METALLIC GLASS STRUCTURE: Efficient Packing of Unequal Spheres

Finding Order Within Disorder

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29 April 2010

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Thanks to:
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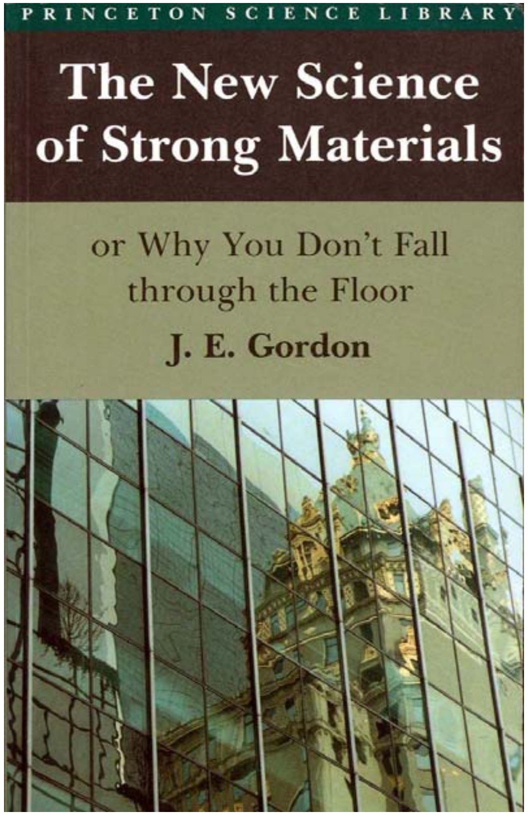
AFRL
THE AIR FORCE RESEARCH LABORATORY

The Entropy Club

"~~metallurgists~~ ^ experimentalists are apt to be practical down-to-earth people who stand no nonsense, but the ~~non-metallurgists~~ ^ theoriticians are probably more lyrical and imaginative"



STRUCTURE

PROPERTIES

potentials

EYESIGHT vs INSIGHT
Why not measure structure directly?

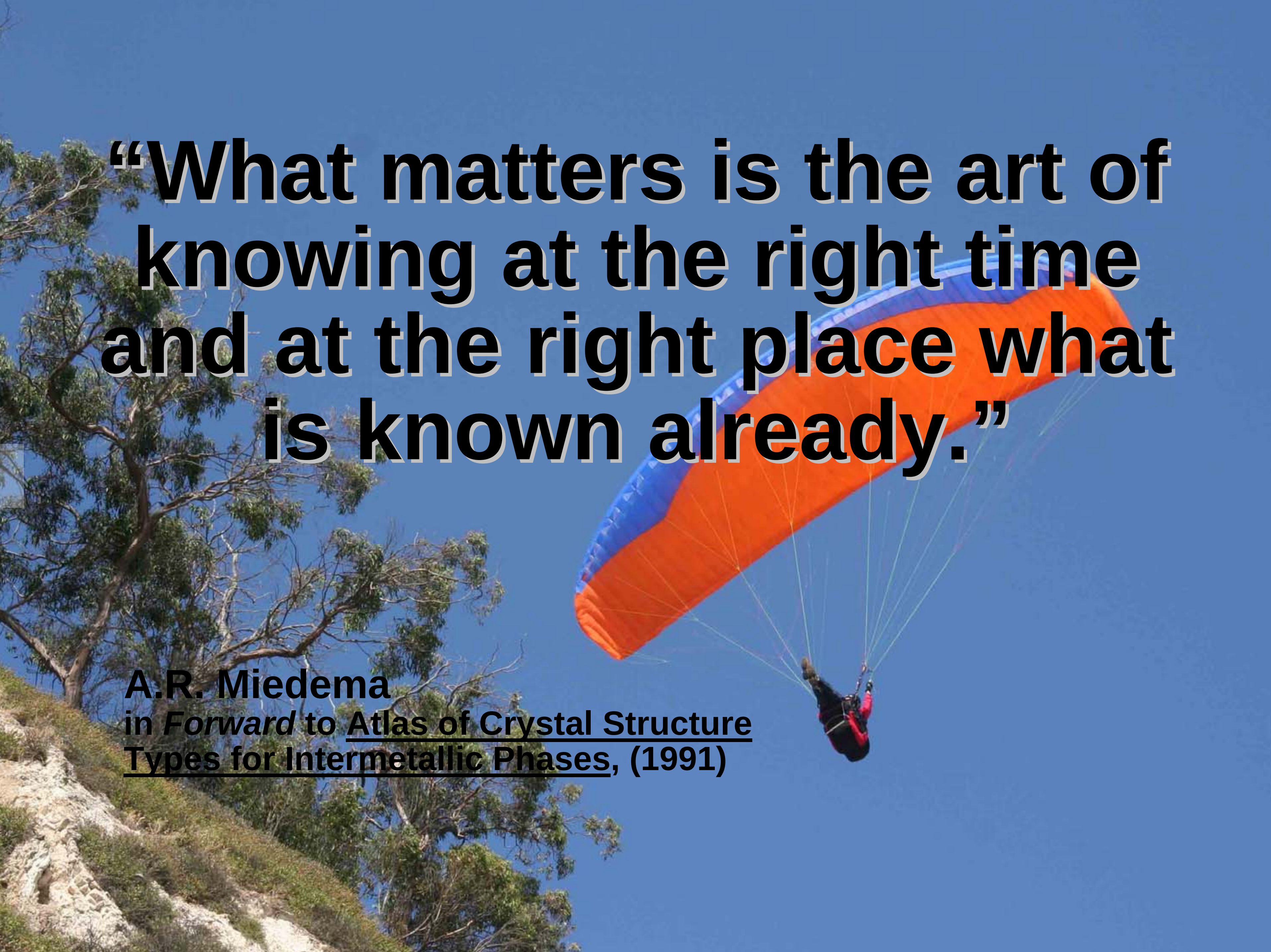
Early investigations used ‘eyesight’
- State-of-the-art experimental methods nevertheless lose important details
- Low spatial resolution provides globally averaged signals
- Reliable information primarily available for first few atomic coordinations
- Deconvolution of overlapping signals is required to quantify atomic coordinations and separations
- Large integration limits produce non-unique results

Direct experiment gives only broad statistical descriptions

Computations provide an alternate approach to describe structure
- Individual simulations are ultimately system-specific
- The information produced is overwhelming, so that a system for organizing results is needed

“The greatest strength of atomic simulations is that they give the (x,y,z) coordinates of every atom in the system.”

“The greatest weakness of atomic simulations is that they give the (x,y,z) coordinates of every atom in the system.”


"What matters is the art of knowing at the right time and at the right place what is known already."
A.R. Miedema
in *Forward* to Atlas of Crystal Structure Types for Intermetallic Phases, (1991)

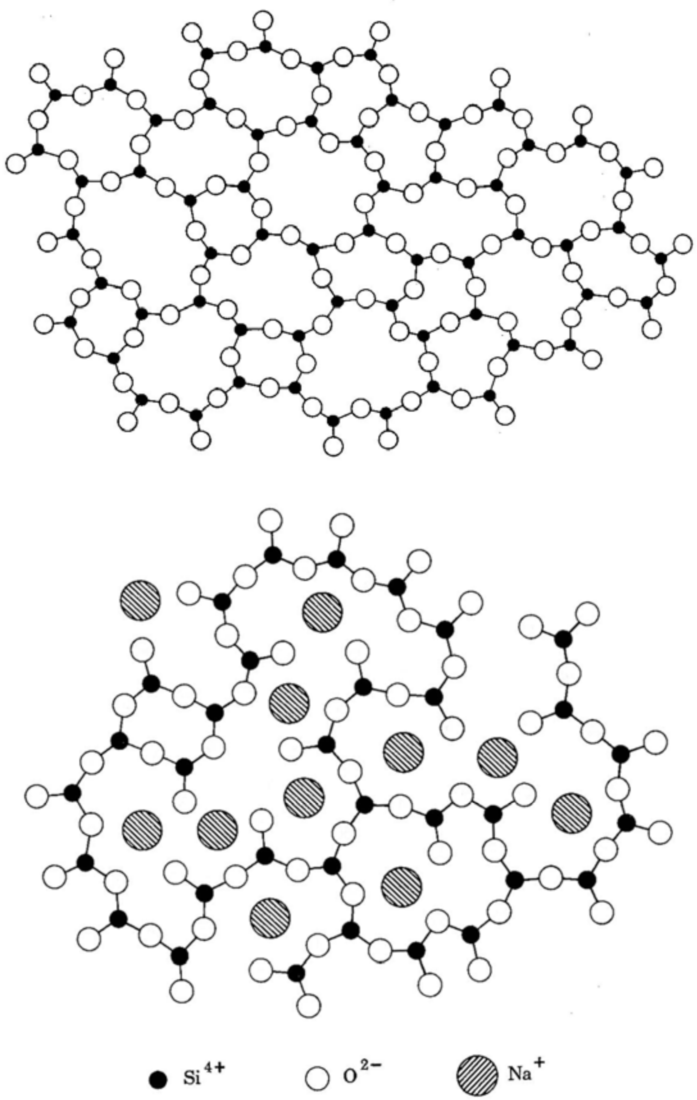
CONTINUOUS RANDOM NETWORK (CRN) MODEL

Efficiently-packed atomic clusters form the basis of the CRN model

- SiO_4 and BO_3 polyhedra form local representative structural elements (RSEs)
- vertex-sharing between adjacent RSEs establishes approach for building structure beyond the nearest neighbor shell

Important differences exist for metallic glasses

- predominantly non-directional metallic bonding *vs.* significant directional covalent bonding in oxide glasses
  - ➢ *efficient filling of space expected in metallic glasses*
- conservation of charge is not a constraint
- smaller variation in atom sizes (<40%)
  - ➢ *radius ratios in metallic glasses range from $0.6 < R < 1.4$*

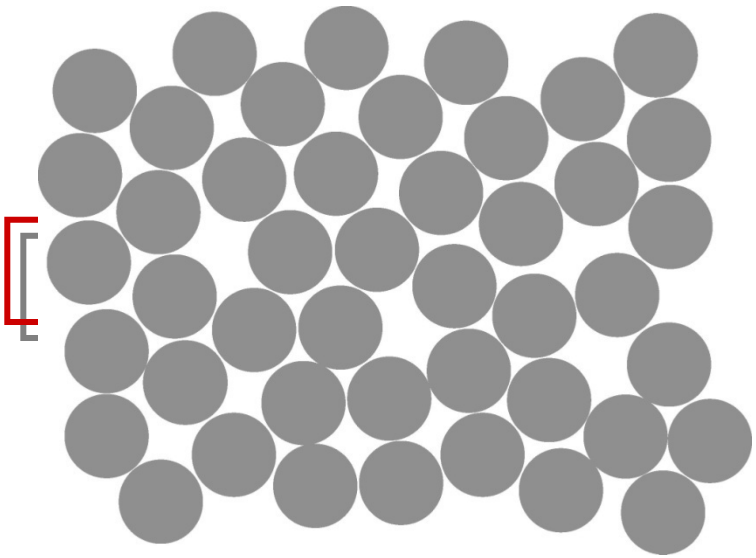


Zachariasen; *J. Am. Chem. Soc.*, **54**, (1932)

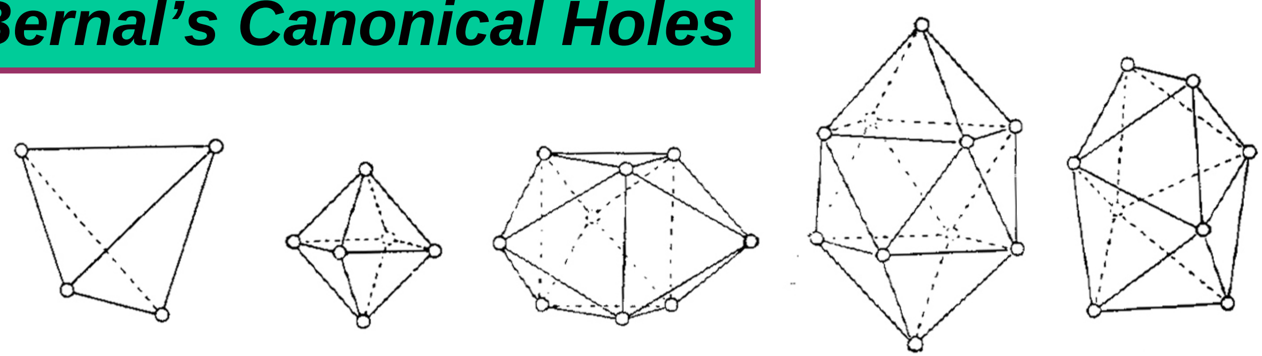
DENSE RANDOM PACKING
A Statistical Model

A dense random packed structure of equal-sized spheres is characterized by:

- a packing fraction of 0.6366
- frequently observed specific local atomic clusters
  - *tetrahedra, half-octahedra, trigonal prisms, Archimedian antiprisms, tetragonal dodecahedron*
- the absence of medium-and long-range order



Bernal's Canonical Holes



Bernal; *Nature*, **185**, (1959)

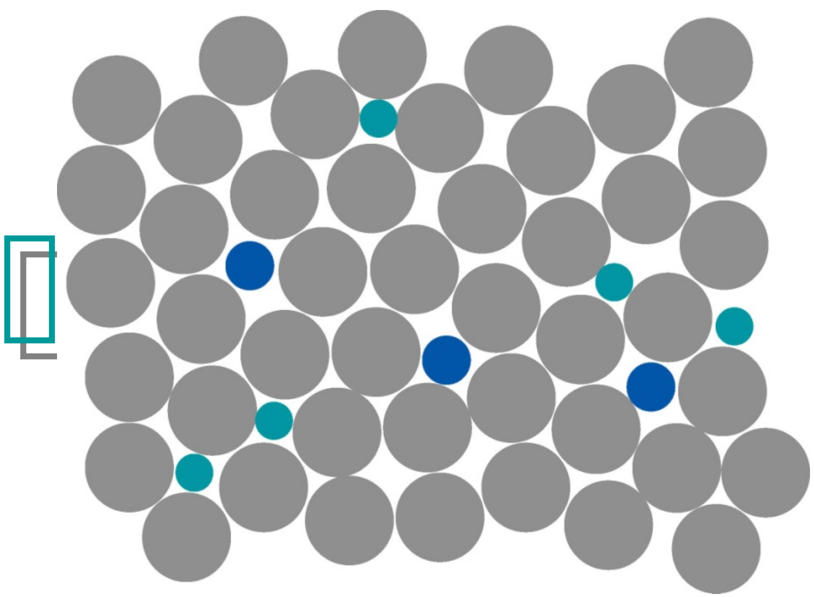
DENSE RANDOM PACKING
Interstitial Model

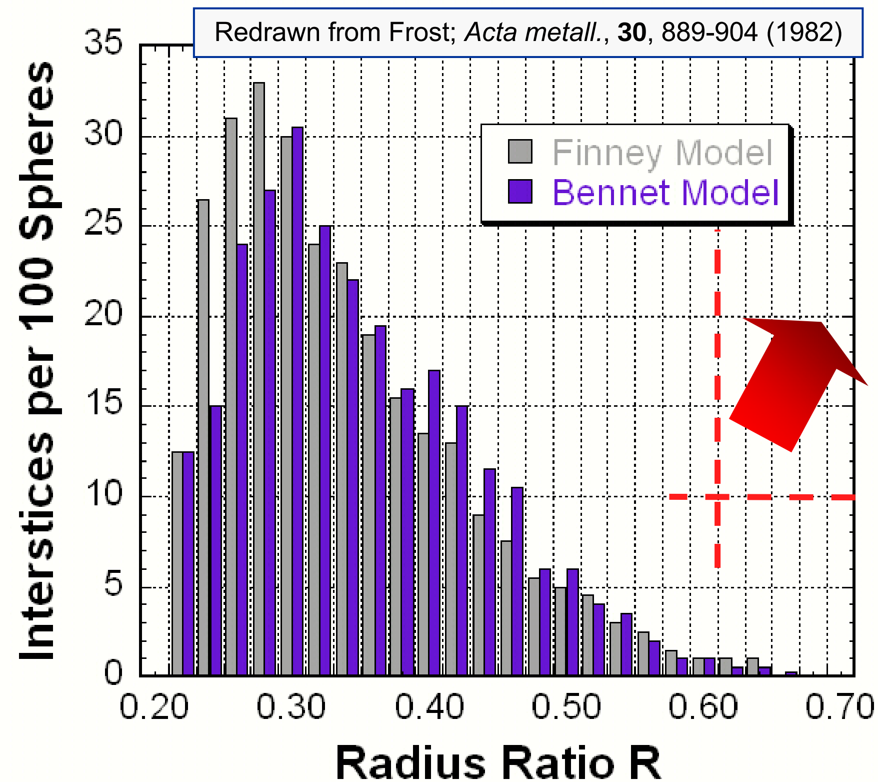
Polk proposed that solutes fill 'holes' left in solvent array

– subsequent analysis showed that the 'holes' are too small and too few to account for observed constitutions of metallic glasses

  - *solute radius ratios are ~0.6 ≤ R ≤ 1.4 and concentrations are ~10% ≤ C ≤ 40%*

– computer simulation of 'hard' and 'soft' spheres confirms this result

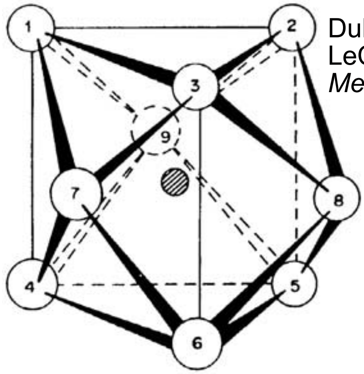




STEREO-CHEMICALLY DEFINED (SCD) MODEL

Local structures show similarity to those in the crystalline state

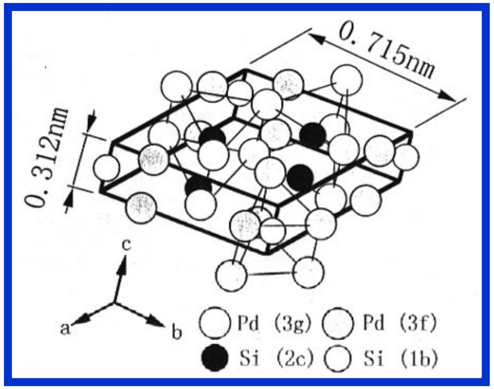
- Short-range atomic forces are similar in crystal and amorphous states
- Capped trigonal prism in metal–metalloid glasses similar to structure of Fe_3C, Pd_3Si etc.



