Glass Properties Course: Lecture 2

Density, Volume, and Packing: Part 1

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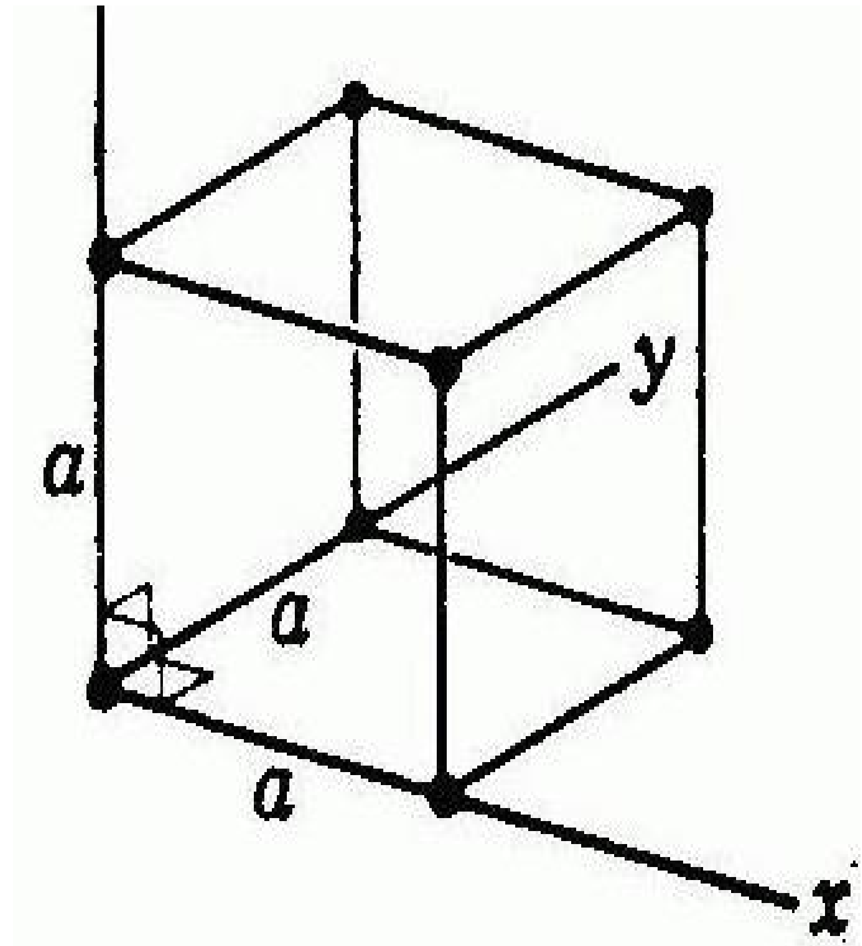
see http://www.lehigh.edu/imi/GlassPropertiesCourse.htm for archived version of lecture

Packing in Crystals

- Simple Cubic Crystal
- packing can be determined exactly
- If these were atoms then there would be 8(1/8) atoms per cell or 1 atom per cell.



