, transport coeff.



if necessary go to Force field

The force field

empirical potentials
∑ atom-atom pair potentials ➡

$U_{ij} = U_{ij}^{Rep} + U_{ij}^{Elec} + U_{ij}^{Disp} + U_{ij}^{Cov}$

U_{ij}^{Rep} = repulsion energy ($\approx e^{-r/\rho}$, $1/r^{12}$)

U_{ij}^{Elec} = electrostatic energy ($\approx z_i z_j / r_{ij}$) *

U_{ij}^{Disp} = dispersion energy ($\approx -1/r^6$)

U_{ij}^{Cov} = covalent bond ($\approx D_e\,[(1- e^{-(r-l)/\lambda})^2 -1]$)

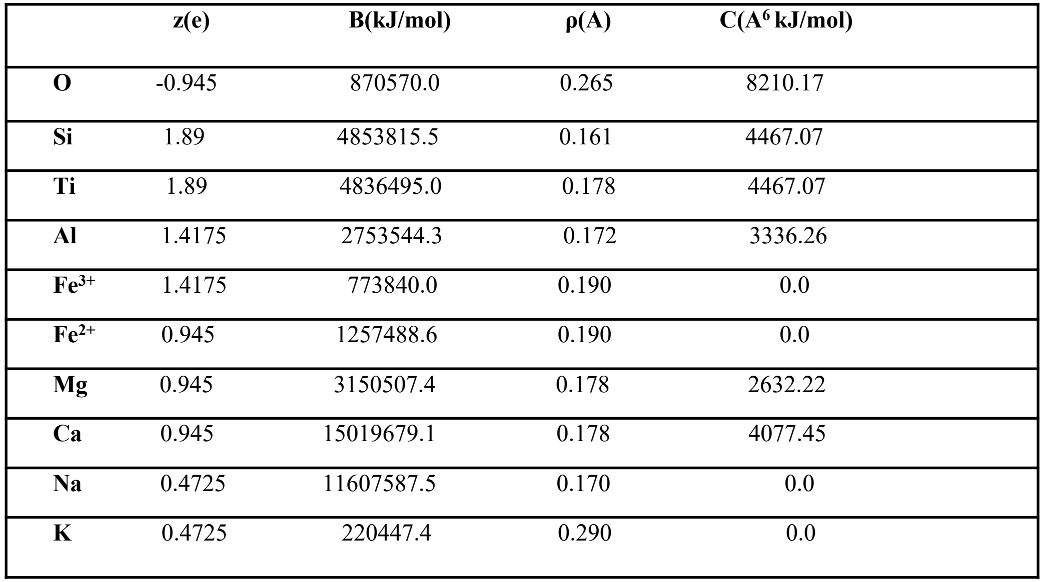
Other choice:

- electronic structure calculation by AIMD (much more expensive x 10^3-10^4)

Requirements: evaluation of transport properties, phase equilibria, reactive species,..
large system size + long time dynamics → Classical MD with empirical potentials

**Note*: the use of effective charges (z_i) in empirical potentials is crucial to account (up to some extent) for polarization effects other choice: force field with explicit polarization (e.g. PIM , Madden et al. Faraday Disc. 2003)*

A force field for silicates



	z(e)	B(kJ/mol)	ρ(A)	C(A^6 kJ/mol)
O	-0.945	870570.0	0.265	8210.17
Si	1.89	4853815.5	0.161	4467.07
Ti	1.89	4836495.0	0.178	4467.07
Al	1.4175	2753544.3	0.172	3336.26
Fe^{3+}	1.4175	773840.0	0.190	0.0
Fe^{2+}	0.945	1257488.6	0.190	0.0
Mg	0.945	3150507.4	0.178	2632.22
Ca	0.945	15019679.1	0.178	4077.45
Na	0.4725	11607587.5	0.170	0.0
K	0.4725	220447.4	0.290	0.0

Guillot and Sator, GCA 2007

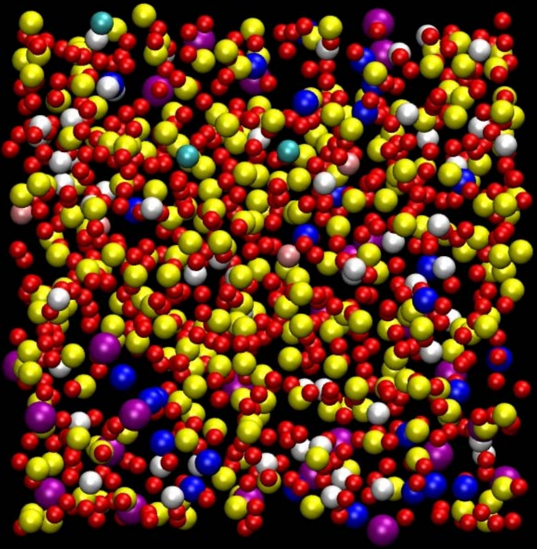
Since then: new parameters for repulsion-dispersion forces (B,ρ,C) and introduction of X-O covalent forces
→ drastic improvement of transport properties for silicate melts
Dufils et al., Chem. Geol. 2017

Chemical compositions (weight fraction) of the silicate melts investigated in this study

Silicate	SiO_2 (wt%)	TiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	FeO (wt%)	MgO (wt%)	CaO (wt%)	Na_2O (wt%)	K_2O (wt%)	Total
Rhyolite (Ry)	74.51 (257)	0.10 (0)	13.25 (54)	0.32 (1)	1.28 (3)	0.08 (0)	0.75 (3)	4.15 (28)	5.64 (25)	100.08 (1000)
Andesite (And)	56.65 (203)	1.01 (3)	17.41 (73)	4.63 (12)	3.53 (11)	4.30 (23)	7.38 (28)	3.23 (22)	1.56 (7)	99.70 (998)
Basalt(MORB)	50.59 (185)	1.52 (4)	15.11 (65)	1.15 (3)	8.39 (26)	7.77 (42)	11.87 (47)	2.94 (21)	0.13 (1)	99.47 (1000)
Mars basalt (BM)	47.68 (176)	0.54 (1)	10.96 (48)	3.09 (9)	15.82 (49)	12.62 (69)	7.96 (31)	2.68 (19)	0.06 (0)	101.41 (1000)
Green glass (LG15)	48.00 (179)	0.26 (1)	7.74 (34)		16.50 (52)	18.20 (101)	8.57 (34)			99.27 (999)
Black glass (LG14)	34.00 (136)	16.40 (50)	4.60 (22)		24.50 (83)	13.30 (79)	6.90 (30)	0.23 (2)	0.16 (0)	100.09 (1000)
Komatiite (Ko)	46.73 (168)	0.31 (1)	6.30 (27)		10.76 (32)	28.42 (152)	6.29 (24)	0.85 (6)	0.13 (1)	99.79 (1001)
Peridotite (Pe)	45.10 (159)		2.80 (12)		10.40 (31)	38.40 (203)	3.40 (13)			100.10 (1001)
Olivine (Ol)	40.68 (142)		0.01 (0)		8.76 (25)	50.52 (262)	0.06 (0)			100.03 (1000)
Allende m. (All)	38.57 (147)	0.14 (0)	3.71 (17)		24.79 (79)	29.23 (166)	2.62 (11)	0.48 (3)		99.54 (1000)
Fayalite (Fa)	29.49 (143)				70.51 (286)					100.00 (1001)

Rhyolite

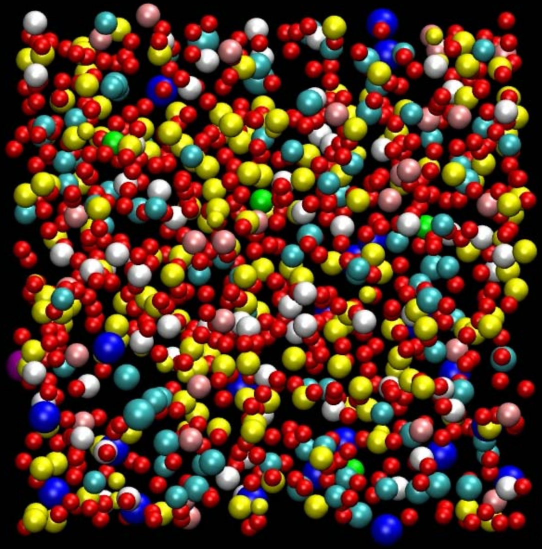
~75 wt% SiO_2



2.23 g/cm^3

MORB

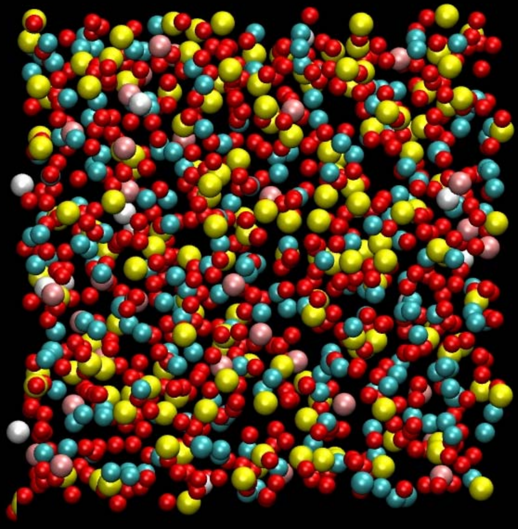
~50 wt% SiO_2



2.55 g/cm^3

Peridotite

~45 wt% SiO_2



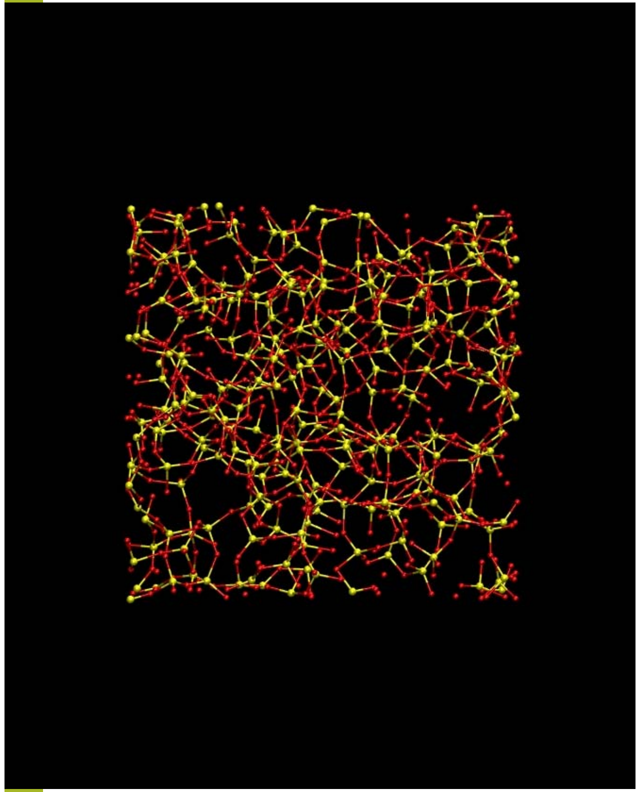
2.61 g/cm^3

O red
Si yellow
Ti green
Al white
Fe pink

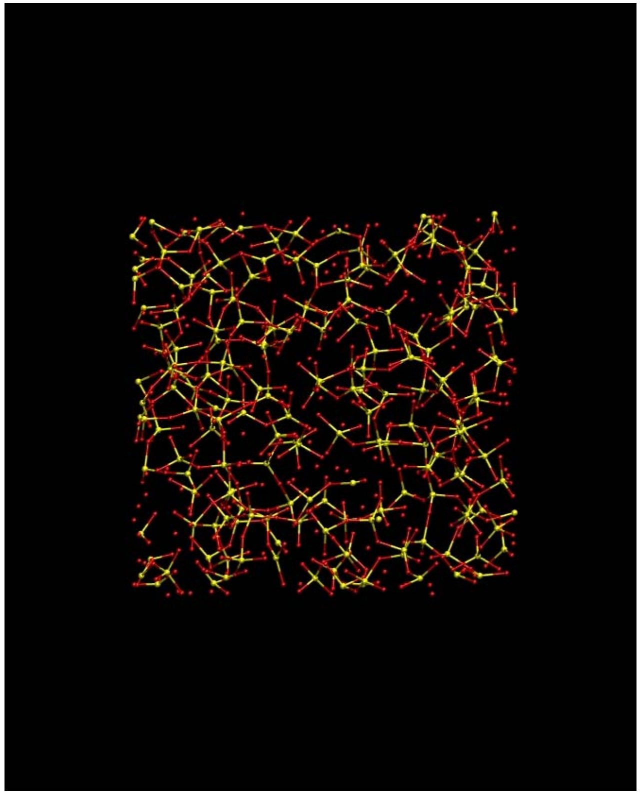
Mg light blue
Ca light blue
Na blue
K purple