DuBois and LeCaer; *Acta Metall.*, (1984)

The SCD model is similar to the CRN model

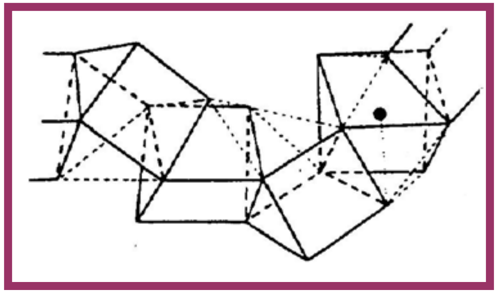
- Representative structural element (solute-centered atomic cluster) is repeated to fill space
- No preferred bond angle and adjacent clusters share edges or faces to conserve volume



Hirotsu *et al.*; *Mat. Sci Eng.*, (1997)

Efforts to extend model beyond 1st shell have been only marginally successful

- simple chemical twinning applied to binary glasses
- extensive curve fitting with arbitrary adjustable parameters required to match observed MRO
- extension to other local coordination numbers and higher order systems is problematic



Gaskell; Glasy Metals II, (1983)

CONFUSION PRINCIPLE

Simply states that the greater is the number of alloy constituents and the difference in relative sizes of atoms, the greater is the tendency to form a glass

- based on observation that best glasses often have many constituents of significantly different sizes
- the atoms become ‘confused’ and don’t know where to go
- not supported by the single controlled experiment to validate this concept
- the ‘Miracle Corollary’ states that the atoms know exactly what they are doing, and that it is the scientists who are confused!

Not a structural model since atomic configurations in the amorphous state are not described

METALLIC GLASS FEATURES

What is known already?

A credible structural model must show agreement with established metallic glass characteristics:

- randomness is a dominant and defining feature
- efficient atomic packing is required over all length scales
  - *low molar volume, small density decrease upon solidification and crystallization and quantification of locally efficient atomic packing are all observed*
- strong short range ordering (compositional and topological)
- significant medium range order (compositional and topological)
- significant size difference (≥12%) between solvent and solute atoms
- large negative enthalpy of mixing of constituent elements
- three or more solutes
- relative sensitivity in some glasses to small composition changes (~1%)
- relative insensitivity in some glasses to large composition changes (~10%)

A compelling structural model will give a predictive capability for many of these features

METALLIC GLASSES HAVE HIGH RELATIVE DENSITY

Metallic glasses have an exceptionally high density relative to the crystalline state of the same alloy

– relative density is typically ≥97%, and is ≥99.5% for BMGs

ALLOY	Δρ (%)
$Zr_{60}Al_{10}Cu_{30}$	0.30
$Zr_{60}Al_{15}Cu_{25}$	0.31
$Zr_{55}Al_{10}Cu_{30}Ni_5$	0.44
$Zr_{55}Ti_5Al_{10}Cu_{20}Ni_{10}$	0.30
$Zr_{52.5}Ti_5Al_{12.5}Cu_{20}Ni_{10}$	0.45
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	0.54
$Al_{85}Ni_6Fe_3Gd_6$	3.31
$Al_{87}Ni_6Fe_1Gd_6$	2.80
$Al_{85}Ni_5Fe_2Gd_8$	1.85

Density increase for crystallization of most metals ranges between 4–12%

COMPARISON WITH METALLIC GLASS CHARACTERISTICS

Metallic Glass Characteristics

Structural Concepts

	Randomness	Global Packing Efficiency	Local Packing Efficiency	SRO	MRO	ΔH	# Solutes	ΔR	R*	Constitution
DRP	✓✓	X	X	✓	X	NA	X	X	X	X
DRP/Finney	✓✓	✓	X	✓	X	X	NA	X	X	X
SCD/SCT	✓	X	✓	✓✓	✓	✓	X	X	X	X
Confusion Principle	✓	NA	NA	NA	NA	NA	✓	✓	NA	NA
Critical Strain	NA	NA	NA	NA	NA	NA	X	✓✓	X	✓
Universal MRO	NA	NA	NA	✓	✓	NA	NA	NA	NA	NA

NA–Not Addressed X – Inconsistent ✓ – Consistent ✓✓ – Predictive

“Gentleman, we have

models ^

run out ~~of mo~~ney. Now

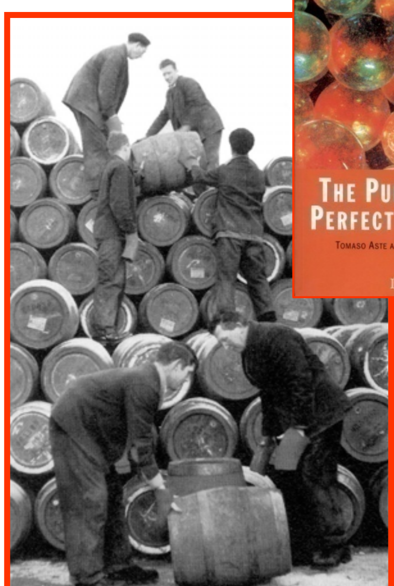
we must think.”

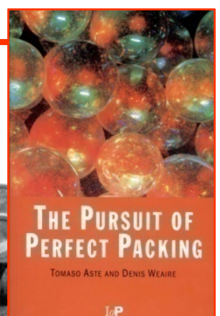
Winston Churchill

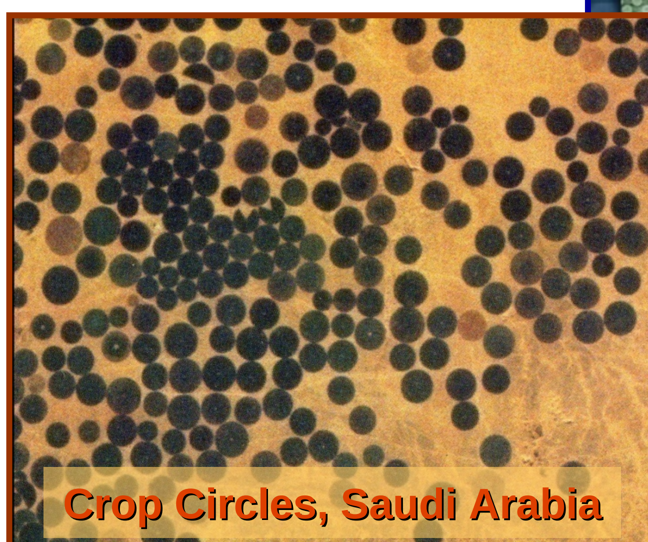
EFFICIENT FILLING OF SPACE

A problem of broad commercial & technological importance

- Agriculture
- Biology
- Civil Engineering
- Communication Theory
- Materials Science
- Mathematics
- Packaging and Shipping
- Physics







Crop Circles, Saudi Arabia

HISTORY OF EFFICIENT PACKING

Kepler Conjecture is an intuitive solution to a 'simple' problem

David Hilbert highlighted efficient packing in a list of problems to guide mathematics in the 20th century

– "How can one arrange most densely in space an infinite number of equal solids of given form?"

Mathematics has extended intuition and experience

– Solution to Kepler Conjecture claimed in 1998

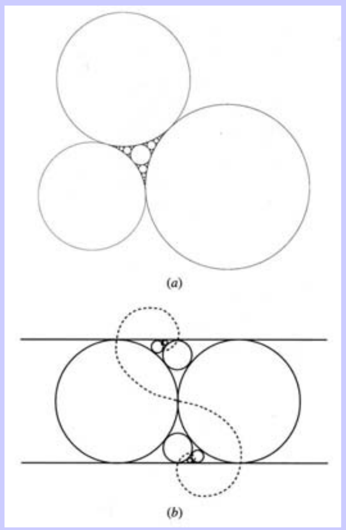
Significant additional complexity exists in systems of *unequal spheres*

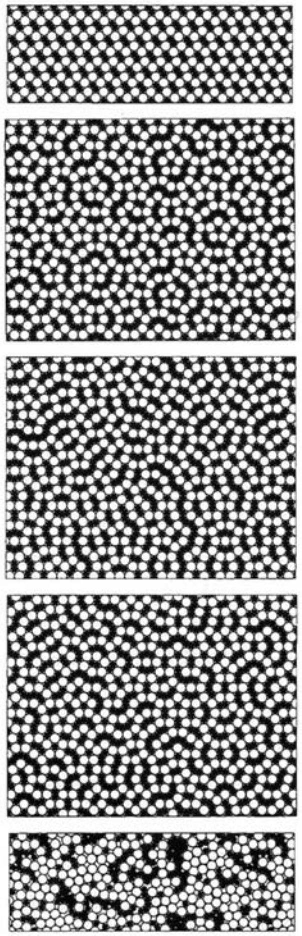
– the number and relative sizes of spheres becomes important

– binary or complex size distributions may exist

– relevant in problems from concrete to cosmology

Figure 3.8. Johannes Kepler (1571–1630).





“When complexity assails, let insight prevail.”

EARLIER INSIGHTS

"This, in turn, suggests correlated rather than random arrangements of local structural units." (P.H. Gaskell, 1983)

"We can no longer assume, I believe, that we can think in the seductive simplicity of the language of randomness alone." (P.H. Gaskell, 1991)

". . . the amorphous state is in reality not a disordered state, but a rather well organized arrangement of atoms. . ." (S. Steeb and P. Lamparter, 1993)

"But more recent work has shifted the balance of evidence towards structures that are more complicated, more diverse and more ordered– at least in the sense that there may be an underlying ordering or structure-forming principle." (P.H. Gaskell, 1991)

"My own view is that simple geometry. . . atomic sizes. . . will prove to be the main criterion that in various subtle ways incorporates the others." (R.W. Cahn, 1991)

OUTLINE

LOCAL STRUCTURE
Efficiently-packed solute-centered clusters

EXTENDED STRUCTURE

VALIDATION

ADDITIONAL TOPICS

REMAINING ISSUES

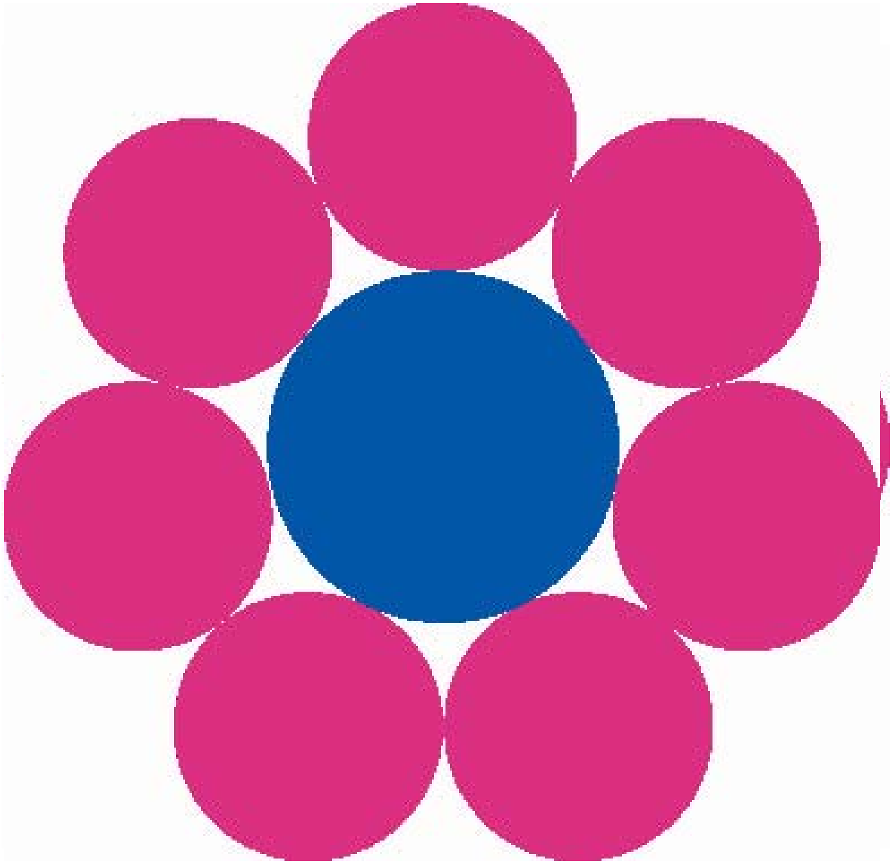
EFFICIENT LOCAL PACKING

Influence of Relative Atomic Size

Look for structural insights from the efficient filling of space by unequal spheres

Choose relative size as first variable

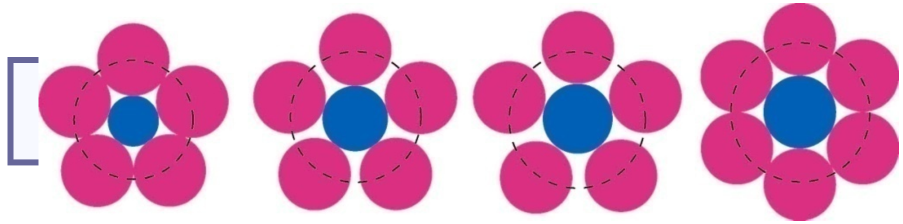
Start with 2D model



TOPOLOGICAL MODEL
Efficient Atomic Packing (2D)

The 2D theoretical coordination number (N^T) is the number of circles of radius r_j that can be placed around a central circle of radius r_i, where $R = r_i/r_j$.

– N^T is a real number



$$N^T = \pi/\arcsin[1/(1+R)]$$

Egami and Waseda; *J. Non-Cryst. Sol.*, **64**, 113–134(1984)

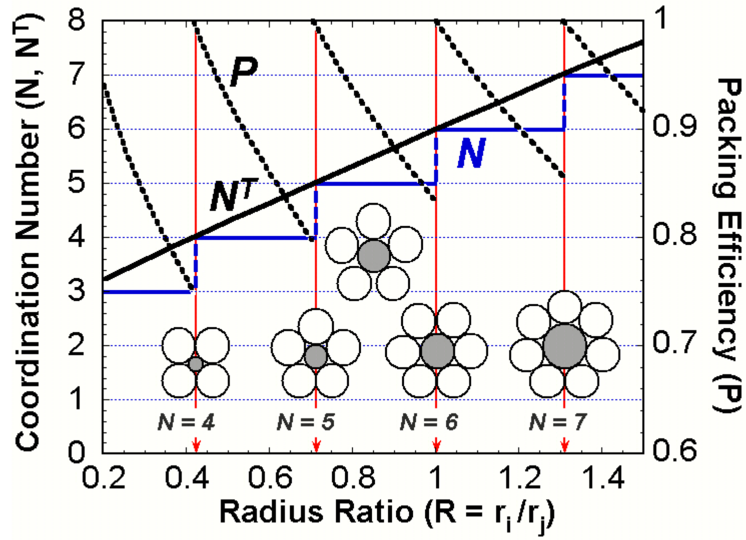
Packing Efficiency (P) is the maximum number of full circles of radius r_j that can be placed around a central circle of radius r_i, normalized by N^T

$$P = Trunc(N^T)/ N^T$$

Packing efficiency varies with R

– P is highest when the first shell is completely 'filled' with no gaps

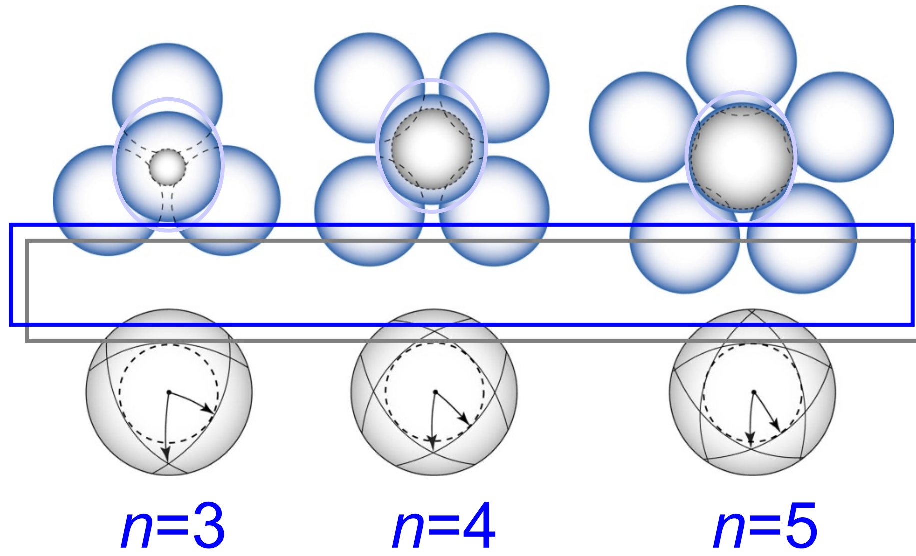
– P is highest for specific values of R where N^T is an integer (R^*)