Packing Fraction of Simple Cubic Lattice

- The packing fraction would be

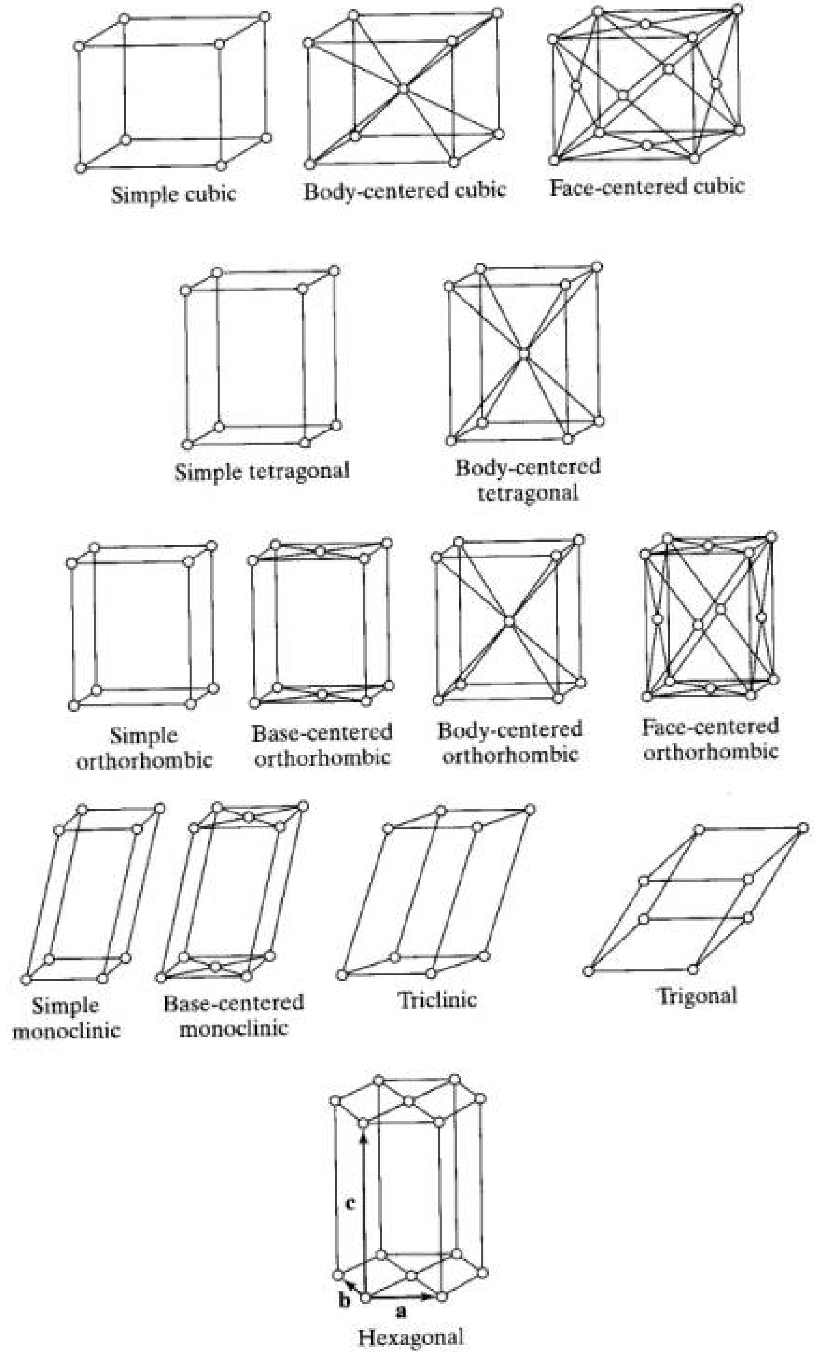
$(4/3)\pi r^3/d^3$

r is related to d, $r = d/2$

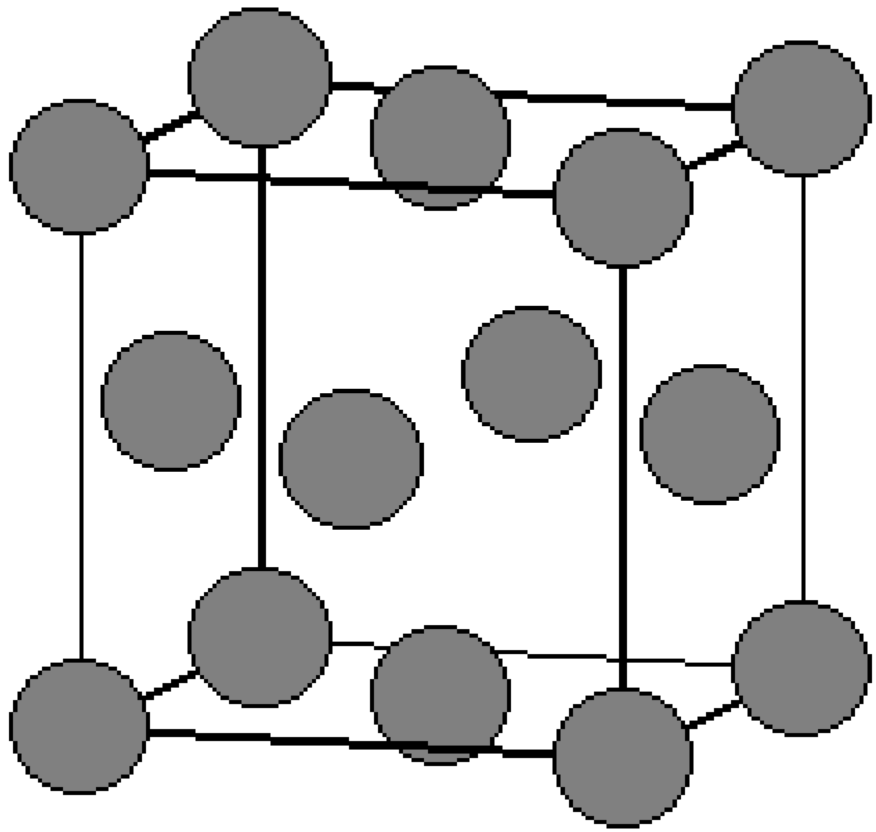
Therefore, the packing is
$(4/3)\ \pi(d/2)^3/d^3 = 4\pi/24 = \pi/6 = 0.52$

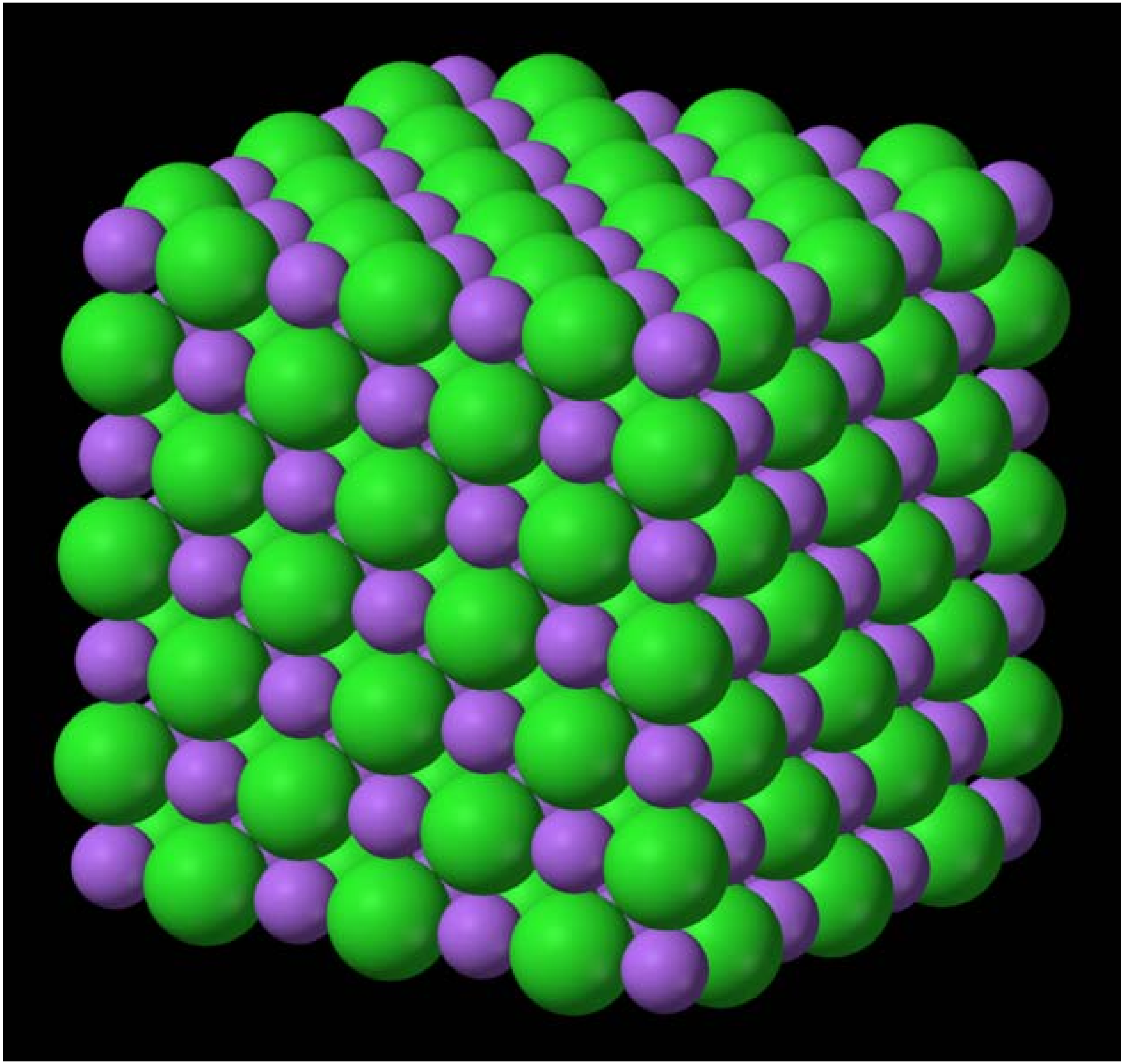
Some Observations

- Since a crystal structure is a lattice + basis the packing fraction of the simple cubic lattice can go beyond one atom bases.
- However, some crystal structures that appear simple cubic are in fact not: The sodium chloride structure is actually face centered cubic with a basis of two atoms.
- Crystal structure, in itself, is a course.


Simple cubic
Body-centered cubic
Face-centered cubic
Simple tetragonal
Body-centered tetragonal
Simple orthorhombic
Base-centered orthorhombic
Body-centered orthorhombic
Face-centered orthorhombic
Simple monoclinic
Base-centered monoclinic
Triclinic
Trigonal
c
b
a
Hexagonal

Face-Centered Cubic





Questions

- 1. What is the packing of the face centered cubic structure?
- Answer: 0.74.

- 2. Find the crystal structure of aluminum and using its packing fraction from this known structure and its atomic mass predict the density. Compare with experiment.
- Final Answer: 2.70 g/cc

How to Measure Density

- M/V if the geometry is high
- Archimedes wet/dry
- Sink float
- Pycnometry
- Density gradient

How to Measure Density

- M/V if the geometry is high
- **Archimedes wet/dry**
- Sink float
- Pycnometry
- Density gradient

Archimedes Principle

- An object of density, ρ, in a fluid has a buoyant force, B, equal to the weight of the displaced fluid.
- Define:

  Wa = Apparent weight in fluid of density ρ_o

  W = Weight of object determined in air

Then Wa = W – B

and $B = \rho_o V g$

Archimedes Principle

$Wa = W - B$ and $B = \rho_o Vg$

$W = Wa + B = Wa + \rho_o Vg$

$V = M/\rho = W/\rho g$

Or $W = Wa + \rho_o Wg/\rho g = Wa + W\rho_o/\rho$

Archimedes Principle

- $W = Wa + W\rho_o / \rho$

- Solve for ρ:

- **$\rho = \rho_o W/(W - Wa)$ (working equation)**

Archimedes Principle

- High quality water is often used (ρ_o = 1 g/cc).
  Other fluids (up to ρ_o = 3.32 g/cc for diiodomethane) may be used for dense objects since the method is more accurate for denser liquids. This is because the weight changes will be greater in denser fluids.