2273K, ~1 bar

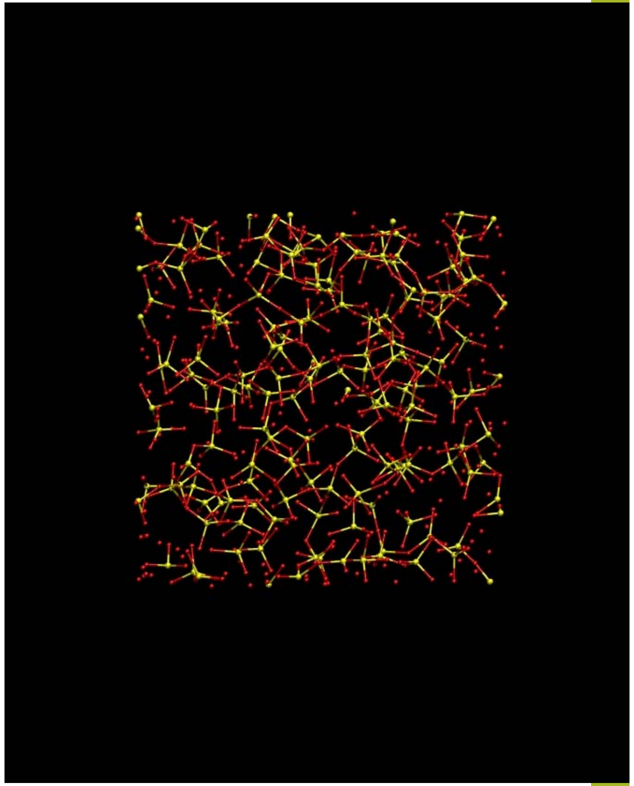
Fragility →



Rhyolite
75% SiO_2

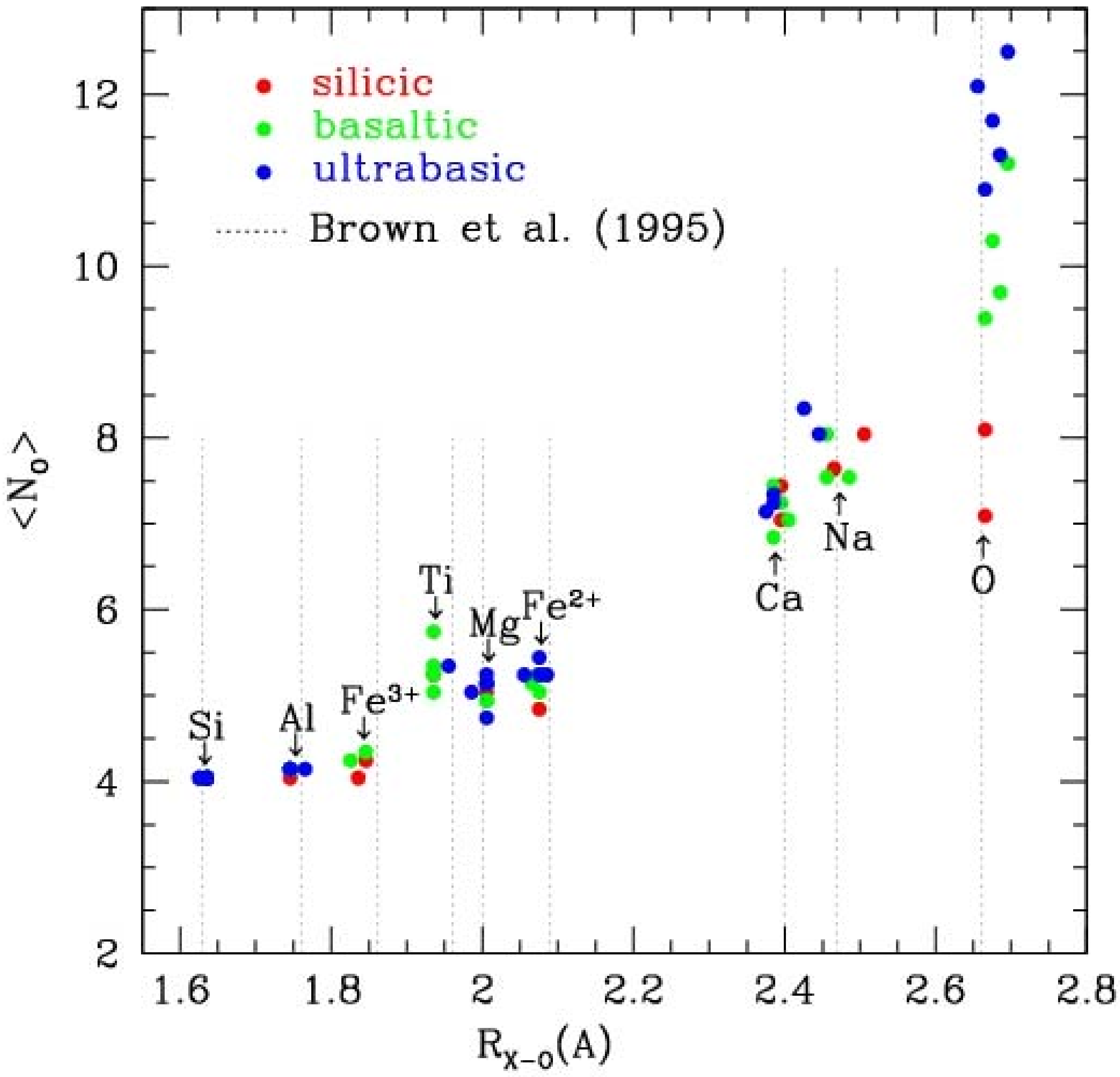


MORB
50% SiO_2

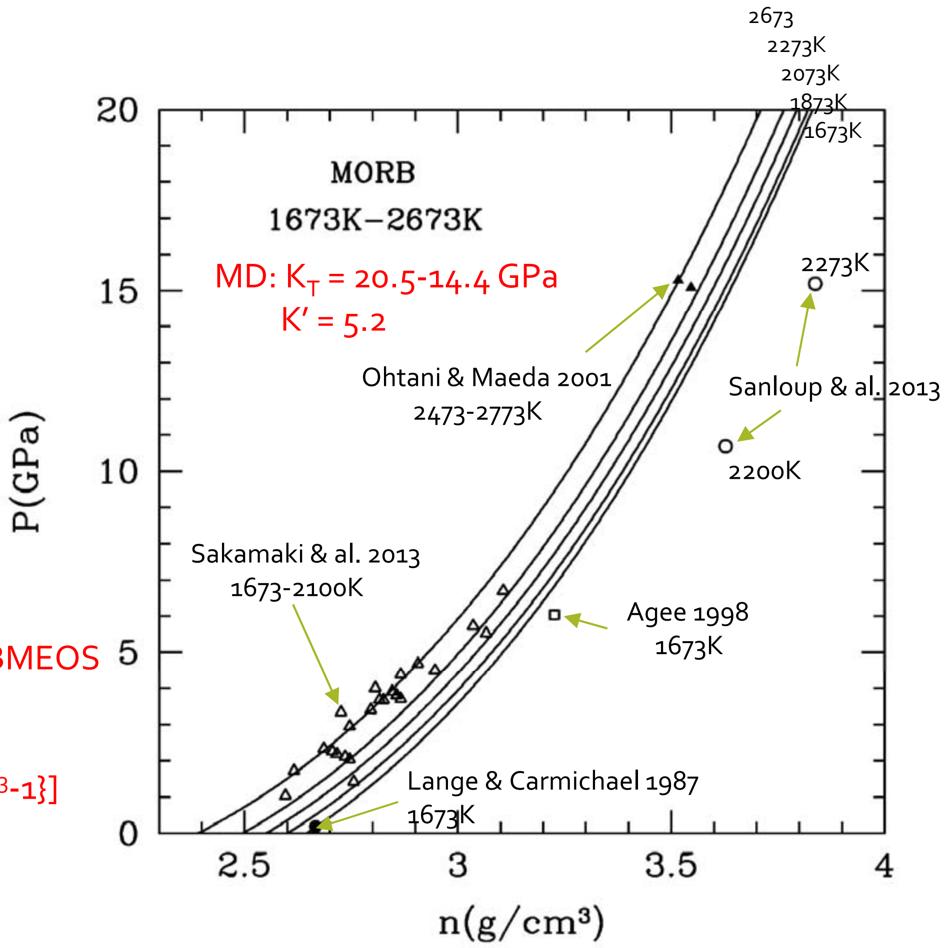


Peridotite
45% SiO_2

O red
Si yellow



● silicic
● basaltic
● ultrabasic
Brown et al. (1995)
Si
Al
Fe^{3+}
Ti
Mg
Fe^{2+}
Ca
Na
O
12
10
8
6
4
2
1.6
1.8
2
2.2
2.4
2.6
2.8
$\langle N_o \rangle$
R_{X-O}(A)



MD: K_T = 20.5-14.4 GPa
K' = 5.2

Ohtani & Maeda 2001
2473-2773K

Sanloup & al. 2013
2273K
2200K

Sakamaki & al. 2013
1673-2100K

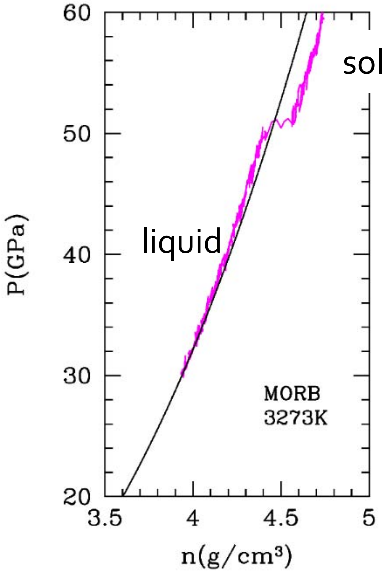
Agee 1998
1673K

Lange & Carmichael 1987
1673K

Note: MD results fitted by BMEOS

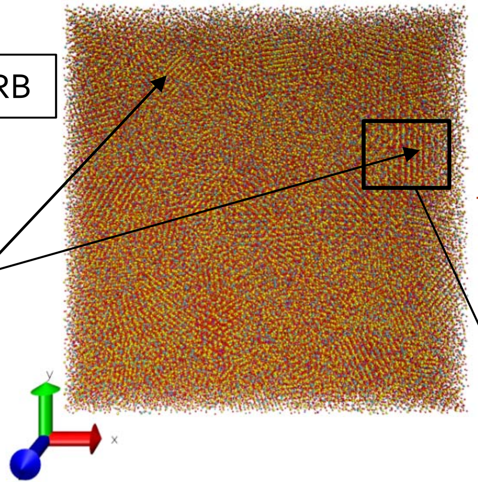
$$P=1.5K_T\{(\rho/\rho_o)^{7/3}-(\rho/\rho_o)^{5/3}\}\times[1-0.75(4-K')\{(\rho/\rho_o)^{2/3}-1\}]$$

Partial crystallization of a MORB

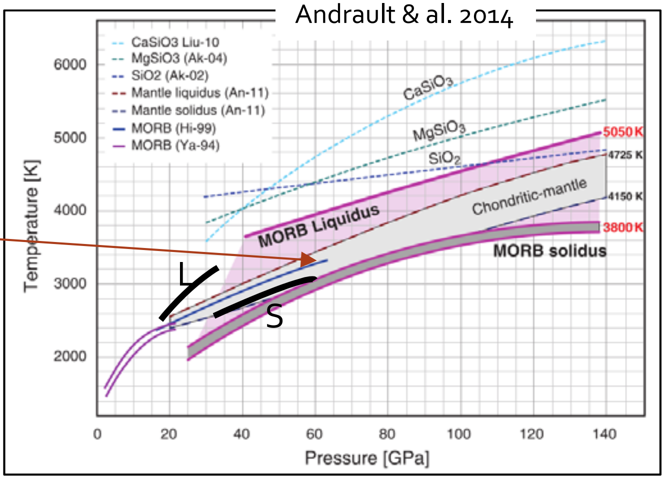


solid

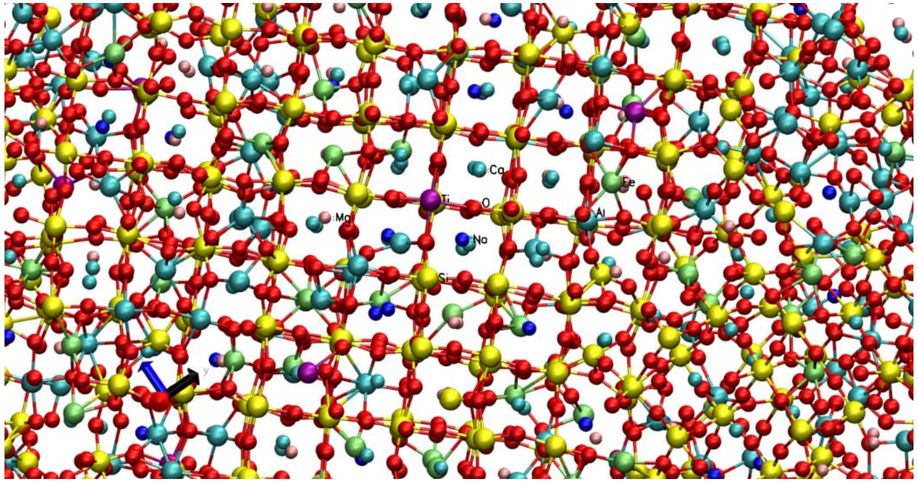
N = 650,000 atoms



Andrault & al. 2014



Pv

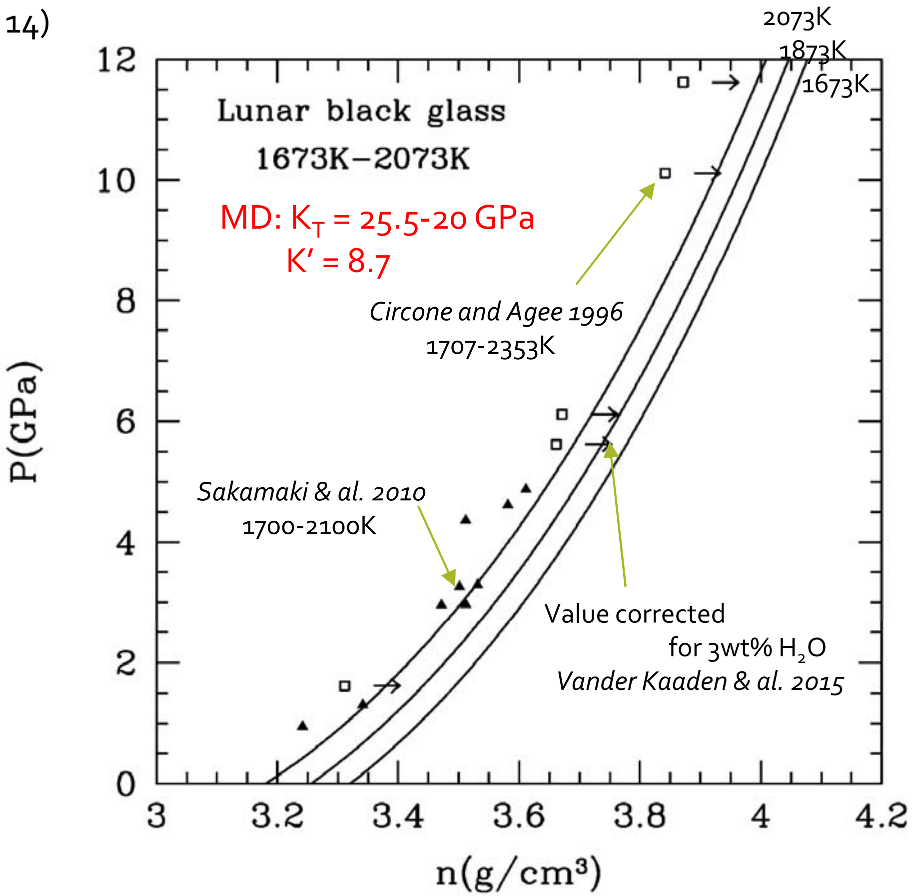


Lunar black glass (Apollo 14)

Basalt

Ti-rich (16.4 wt%)

Fe-rich (24.5 wt%)



