Zeolite Collapse, Polyamorphism and the Role of Low Frequency Modes

Neville Greaves University of Wales, Aberystwyth, UK
gng@aber.ac.uk

Florian Meneau DUBBLE CRG/ESRF, Grenoble, France
Odile Majérus, Ecole Nationale Supérieure de Chimie de Paris (ENSCP)

Jon Taylor ISIS, Rutherford Appleton Laboratory, UK

Glass Lecture Series: prepared for and produced by the International Material Institute for New Functionality in Glass
An NSF sponsored program – material herein not for sale
Available at www.lehigh.edu/imi
Contents

Introduction
Melting v Amorphisation, Microscopy

Low temperature dynamics
Anomalous $C_p$, Boson Peak, TLS

Zeolites and Amorphisation
Structure, Collapse, SAXS/WAXS

Low Frequency Modes
Inelastic Neutron Scattering, Boson Peak, Librational Modes, Anharmonicity, LDA-HDA transition

Rheology of collapsing zeolites amorphised by temperature and pressure
GN Greaves,
F Meneau, A Sapelkin, LM Colyer, I ap Gwynn, S Wade, G Sankar


Identifying the vibrations that destabilize crystals and that characterize the glassy state
GN Greaves, F Meneau, O. Majérus, D.G. Jones, J. Taylor
Science, 308, 1299-1302 (2005)
Introduction

Amorphisation

Normal Melting v Pressure induced Melting

Clapeyron's Equation
\[ \frac{dT}{dP} = \frac{\Delta V}{\Delta S} = \frac{T}{\Delta V/\Delta H} \]

…….. amorphisation results from instabilities, usually volume decreases and entropy increases
Potential energy landscape

- Strong/fragile liquid behaviour
- Kauzmann paradox and perfect glasses
- Glass transition

Formation of Glasses from Liquids and Biopolymers
C.A. Angell, Science 267, 1924-1935
Introduction

Zeolite Collapse - Microscopy

Temperature induced amorphisation – T<T<sub>g</sub>

1. 100% Na zeolite Y
2. 3000Å
3. 25% Na zeolite Y

amorphised Na zeolite Y
Zeolite Collapse – Microscopy

Zeolites & Amorphisation

pressure amorphisation

1. 100% Na zeolite Y
   3000Å

2. 10% Na zeolite Y
   amorphised Na zeolite Y
   300Å

3. amorphised Na zeolite Y
polyamorphism & amorphisation

Ponyatovsky Model

EG Ponyatovsky and OI Barkolov, Pressure-induced amorphous phases, Materials Science Reports 8, 147-191 (1992)

- Instabilities triggering amorphisation relate to the presence of two amorphous phases: a high density amorphous phase (HDA) and a low density amorphous phase (LDA).

- Clapeyron crystalline melting curve replaced by free energy maximum for 50/50 mixture, with boundaries determined by the spinodal turning points.

\[ G(c) = (\Delta U - T \Delta S + P \Delta V)c + U_{\text{mix}}(1-c) + RT[c \ln c + (1-c) \ln(1-c)] \]

\( \Delta S \) is difference in configurational entropy between HDA and LDA phases.
Introduction

polyamorphism and zeolite collapse

Which vibrations promote polyamorphism and trigger zeolite collapse?

T-P diagram: $\Delta U$, $\Delta S$, $\Delta V$ and $U_{\text{mix}}$ parameterised from experimental T-P results

E. Rapoport, J. Chem. Phys. 46, 2891 (1967); ibid 48, 1433 (1968)
Anomalous Specific Heat

Enhancement over Debye $T^3$ behaviour

Low frequency Modes in crystals and glasses

Low temperature dynamics

Floppy Modes

Rigid Unit Modes

ν < 4 meV

P-sodalite


Low temperature dynamics

Two Level Systems


Angell cartoon of Energy Landscape
Librational Modes

1 meV < \nu < 3 meV

Zeolite Structure and Secondary Building Units

- Density: \(1.5 \text{ g cm}^{-3}\)
- Sodalite cage: \(~7\text{Å}~\) diameter
- Double ring: \(~6\text{Å}~\) diameter
- Supercage: \(~11\text{Å}~\) diameter

Zeolite A: \(\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\)

NB density of glass: \(2.5 \text{ g cm}^{-3}\)
\(\Delta V_A \sim 40\%\)
Zeolites and Amorphisation

X-ray Diffraction and Small Angle X-ray Scattering SAXS
Modelling 3 phases from SAXS & XRD

Na zeolite Y

Evidence for Low and High Density Phases

Zeolites & Amorphisation

$Q \sim \propto x \cdot x_{LDA}(\rho_{Z} - \rho_{LDA})^2 + x_{LDA} \cdot x_{HDA}(\rho_{LDA} - \rho_{HAD})^2 + x \cdot x_{HDA}(\rho_{Z} - \rho_{HDA})^2$