Questions

- 1. Imagine a 0.7 cc of a lead silicate glass of density 7.5 g/cc. What is its apparent weight in

  a) water

  b) diiodomethane

  c) carbon tetrachloride

  2. What temperature control of the fluid would it take to allow measurements with an error no more than 0.5 %.

How to Measure Density

- M/V if the geometry is high
- Archimedes wet/dry
- **Sink float**
- Pycnometry
- Density gradient

Sink float

- In the Sink float **method the density of several mg of sample is determined by floating the flakes in calibrated miscible fluids.**
- **We use acetone and diiodomethane since the density range is 0.78 g/cc to 3.32 g/cc.**

Sink float

- If the fluids are miscible then:

$V = V_1 + V_2$ and $M = M_1 + M_2$

$\rho = (M_1+M_2)/(V_1+V_2) = (M_1+M_2)/(M_1/\rho_1+M_2/\rho_2)$

$\rho = (1+m)/(1/\rho_1+m/\rho_2)$ where $m = M_2/M_1$

corrected 9/9/08

$\boldsymbol{\rho = \rho_1 (1+m)/(1+m\rho_1/\rho_2)}$

For calibrated fluids one needs only to measure the mass ratio of the two fluids.

Sink float

- Just tens of mg of sample are needed
- Temperature is crucial because of the fluids more than the sample.
- No samples with density greater than 3.32 g/cc can be done.
- Several ways to do the measurement—we prefer the bracketing method.
- We use stirrer and add diiodomethane to acetone drop by drop. Need a cap because acetone is volatile.

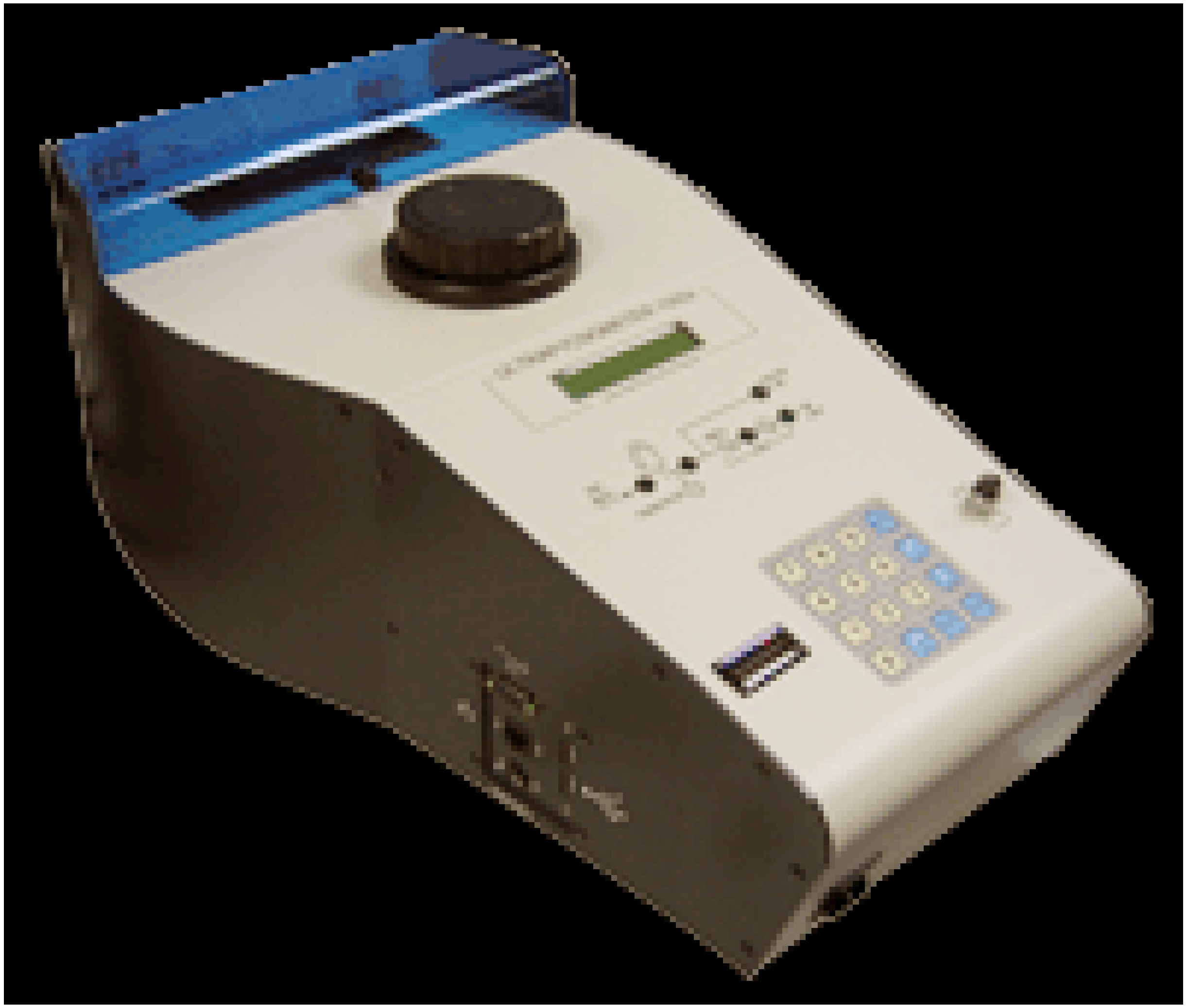
Question

- Plot the densities of liquid mixtures of acetone and diiodomethane as a function of the mass ratio of diiodomethane to acetone assuming they are fully miscible.
- This plot serves as a useful way to estimate needed masses of the two fluids in the sink float method.

How to Measure Density

- M/V if the geometry is high
- Archimedes wet/dry
- Sink float
- **Pycnometry**
- Density gradient

Pycnometry



Pycnometry

- Uses Ideal Gas Law (we use He)
- PV= nRT
- There are two calibrated volumes: the reference (Vr) and cell (Vc) volumes. Calibration is done with two reference steel spheres.
- Sample volume is defined by Vs.

Pycnometry

- Put sample in Vc
- Pressurize Vr and measure pressure, P_1
- Let gas fill both chambers and measure pressure, P_2
- Then if T = constant,

  $P_1 Vr = P_2(Vr + Vc - Vs)$
- Solve for **$Vs = Vc + (1 - P_1/P_2)Vr$**

Pycnometry

- Find mass on a balance (usually done before volume measurement)
- Need a certain critical volume for sample. We use 0.5 cc, minimum.
- Pycnometers come automated or manual.
- No limitation on density range.
- Temperature dependent due to ideal gas law. We calibrate all densities against high purity aluminum.