MD: K_T = 25.5-20 GPa

K' = 8.7

Circone and Agee 1996

1707-2353K

Sakamaki & al. 2010

1700-2100K

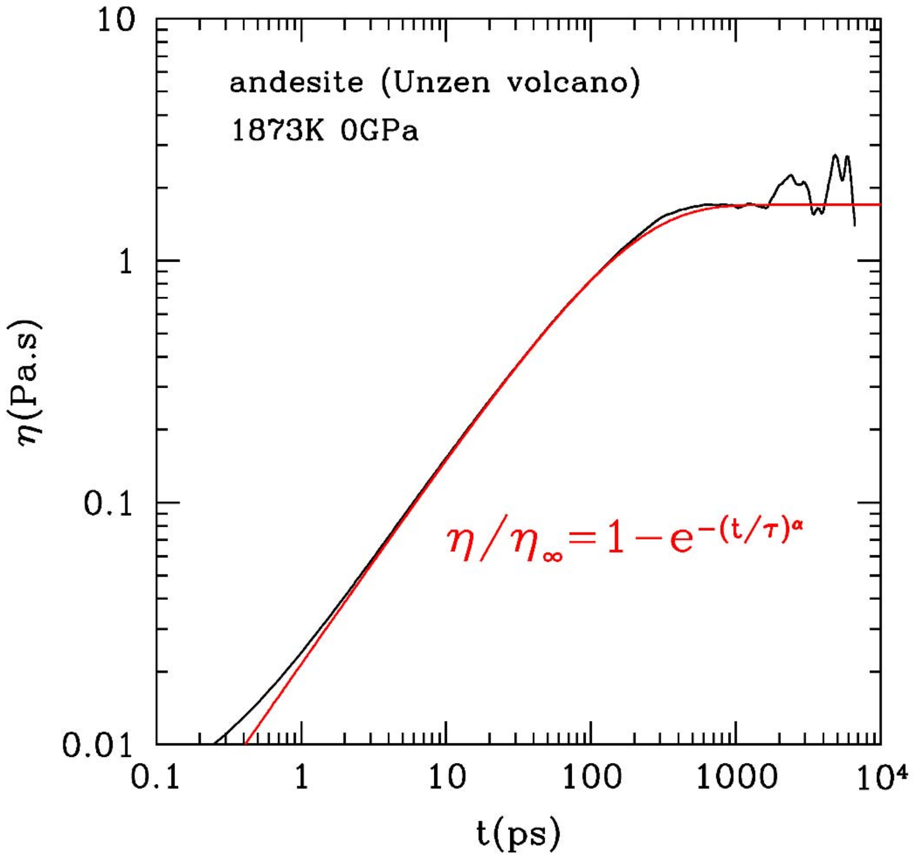
Value corrected

for 3wt% H_2O

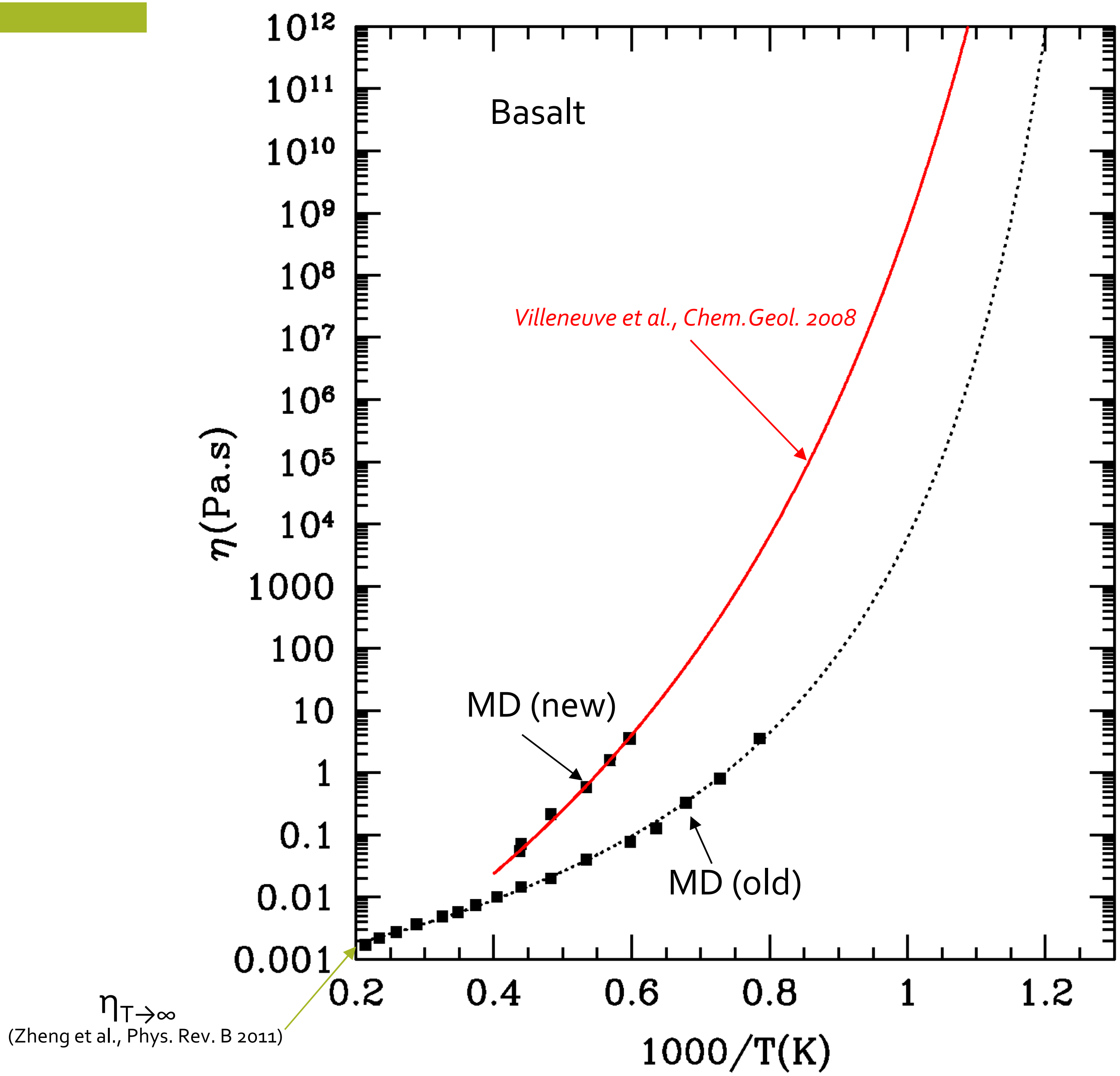
Vander Kaaden & al. 2015

$$\eta = \frac{1}{k_B T V}\int_0^{t\to\infty} S(t)\,dt$$

where $S(t) = \sum_{\alpha\neq\beta} < P_{\alpha\beta}(t).P_{\alpha\beta}(0) >$, $P_{\alpha\beta} = \sum_i m_i v_i^{\alpha} v_i^{\beta} + \frac{1}{2}\sum_{i\neq j} r_{ij}^{\alpha}\, F_{ij}^{\beta}$



Note: $G_\infty = \eta_\infty/\tau$ = 28 GPa



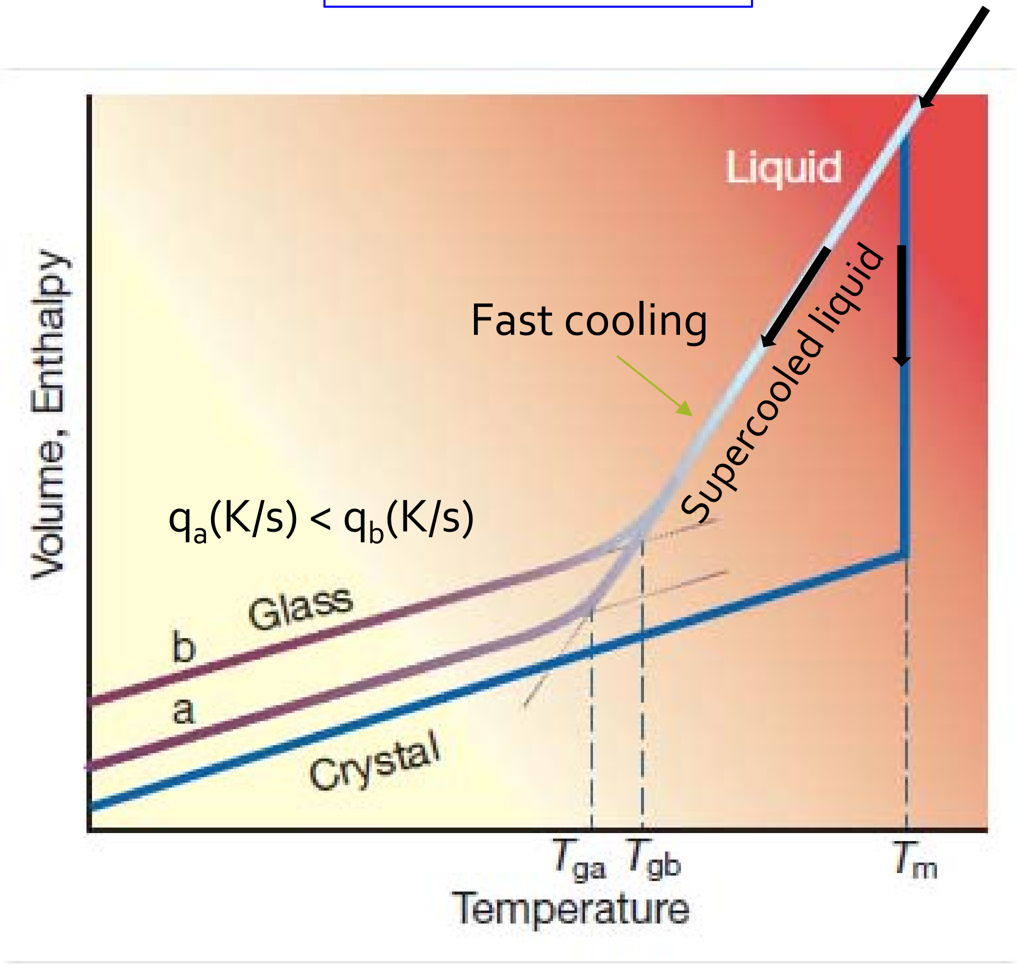
Villeneuve et al., Chem.Geol. 2008

MD (new)

MD (old)

$\eta_{T \to \infty}$
(Zheng et al., Phys. Rev. B 2011)

