

# Influence of initial packing, pore formers and sintering on mechanical properties of porous ceramics: Discrete Element Method simulations

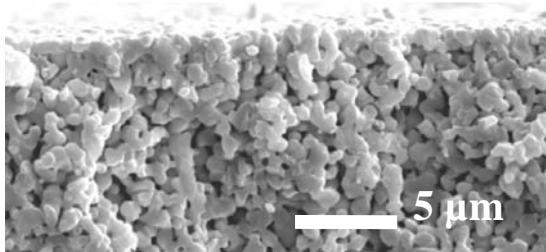
David Jauffrès, Christophe L. Martin



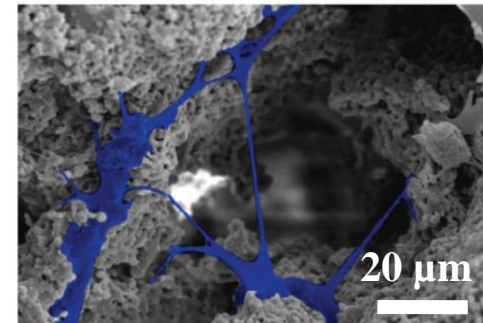
Rajendra K. Bordia



- Functional porous ceramics obtained via partial sintering



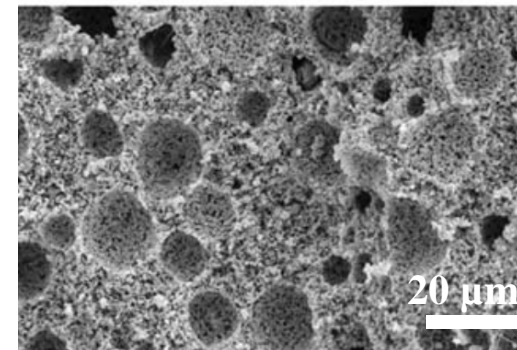
Solid Oxide Fuel Cell electrode  
From J. Laurencin CEA, unpublished



Bone scaffold

A. Bignon et al., J. Mater. Sci. Mater. Med. 14, 1089–97, 2003

- ✓ Pore surface or volume for functionality
- ✓ Porosity obtained via partial sintering
- ✓ Particulate nature is retained
- ✓ Pore formers can be used

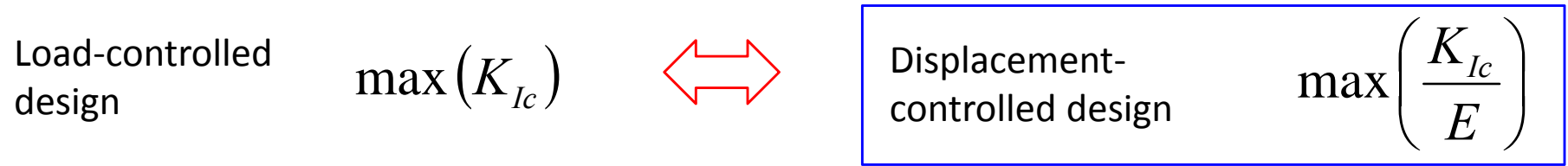


SiC filter

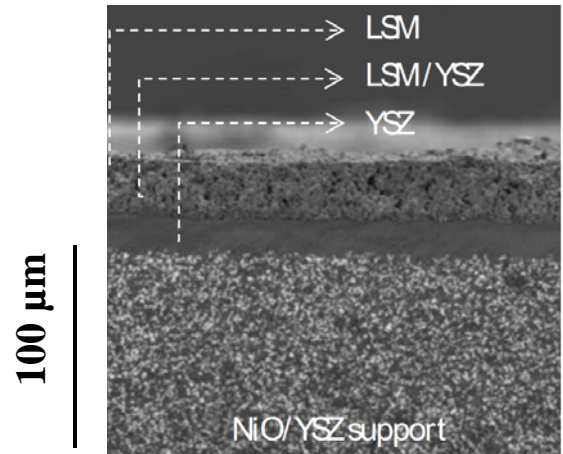
Y. W. Kim et al., J. Mater. Sci. 45, 2808–2815, 2010

- Strain tolerance

Minimum mechanical requirement to sustain handling, self-support or thermal cycling.