Pycnometry

- Typical pressure to use is about 17 psi for P_1 with P_2 being in the 8 psi range, depending on V_1 and V_2.
- We typically perform 10-15 density determinations per sample averaging the last 5 for the final result (after doing a temperature correction).

How to Measure Density

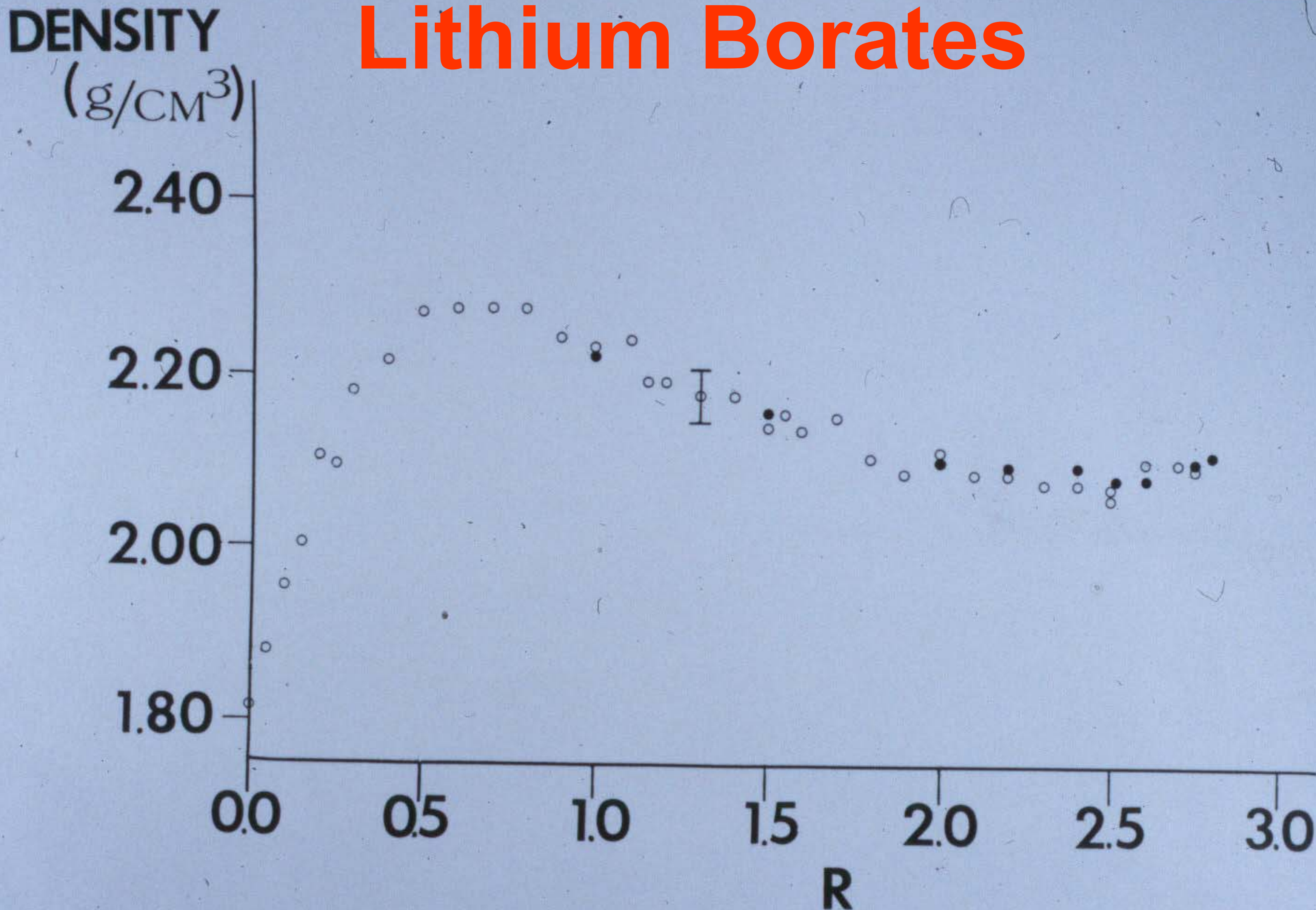
- M/V if the geometry is high
- Archimedes wet/dry
- Sink float
- Pycnometry
- **Density gradient**

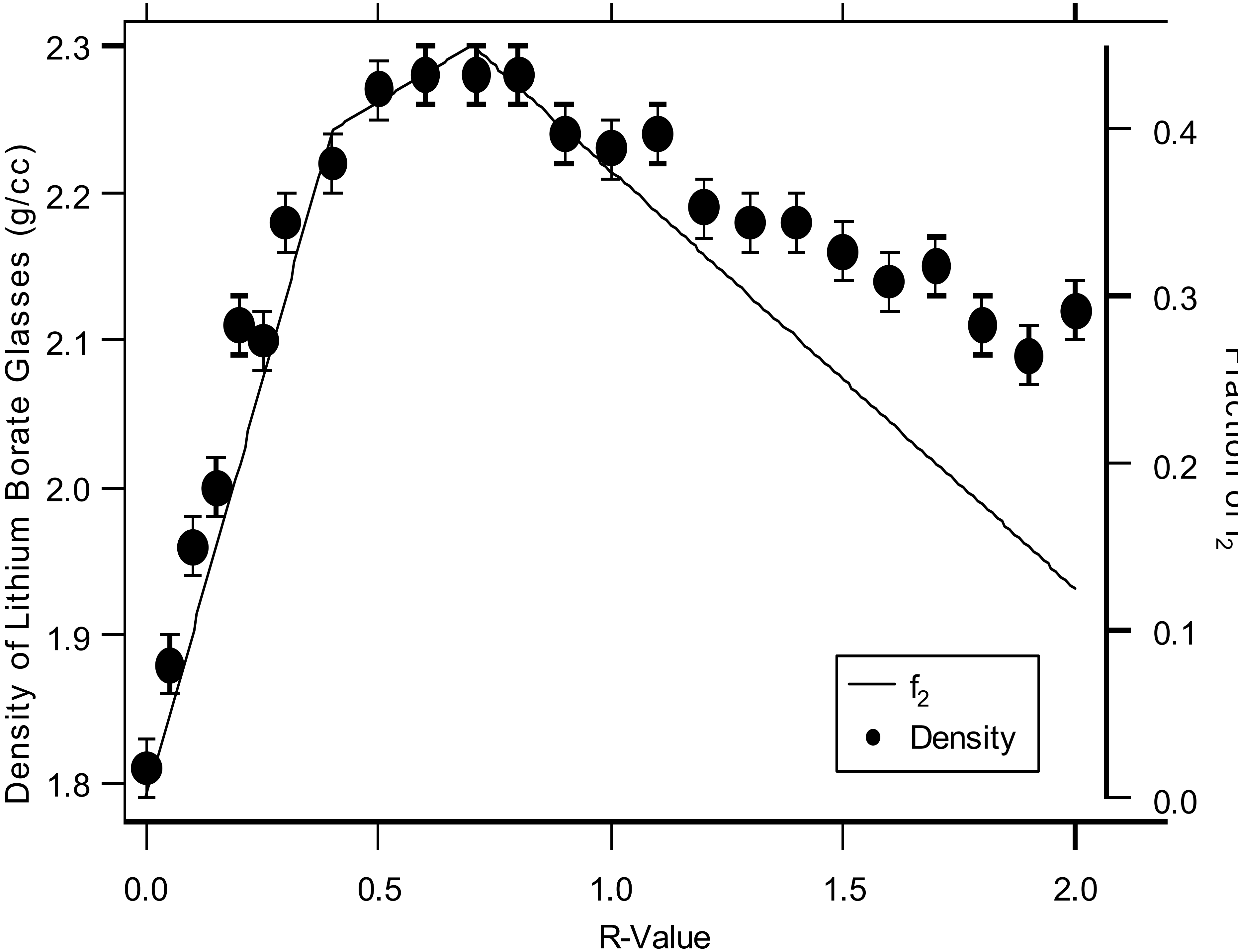
- http://www.ides.com/property_descriptions/ASTMD1505.asp