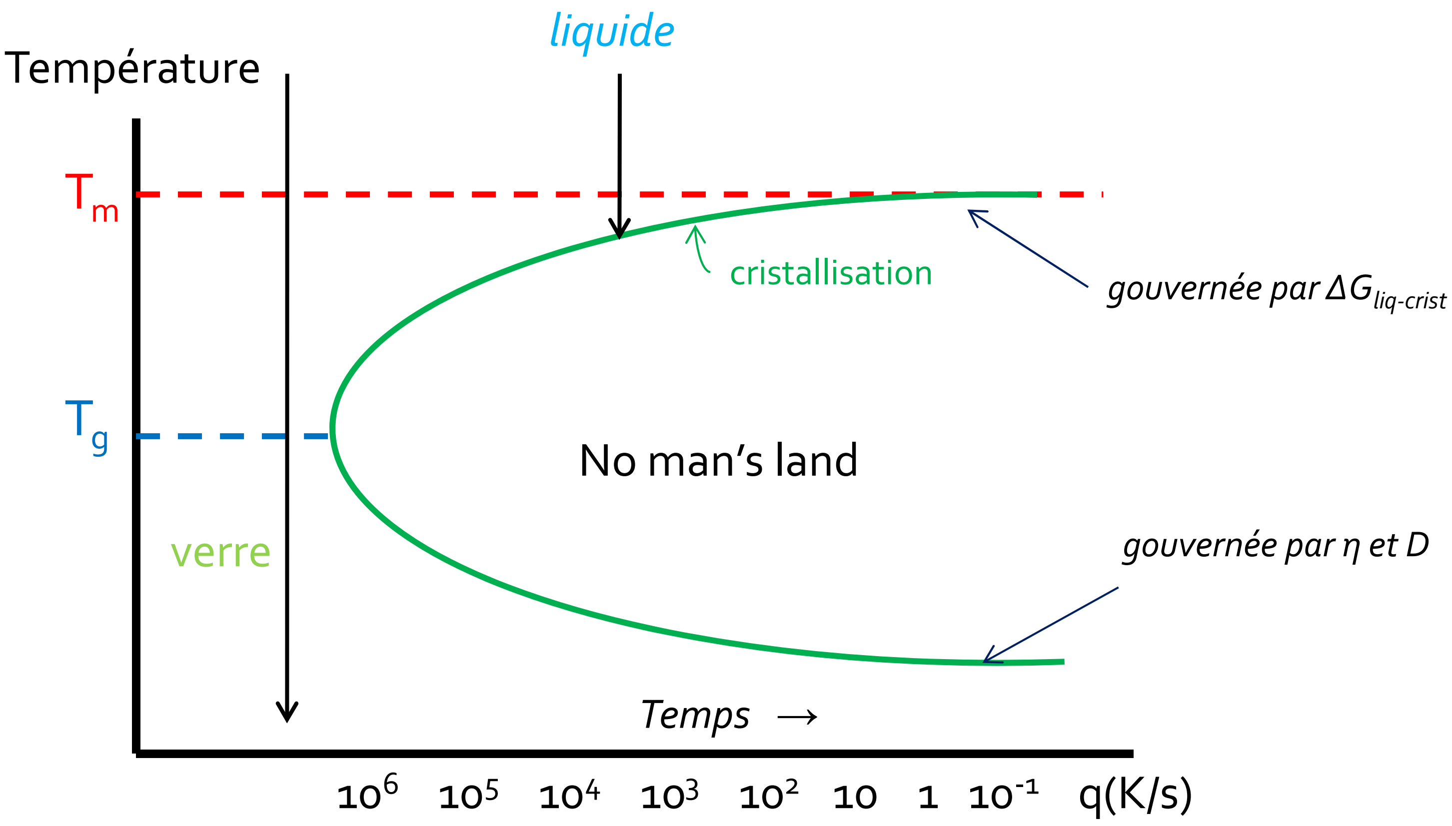
The glass transition



Fast cooling

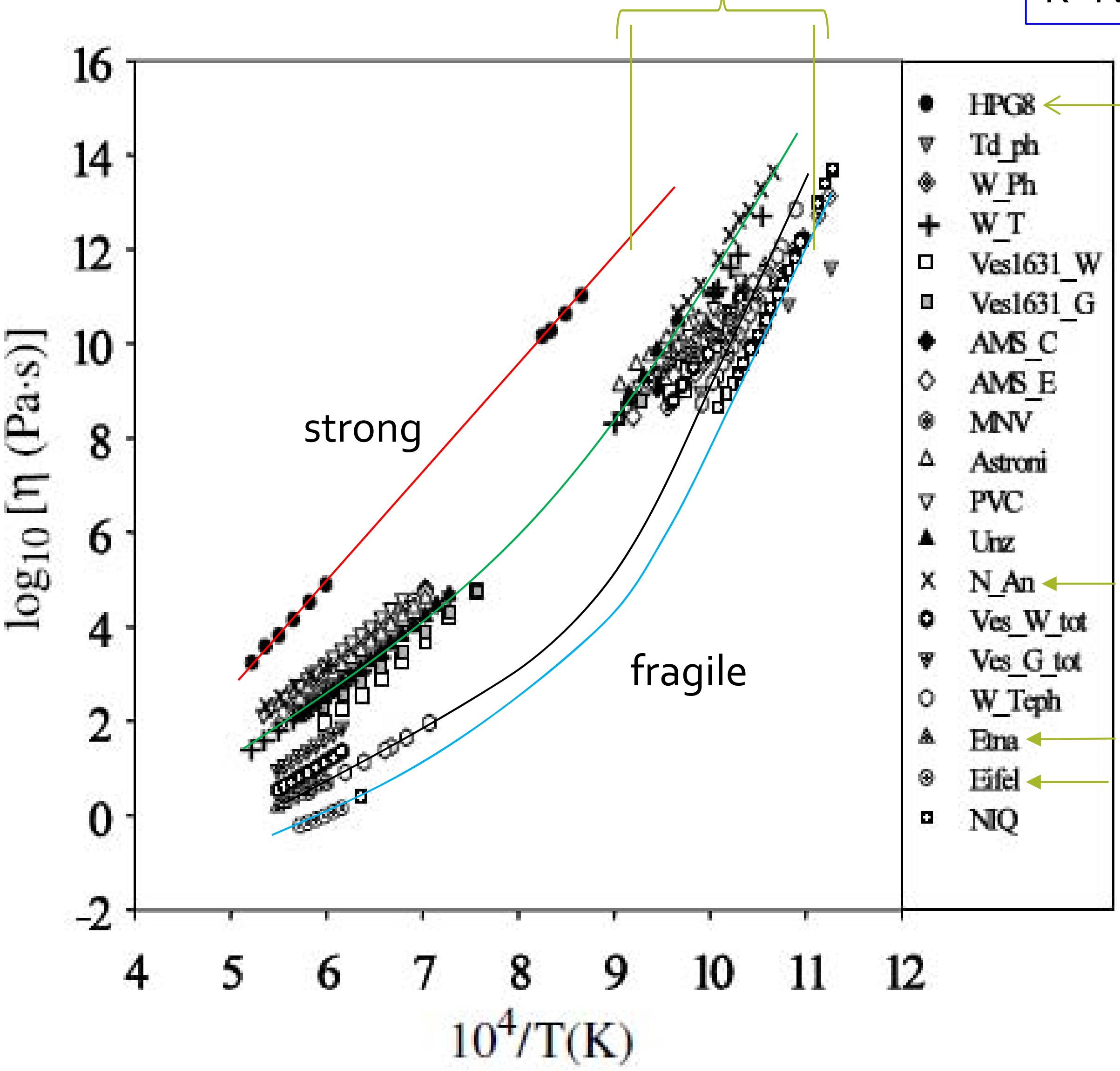
$q_a(K/s) < q_b(K/s)$

Courbe de transformation temps-température



T_g = 1150 – 900 K

R=NBO/T= (2*O-4*T)/T



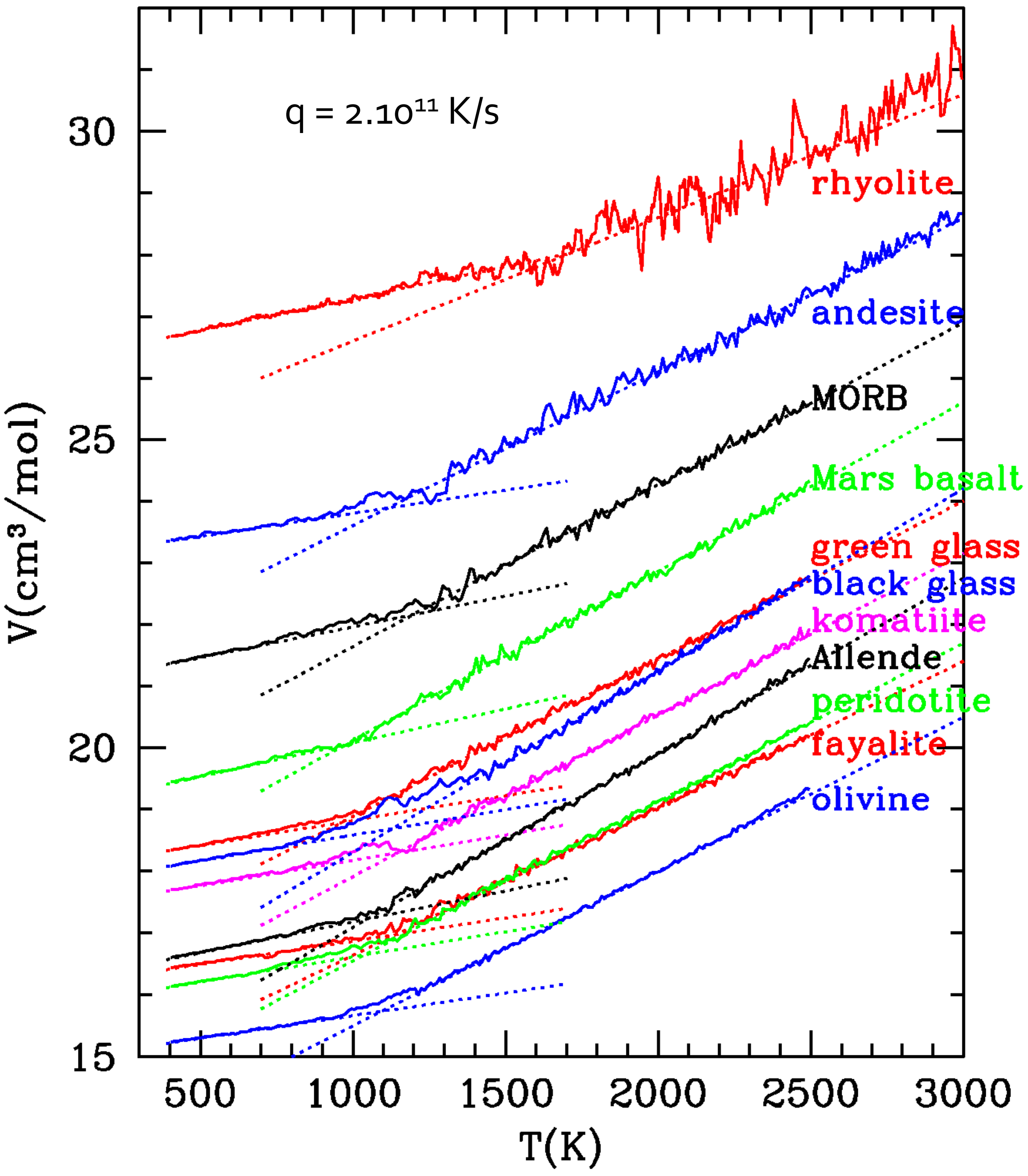
Granite (84% SiO_2, R=0.02)

Andesite (66% SiO_2, R=0.28)

Basalt (51.9% SiO_2, R=0.43)

Basanite (43% SiO_2, R=1.16)

Giordano and Dingwell, J. Phys.: Condens. Matter 15 (2003), S945


q = 2.10¹¹ K/s
rhyolite
andesite
MORB
Mars basalt
green glass
black glass
komatiite
Allende
peridotite
fayalite
olivine
V(cm³/mol)
T(K)
30
25
20
15
500
1000
1500
2000
2500
3000

La transition vitreuse: un réel problème en MD

Quelques données clés des simulations …

Les ressources informatiques sont limitées $\Longrightarrow$ $N = 10^3 - 10^6$ atomes, $t_{max} \sim 100$ ns

$D_{min} = \langle R_{min}{}^2 \rangle / 6t_{max}$ $\sim 10^{-13}$ m²/s pour un déplacement carré moyen de 6 A²

D'où (d'après Eyring) $\eta_{max} = k_B T / \lambda D_{min}$ = 300 Pa.s (!!)

$\lambda = 2.8$ A pour les silicates

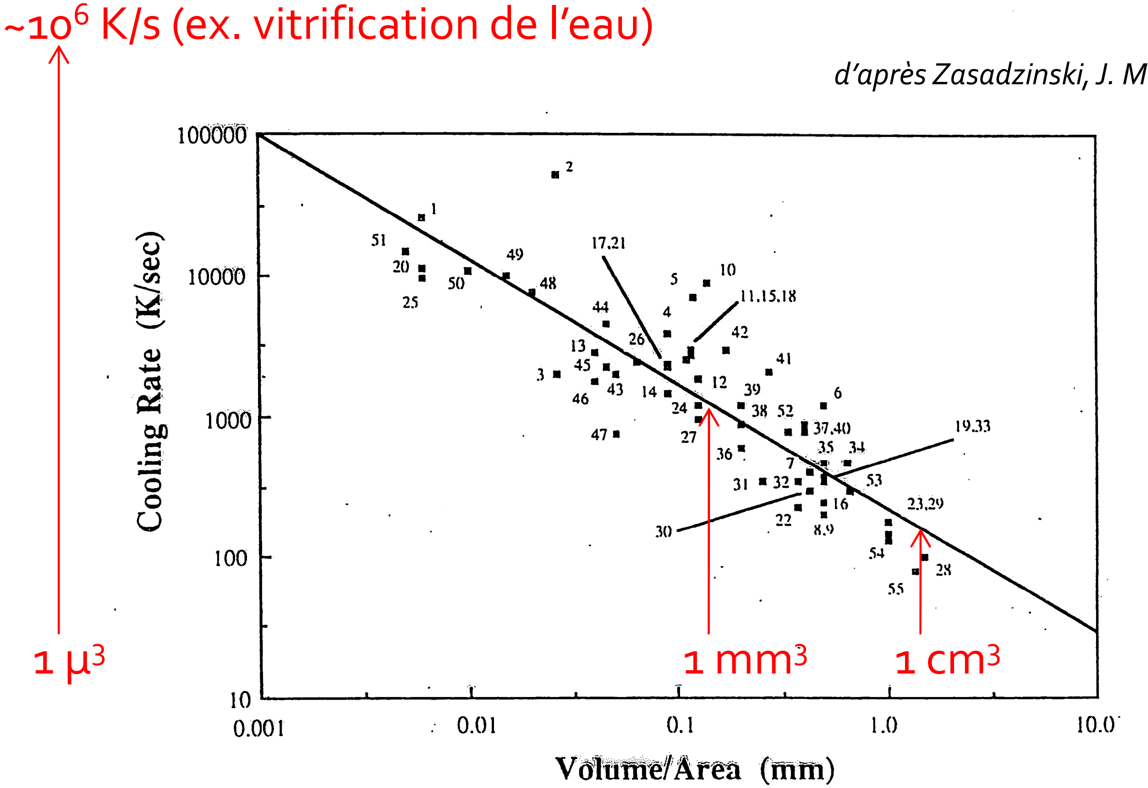
Vérification: (d'après Maxwell) $\tau_{relax} = \eta / G_\infty$ = 10 -100 ns

avec $G_\infty = 0.3\ 10^{10} - 3.\ 10^{10}$ Pa

Remarque : à T_g $\eta \approx 10^{12}$ Pa.s il faudrait une simulation de 300 - 3000 s

Vitesse de trempe la plus lente: $10^2 - 10^3$ K/100 ns = $10^9 - 10^{10}$ K/s

est-ce bien raisonnable ?

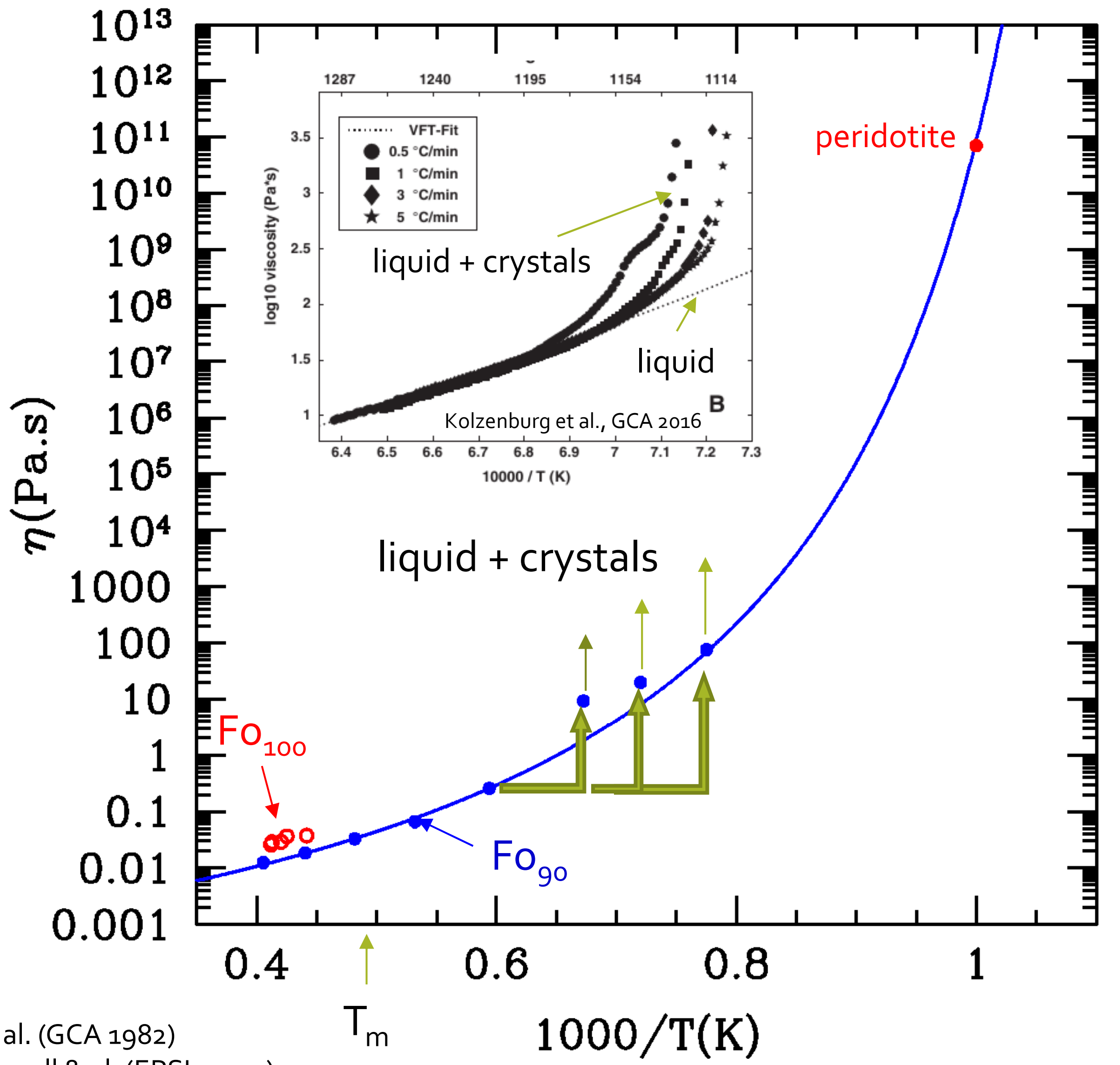


~10^6 K/s (ex. vitrification de l'eau)

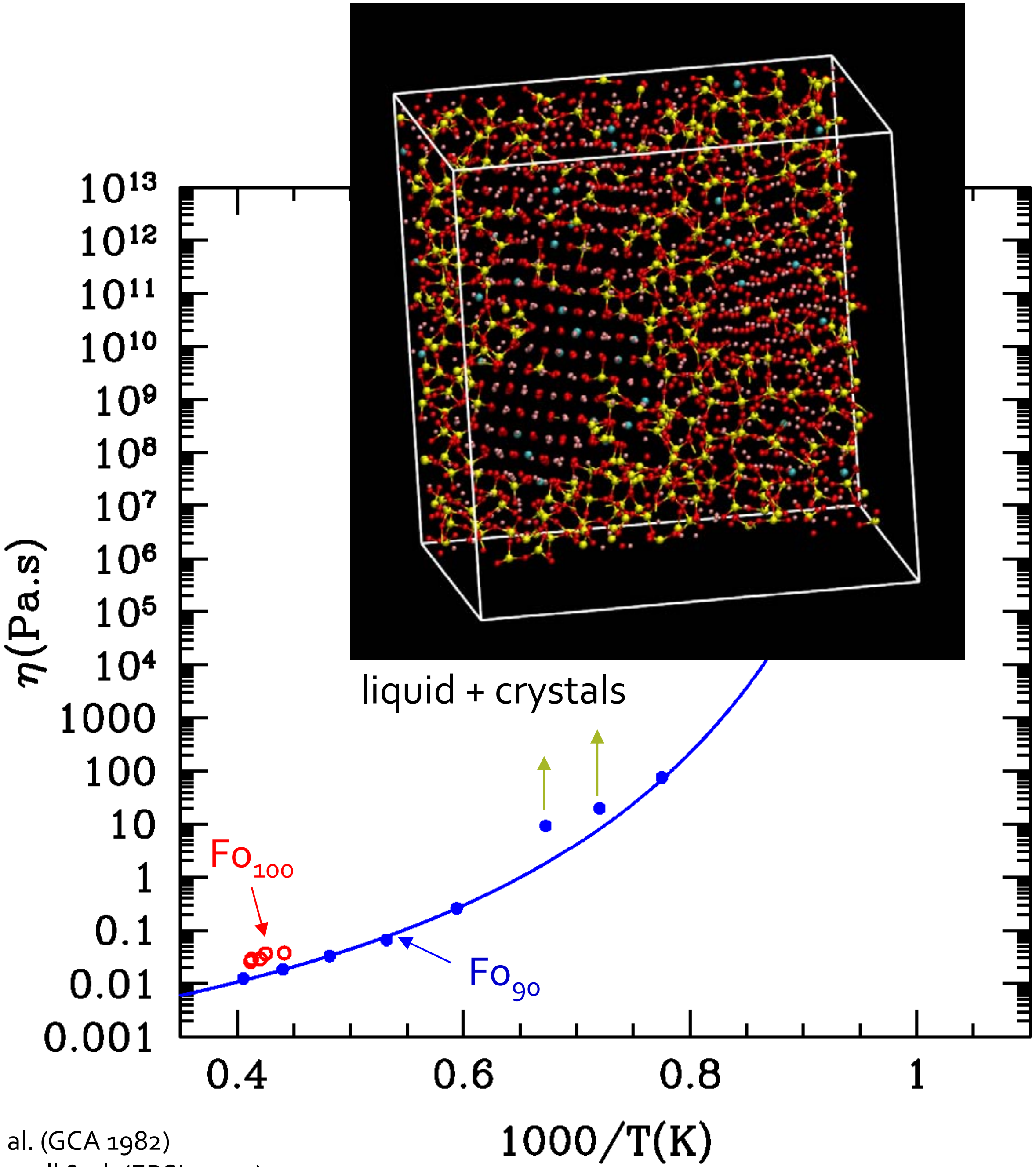
d'après Zasadzinski, J. Microsc. 150 (1988), 137

Pour un échantillon nanométrique (20 A)^3 l'extrapolation donne 10^9K/s (!)