Example of displacement-controlled design: SOFC



A. Suresh et al., Electrochem. Solid-State Lett. 12, B176, 2009.

Thermal cycling + CTE mismatch

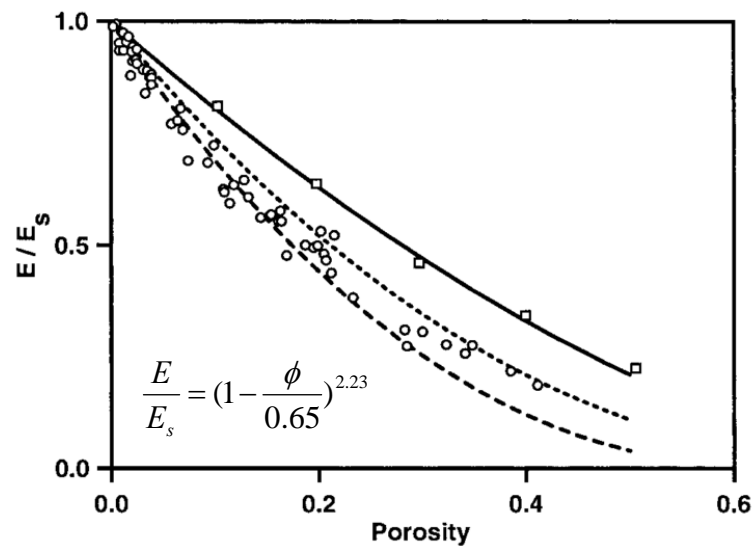


Thermal strains

↓  
Strain tolerance parameter

- Towards more strain tolerant porous ceramics ?

Authors typically relate mechanical properties to porosity ...



Empirical or semi-empirical relationships have been proposed...

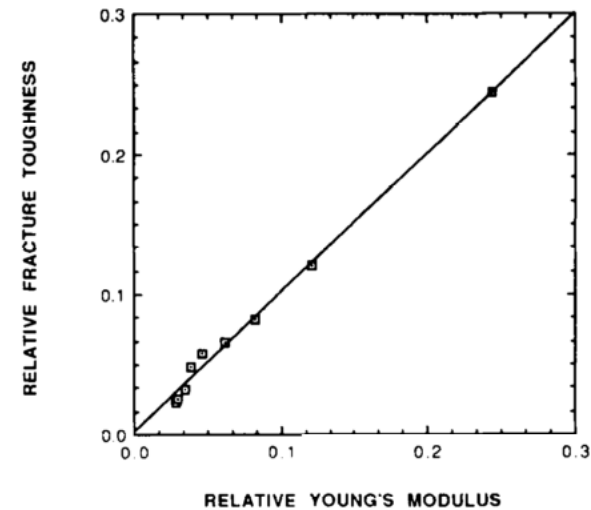
A. P. Roberts and E. J. Garboczi, J. Am. Ceram. Soc., 83, 3041–3048, 2000.

- Towards more strain tolerant porous ceramics ?

Toughness versus Young's modulus

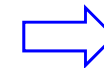
$$\frac{K_{Ic}}{E} = \text{constant} ?$$

No freedom for  
microstructural design ?



D. Hardy and D. J. Green, J. Eur. Ceram. Soc., 15, 769–775, 1995.

- Is it possible to improve mechanical properties at a fixed value of porosity via microstructural design ?
- Is it possible to optimize the strain tolerance ?



Need for sound relationships  
between microstructure and  
mechanical properties

## Outline

- Methods: from particles to mechanical properties of porous ceramics
  - Discrete Element Method
  - Compaction & sintering
  - Elasticity & fracture
- Results: design of strain tolerant porous ceramics
  - Scaling laws for homogeneous microstructures
  - Influence of heterogeneity: pore formers and powder pre-calcination
  - Toward an experimental validation ?
- Conclusion