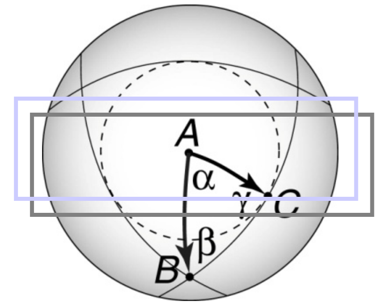


3D COORDINATION NUMBER

Accurate evaluation of N^T is needed in 3D to determine R^*

- consider sphere packing on a curved surface
- tesselate curved surface by constructing planes that are perpendicular bisectors of lines joining atom centers in the 1st coordination shell
  - *the intersection of these planes with the solute surface form great circles which define the area associated with a surface sphere*
  - *the area associated with a sphere on a curved surface depends onthe number of nearest neighbors in the 1st coordination shell, n*
  - *n is the surface symmetry, and n = 6 for R = ∞, n = 3, 4, or 5 for R < ∞*
- closed-form solution for the area bounded by great circles is given by spherical trigonometry





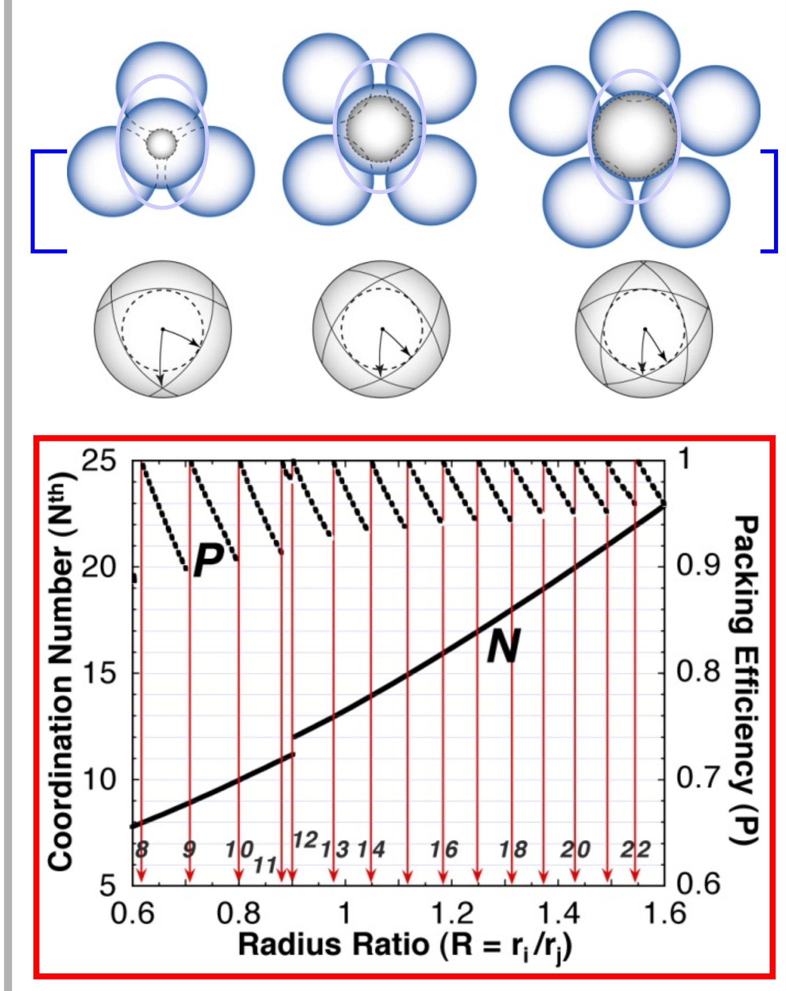
$$N^T = \frac{4\pi}{\{\pi(2-n)+(2n)\arccos[\sin(\pi/n)(1-1/(1+R)^2)]\}}$$

TOPOLOGICAL MODEL
Efficient Atomic Packing (3D)

3D relationship given between *R* and packing efficiency in 1st atomic shell

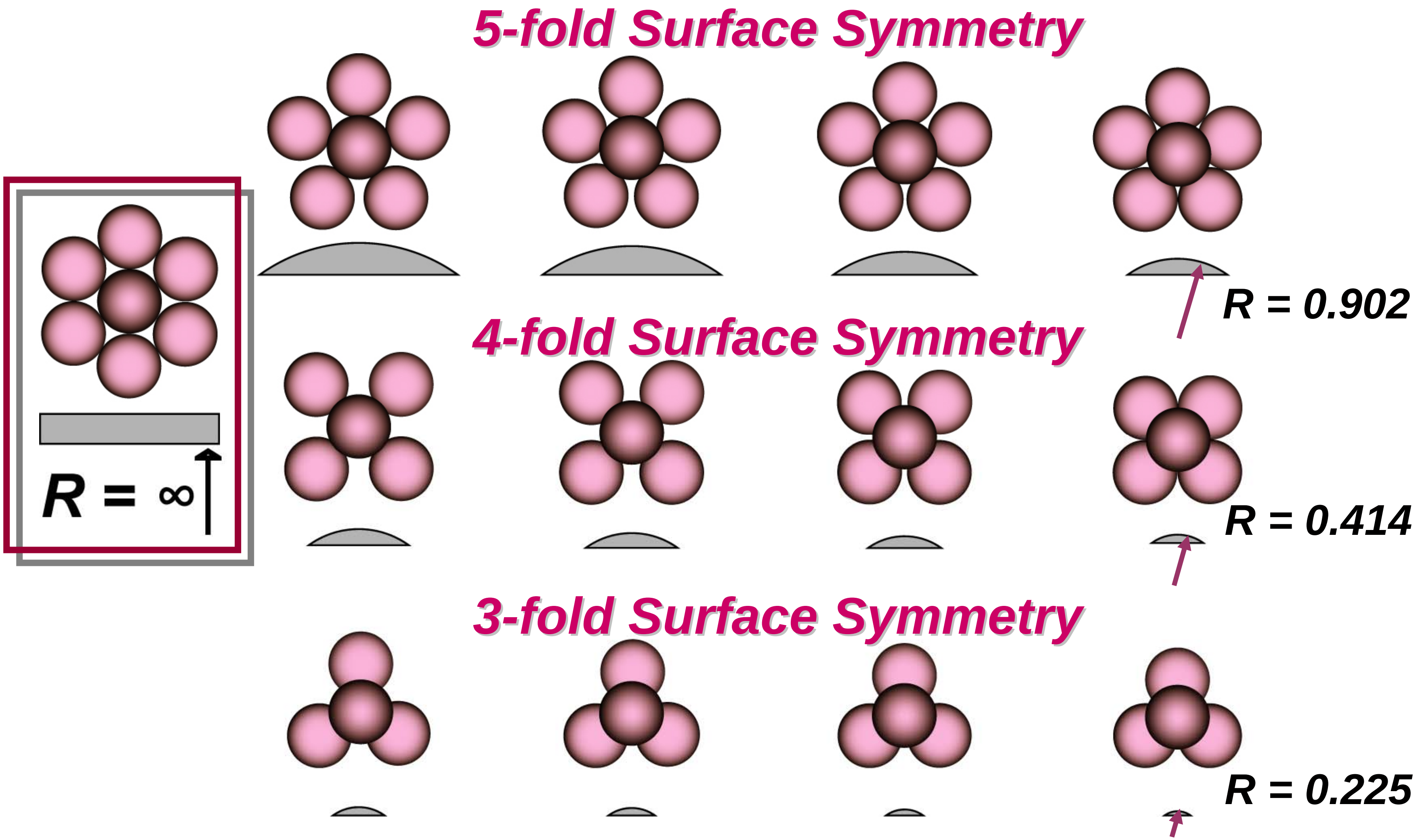
- Packing efficiency is a maximum when N^T is an integer
- N^T is an integer for specific ratios, R^*
- Suggests that specific radius ratios R^* may be preferred in metallic glasses

N^T	R^*	N^T	R^*
6	0.414	**14**	1.047
7	0.515	**15**	1.116
8	0.617	**16**	1.183
9	0.710	**17**	1.248
10	0.799	**18**	1.311
11	0.884	**19**	1.373
12	0.902	**20**	1.433
13	0.976	**21**	1.491



Miracle, Sanders and Senkov; *Phil Mag. A*, **83**, (2003)

SURFACE SYMMETRY

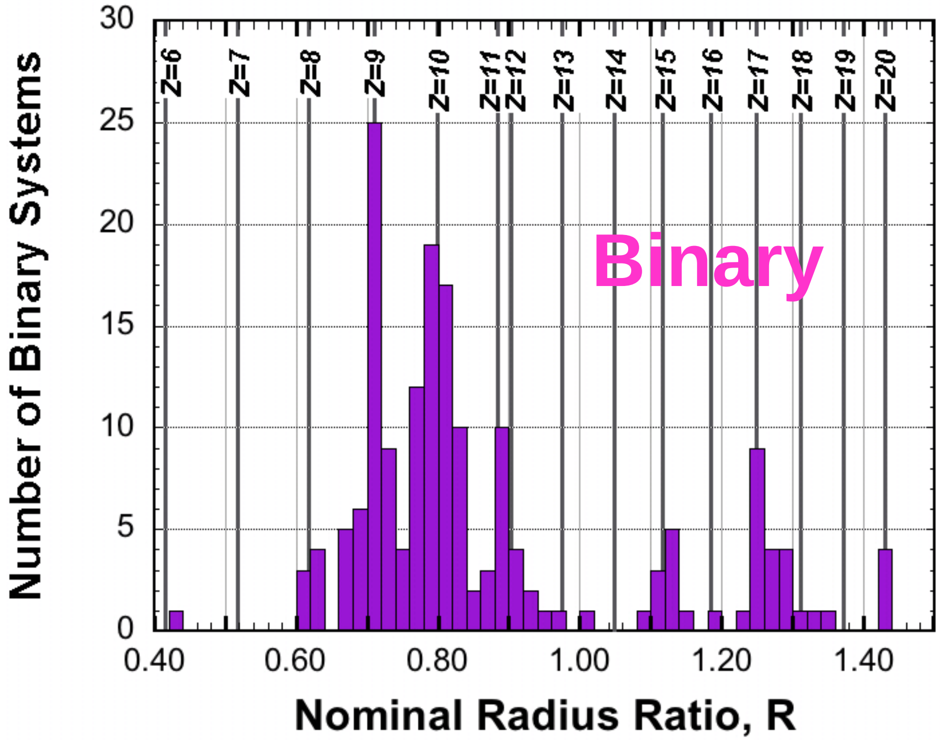


Surface symmetry decreases discontinuously with radius ratio

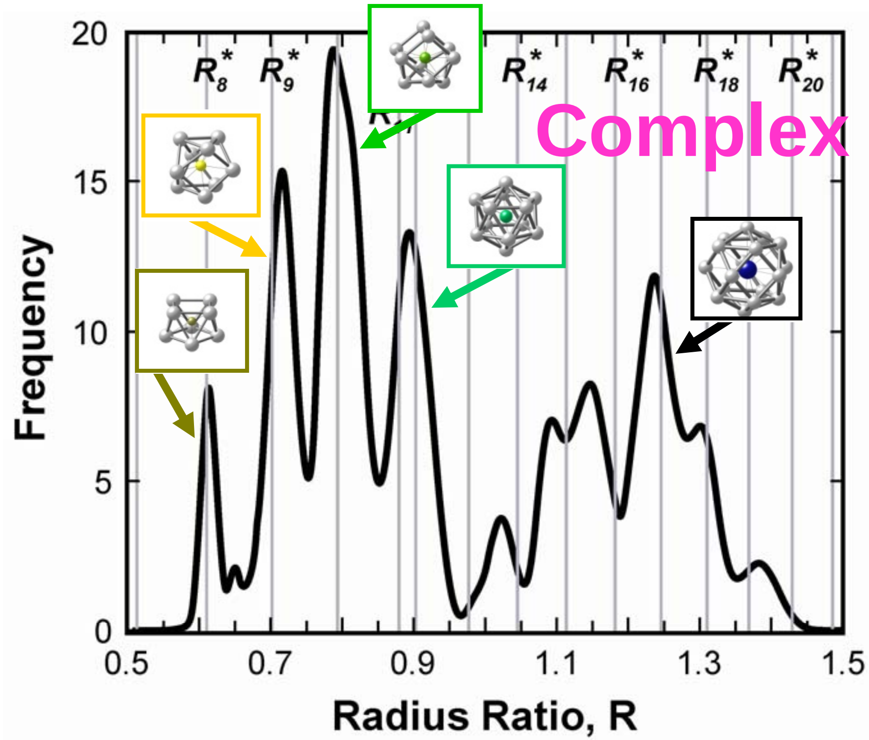
R* VALIDATION

Analysis of >400 radius ratios in metallic glasses confirms strong preference for *Rvalues**

– Efficient local atomic packing is concluded to be important in the formation of metallic glasses



Miracle, Louzguine, Louzguina, Inoue; *Int'l Mater. Rev.*, In Press.



Miracle, Sanders and Senkov; *Phil. Mag.,* **83A**, (2003)

EFFICIENT LOCAL ATOMIC PACKING : Implications

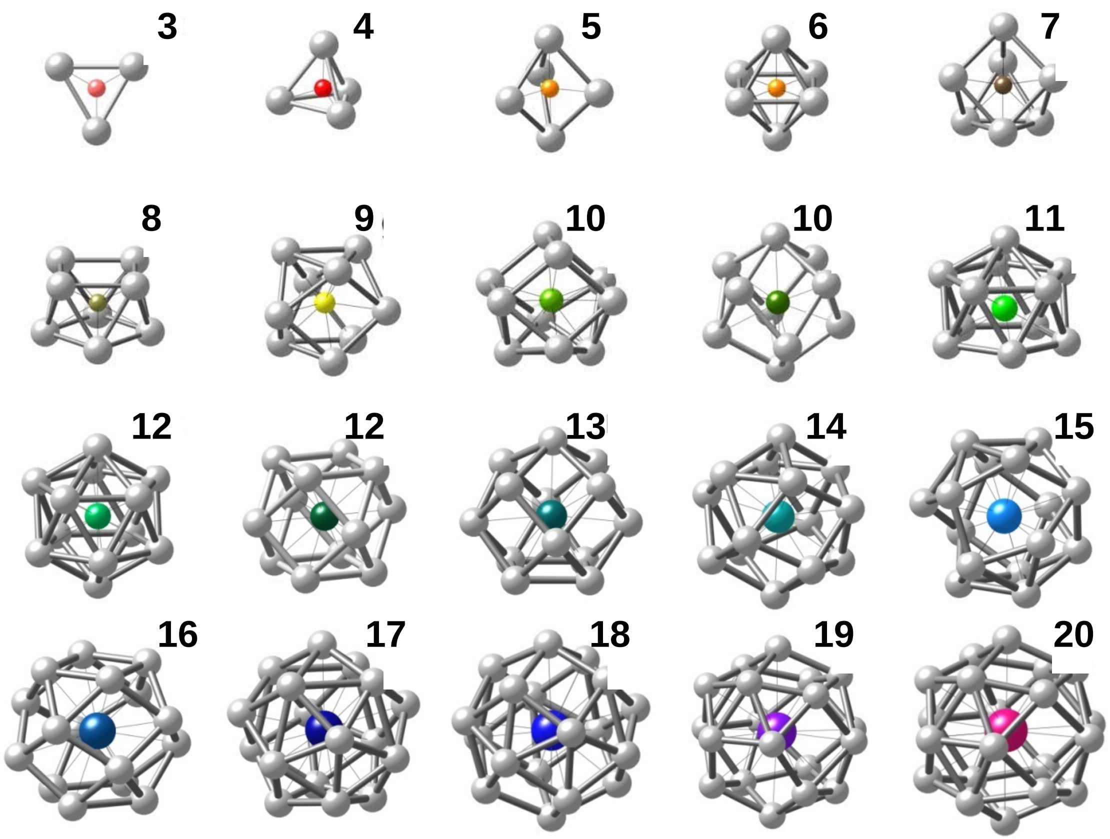
Changing solute-to-solvent radius ratio enables efficient atomic packing in the 1st coordination shell

- Specific solute-to-solvent radius ratios are preferred

Efficiently packed solute-centered canonical clusters with specific *N, R*

- Can be considered as local representative structural elements
- Each *N* introduces a family of clusters
- Many different local clusters

Miracle, Lord and Ranganathan; *Trans. JIM*, **47**, 1737 (2006)



ASSESSED ATOMIC RADII

Miracle, Louzguine, Louzguina, Inoue; *Inter. Mater. Review*, In press.