$x + x_{LDA} + x_{HDA} = 1$
Dynamics of T-induced amorphisation

Amorphisation temperature depends on the rate at which temperature is applied.
Dynamics of P-induced amorphisation

Amorphisation pressure depends on the rate at which the pressure is applied.
Zeolite collapse –

Temperature and Pressure-induced Amorphisation are equivalent

\[ P_A \Delta V_A \sim 3RT_A \]
Universal curve for zeolite collapse

\[ x = \exp\left(-\frac{t}{\tau_\text{A}}\right)^n \]

Avrami-like \( n \sim 4 \)

(3D nucleation, 1 process)

temperature and pressure induced amorphisation are equivalent processes
Rheology of Amorphisation

Different Angell plot

Zeolites &

Amorphisation

Slopes of viscosity curves for collapse (LDA) are less even than SiO₂, the classic strong liquid i.e. character of super string liquid

\[ \eta = G_\infty \tau \]

\( T < T_g \) collapse is faster than relaxation of equilibrium glass (HDA)

Crystalline chemical order should be retained and a perfect glass formed avoiding Kauzmann Paradox

Glasses made by quenching approach \( T_g \) from the liquid state whereas glasses produced by amorphisation approach \( T_g \) from the crystalline state

Zeolite collapse –

T & P –induced amorphisation

ΔVA ≈ 3RTA

Temperature and Pressure-induced Amorphisation are equivalent

PAΔVA ≈ 3RTA
Zeolite Collapse -
T-P relationships

P₁-T₁ and P₂-T₂ point to a Critical Point at negative pressure

Zeolites &
Amorphisation
Prologue

polyamorphism and zeolite collapse

Which vibrations promote polyamorphism and trigger zeolite collapse?

T-P diagram: $\Delta U$, $\Delta S$, $\Delta V$ and Umix parameterised from experimental T-P results

E. Rapoport, J. Chem. Phys. 46, 2891 (1967); ibid 48, 1433 (1968)
Inelastic neutron scattering

Low frequency modes

Zeolite modes relate to Secondary Building Units SBU’s

low frequency mode

\[ \nu = \frac{V_{tl}}{\lambda} \]

\( V_{tl} \), speed of sound:

- longitudinal 5181 ms\(^{-1}\)
- transverse 3358 ms\(^{-1}\)

\( \lambda \) = circumference of SBU

microporous enhancement

Boson Peak
Low Frequency Modes

Inelastic neutron scattering

$S(Q,E) \propto Q^2$

1 – 3 meV

sound propagating acoustic modes

$S(Q,E) \propto Q$

localised modes

microporous enhancement
Low frequency modes

both sound propagating and localised modes are anharmonic

Temperature Dependence

A

Zeolite

\[ \Delta E = 0.2 \text{ meV} \]

20% amorphous

B

Zeolite

\[ \Delta E = 0.8 \text{ meV} \]

20% amorphous

20K

290K

Inelastic Neutron Scattering

Energy Loss (meV)

100% amorphous

amorphisation
Low frequency modes

Decrease in $S(Q,E)$ with amorphisation

$S(Q,E)$ decreases non-linearly with amorphisation

$ΔE=0.2$ meV

$ΔE=0.8$ meV

Boson Peak

Amorphization (%)

Peak Area

Decrease in $S(Q,E)$ with amorphisation

$4.5$ meV

$1.8$ meV

α-cage

librational modes

librational

Low frequency modes

$ΔE=0.2$ meV
Amorphous contribution

Total – Zeolite contribution

Low frequency modes

Boson Peak

librational modes

Amorphization (%)
S(Q,E) for Amorphous contribution

\[ S(Q,E)_{\text{Total}} - S(Q,E)_{\text{Zeolite}} \]

Low frequency modes

- \( \alpha \)-cage
- \( \beta \)-cage

60% amorphous

90% amorphous

because \( S(Q,E)_{\text{HDA}} \) is very small

\[ S(Q,E)_{\text{Total}} - S(Q,E)_{\text{Zeolite}} \approx S(Q,E)_{\text{LDA}} \]
29Si NMR

1 Si and Al are ordered in zeolites and Si NMR is structured

2 Si and Al are disordered in HDA glass and Si NMR comprises a single peak

3 Conversion of zeolite spectrum into glass spectrum through amorphisation is not linear and intermediate states are structured
Conclusions

• Introduction
  Melting v Amorphisation, Microscopy

• Low temperature dynamics
  Anomalous CP, TLS, Boson Peak

• Zeolite Collapse
  SBUs, SAXS/WAX, Low Density and High Density Phases (LDA, HDA)

• Low frequency Modes -
  Boson Peak enhancement, surface modes, anharmonicity, TLS and microporous instability, evidence for LDA

Na Zeolite Y - ambient pressure
Zeolite amorphisation is a catastrophic and irreversible order transition.

this is the supercage

Na Zeolite Y - ambient pressure
this was the supercage