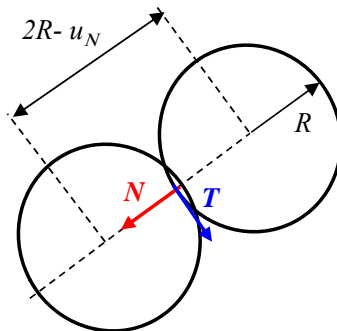


- Compaction

### Hertz-Mindlin contact

$$N = \frac{4}{3} \frac{E}{1-\nu} R^{\frac{1}{2}} u_N^{\frac{3}{2}}$$

$$T = 8 \frac{G}{2-\nu} (R u_N)^{\frac{1}{2}} u_T$$





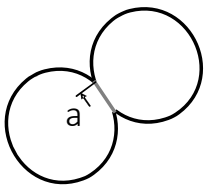
- Sintering

### Viscous normal and tangential forces

$$N = \frac{\pi a^4}{8\Delta_b} \frac{du_N}{dt} + \frac{9}{8} \pi R \gamma_s$$

$$T = -\eta \frac{\pi a^2 R^2}{8\Delta_b} \frac{du_T}{dt}$$

$D_b/D_s = 2$



$\Delta_b = \Delta_b(\delta, D_{0b}, R, T, Q_b, \Omega) =$  GB diffusion parameter

$\gamma_s =$  surface energy

$\eta =$  viscous parameter (phenomenological)

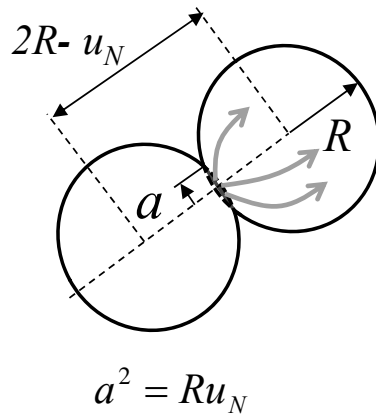
D. Bouvard and R. M. McMeeking, J. Am. Ceram. Soc., 79, 666–672, 1996.  
 C. L. Martin et al., Scr. Mater., 55, 425–428, 2006.



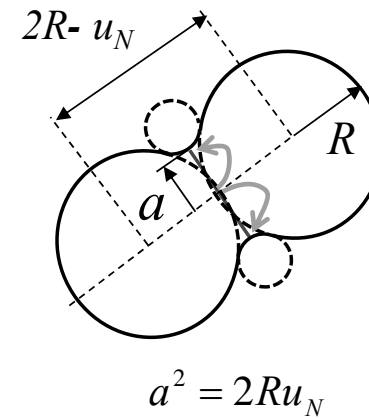
- Sintering

Neck size  $a$  ?

2 possible assumptions for matter redistribution



Truncated Spheres (TS)

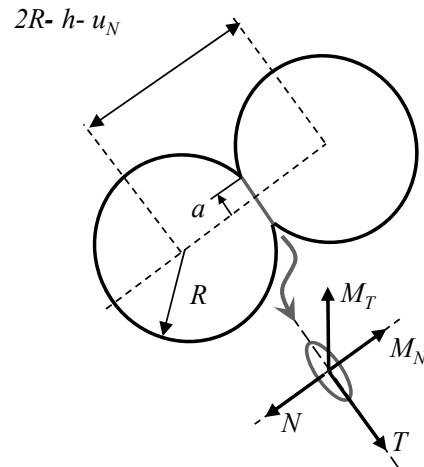


Tangent Torus (TT)