Element	At #	Radius (pm)	Element	At #	Radius (pm)	Element	At #	Radius (pm)
Li	3	152	**Se**	34	118	**Tb**	65	176
Be	4	112	**Rb**	37	244	**Dy**	66	175
B	5	88	**Sr**	38	212	**Ho**	67	177
C	6	77	**Y**	39	179	**Er**	68	175
N	7	72	**Zr**	40	158	**Tm**	69	175
O	8	64	**Nb**	41	143	**Yb**	70	190
Na	11	180	**Mo**	42	139	**Lu**	71	175
Mg	12	160	**Tc**	43	136	**Hf**	72	158
Al	13	141	**Ru**	44	134	**Ta**	73	145
Si	14	110	**Rh**	45	132	**W**	74	135
P	15	102	**Pd**	46	142	**Re**	75	137
S	16	103	**Ag**	47	144	**Os**	76	135
K	19	230	**Cd**	48	157	**Ir**	77	136
Ca	20	201	**In**	49	155	**Pt**	78	139
Sc	21	162	**Sn**	50	155	**Au**	79	143
Ti	22	142	**Sb**	51	155	**Hg**	80	152
V	23	134	**Te**	52	140	**Tl**	81	172
Cr	24	130	**Cs**	55	264	**Pb**	82	174
Mn	25	132	**Ba**	56	223	**Bi**	83	162
Fe	26	125	**La**	57	187	**Po**	84	168
Co	27	125	**Ce**	58	182	**Th**	90	178
Ni	28	126	**Pr**	59	183	**Pa**	91	165
Cu	29	126	**Nd**	60	182	**U**	92	158
Zn	30	140	**Pm**	61	185	**Np**	93	175
Ga	31	134	**Sm**	62	185	**Pu**	94	175
Ge	32	114	**Eu**	63	196			
As	33	115	**Gd**	64	176			

OUTLINE

LOCAL STRUCTURE

EXTENDED STRUCTURE
Filling of space by efficiently-packed clusters

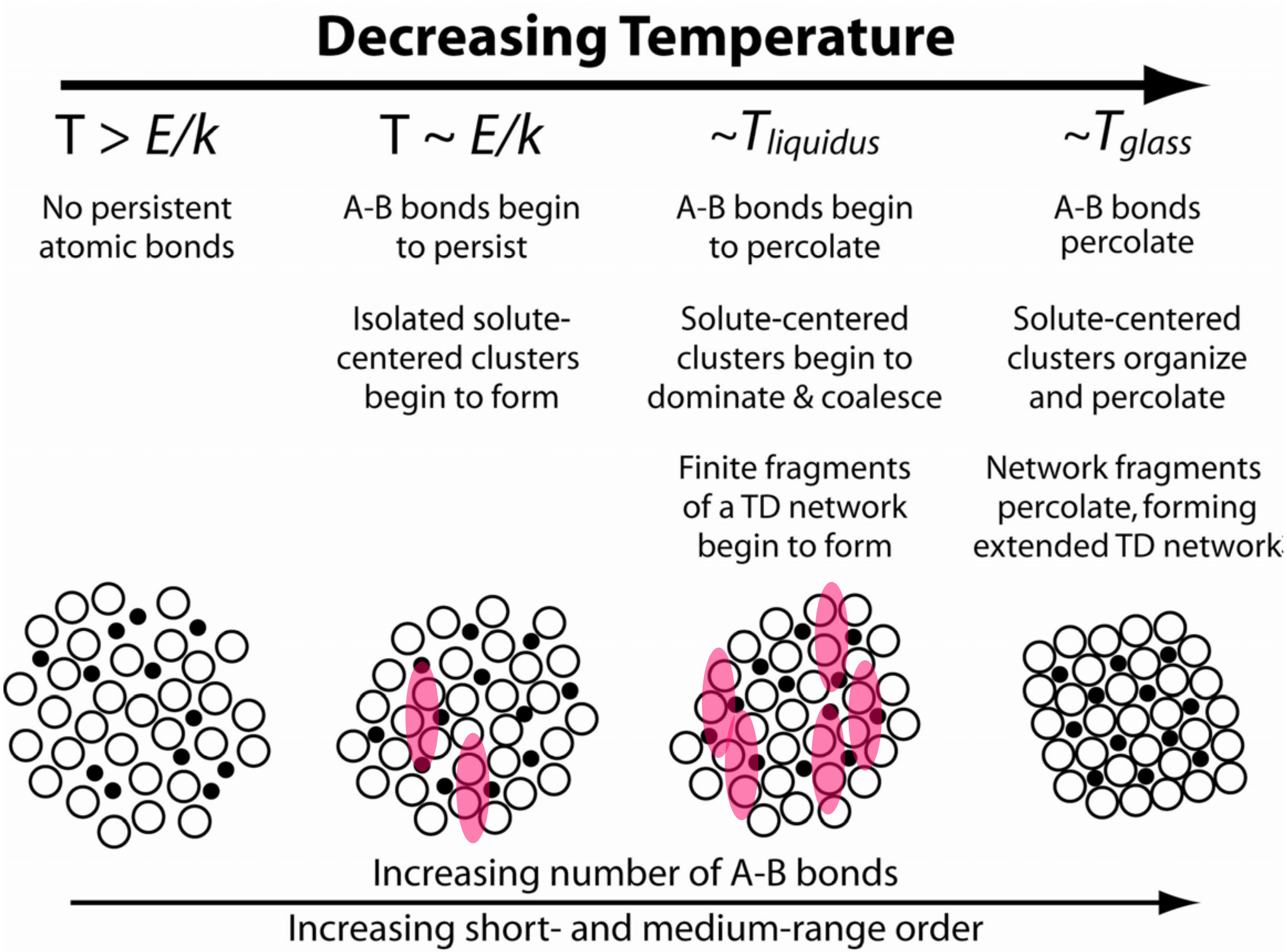
VALIDATION

ADDITIONAL TOPICS

REMAINING ISSUES

Miracle, *Nature Mat*., **3**, 697 (2004); Miracle, *Acta mater*., **54**, 4317 (2006)

CLUSTER ORGANIZATION
Evolution of MRO from the Liquid



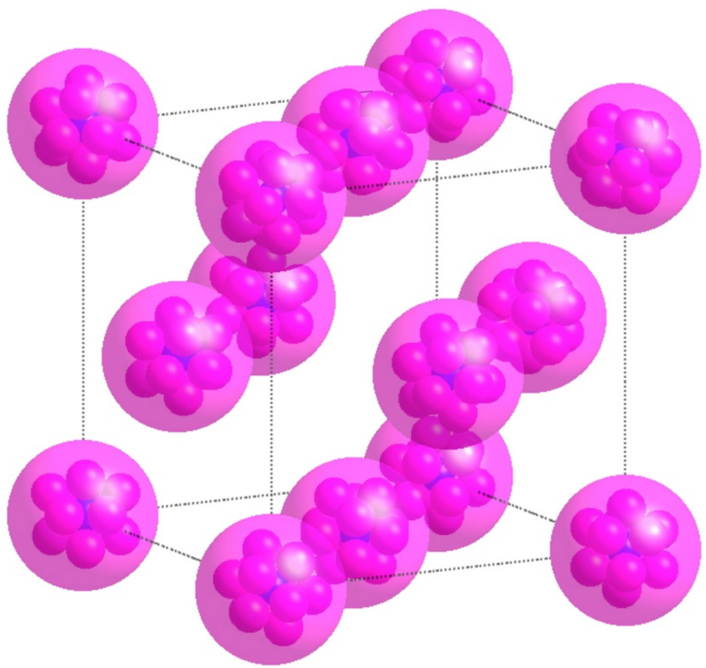
Cluster organization is motivated by solute-solute avoidance

RULE 1
Efficient Packing of Primary Clusters

Efficiently-packed solute-centered atomic clusters are imagined to be sphere-like

Efficient atom packing beyond the 1st atomic shell achieved by dense packing of these sphere-like clusters

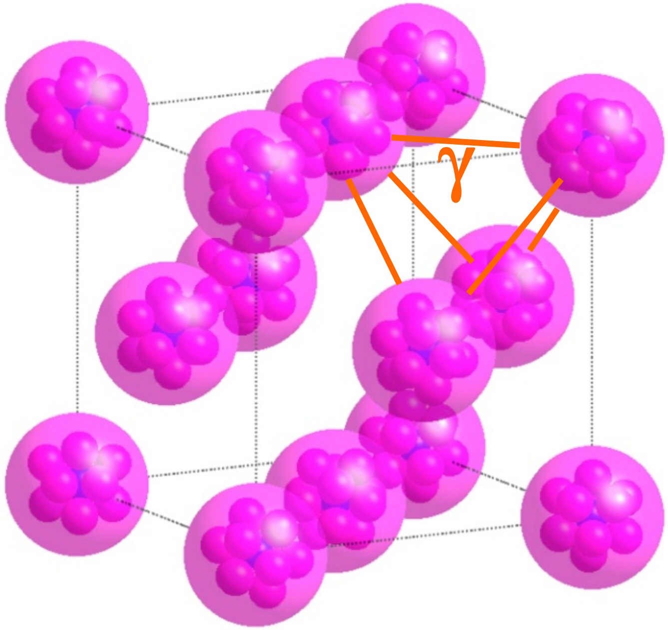
- fcc, bcc, hcp, sc, icosahedral and random cluster packing considered
- fcc cluster packing gives the most efficient packing of equal-sized spheres and best agreement with measured MRO



Efficiently-packed, solute-centered clusters are organized in space to achieve efficient cluster packing

RULE 1 CONSEQUENCES
Efficient Packing of Primary Clusters

Four topologically distinct atomic species and sites
- Solvent atoms (Ω)
- Primary (α) solutes produce the structure-forming unit clusters
- Cluster-octahedral interstices (β)
- Cluster-tetrahedral interstices (γ)
- $r_\alpha > r_\beta > r_\gamma$



Solute atoms occupy ~ordered sites
- Provides basis for observed medium range atomic ordering (MRO)
- Variable cluster-cluster separation degrade cluster ordering beyond a few cluster diameters

Preferred atom positions introduces the possibility of structural defects
- Vacancy and anti-site point defects
- Constitutional and thermal

“Ninety-nine percent loyalty is 100% disloyalty.”

Napoleon Bonaparte

“He’s not dead. I said he’s *mostly* dead. BIG difference.”

Miracle Max, from “The Princess Bride”

“The Pirate’s Code is more what you’d call ‘guidelines’ than actual rules.”

Captain Barbossa, from “The Pirates of the Caribbean”

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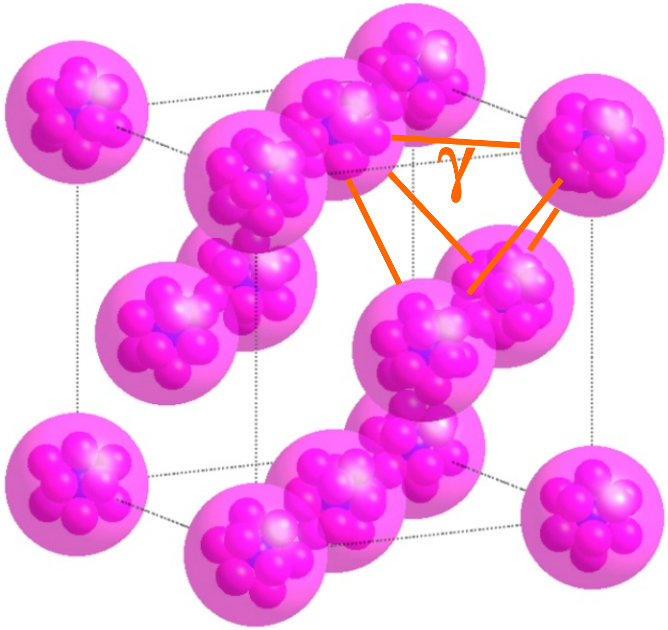

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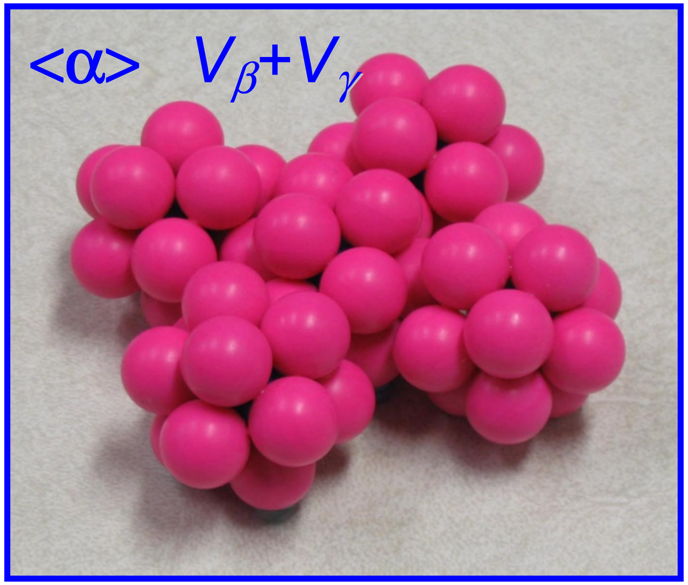
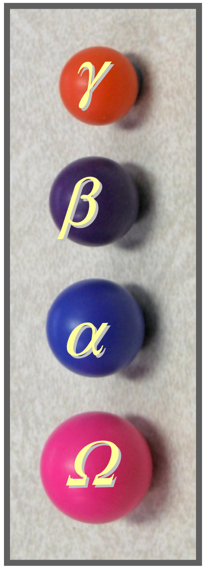
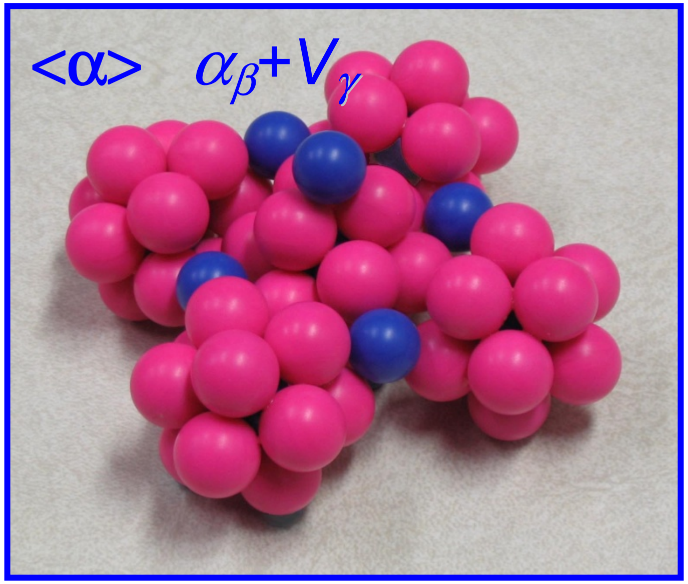
CONSTITUTIONAL STRUCTURAL DEFECTS







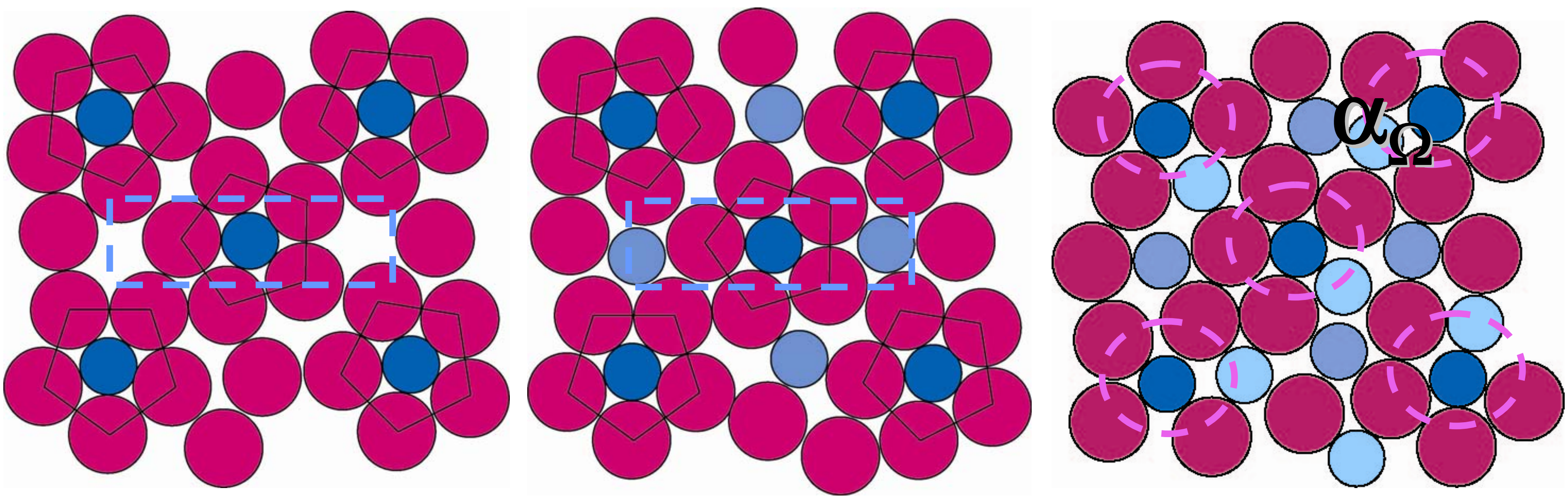
STRUCTURE AND BONDING
α–α Bonds in Solute-Rich Glasses

Solute-centered clusters are the primary structural unit

- The first shell of solutes (α) are filled only by solvent atoms (Ω)
- Inter-cluster sites (β and γ) can also be filled by solutes
  - *Increases number of α–Ω bonds without forming α–α bonds*

Solute-rich glasses can have a significant number of α_Ω anti-site defects, *S*(α_Ω)

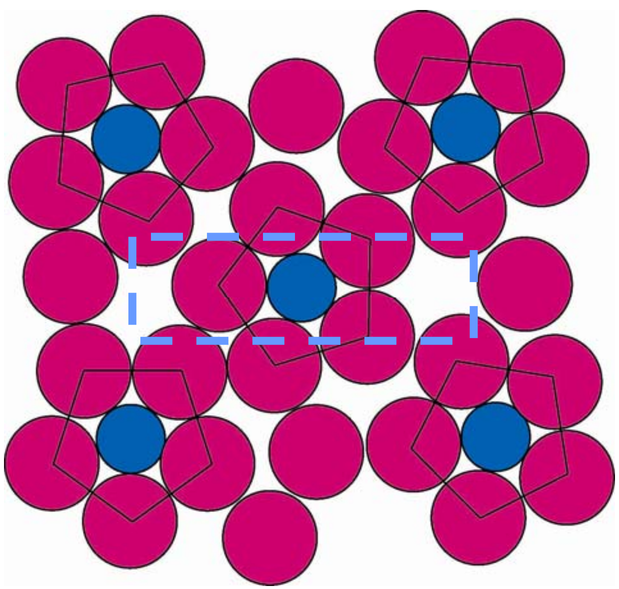
- The first shell of α sites has mixed α + Ω occupancy
- Produces α–α nearest neighbor bonds