Some Results

- Borates
- Silicates
- Germantes
- Others

Lithium Borates





Density of Lithium Borate Glasses (g/cc)
1.8
1.9
2.0
2.1
2.2
2.3
0.0
0.5
1.0
1.5
2.0
R-Value
Fraction of f_2
0.0
0.1
0.2
0.3
0.4
f_2
Density

What Happens to a Density Measurement

- Density itself can be used

  1. Needed in diffraction experiments of all kinds: neutron, X-Ray, electron.

  2. Needed in MD calculations

  3. Density is a simple and essential test for any structural modeling.

  4. Density can reveal structural origins.

What Happens to a Density Measurement

- Density itself can be used to compare with structure.

$$\rho = M/V$$

$$= \Sigma M/(Vi)$$

In a given glass system one needs to know the short range structures and their fractions.

$$\rho = \Sigma M/(f_i V_i)$$

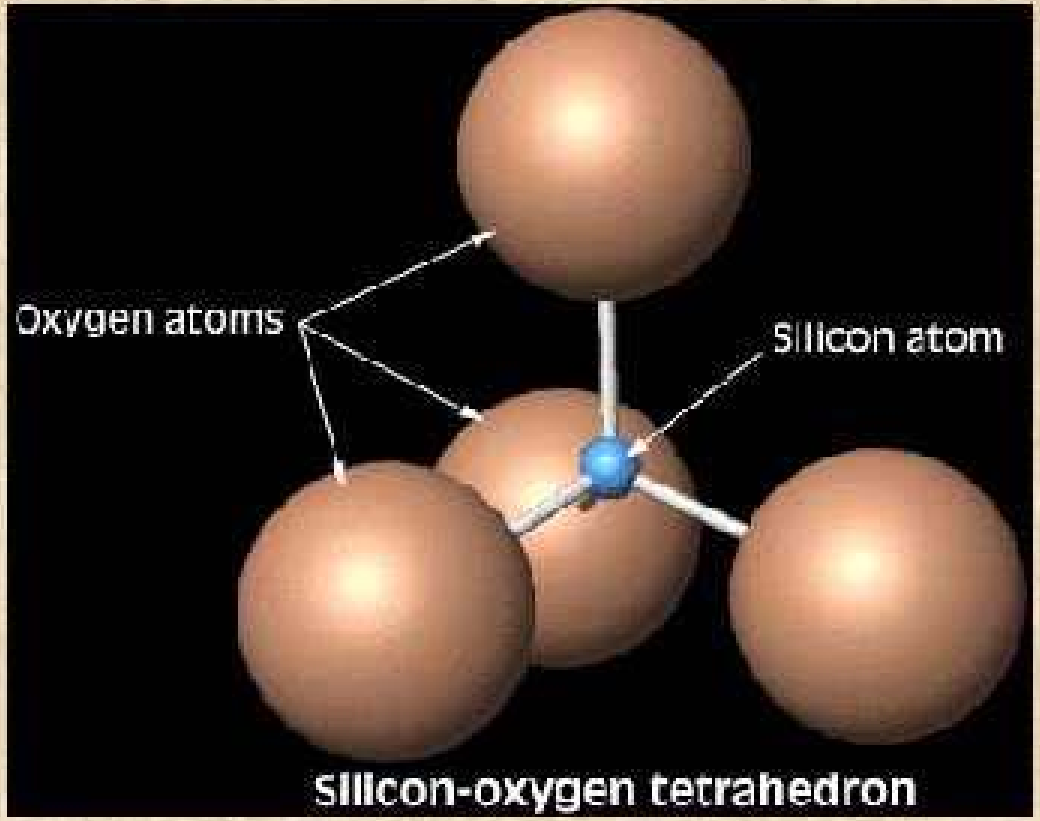
A least squares fit of the density yields the values for V_i. These are the volumes of the individual structural groupings. This is model dependent since the units and the fractions of the units are from models.

Glass Structure

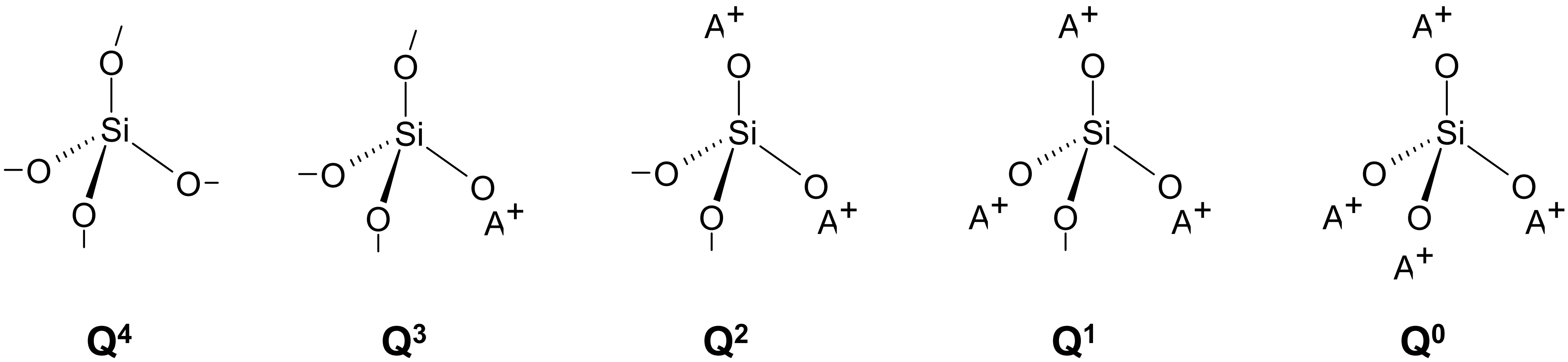
- Silicates: Tetrahedral
- Borate: Trigonal and Tetrahedral
- Germanates: Tetrahedral and Octohedral
- Phosphates: Distorted Tetrahedral
- Vanadates: 5 and 4-coordinated V

Silica Tetrahedra

- The basic building block of all silicates



Background: Q-Units



- **Structural Model for Silicate Glasses:** Alkali oxide enters the silicate network, converting bridging oxygens to non-bridging oxygens while maintaining silica tetrahedra. The result is a glass with a mixture of Q^n tetrahedra where n represents the number of bridging oxygens per silicon and may take values of 0 to 4 in integer steps.