- Elastic behavior of bonded particles

## Bond contact model

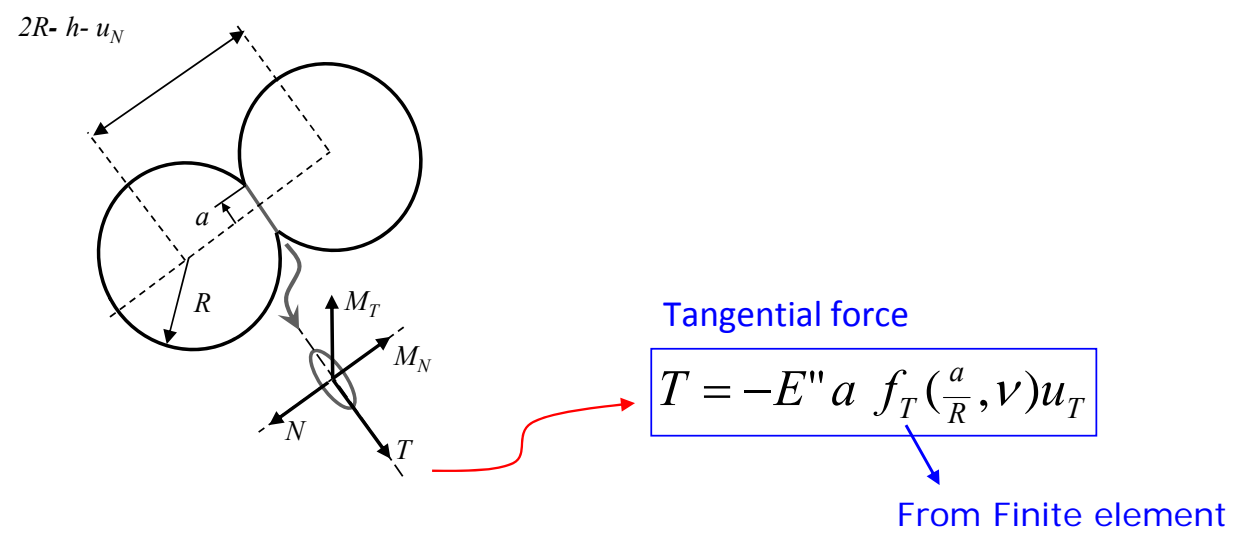
*G. Jefferson et al., 2002, J Mech Phys Solids, 50 2539-75*  
*D.O. Potyondy and P.A. Cundall, 2004, Int J Rock Mech & Mining Sci 41, 329-1364*  
*D. Jauffres et al., 2012, MSMSE 20, 045009*



- Elastic behavior of bonded particles

### Bond contact model

G. Jefferson et al., 2002, *J Mech Phys Solids*, 50 2539-75  
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 D. Jauffres et al., 2012, *MSMSE* 20, 045009



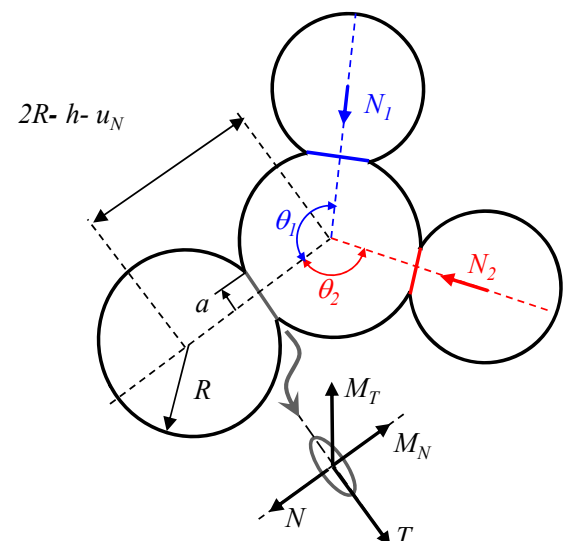




- Elastic behavior of bonded particles

### Bond contact model

G. Jefferson et al., 2002, *J Mech Phys Solids*, 50 2539-75  
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 D. Jauffres et al., 2012, *MSMSE* 20, 045009