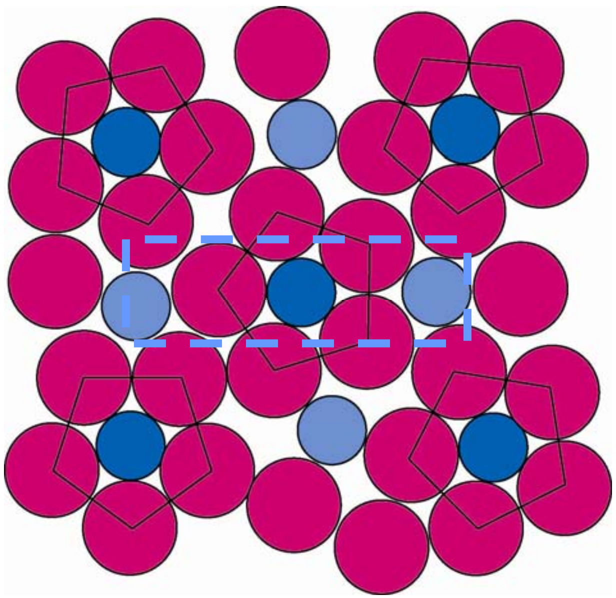


RULE 2
Structure-Forming Clusters Don't Overlap

Structure-forming α clusters do not overlap

- Gives largest number of Ω atoms bonded to each α atom
  - ➢ *QX glass model consists of non-overlapping icosahedra*
- This can be validated experimentally
  - ➢ *Gives* smaller critical α *concentrations for glass formation*
  - ➢ *Partial coordination numbers and density*
- Additional solutes occupy cluster-interstitial sites that bind structure-forming clusters and produce overlapping clusters

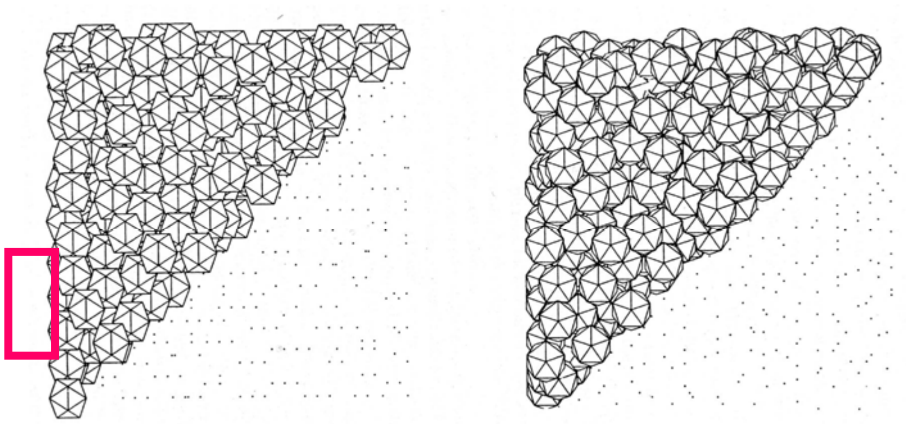




RULE 3
No Cluster Orientational Order

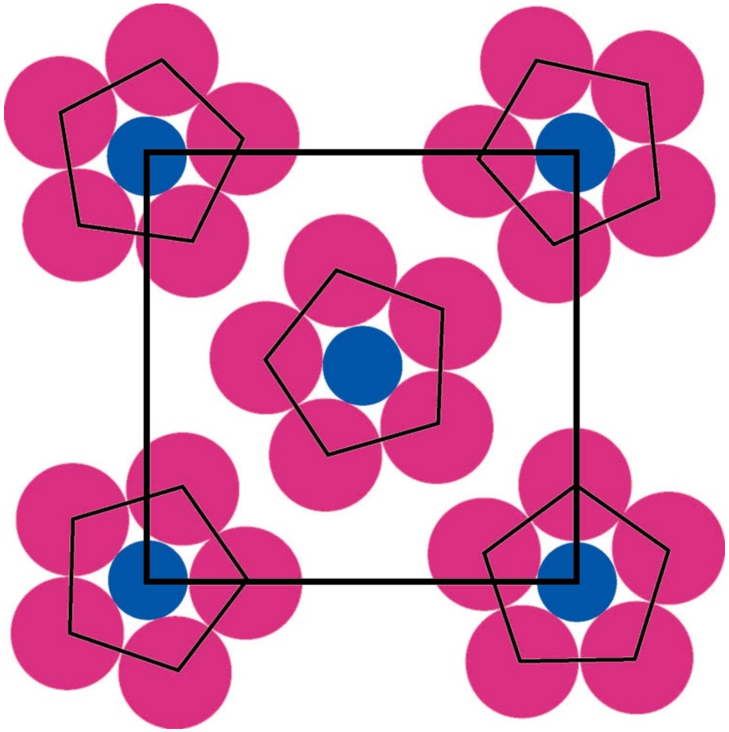
No orientational order exists amongst α clusters

- point group symmetries of efficiently packed clusters are incommensurate with a cubic lattice
- enforces randomness of solvent atoms
- provides important distinction from ‘icosahedral glass’ model for quasicrystals



Images of icosahedral glass along 2-fold and 5-fold axes

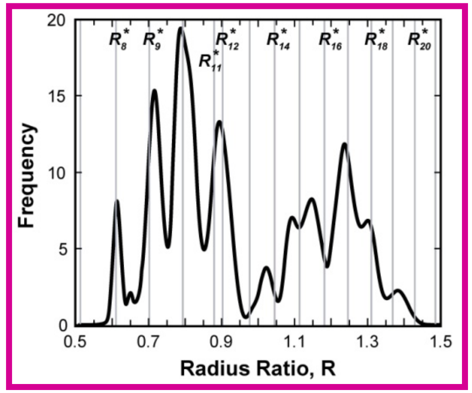
Stephens; in *Aperiodicity and Order*, **V.3**, (1989)



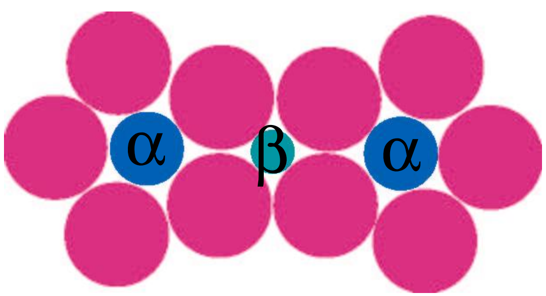
RULE 4
Specific Solute Sizes

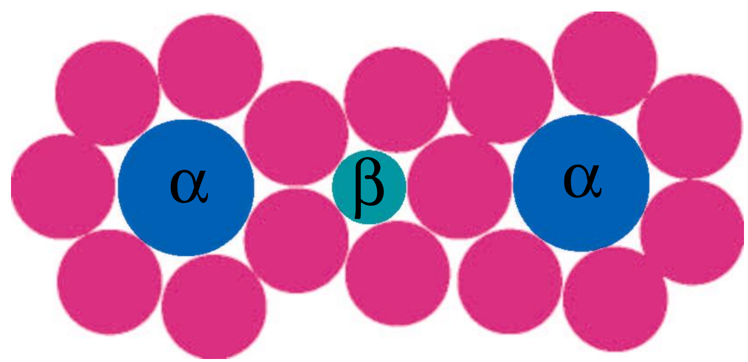
All solutes possess specific atomic radius ratios R^* relative to solvent atoms

- enables efficiently packed configurations in the first coordination shell of α, β and γ solutes
- atoms with radius ratios within 2% of one another are topologically equivalent
  - ➢ *provides reasonable bound to account for changes in atomic radii due to local structure and chemistry*
  - ➢ *provides important simplification for structural description of multi-component glasses*



N	*R*±2%*
8	0.62
9	0.71
10	0.80
12	0.90
15	1.12
16	1.18
17	1.25
18	1.31
19	1.37





Miracle, Sanders and Senkov; *Phil Mag. A*, **83**, (2003)

CONVENTIONS
Glass Designations

List alloy compositions with Ω first, followed by solutes in decreasing order of size: Ω-α-β-γ

Combine topologically equivalent solutes in parentheses

- Zr-Al-Ti-Cu-Ni-Be is a topological quaternary Zr-(Al,Ti)-(Cu,Ni)-Be

Structures are designated by the coordination numbers of solutes present <Z_α, Z_β, Z_γ>

- Zr-(Al,Ti)-(Cu,Ni)-Be are designated as <12,10,9> glasses
  - $R_{Al,Ti}$ = *0.905,* $R_{Cu,Ni}$ = *0.807 and* R_{Be} = *0.709*
  - $Z_{Al,Ti}$ = *12,* $Z_{Cu,Ni}$ = *10 and* Z_{Be} = *9*
- Ca-Mg-Zn-Cu are designated as <10,9,8> glasses
  - $R_{Mg} \cong 0.8$, $R_{Zn} \cong 0.7$ *and* $R_{Cu} \cong 0.64$
  - Z_{Mg} = *10,* Z_{Zn} = *9 and* Z_{Cu} = *8*

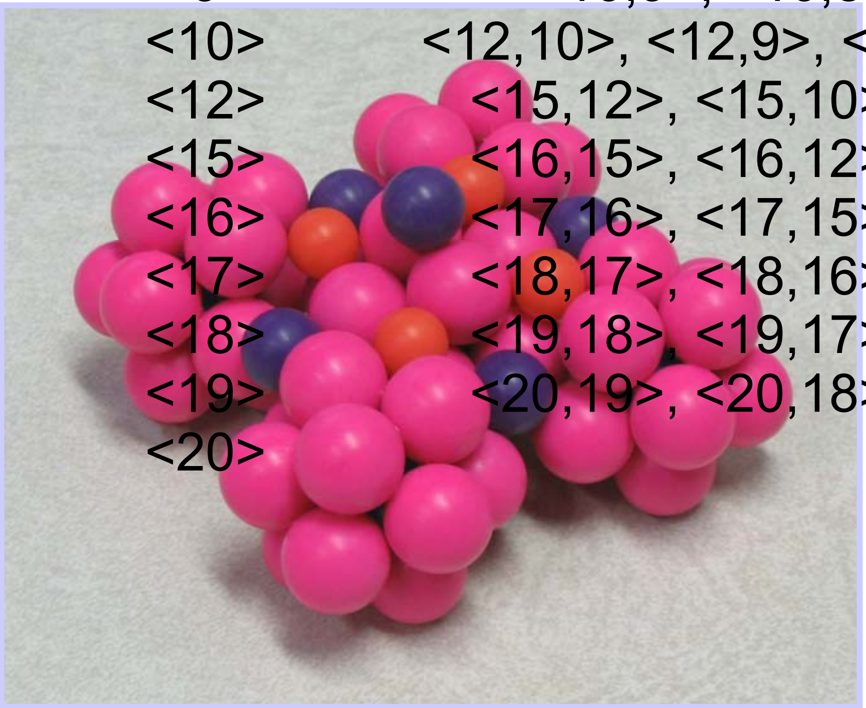
N	*R**
6	0.414
7	0.515
8	0.617
9	0.710
10	0.799
11	0.884
12	0.902
13	0.976
14	1.047
15	1.116
16	1.183
17	1.248
18	1.311
19	1.373
20	1.433

STRUCTURAL TOPOLOGIES

A wide range of glass topologies (276) are possible

BINARY	TERNARY	QUATERNARY
<8>	<9,8>	<10,9,8>
<9>	<10,9>, <10,8>	<12,10,9>, <12,10,8>, <12,9,8>
<10>	<12,10>, <12,9>, <12,8>	<15,12,10>, <15,12,9> …
<12>	<15,12>, <15,10> …	<16,15,12>, <16,15,10> …
<15>	<16,15>, <16,12> …	<17,16,15>, <17,16,12> …
<16>	<17,16>, <17,15> …	<18,17,16>, <18,17,15> …
<17>	<18,17>, <18,16> …	<19,18,17>, <19,18,16> …
<18>	<19,18>, <19,17> …	<20,19,18>, <20,19,17> …
<19>	<20,19>, <20,18> …	
<20>		

<12-10-9> Glass

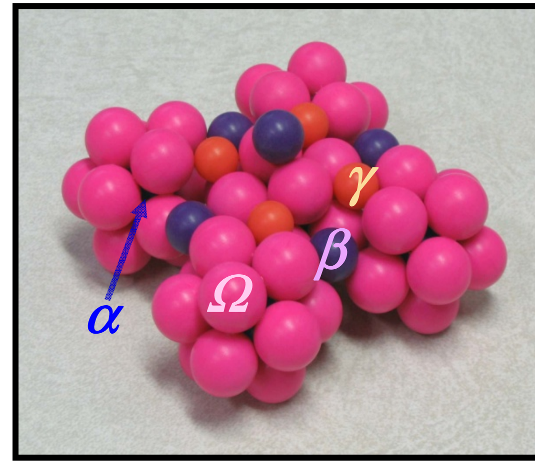


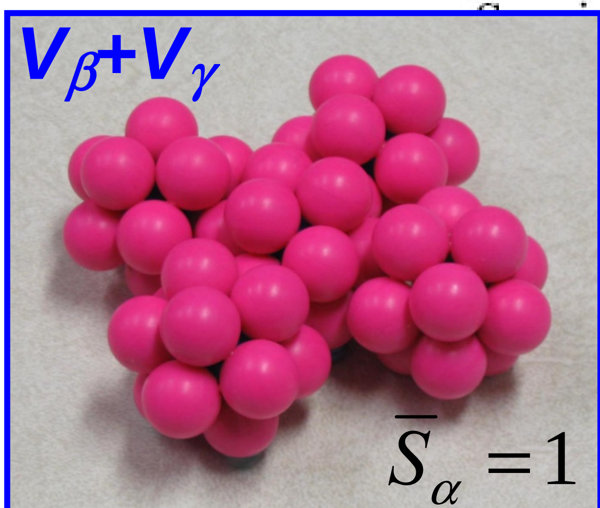
<17-12-10> Glass

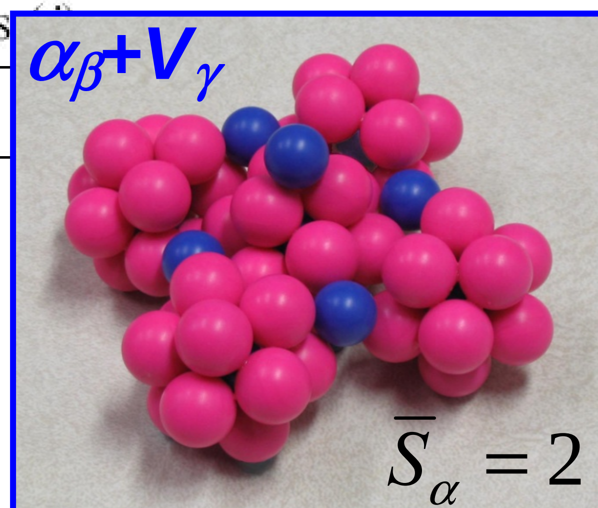
STRUCTURAL CHARACTERIZATION

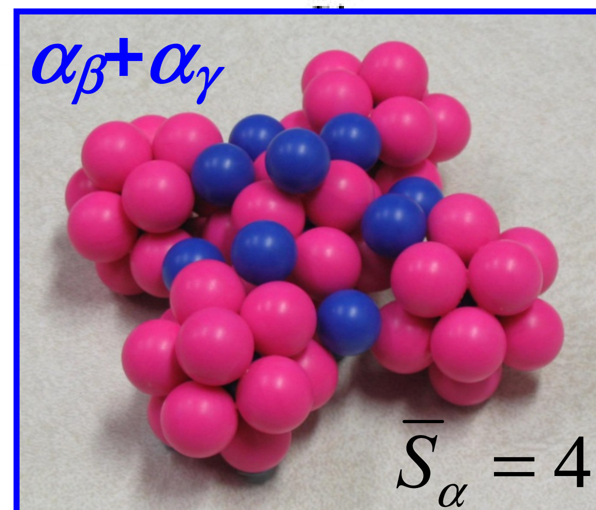
Site occupancies *S(i_j)* are the primary structural descriptors

- *S(i_j)* is the number of species, *i*, that occupy sites, *j*, <u>per α site</u>
- There are 4 structural sites: $j = \Omega,\ \alpha,\ \beta$ and γ
- There are 4 structural species: $i = \Omega,\ \alpha,\ \beta$ and γ
- *S(i_j)* is obtained by matching composition
  - *Fill solute sites in the order* α, β, γ, Ω
- $\bar{S}_\alpha = \left(F_\alpha / F_\Omega\right)\left(\hat{S}_\Omega - S(\alpha_\Omega)\right)$









BINARY STRUCTURE FROM CONSTITUTION

<9> $R^* = 0.710$ (Co-B, Fe-B, Pd-Si)

- When $f_\alpha = 0.10 = 1/(1+9)$, all α sites are just filled
- When $f_\alpha = 0.18 = 2/(2+9)$, all α and β sites are just filled
- When $f_\alpha = 0.31 = 4/(4+9)$, all α, β and γ sites are just filled
- When $f_\alpha > 0.31$, all α, β and γ sites are filled and α_Ω defects are formed