Q Units

- $Q^4 = (SiO_2)^0$
- $Q^3 = (SiO_{2.5})^{-1}$
- $Q^2 = (SiO_3)^{-2}$
- $Q^1 = (SiO_{3.5})^{-3}$
- $Q^0 = (SiO_4)^{-4}$

Background: Binary Rule

- Simplest model which describes the structure of alkali silicate glasses as the amount of alkali modifier is increased.
- Assumes sequential conversion of the silica tetrahedra:

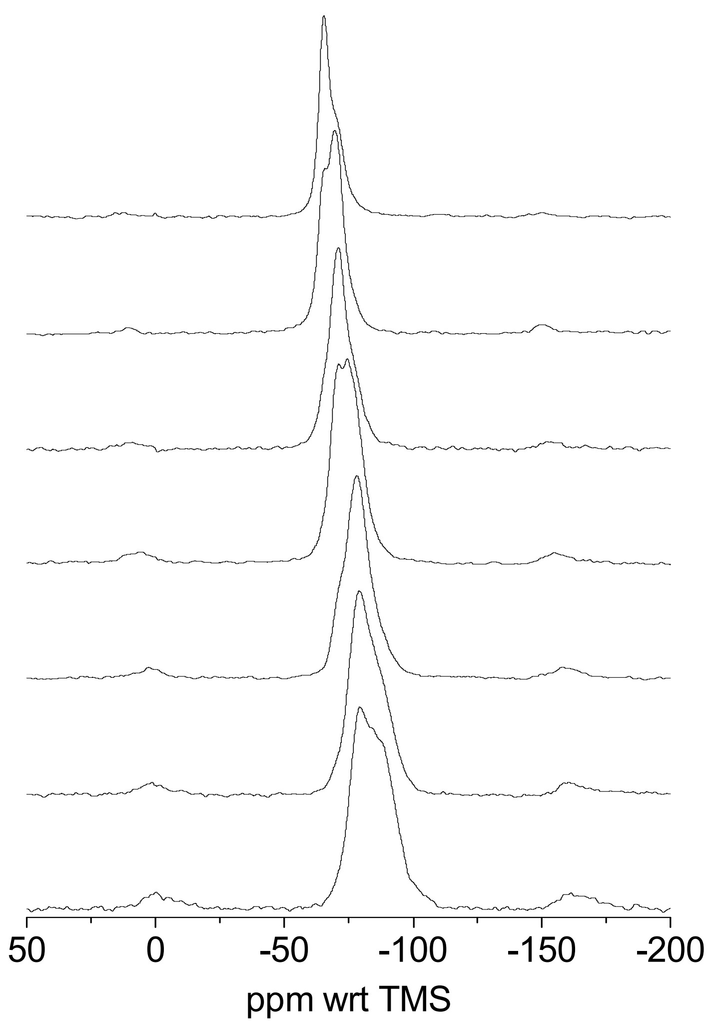
$$Q^n \rightarrow Q^{n-1}$$

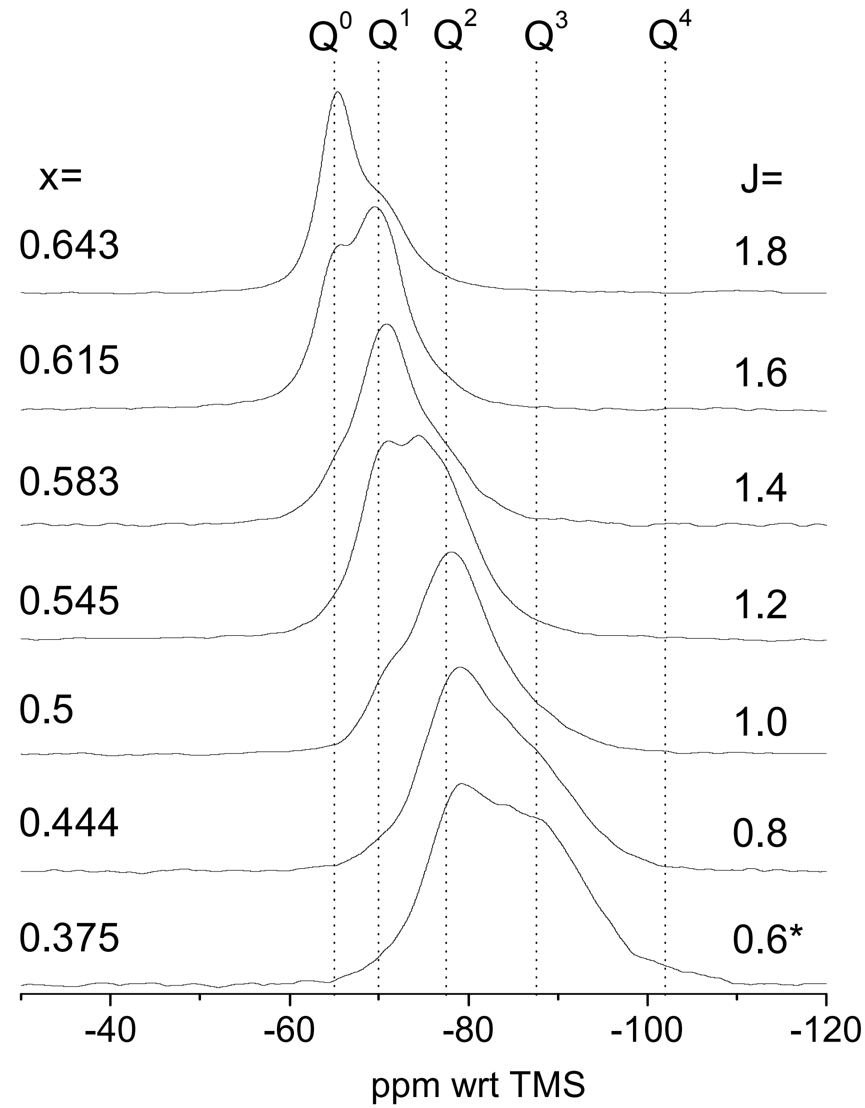
- Fractional abundances of the units in terms of J, the molar ratio of alkali oxide to SiO_2:

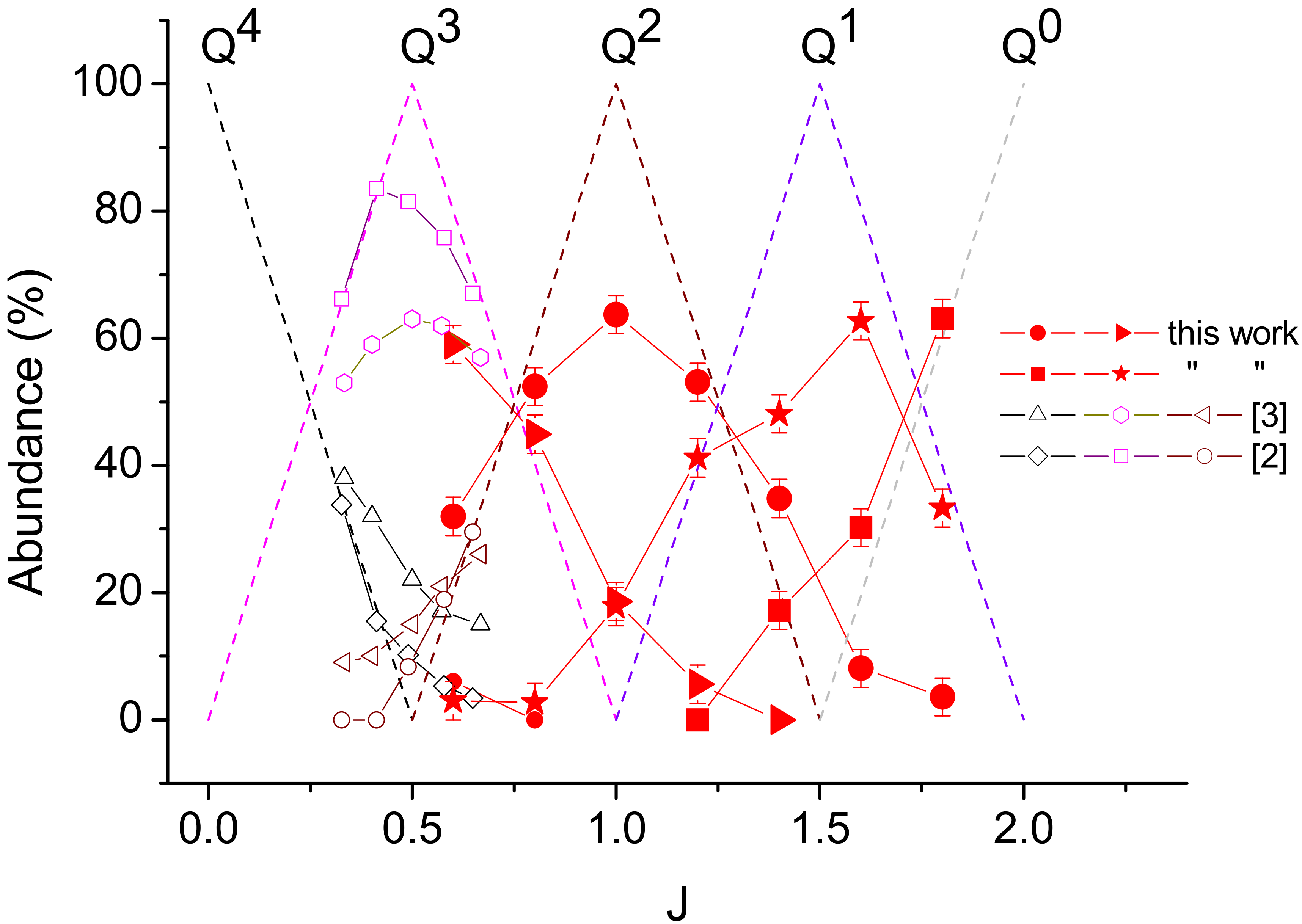
$Q^4 = 1 - 2J$	**$Q^3 = 2J$**	**$0.0 \leq J \leq 0.5$**
$Q^3 = 2 - 2J$	**$Q^2 = 2J - 1$**	**$0.5 \leq J \leq 1.0$**
$Q^2 = 3 - 2J$	**$Q^1 = 2J - 2$**	**$1.0 \leq J \leq 1.5$**
$Q^1 = 4 - 2J$	**$Q^0 = 2J - 3$**	**$1.5 \leq J \leq 2.0$**

- Given a J value, we can predict the abundance of each Q-unit for the glass using this model.

^{29}Si MAS NMR of Lithium Silicates







Q4
Q3
Q2
Q1
Q0
Abundance (%)
100
80
60
40
20
0
0.0
0.5
1.0
1.5
2.0
J
this work
"   "
[3]
[2]

Disproportionation

- **$2Q^n \rightarrow Q^{n+1} + Q^{n-1}$**.
- Can also go further than this

Short Ranges Structures

Short-range borate units,

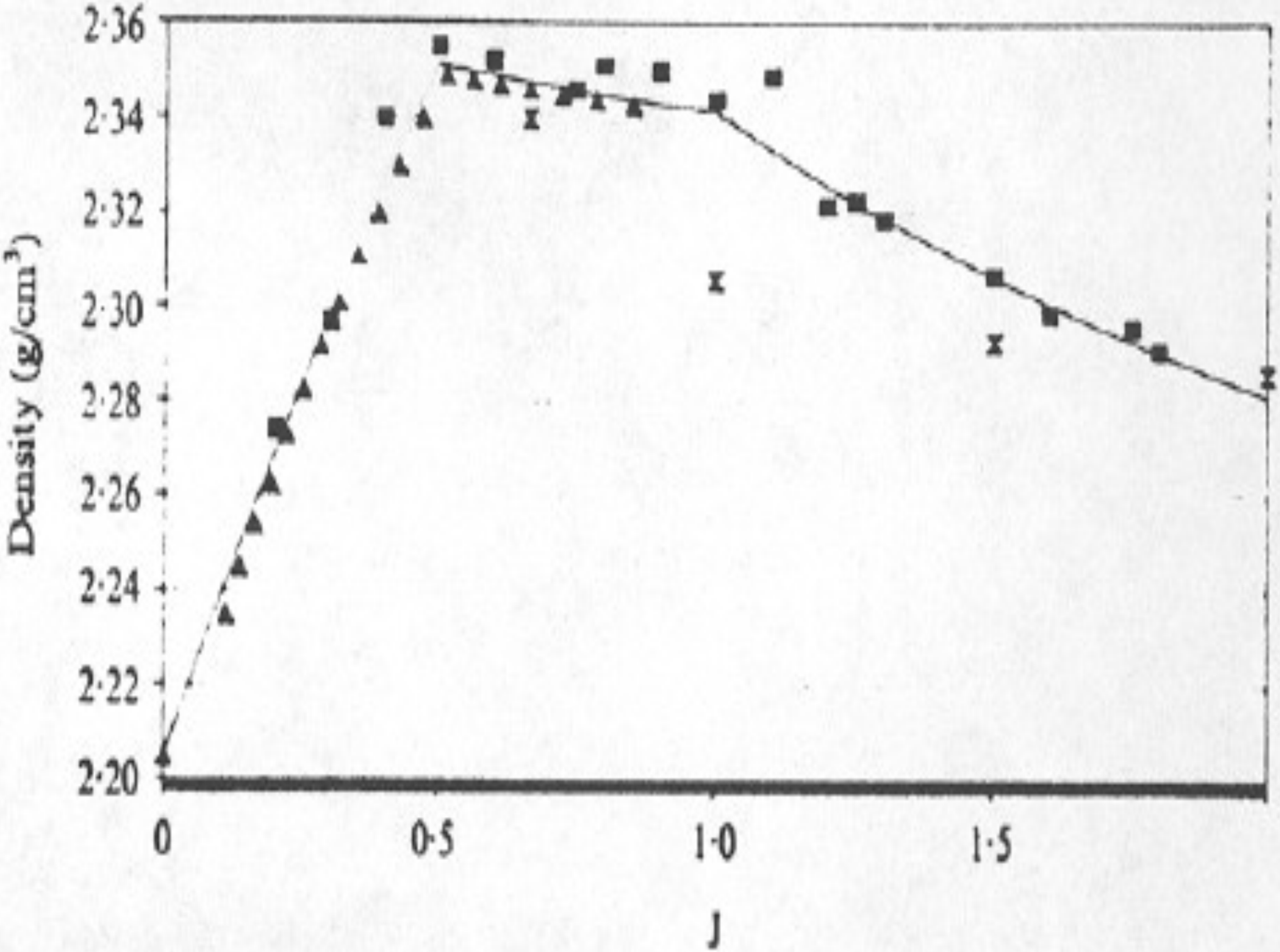
$$R = \frac{molar\ \%\ MO}{molar\ \%\ B_2O_3}$$