Supercooled liquid versus crystal: the example of molten olivine (Fo$_{90}$)



Fo$_{100}$: Urbain & al. (GCA 1982)
Peridotite: Dingwell & al. (EPSL 2004)



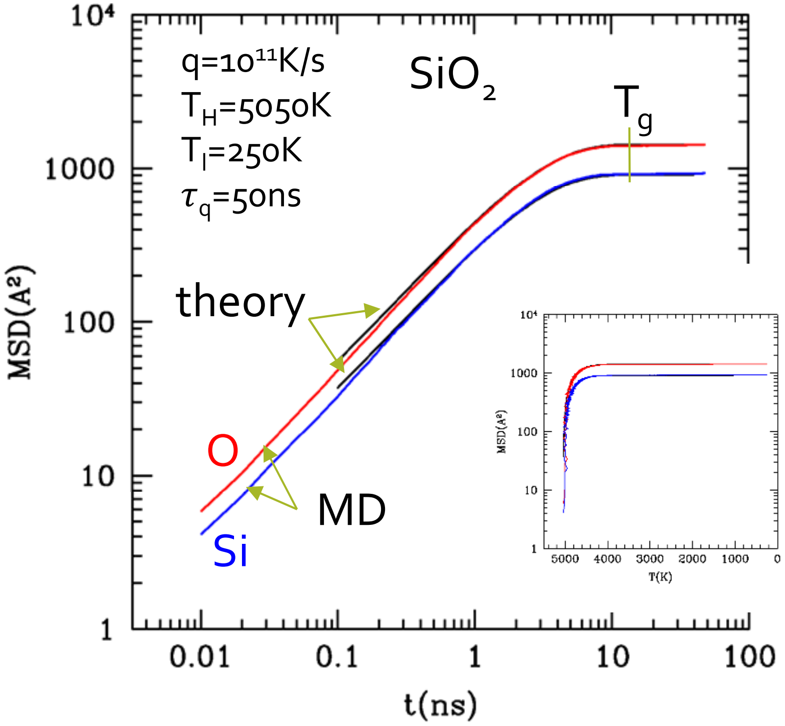
Fo_{100}: Urbain & al. (GCA 1982)
Peridotite: Dingwell & al. (EPSL 2004)
Stromboli, Etna: Vona & al. (GCA 2011)

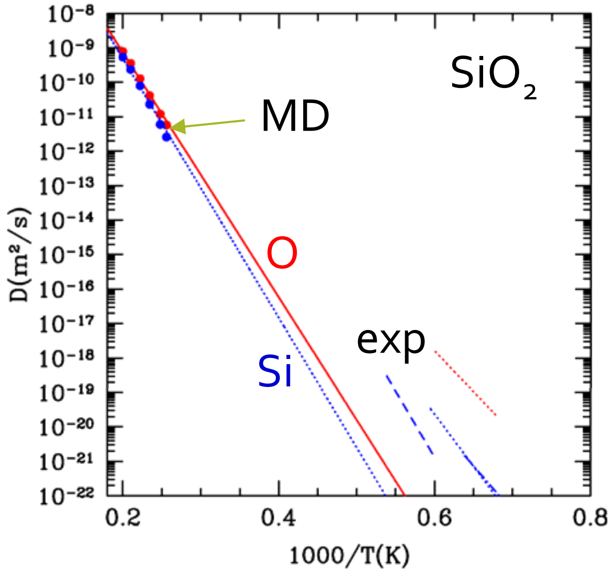
Kinetic arrest and cooling rate: A simple way to estimate T_g (or T_f)

$R^2(t)=6Dt$ ⟹ $2RdR=6Ddt$ with $D(t)=A\ e^{-Ea/k_B T_q}$

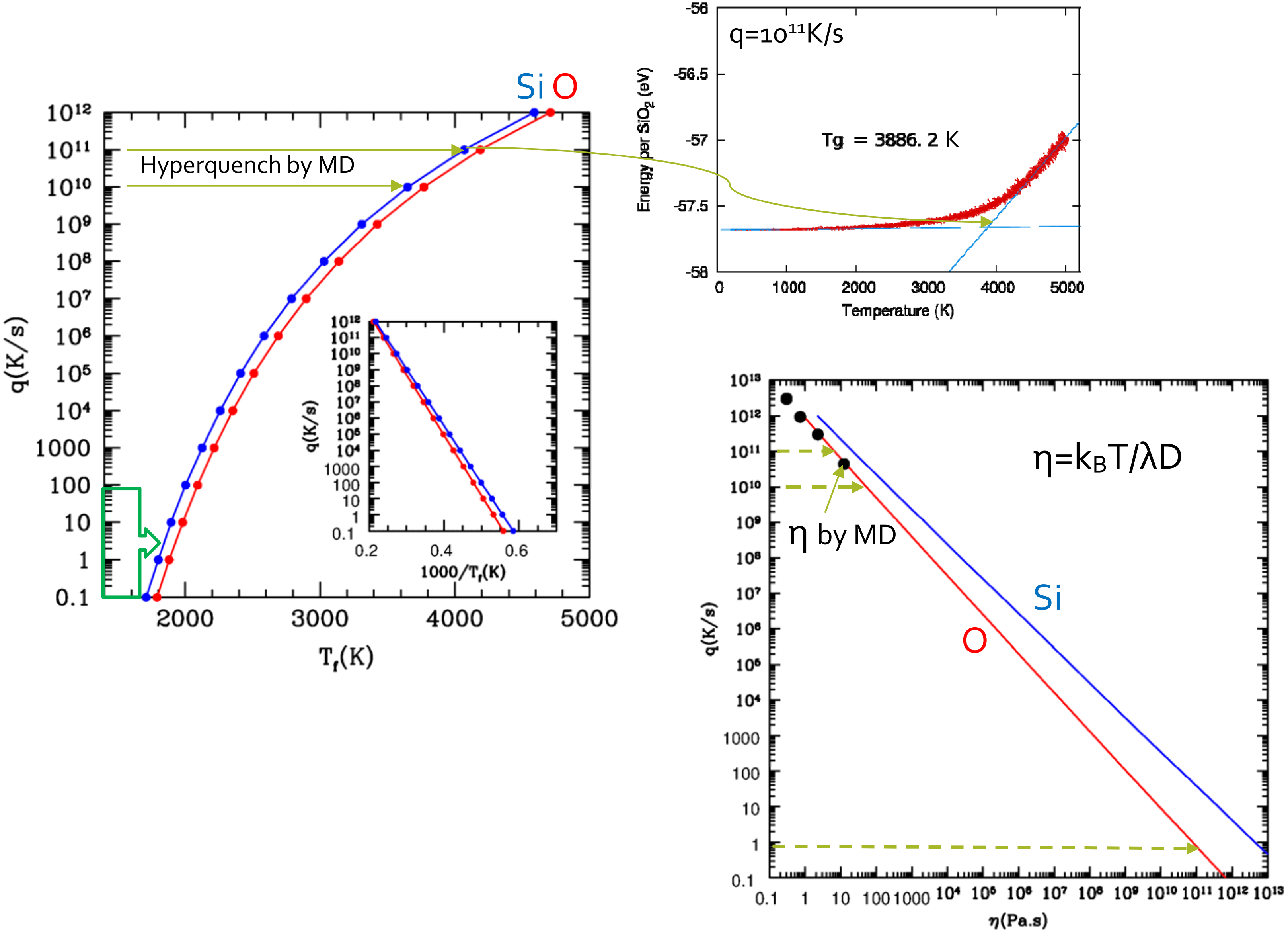
where $T_q=T_H-qt\quad 0<t<\tau_q\ ,\ T_H<T_q<T_l$

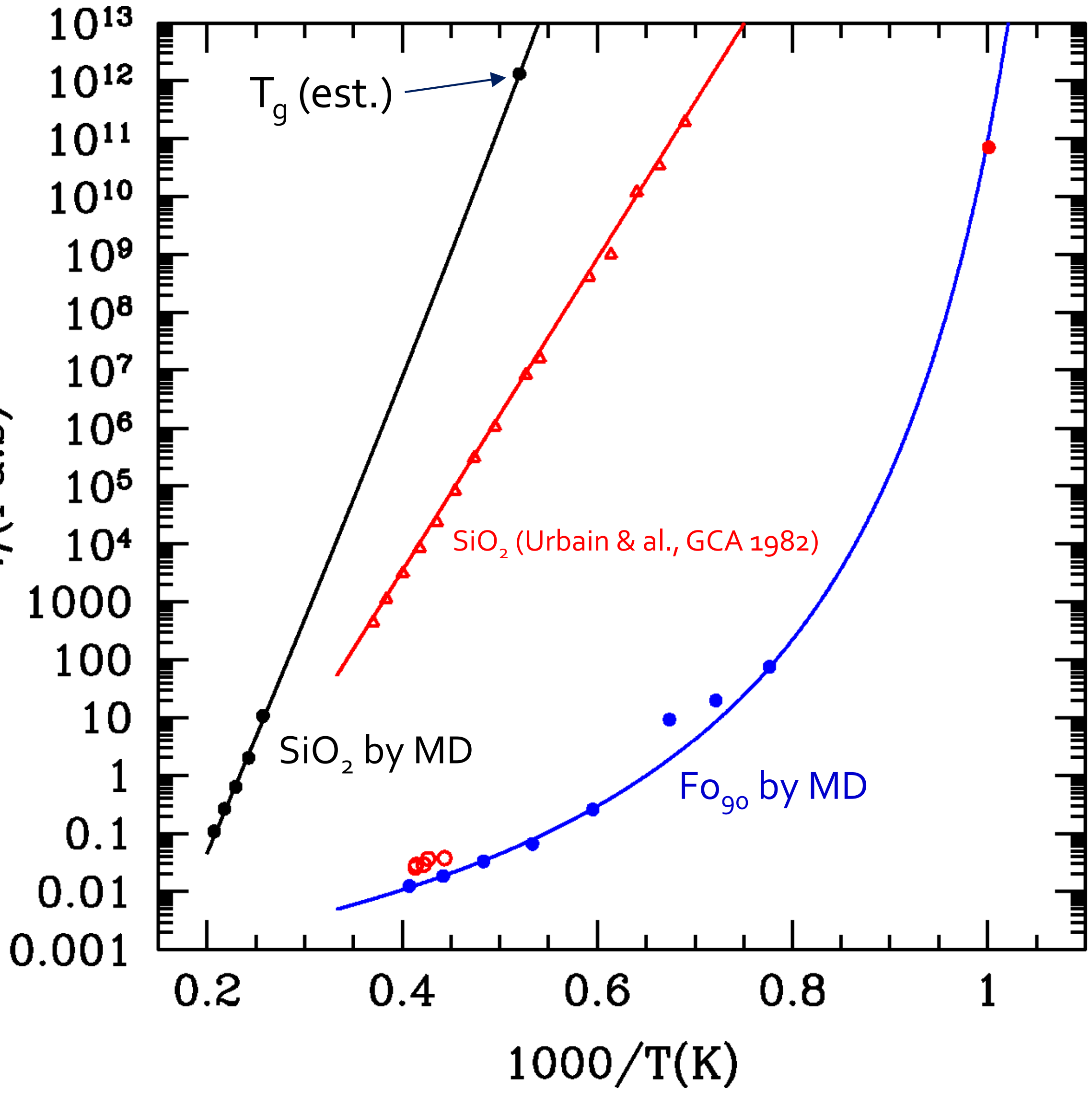
Kinetic arrest ⟹ $R^2(t)=\int_0^t 6Ddt \rightarrow constant\ value\ when\ t \rightarrow \tau_q$





$$T_g(q) \rightarrow \frac{dR^2}{dT} = \frac{6D(T)}{q} \sim 0.1\ A^2/K$$


Si O
Hyperquench by MD
q(K/s)
10¹² 10¹¹ 10¹⁰ 10⁹ 10⁸ 10⁷ 10⁶ 10⁵ 10⁴ 1000 100 10 1 0.1
2000 3000 4000 5000
T_f(K)
1000/T_f(K)
0.2 0.4 0.6
q=10¹¹K/s
Tg = 3886.2 K
Energy per SiO₂ (eV)
-56 -56.5 -57 -57.5 -58
0 1000 2000 3000 4000 5000
Temperature (K)
η=k_BT/λD
η by MD
Si
O
10¹³
0.1 1 10 100 1000 10⁴ 10⁵ 10⁶ 10⁷ 10⁸ 10⁹ 10¹⁰ 10¹¹ 10¹² 10¹³
η(Pa.s)


η(Pa.s)
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
1000
100
10
1
0.1
0.01
0.001
0.2
0.4
0.6
0.8
1
1000/T(K)
T_g (est.)
SiO_2 (Urbain & al., GCA 1982)
SiO_2 by MD
Fo_{90} by MD