<12> $R^* = 0.902$ (Nb-Ni, Nb-Rh, Ti-Cu)

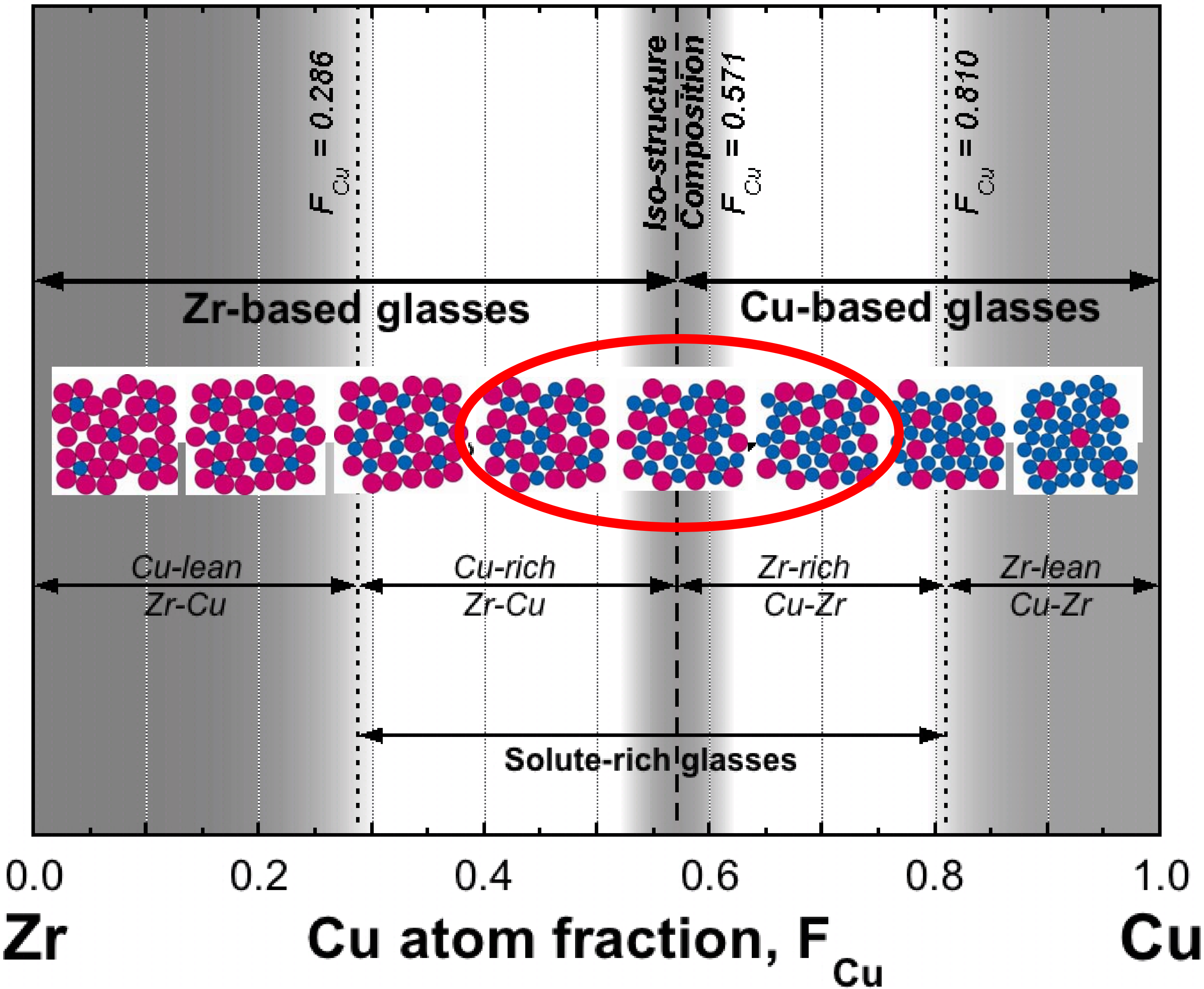
- When $f_\alpha = 0.08 = 1/(1+12)$, all α sites are just filled
- When $f_\alpha = 0.14 = 2/(2+12)$, all α and β sites are just filled
- When $f_\alpha = 0.25 = 4/(4+12)$, all α, β and γ sites are just filled
- When $f_\alpha > 0.25$, all α, β and γ sites are filled and α_Ω defects are formed

<17> $R^* = 1.248$ (Al-Gd, Al-Y, Cu-Hf, Cu-Zr, Ni-Hf, Ni-Zr)

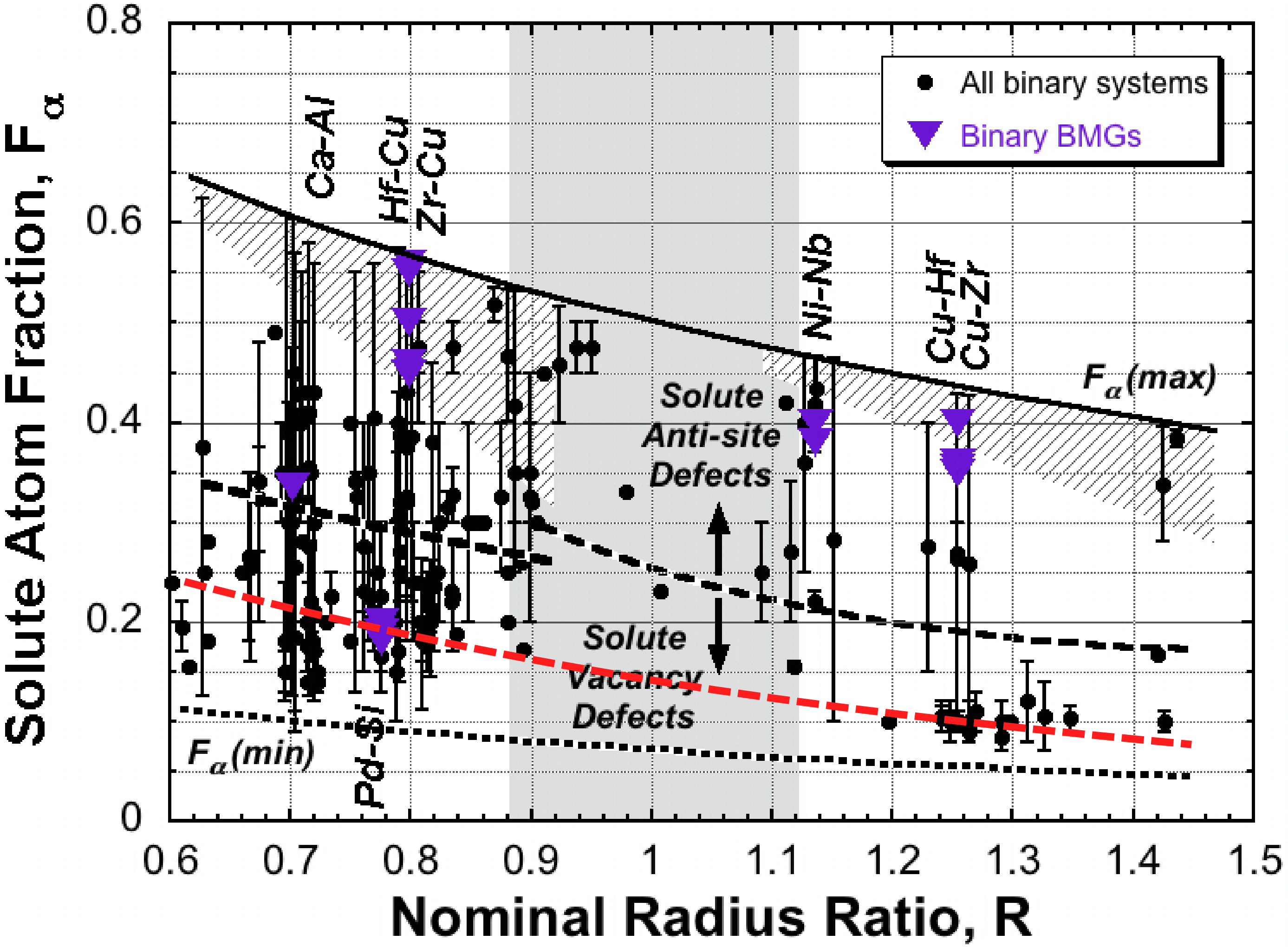
- When $f_\alpha = 0.06 = 1/(1+17)$, all α sites are just filled
- When $f_\alpha = 0.11 = 2/(2+17)$, all α and β sites are just filled
- When $f_\alpha = 0.19 = 4/(4+17))$, all α, β and γ sites are just filled
- When $f_\alpha > 0.19$, all α, β and γ sites are filled and α_Ω defects are formed

BINARY GLASS TOPOLOGIES

Miracle, Louzguine, Louzguina, Inoue; *Inter. Mater. Review*, In press.



BINARY GLASS TOPOLOGIES



Miracle, Louzguine, Louzguina, Inoue; *Inter. Mater. Review*, In press.

TERNARY STRUCTURE FROM CONSTITUTION

Zr-Al-(Cu,Ni) $R_{\alpha}^{*} = 0.902$ $Z_{\alpha} = 12$

α-centered clusters form the scaffold of the metallic glass structure

- Each α site creates 12 Ω sites, 1 β site and 2 γ sites for 16 total structural sites
- A minimum f_{α} of 1/13 = 0.077 is needed to fill α sites

Al atoms are distributed on α sites and then progressively on β, γ and Ω sites until all the Al is used up

- If $f_{Al} < 0.077$, then β solutes are placed on α sites

The remaining solutes occupy β and γ sites

- No account of the relative size is necessary from a site occupancy point of view, since β and γ sites do not create new Ω sites
  - ➢ *The solute size is important for local strain considerations*

These ideas have not yet been validated by comparison with actual glass compositions

OUTLINE

LOCAL STRUCTURE

EXTENDED STRUCTURE

VALIDATION

Partial coordination numbers

Cluster organization via diffraction

ADDITIONAL TOPICS

REMAINING ISSUES

SHORT RANGE ORDER
α Nearest-Neighbor Coordinations

artial coordination of α around α ($N_{\alpha-\alpha}$)

$$N_{\alpha-\alpha} = \phi \cdot S(\alpha_\Omega)[S(\alpha_\alpha) + S(\alpha_\beta) + S(\alpha_\gamma)] \big/ \hat{S}_\Omega$$

- Can be checked against experimental measurements
- A single value of $S(\alpha_\Omega)$ gives consistent fit to height of solute-solute nearest-neighbor peak and $N_{\alpha-\alpha}$ for $Ni_{81}B_{19}$, $Fe_{80}B_{20}$, $Ni_{80}P_{20}$, $Zr_{65}Ni_{35}$ and $Nb_{60}Ni_{40}$ but not for $Ni_{63}Nb_{37}$ or $Al_{90}Y_{10}$

Partial coordination of Ω around α ($N_{\alpha-\Omega}$)

- Given directly from N(R^*) for binary glasses when $S(\alpha_\Omega)$=0
- Non-integer values of $N_{\alpha-\Omega}$ are anticipated for $R \approx R^*$ via the concept of quasi-equivalent clusters (Sheng *et al.*, *Nature*, **439**, 2006 419)
- When (α_Ω) defects are present,

$$\boxed{N_{\alpha-\Omega} = N(R^*) - N_{\alpha-\alpha}}$$

N	R^*
8	0.617
9	0.710
10	0.799
11	0.884
12	0.902
13	0.976
14	1.047
15	1.116
16	1.183
17	1.248
18	1.311
19	1.373

SHORT RANGE ORDER
Ω Nearest-Neighbor Coordinations

artial coordination of *Ω* around *Ω* ($N_{\Omega-\Omega}$)

- For vertex-sharing between adjacent clusters,

$$\boxed{N_{\Omega-\Omega} \cong 2(q+1) - S(\alpha_\Omega)[N_{\alpha-\Omega}/\hat{S}_\Omega]}$$

Partial coordination of *α* around *Ω* ($N_{\Omega-\alpha}$)

$$\boxed{N_{\Omega-\alpha} = 2\phi[S(\alpha_\alpha) + S(\alpha_\beta) + S(\alpha_\gamma) + S(\alpha_\Omega)\cdot(q/\hat{S}_\Omega)]/N_{\alpha-\Omega}}$$

q is 'surface coordination' from Frank and Kasper

ϕ is the number of nearest-neighbor clusters

SHORT RANGE ORDER
Predictions vs. Experiment

Experimental and predicted partial coordination numbers

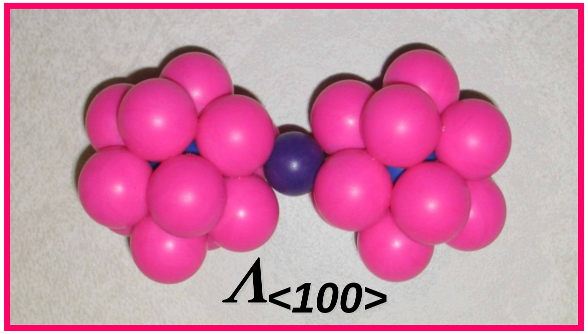
Glass		$N_{\Omega-\Omega}$	$N_{\Omega-\alpha}$	$N_{\alpha-\alpha}$	$N_{\alpha-\Omega}$	Ref.
$Ni_{81}B_{19}$ $\langle 9\rangle_{sc}$	Expt.	10.8	2.2	0	9.3	[4]
	Pred.	10.0	1.93	0	8.62	
$Ni_{64}B_{36}$ $\langle 9\rangle_{sc}$	Expt.	9.2	4.9	1.1	8.7	[84]
	Pred.	9.07	4.78	1.94	6.67	
$Fe_{80}B_{20}$ $\langle 9\rangle_{sc}$	Expt.	12.4	2.16	0	8.64	[85]
	Pred.	10.0	2.11	0	8.52	
$Ni_{80}P_{20}$ $\langle 10\rangle_{sc}$	Expt.	9.4	2.33	0	9.3	[76]
	Pred.	10.00	2.50	0	9.80	
$Zr_{65}Ni_{35}$ $\langle 10\rangle_{sc}$	Expt.	9.0	2.9	2.3	5.4	[74]
	Pred.	7.50	2.59	1.88	8.65	
$Nb_{60}Ni_{40}$ $\langle 12\rangle_{fcc}$	Expt.	9.0	5.5	3.8	8.2	[72]
	Pred.	8.63	6.21	3.44	7.03	
$Ni_{63}Nb_{37}$ $\langle 16\rangle_{fcc}$	Expt.	6.6	5.9	5.6	10.0	[72]
	Pred.	10.19	6.56	5.23	11.40	
$Al_{90}Y_{10}$ $\langle 17\rangle_{fcc}$	Expt.	10.7 ± 0.8	1.6 ± 0.2	1.2 ± 0.9	14.2 ± 1.3	[86]
	Pred.	11.81	1.47	0.13	17.04	

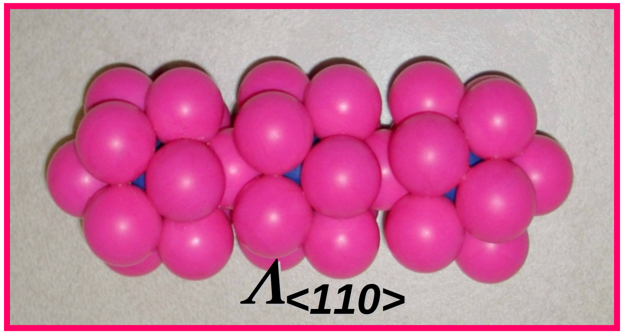
Miracle, *Acta mater.*, **54**, 4317 (2006)

SOLUTE-SOLUTE MRO
Introduction

The degree to which solute organization represents MRO can be studied directly

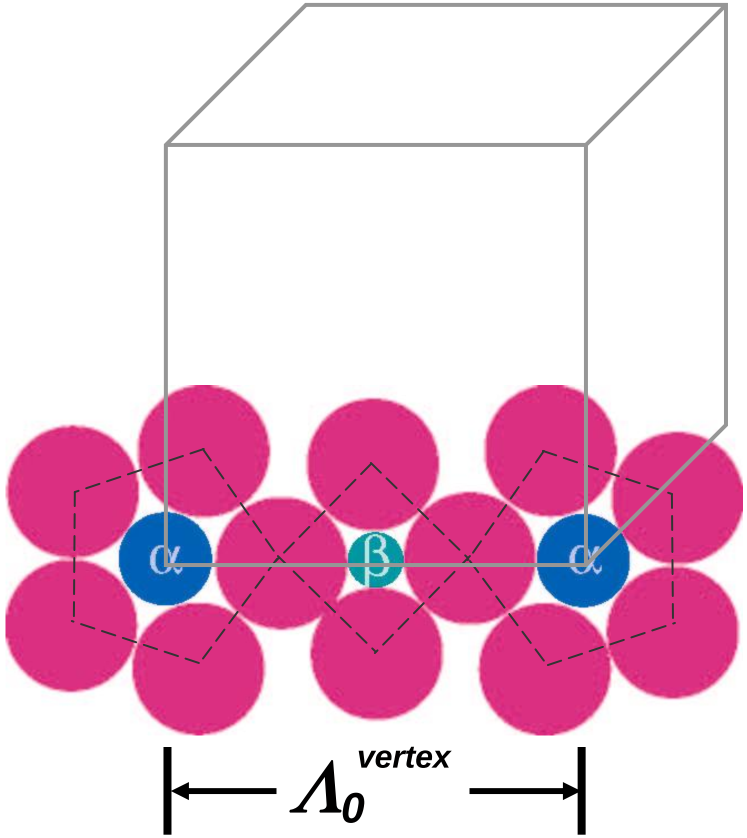
- Expand the structure factor for candidate cluster organizations by a length scale representing the cluster size
  - ➢*Cluster packing symmetries considered include fcc, bcc, sc, hcp, icosahedral (Bergman and Mackay) and dense random*
- The length scale is the cluster unit cell length, Λ_0, which can be estimated from the packing of hard spheres
- Compare predicted structure factors with **solute-solute** partial pair distribution functions