Normal force

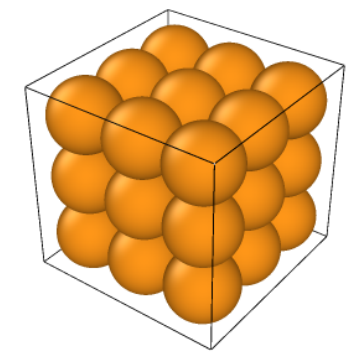
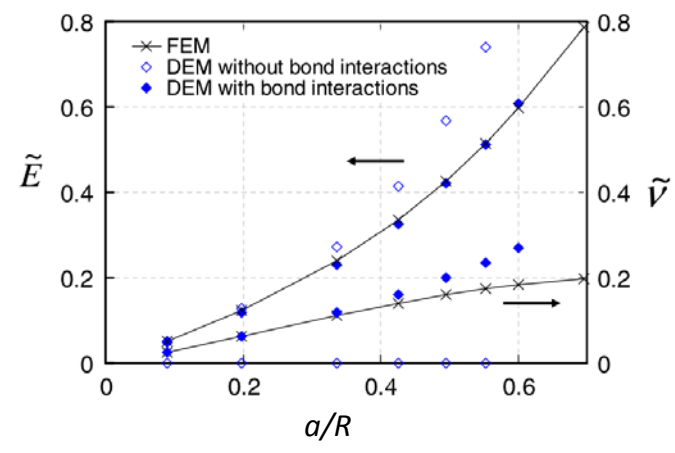
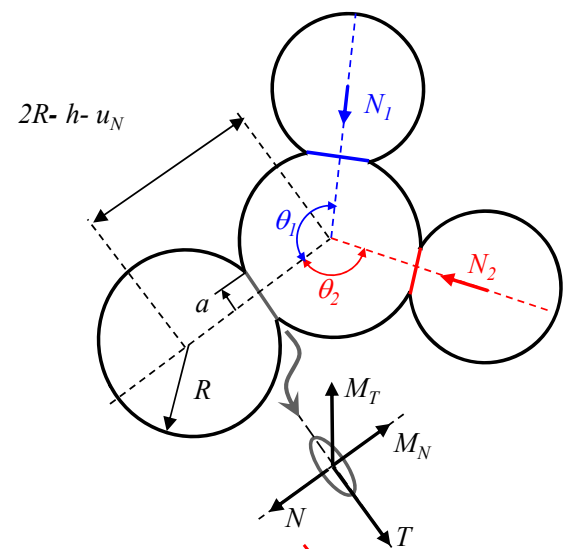
$$N = E' a f_N \left( \frac{a}{R}, \nu \right) [u_N + g(N_i, \theta_i)]$$

Contact interaction term, accounts for sphere deformation under multiples contacts

- Elastic behavior of bonded particles

### Bond contact model

G. Jefferson et al., 2002, *J Mech Phys Solids*, 50 2539-75  
 D.O. Potyondy and P.A. Cundall, 2004, *Int J Rock Mech & Mining Sci* 41, 329-1364  
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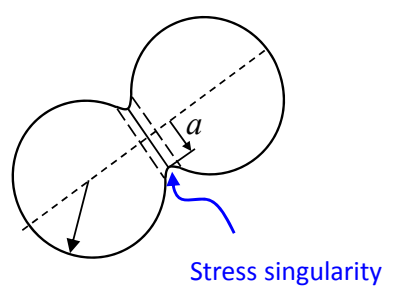
Normal force

$$N = E' a f_N \left( \frac{a}{R}, \nu \right) [u_N + g(N_i, \theta_i)]$$

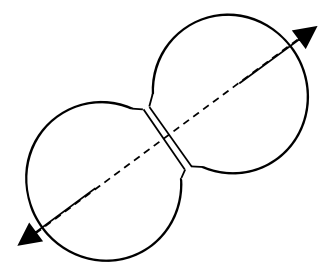
Contact interaction term, accounts for sphere deformation under multiples contacts

- Toughness of bonded particles

### Bond fracture criteria



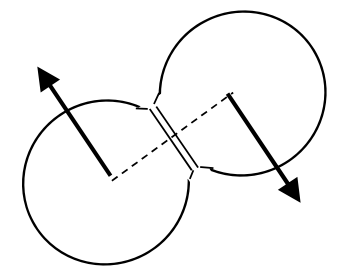
$$\sigma_b > \sigma_c$$



Fracture energy  
 $\Gamma = 2\gamma_s \sim 2\text{J/m}^2$

$$\sigma_c = 2\sqrt{\frac{E}{1-\nu^2} \frac{\Gamma}{\pi a} f_N}$$

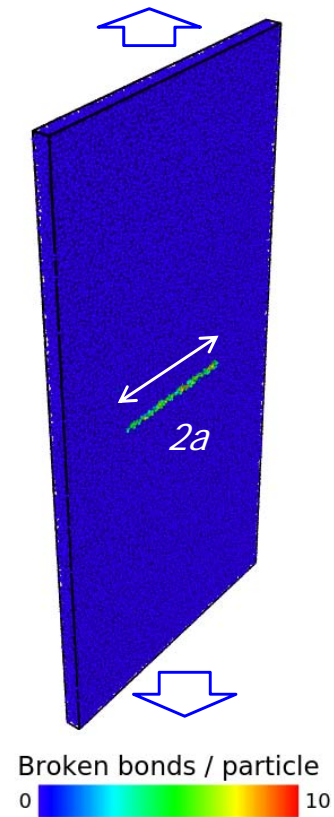
+ Similar in tangential mode (mode II)