F_i unit	Structure	R value
F_1	trigonal boron with three bridging oxygen	0·0
F_2	tetrahedral boron with four bridging oxygen	1·0
F_3	trigonal boron with two bridging oxygen (one NBO)	1·0
F_4	trigonal boron with one bridging oxygen (two NBOs)	2·0
F_5	trigonal boron with no bridging oxygen (three NBOs)	3·0

Short-range silicate units,

$$J = \frac{molar\ \%\ MO}{molar\ \%\ SiO_2}$$

Q_i unit	Structure	J value
Q_4	tetrahedral silica with four bridging oxygen	0·0
Q_3	tetrahedral silica with three bridging oxygen (one NBO)	0·5
Q_2	tetrahedral silica with two bridging oxygen (two NBOs)	1·0
Q_1	tetrahedral silica with one bridging oxygen (three NBOs)	1·5
Q_0	tetrahedral silica with no bridging oxygen (four NBOs)	2·0


2·36
2·34
2·32
2·30
2·28
2·26
2·24
2·22
2·20
Density (g/cm³)
0
0·5
1·0
1·5
J

Method of Least Squares

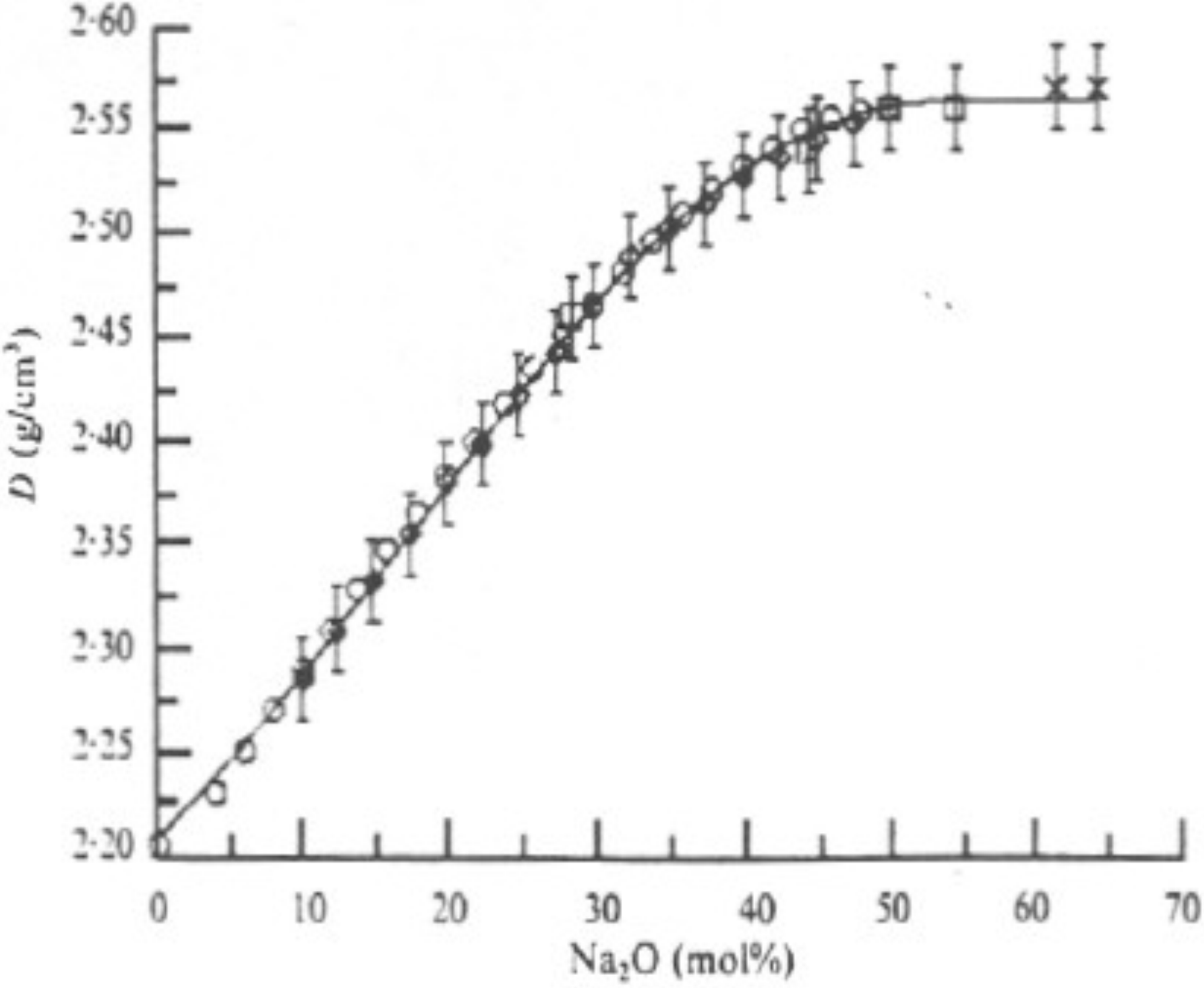
- Take $(\rho_{mod} - \rho_{exp})^2$ for each data point
- Add up all terms
- Vary volumes until a least sum is found.
- Volumes include empty space.

- ρ_{mod} **= $\Sigma M/(f_i V_i)$**

Example: Li-Silicates

- $V_{Q4} = 1.00$
- $V_{Q3} = 1.17$
- $V_{Q2} = 1.41$
- $V_{Q1} = 1.69$
- $V_{Q0} = 1.95$

- $V_{Q4}(J = 0)$ defined to be 1.
- The $J = 0$ glass is silicon dioxide with density of 2.205 g/cc



2·60
2·55
2·50
2·45
2·40
2·35
2·30
2·25
2·20
D (g/cm³)
0
10
20
30
40
50
60
70
Na₂O (mol%)

Borate Structural Model

- $R < 0.5$
- $F_1 = 1-R$, $F_2 = R$

- $0.5 < R < 1.0$
- $F_1 = 1-R$, $F_2 = -(1/3)R + 2/3$, $F_3 = +(4/3)R - 2/3$

- $1.0 < R < 2.0$
- $F_2 = -(1/3)R + 2/3$, $F_3 = -(2/3)R + 4/3$, $F_4 = R-1$

Another Example: Li-Borates

- $V_1 = 0.98$
- $V_2 = 0.91$
- $V_3 = 1.37$
- $V_4 = 1.66$
- $V_5 = 1.95$

- $V_1(R = 0)$ is defined to be 1.
- The R = 0 glass is boron oxide with density of 1.823 g/cc

	Barium	Calcium
V_{f1}	0·96	0·99
V_{f2}	1·16	0·96
V_{f3}	1·54	1·29
V_{f4}	2·16	1·68
V_{Q4}	1·44	1·43
V_{Q3}	1.92	1.72
V_{Q2}	2.54	2.09

Densities of Barium Borate Glasses

R = x/(1-x)	Density (g/cc)
0·0	1·82
0·2	2·68
0·2	2·66
0·4	3·35
0·4	3·29
0·6	3·71
0·6	3·68
0·8	3·95
0·8	3·90
0·9	4·09
1·2	4·22
1·3	4·31
1·5	4·40
1·7	4·50
2·0	4·53

Part 1 ended with this slide

Use these data and the borate model to find the four borate volumes. Note this model might not yield exactly the volumes given before.