Kinetic control of the structural relaxation through the glass transition range

Kinetic decoupling between structure makers and structure modifiers when T → T_g

viscosity

$$\tau_\eta = \frac{\eta}{G_\infty} \text{ with } G_\infty \sim 10^{10}\ Pa.s$$

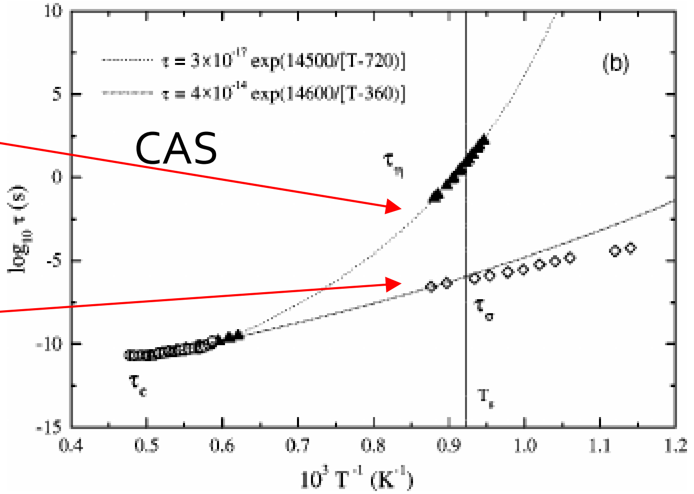
(controlled by slow particles)

conductivity

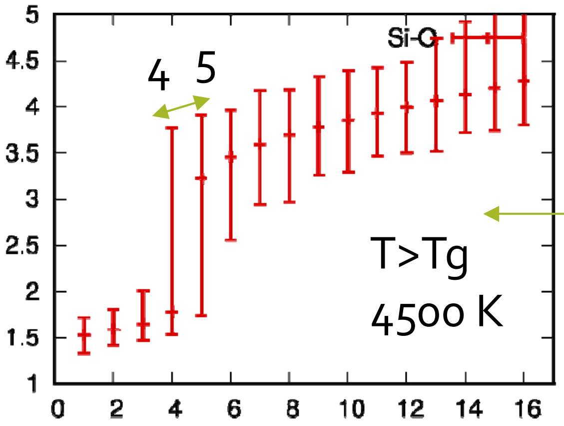
$$\tau_\sigma \rightarrow \sigma(\omega) \text{ with } \sigma(0) \sim \sum z_i^2 D_i$$

(controlled by fast particles)

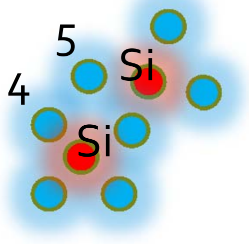
after Gruener et al., Phys. Rev. B (2001)

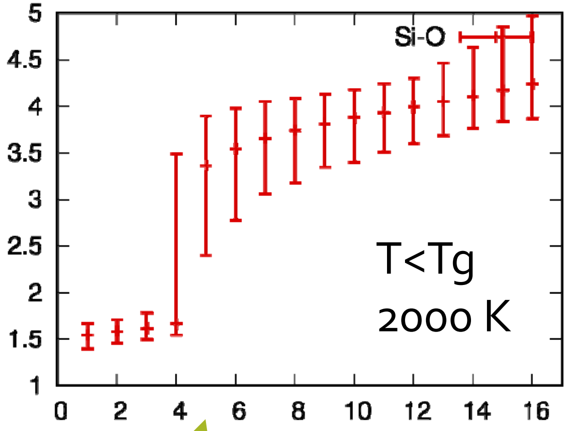


SiO_2 : a strong glass

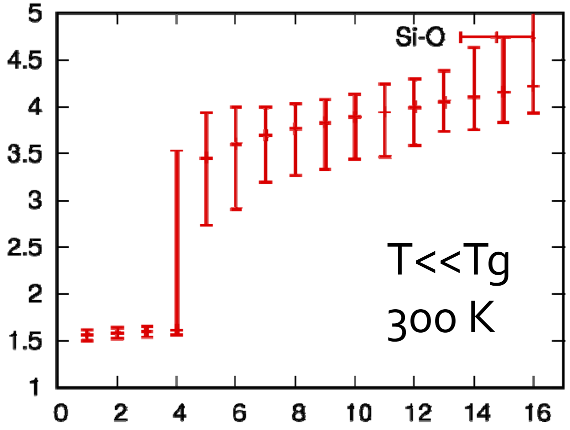


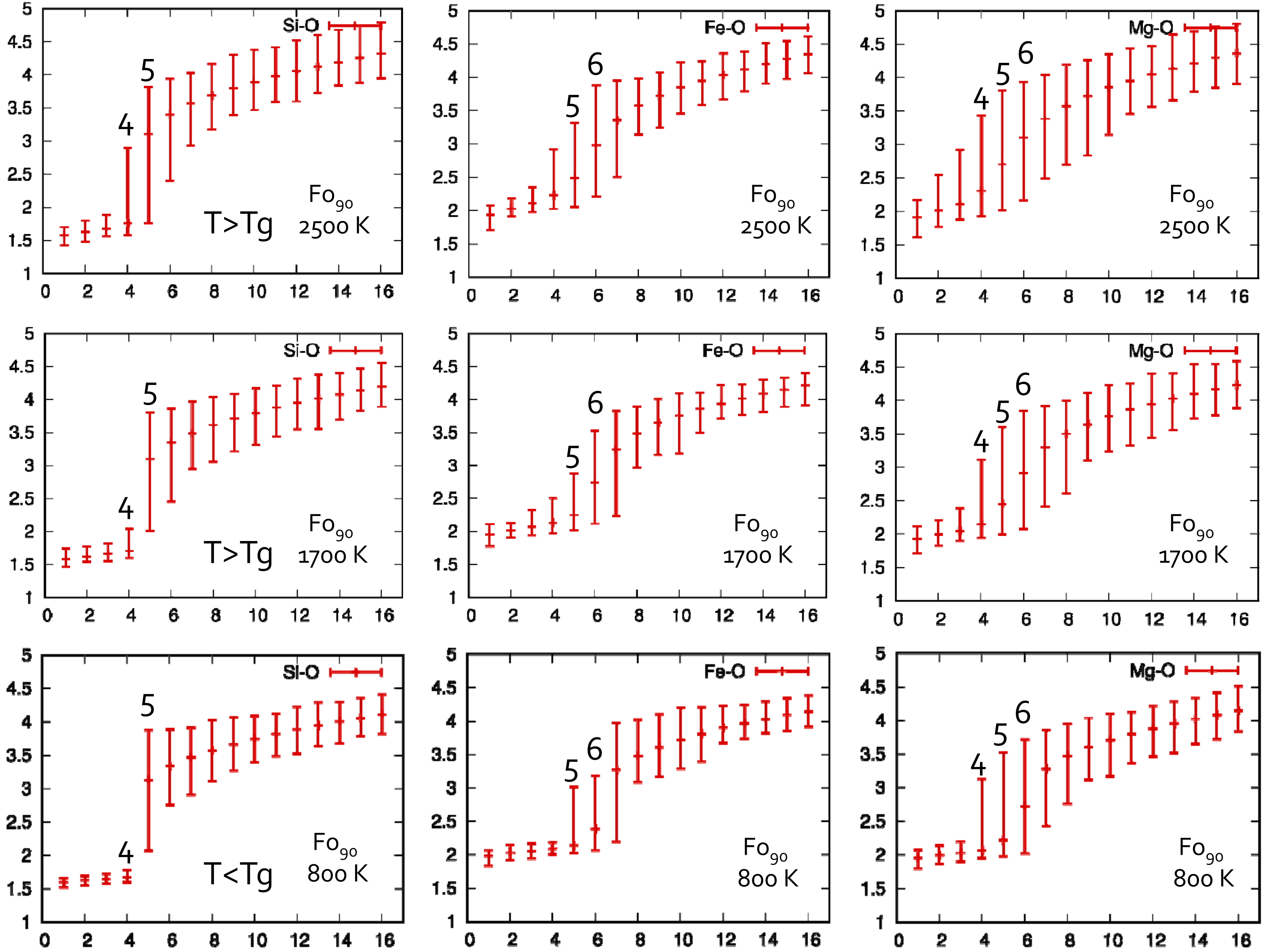
liquid

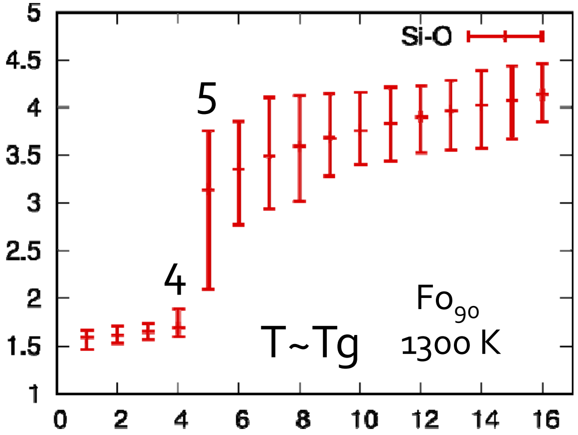


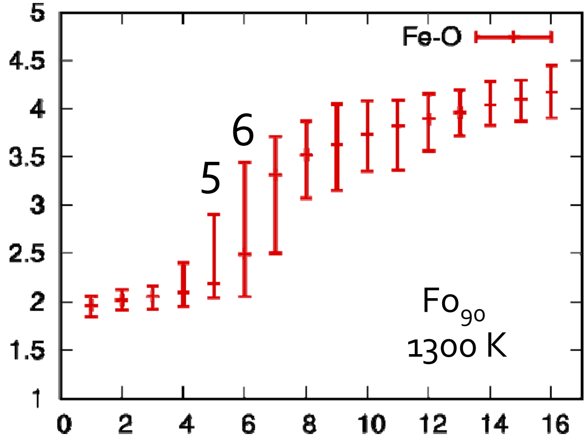


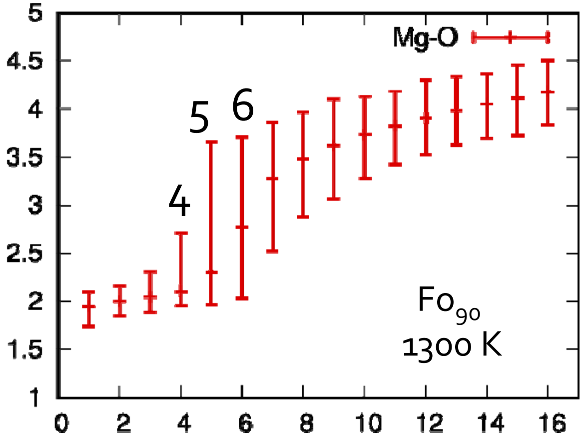
Frozen liquid
(no diffusion)

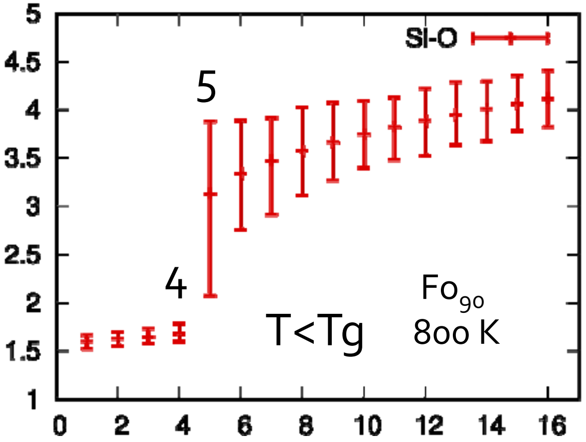


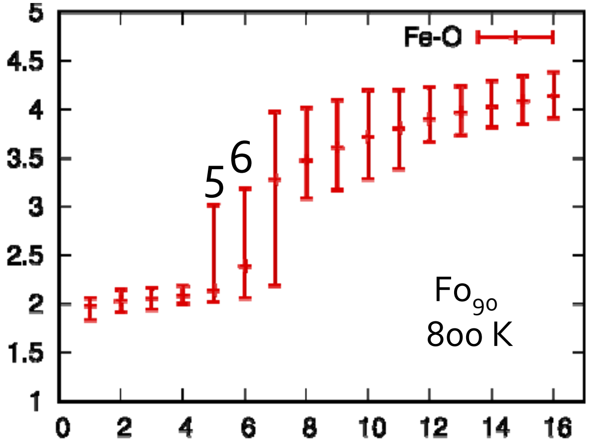

Si-O
Fe-O
Mg-O
Fo$_{90}$
2500 K
1700 K
800 K
T>Tg
T<Tg
4
5
6
0
2
4
6
8
10
12
14
16
1
1.5
2
2.5
3
3.5
4
4.5
5