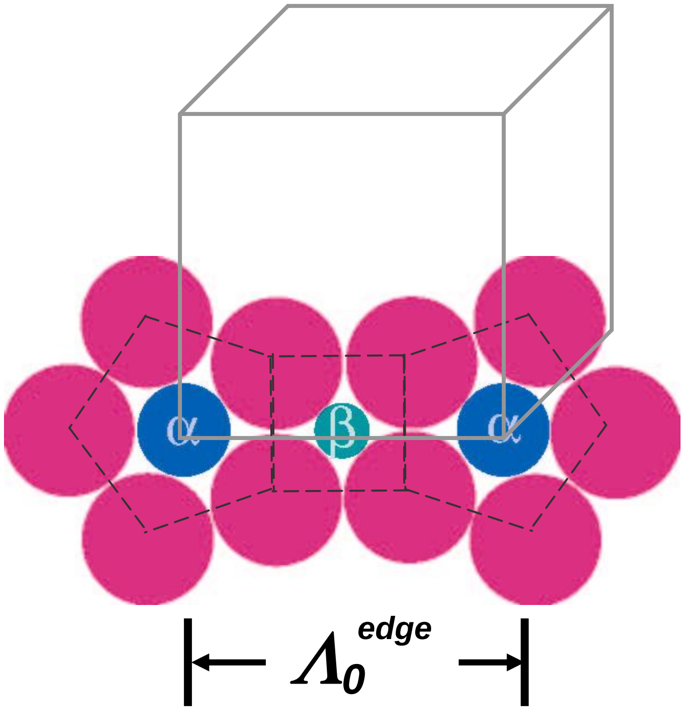




CLUSTER UNIT CELL LENGTH
Cluster Unit Cell Length (Λ_0)

Cluster unit cell length (Λ_0) can be calculated from geometry





$$\Lambda_0^{vertex} = 2[R_\alpha + 2 + R_\beta]$$

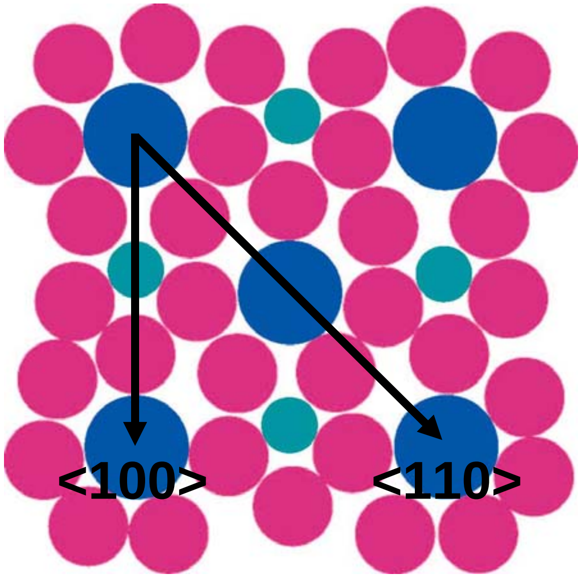
$$\Lambda_0^{edge} = 2[\sqrt{(1+R_\alpha)^2 - 1} + \sqrt{(1+R_\beta)^2 - 1}]$$

$$\Lambda_0^{face} = 2[\sqrt{(1+R_\alpha)^2 - 4/3} + \sqrt{(1+R_\beta)^2 - 4/3}]$$

CLUSTER UNIT CELL LENGTH Λ_0

Cluster unit cell length Λ_0 is calculated from $\Lambda^{<hkl>}$ values

- Determined from unrelaxed hard sphere calculations
- Needed for MRO, density comparisons
- Λ_0 is given as $\Lambda^{<100>}$, $\Lambda^{<110>}/\sqrt{2}$ and $\Lambda^{<111>}/\sqrt{3}$
  - *9 values obtained depend on the relative solute sizes and site occupancy*
  - *Λ_0 is the largest of $\Lambda^{<100>}$, $\Lambda^{<110>}/\sqrt{2}$ and $\Lambda^{<111>}/\sqrt{3}$ for face-sharing clusters*
- tensile strains exist along less densely packed directions
  - *edge and vertex sharing configurations reduce the internal strain*



		Unit Cell Derived From		
		$\Lambda^{<100>}$	$\Lambda^{<110>}$	$\Lambda^{<111>}$
Λ_0 (nm)	**face**	**0.925**	**0.684**	**0.998**
	edge	**0.996**	**0.732**	**1.088**
	vertex	**1.184**	**0.861**	**1.316**

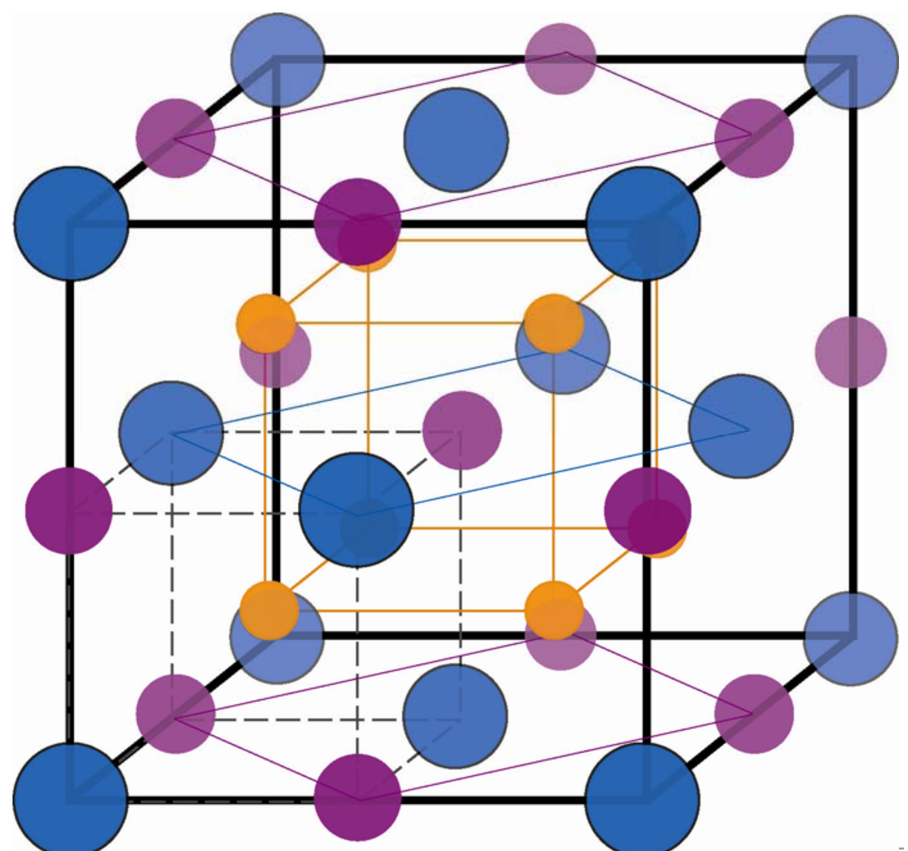
Calculated for <12-10-9> glass with Zr solvent (r_{Zr} = 0.158 nm)

SOLUTE SYMMETRY AND CLUSTER-PACKING SYMMETRY

Solute symmetry depends on cluster-packing symmetry and site occupancy

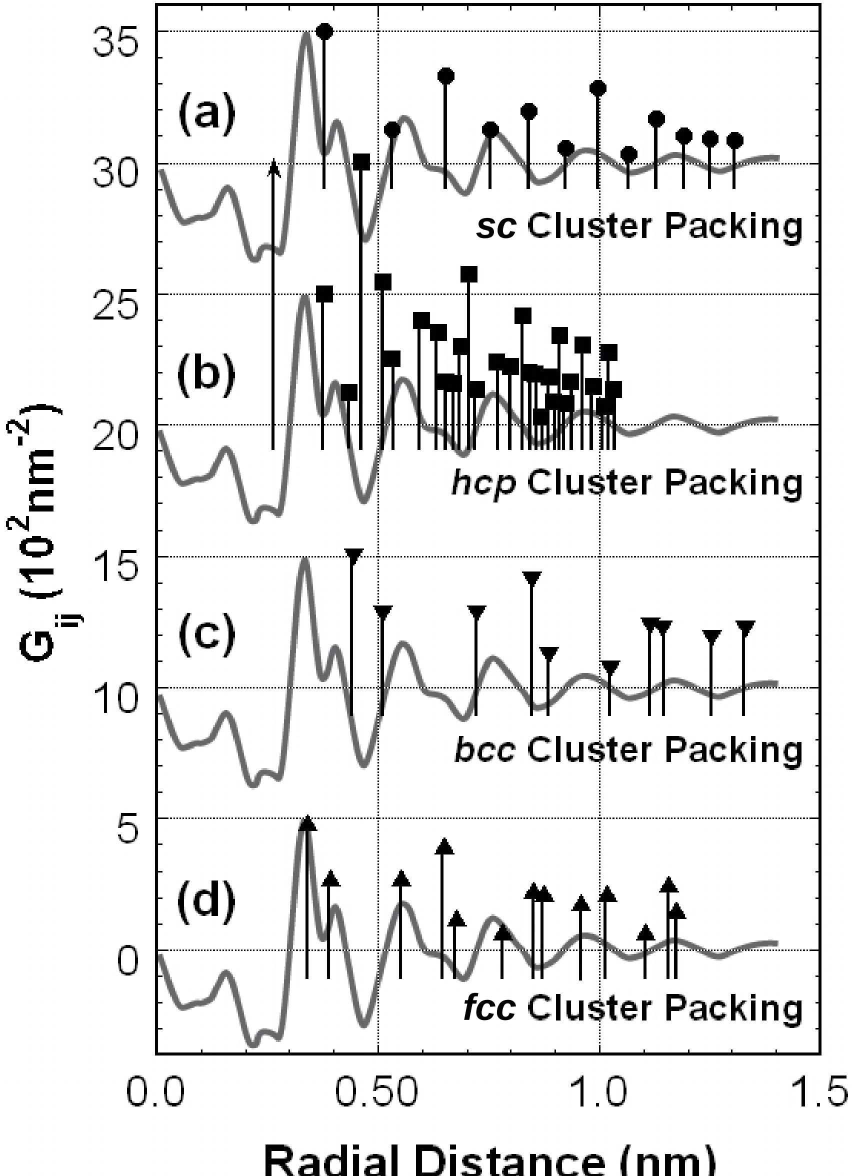
- In binary glasses, the α, β and γ sites are only occupied by α
- For fcc cluster-packing symmetry, the solute symmetry changes with defect structure as shown below

Defect Structure	Solute Symmetry	Length
$V_\beta + V_\gamma$	fcc	Λ_0
$\alpha_\beta + V_\gamma$	sc	$\Lambda_0/2$
$\alpha_\beta + \alpha_\gamma$	bcc	$\Lambda_0/2$



‘PERIODIC’ CLUSTER PACKING

B-B Partial RDF for $Ni_{81}B_{19}$



Cluster packing symmetry is determined by p-RDF

- Overcomes issue of non-uniqueness
- Clear distinction between different cluster packing symmetries

***sc* cluster packing gives good fit**

- Misses splitting of 1^{st} ordering peak

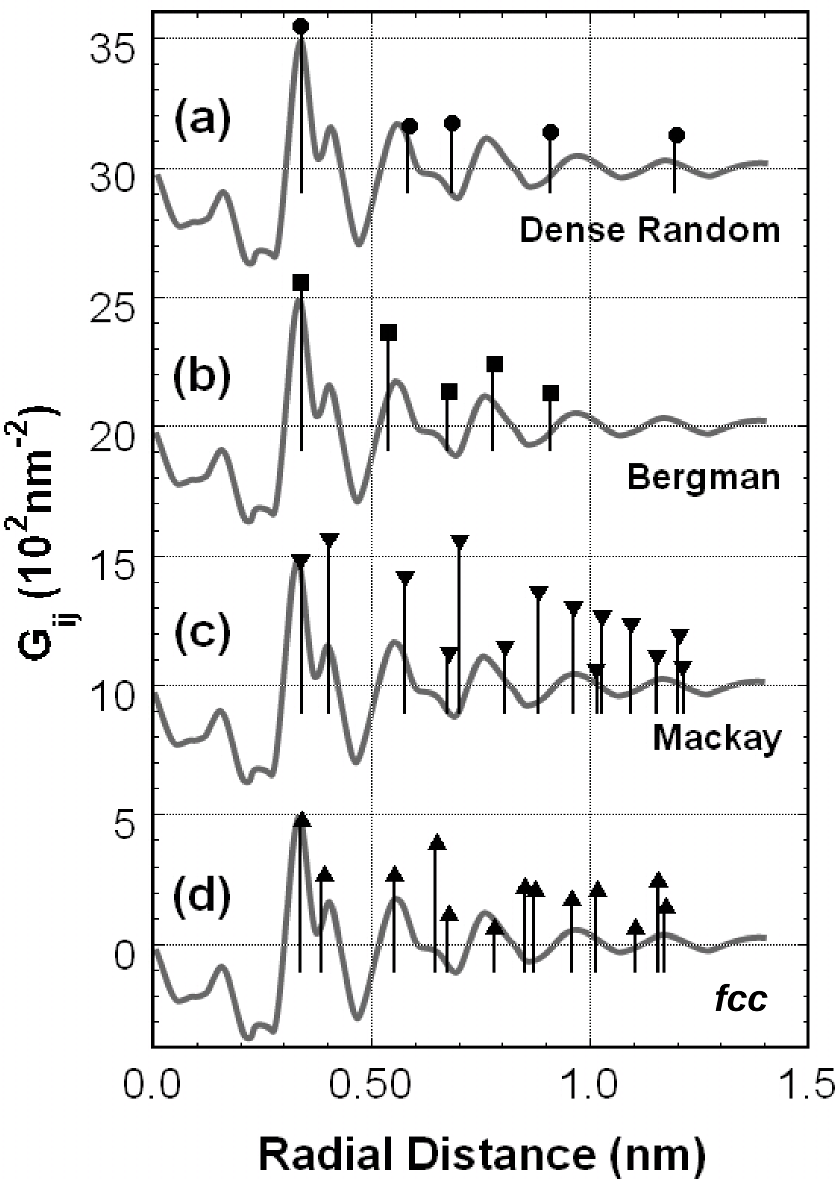
***hcp, bcc* cluster symmetry give poor fit**

***fcc* cluster symmetry gives best fit for periodic cluster packings**

- α_β defect state gives *bcc* solute symmetry
- Edge-sharing of nearest-neighbor clusters gives best fit

Exptl data from Lamparter, *Phys. Scr.*, **T57**, 72 (1995)

ICOSAHEDRAL & RANDOM CP
B-B Partial RDF for $Ni_{81}B_{19}$



Dense random cluster packing (DRCP) gives poor fit
- Misses splitting of 1st ordering peak and the 3rd ordering peak

Bergman cluster packing gives good fit
- Misses splitting of 1st ordering peak

Mackay cluster packing gives better fit
- Captures 1st ordering peak splitting
- Requires edge-sharing of adjacent clusters

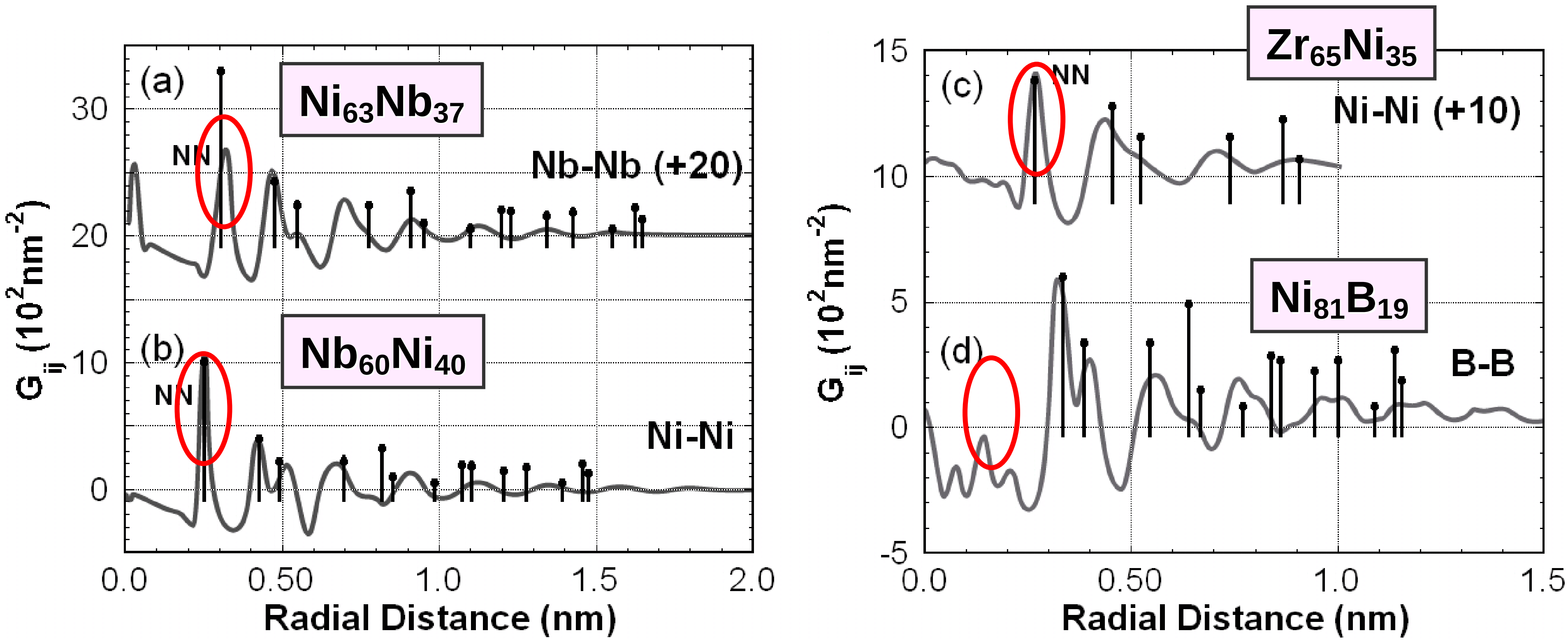
***fcc* cluster symmetry gives best fit**
- Edge-sharing of adjacent clusters