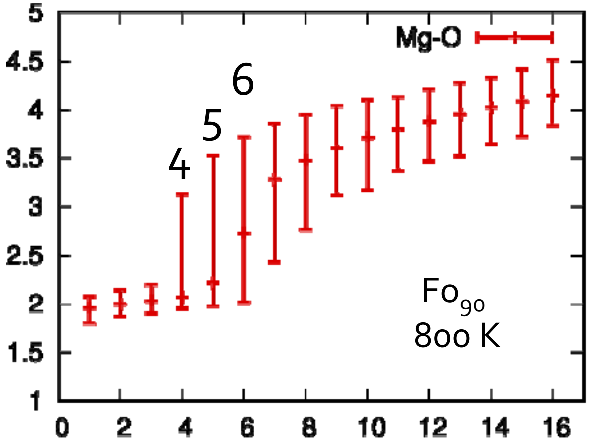

Si-O
5
4
T~Tg
Fo_{90}
1300 K
1
1.5
2
2.5
3
3.5
4
4.5
5
0
2
4
6
8
10
12
14
16


Fe-O
6
5
Fo_{90}
1300 K
1
1.5
2
2.5
3
3.5
4
4.5
5
0
2
4
6
8
10
12
14
16

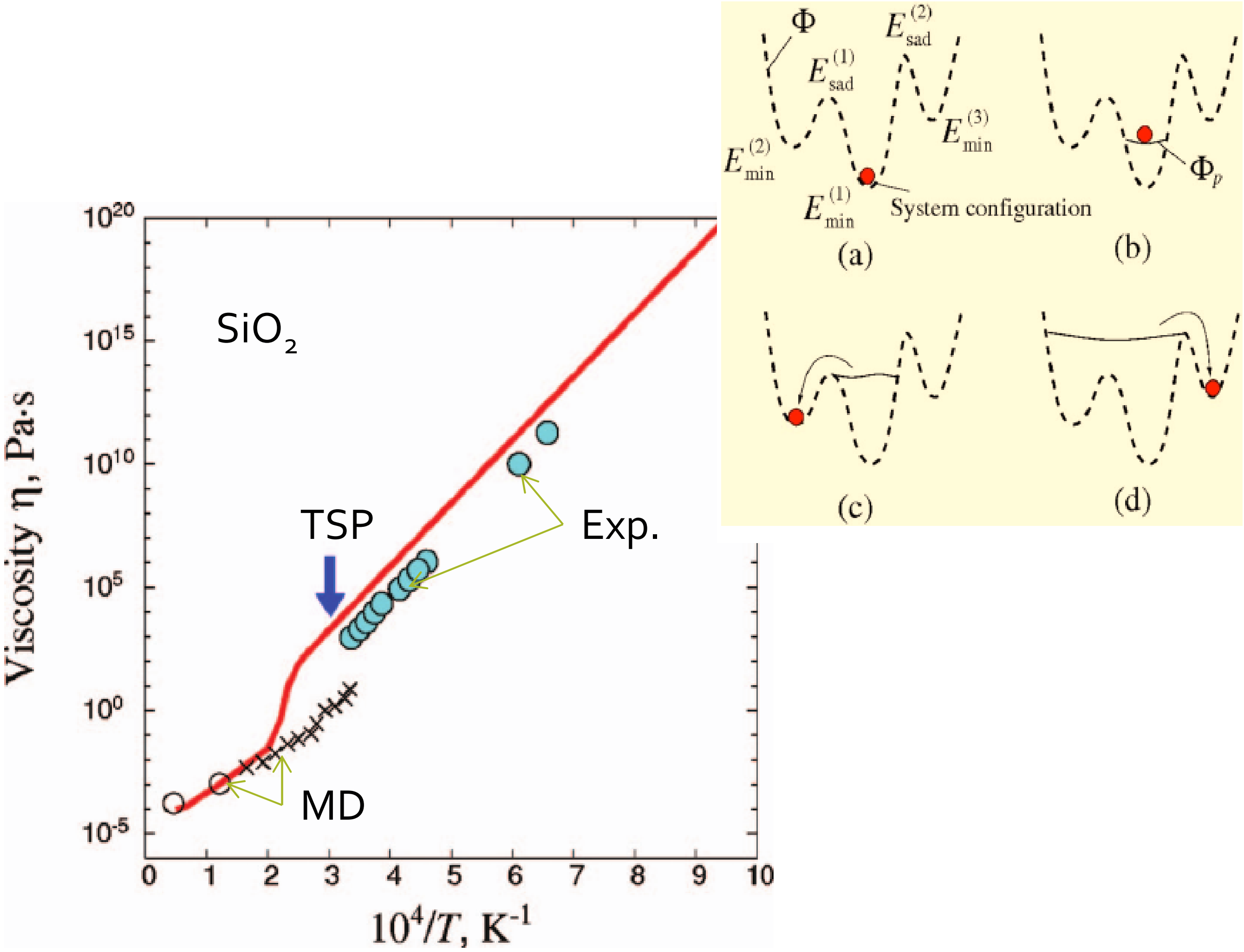

Mg-O
5
6
4
Fo_{90}
1300 K
1
1.5
2
2.5
3
3.5
4
4.5
5
0
2
4
6
8
10
12
14
16


Si-O
5
4
T<Tg
Fo_{90}
800 K
1
1.5
2
2.5
3
3.5
4
4.5
5
0
2
4
6
8
10
12
14
16


Fe-O
5
6
Fo_{90}
800 K
1
1.5
2
2.5
3
3.5
4
4.5
5
0
2
4
6
8
10
12
14
16


Mg-O
6
5
4
Fo_{90}
800 K
1
1.5
2
2.5
3
3.5
4
4.5
5
0
2
4
6
8
10
12
14
16

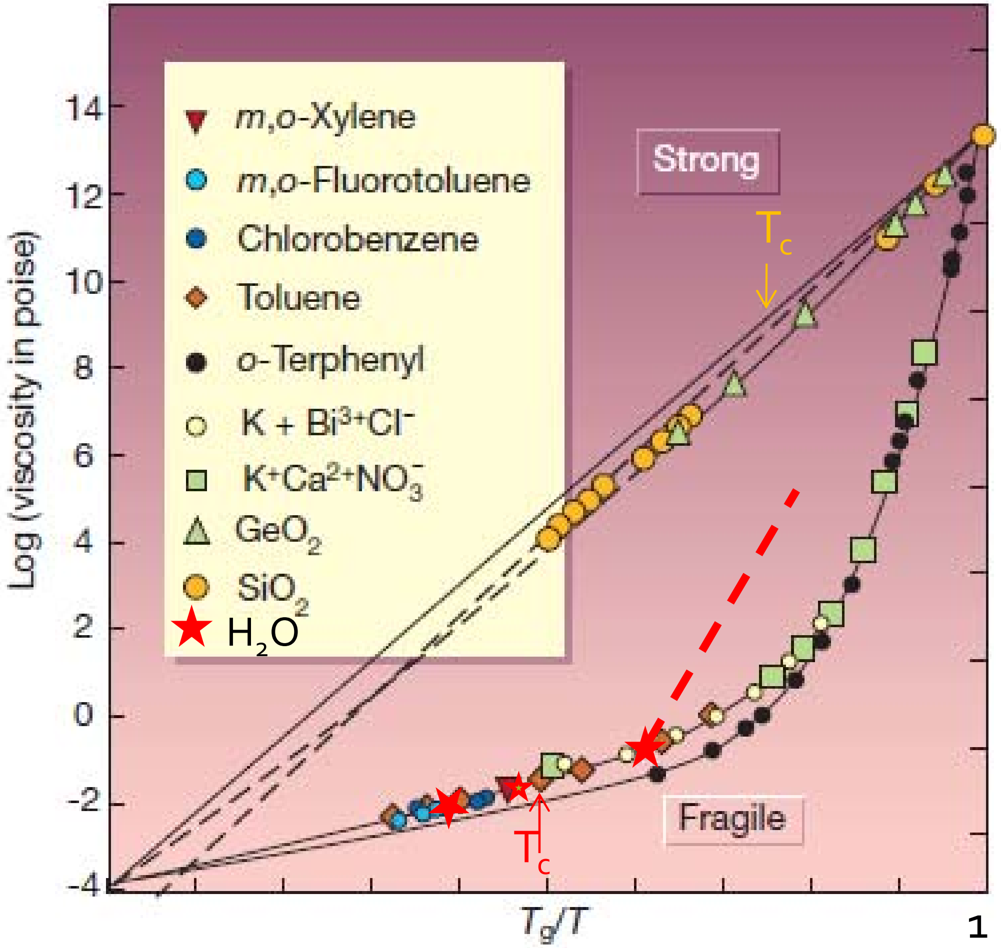
Beyond MD



Kushima et al., J.Chem.Phys. 130, 2009

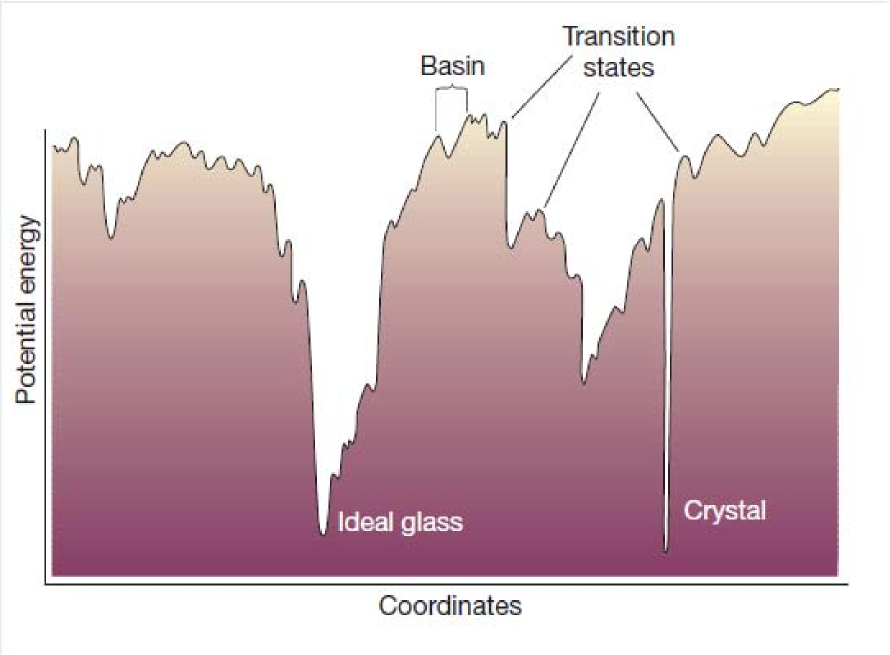
$\mathrm{Log}\ \eta = A + B/(T-T_0)$ $T_0 \sim 0$ pour les liquides forts

$0 < T_0 < T_g$ pour les liquides fragiles



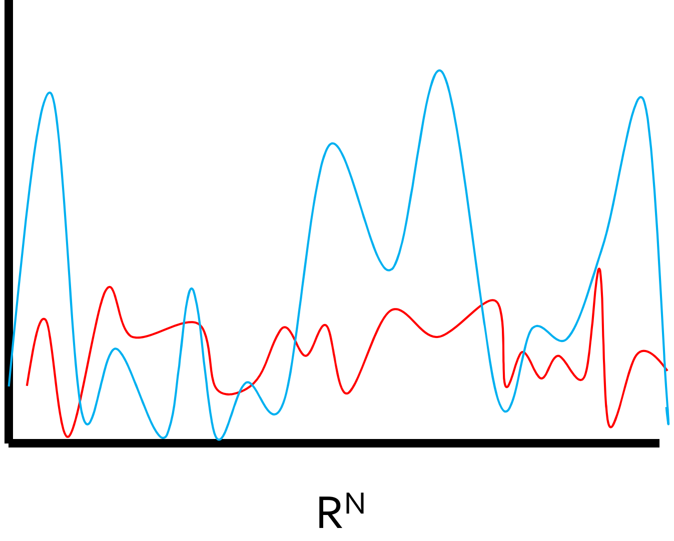
D'après Debenedetti and Stillinger, Nature 410 (2001), 259

Paysage énergétique



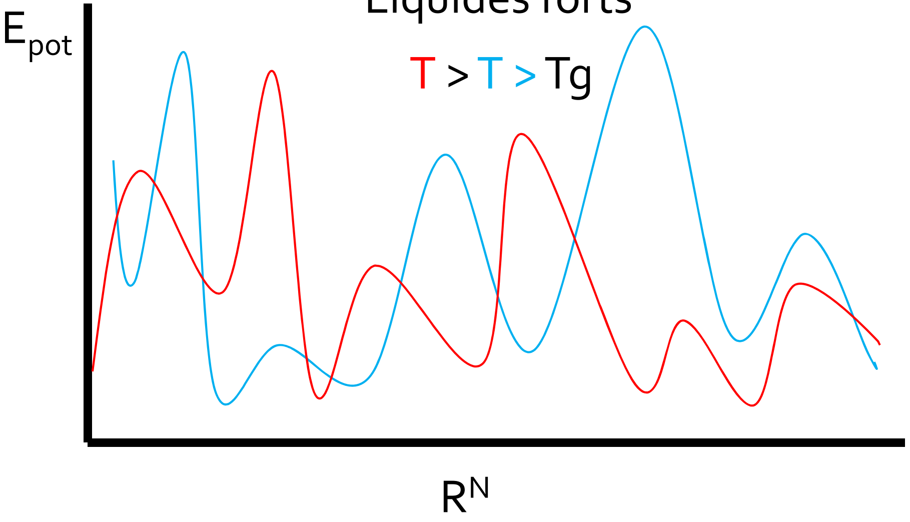
Liquides fragiles

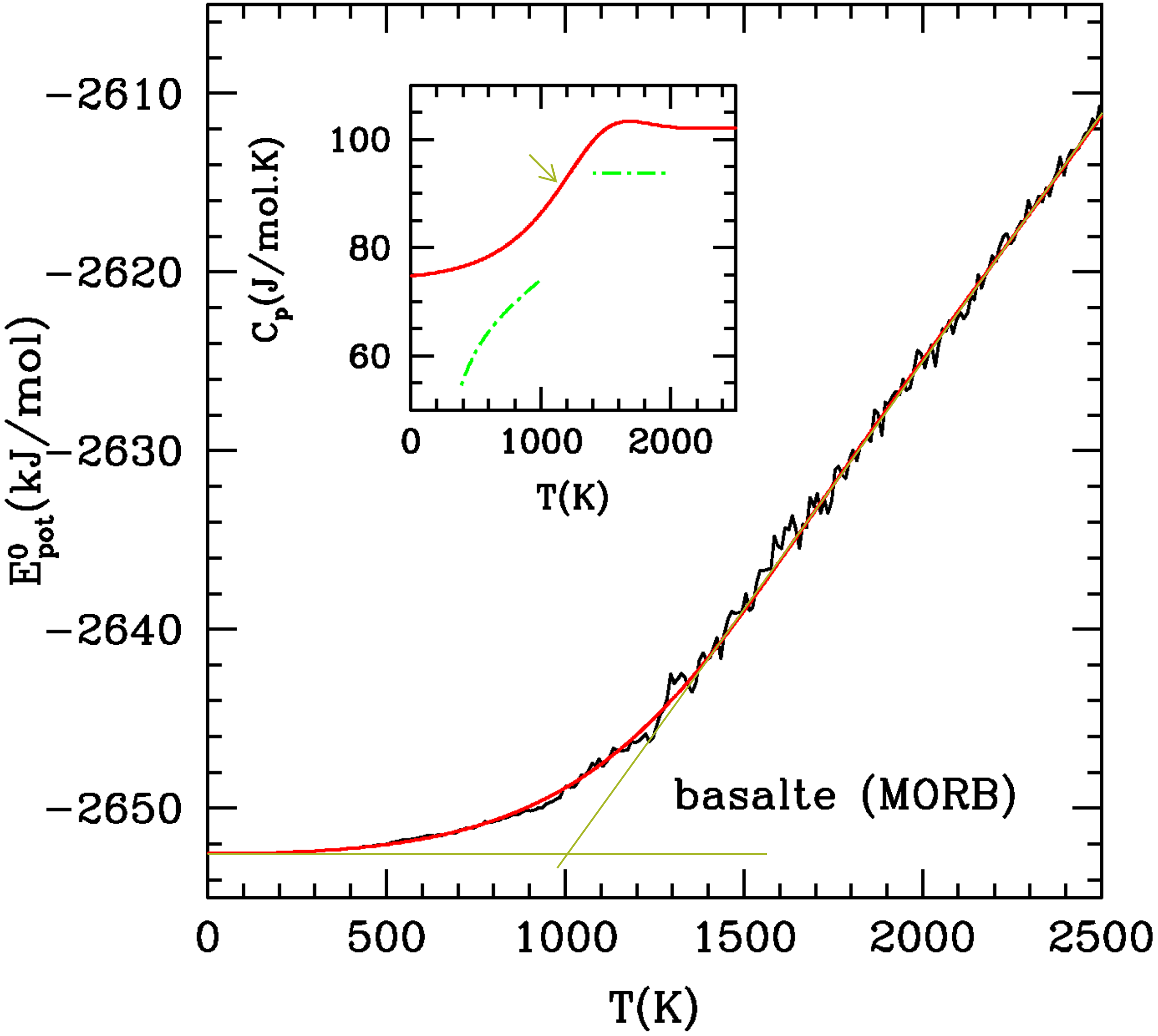
T > T > Tg

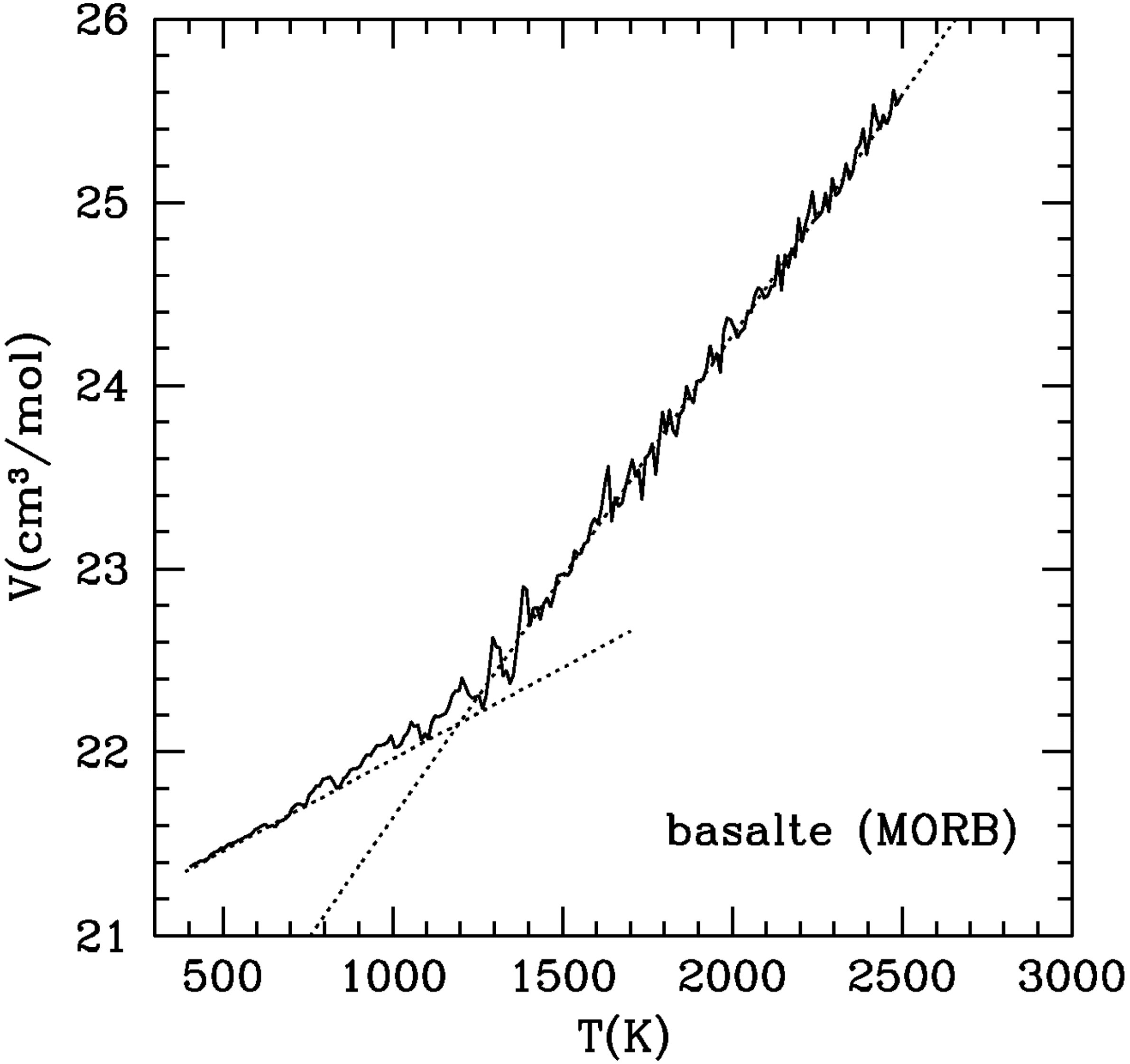


Liquides forts

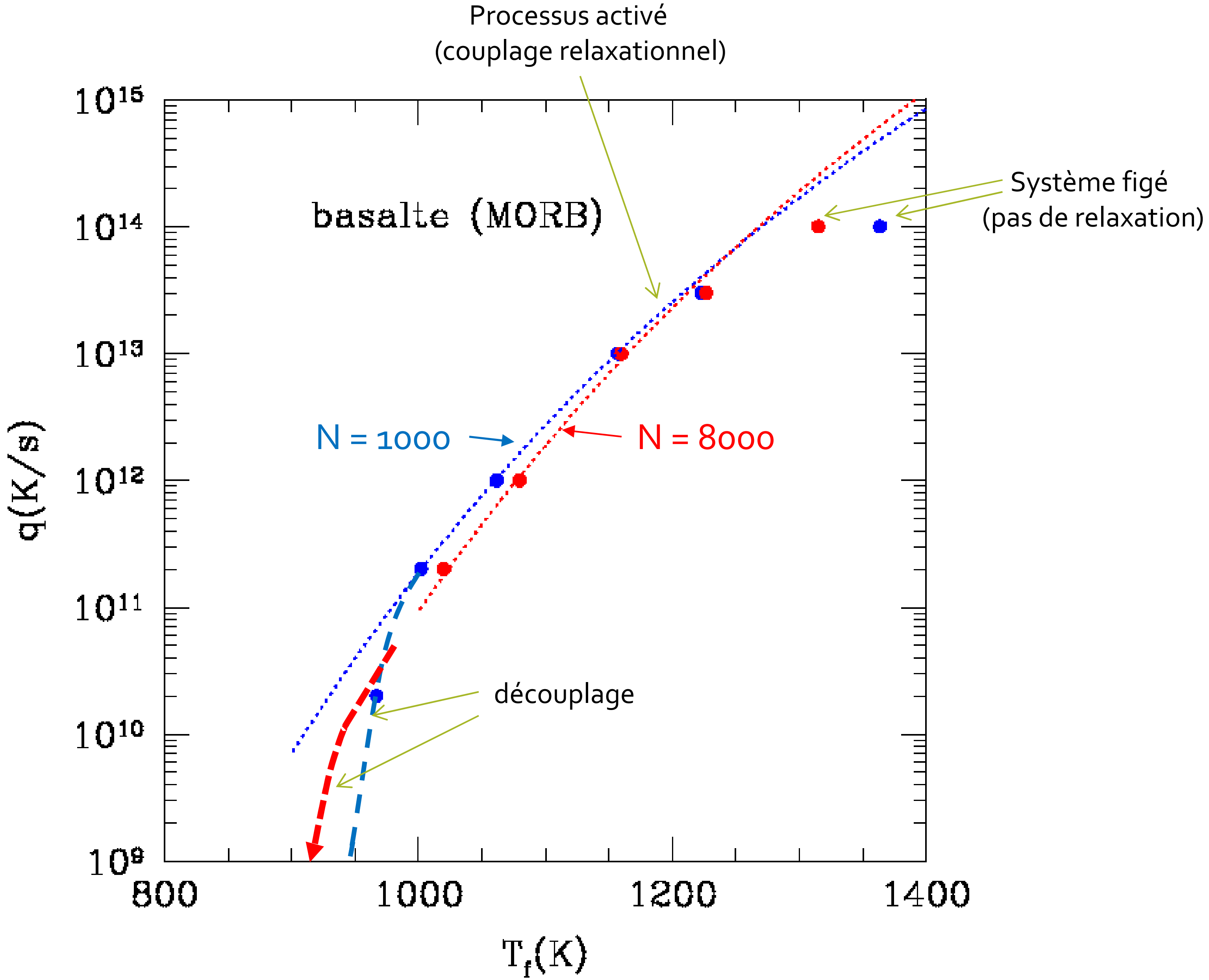
T > T > Tg




−2610
−2620
−2630
−2640
−2650
E^0_{pot}(kJ/mol)
0
500
1000
1500
2000
2500
T(K)
basalte (MORB)
100
80
60
C_p(J/mol.K)
0
1000
2000
T(K)


26
25
24
23
22
21
500
1000
1500
2000
2500
3000
T(K)
V(cm³/mol)
basalte (MORB)

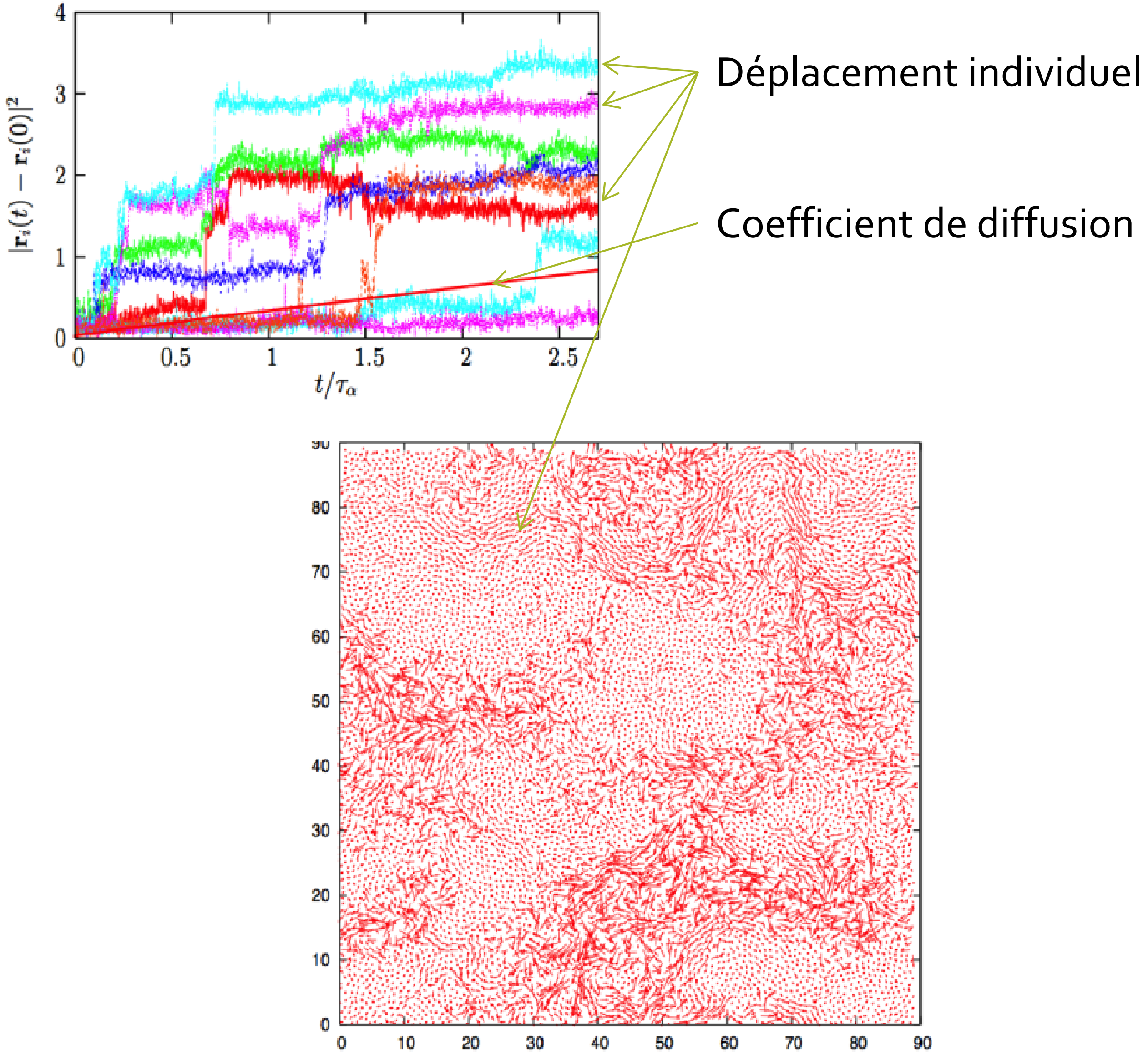
	T_g(K) = (dilatométrie; calorimétrie)	T_g^{exp}
Rhyolite (74.5 wt%SiO_2)	1500; 1600	1125
andesite (56.7 wt%SiO_2)	1116; 1210	1013
MORB (50.6 wt%SiO_2)	1178; 1000	950
Mars (47.7 wt%SiO_2)	960; 940	
Lunar Glass 14 (34.0 wt%SiO_2)	1126; 1020	
Lunar Glass 15 (48.0 wt%SiO_2)	960; 990	
komatite (46.7 wt%SiO_2)	1147; 900	~1000
peridotite (45.10 wt%SiO_2)	1037; 1000	~1000
Allende (38.6 wt%SiO_2)	1043; 900	
olivine (40.7 wt%SiO_2)	1100; 1000	
fayalite (29.5 wt%SiO_2)	1137; 1000	



Processus activé (couplage relaxationnel)

Système figé (pas de relaxation)

découplage



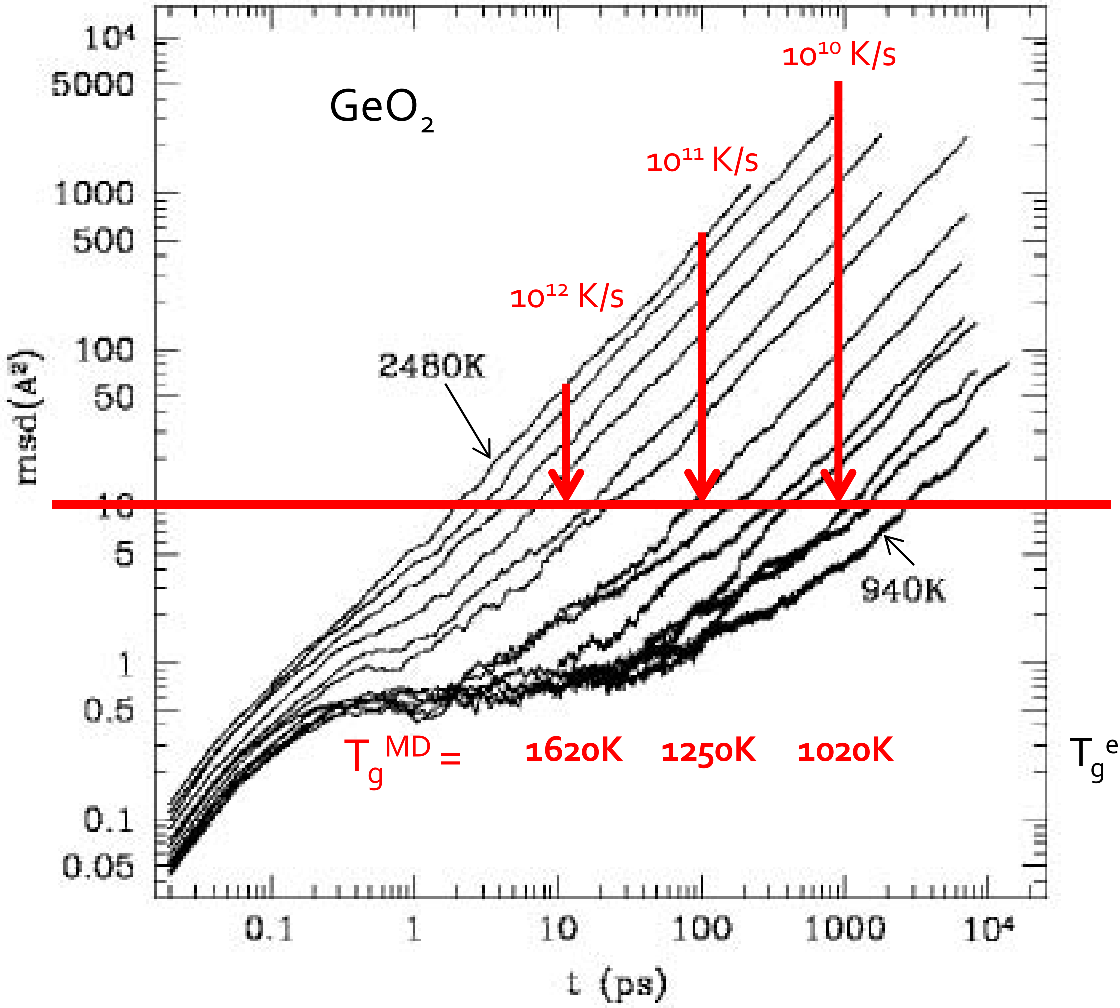
Déplacement individuel

Coefficient de diffusion

Hétérogénéités dynamiques (L-J)

L.Berthier, Physics 4, 2011
Berthier and Biroli, Rev. Mod. Phys. 83, 2011

GeO_2: Micoulaut et al., Phys. Rev. E 73 (2006), 31504



$T_g^{exp} \approx 850K$

Pour un taux ΔT/Δt (K/s) fixé, une estimation de Tg ≈ T ($MSD<10A^2$)