Exptl data from Lamparter, *Phys. Scr.*, **T57**, 72 (1995)

MEDIUM RANGE ORDER
Prediction

Notable results

- *fcc* cluster packing with (α_β+α_γ) defect state for N≥12, *sc* cluster packing for N≤10
- MRO for $Ni_{81}B_{19}$ now well-predicted by ECP model
- Good fit to MRO of solutes to radial distances of ~1nm



Miracle, *Nature Mat.*, **3**, 697 (2004)

DENSITY

Calculated densities and packing fractions

Composition	Actual density (g/cm^3)	Predicted density (g/cm^3)	Density error (%)	Λ_0 Error (%)	Corrected Λ_0 (nm)	Packing fraction	Ref.
$Ni_{81}B_{19}$	8.4	10.92	30.0	−9.1	0.395	0.7420	[4]
$Pd_{79.8}Si_{20.2}$	10.25	13.45	31.2	−9.5	0.663	0.6997	[52]
$Al_{85}Gd_6(Fe_3Ni_6)$	3.51	3.07	−12.6	4.4	0.928	0.7048	[19]
$Al_{85}Gd_8(Fe_2Ni_5)$	3.71	3.23	−12.9	4.5	0.927	0.7223	[19]
$Al_{87}Gd_6(Fe_1Ni_6)$	3.47	2.95	−14.9	5.3	0.920	0.7115	[19]
$Fe_{70}Zr_{10}B_{20}$	7.23	9.52	31.6	9.6	0.855	0.7086	[87]
$Fe_{70}Nb_{10}B_{20}$	7.68	9.07	18.2	−5.7	0.807	0.7183	[87]
$Fe_{70}Cr_{10}B_{20}$	7.34	7.75	5.6	−1.8	0.755	0.7105	[87]
$Mg_{60}Y_{10}Cu_{30}$	3.13	2.71	−13.4	4.7	1.039	0.6784	[88]
$Pd_{77.5}Cu_6Si_{16.5}$	10.48	9.74	−7.1	2.4	0.766	0.7051	[52]
$Pd_{48}Ni_{32}P_{20}$	9.83	6.94	−29.4	11.0	0.768	0.7227	[52]
$Pt_{52.5}Ni_{22.5}P_{25}$	15.85	13.29	−16.1	5.7	0.809	0.6811	[52]
$Zr_{60}Al_{10}Cu_{30}$	6.72	4.60	−31.6	11.9	0.912	0.7254	[21]
$Zr_{60}Al_{15}Ni_{25}$	6.36	4.07	−36.0	13.8	0.896	0.7272	[21]

Miracle, *Acta mater.*, **54**, 4317 (2006)

“There is no problem, no matter how complex, which, upon careful analysis, does not become more complex.”

Anderson’s Law

“For every complex problem there is a solution that is simple, neat, and wrong.”

H.L. Menken

“Everything should be made as simple as possible, but not simpler.”

A. Einstein

OUTLINE

LOCAL STRUCTURE

EXTENDED STRUCTURE

VALIDATION

ADDITIONAL TOPICS

Solute selection: Which solute is α?

Solute site sizes

Partial coordination numbers

Influence of structure on properties: Stability, Density

Defects: Constitutional and Thermal

Deformation: STZ static structure

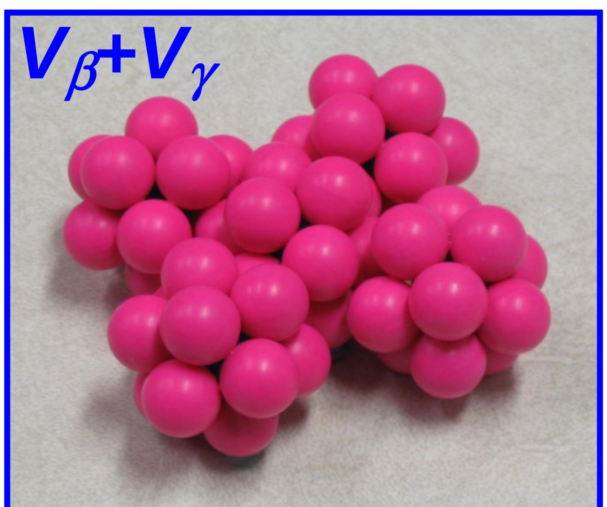
REMAINING ISSUES

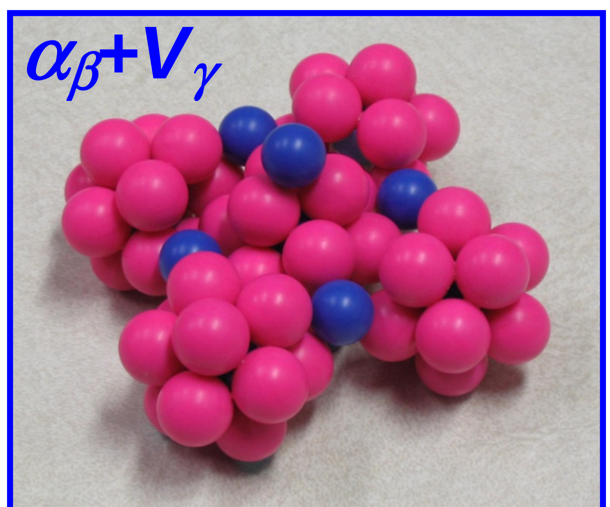
TOPOLOGICAL CONTRIBUTION TO STABILITY

Significant topological complexity is possible

- The ECP model allows quantification of structural topology in metallic glasses
- 276 distinct metallic glass topologies have been defined with the ECP model

Do all topologies have the same stability, or are some intrinsically more stable than others?



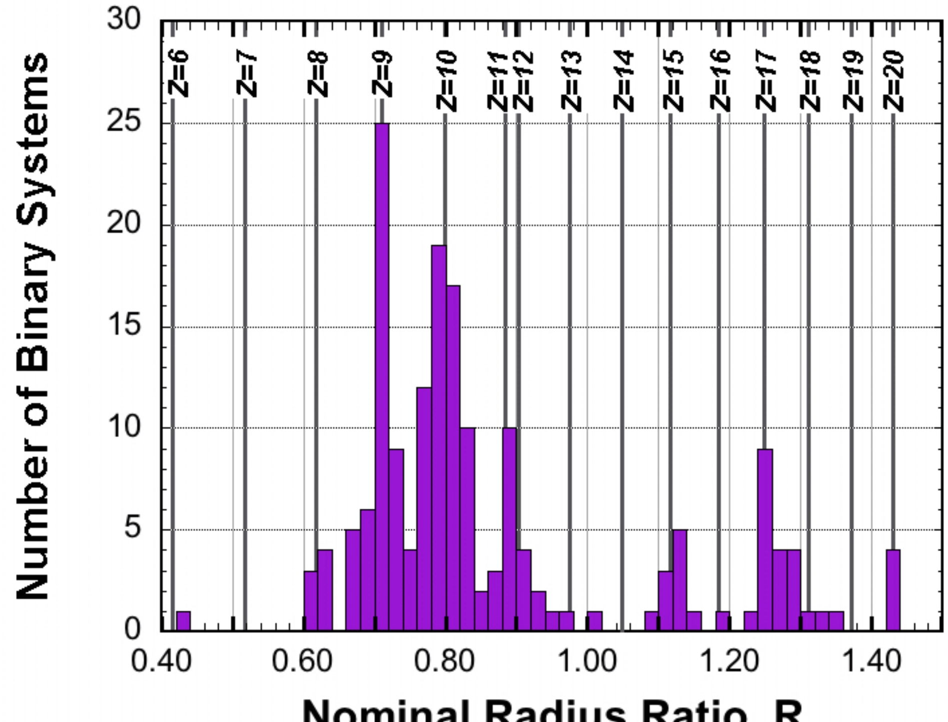


MISSING BINARY TOPOLOGIES

Do all topologies have the same stability, or are some intrinsically more stable than others?

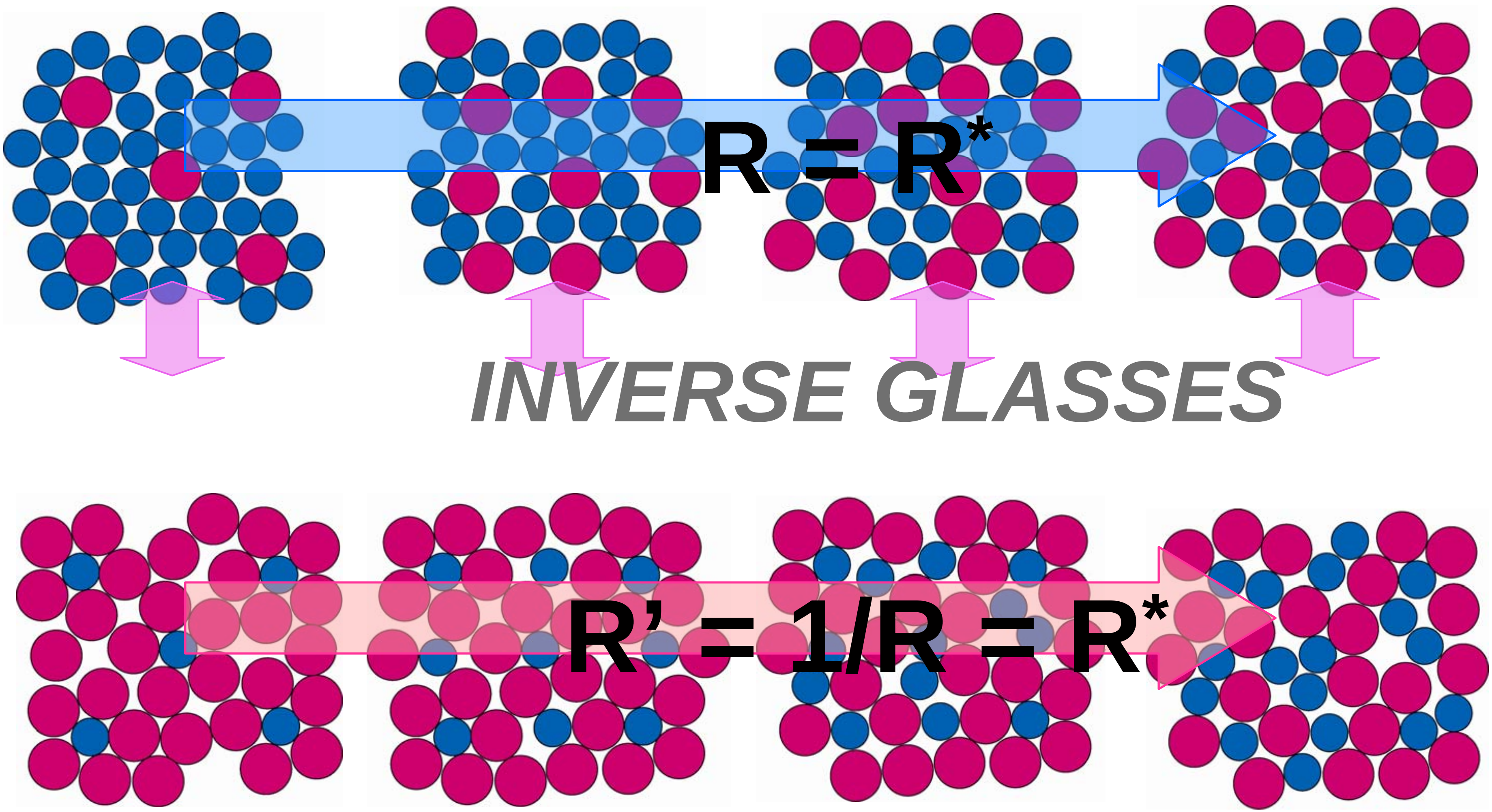
Thirteen values of R* (or <Z>) may be expected in metallic glasses

- 0.617 ≤ *R** ≤ 1.433, which gives 8 ≤ Z ≤ 20
- Only 5 *R** values are common
- <11>, <13> and <14> can be excluded on topological basis
- Preference for <10>, <17>, <12> and <15> may be related to unusual 'inverse' relationship
- Scarcity of <8> and <20> may be related to relatively few candidate systems
- Scarcity of <16>, <18>, <19> not understood



Miracle, Louzguine, Louzguina, Inoue; *Int'l Mater. Rev.*, In Press.

WHEN DOES THE SOLUTE BECOME THE SOLVENT?



TOPOLOGICAL CONTRIBUTION TO STABILITY

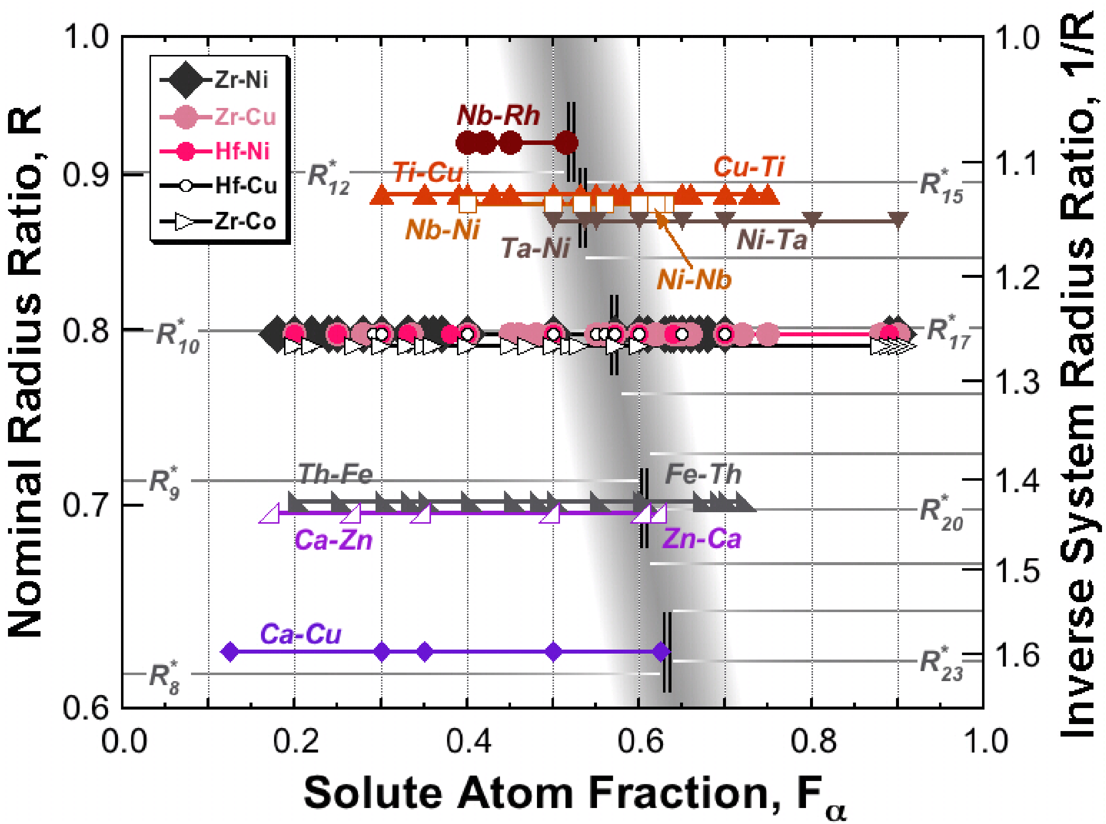
Complementary inverse glasses

– The solute-to-solvent radius ratio and solvent-to-solute radius ratios both match *R** needed for efficient local atomic packing

Two pairs of systems stand out

– The inverse of *R**=0.799 for <10> almost exactly equals *R**=1.248 for <17>

– The inverse of *R**=0.902 for <12> matches *R**=1.116 for <15> almost as well



“This paper is unlikely to be very important in its field, but it could be interesting to a wide spectrum of physicists.”

Unattributed

July 2003

Comment of ‘Referee B’ for manuscript submitted to Phys. Rev. Lett.

OUTLINE

LOCAL STRUCTURE

EXTENDED STRUCTURE

VALIDATION

ADDITIONAL TOPICS

REMAINING ISSUES

Solute-rich structures

Chemical contributions

Strength/Fragility of Supercooled Liquids

CLOSING COMMENTS

Key features and predictions validated by comparison with experimental data

- SRO/ partial coordination numbers
- MRO
- Number of topologically distinct atomic species
- Preference for specific radius ratios

A simple topological model helps organize the way we look at structures

- Has proved useful in computations
- Simplifies the way we ‘bin’ metallic glasses

ECP model has been used to guide exploration of new bulk metallic glasses

- New BMGs based on Ca, Fe, Sc…

A lot of work still needs to be done

THANK YOU!