*D. Jauffres et al., 2012, Acta Mat 60, 4685-4694*

- Toughness of bonded particles

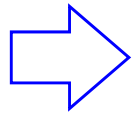
## Fracture mechanics



*D. Jauffres et al., 2012, Acta Mat 60, 4685-4694*

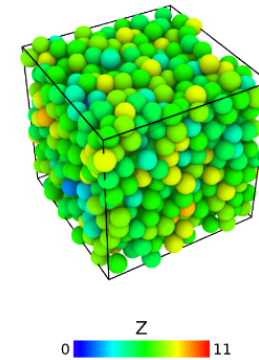


- Methods summary



Generation of **realistic** microstructures via DEM  
**Contact law based on physic** (Hertz, sintering)

Relative density 0.7

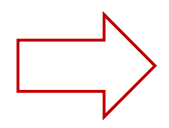






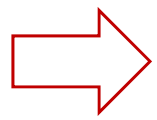
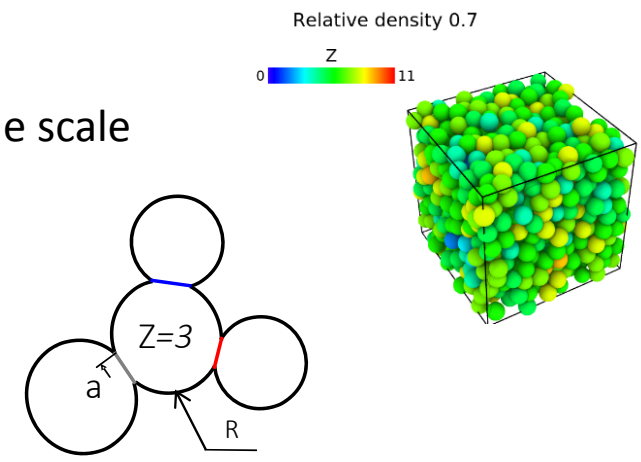


• Results: microstructure – mechanical properties relationships



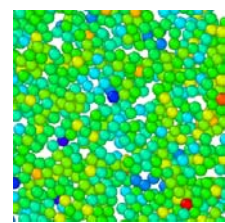
Homogeneous microstructures at the scale of a few particles: no macroporosity

Microstructure parameters:  $\langle Z \rangle$  and  $\langle a/R \rangle$

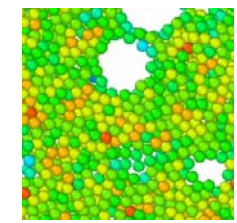


Heterogeneous microstructures with macroporosity

Sintering of pre-calcined powder aggregates



Spherical pore formers





- Homogeneous microstructures: scaling law for  $E$

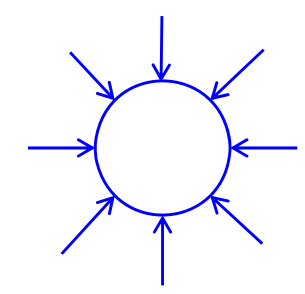
Revisiting Green's analytical work

D. J. Green et al., Mater. Res. Soc. Symp. Proc., 119, 43–48, 1988.

Spheres with  $Z$  contacts under uniform pressure  
 Homogeneous strain (Voigt assumption)  
 Constant Poisson's ratio

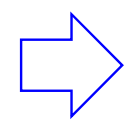
$$E \propto K \propto \frac{Z}{\Phi R}$$

Compliance of the contact



DEM simulations show that homogeneous strain is not a valid assumption  
 Strain distribution is function of  $Z$

$$E \propto K \propto \frac{Z^m}{\Phi R}$$



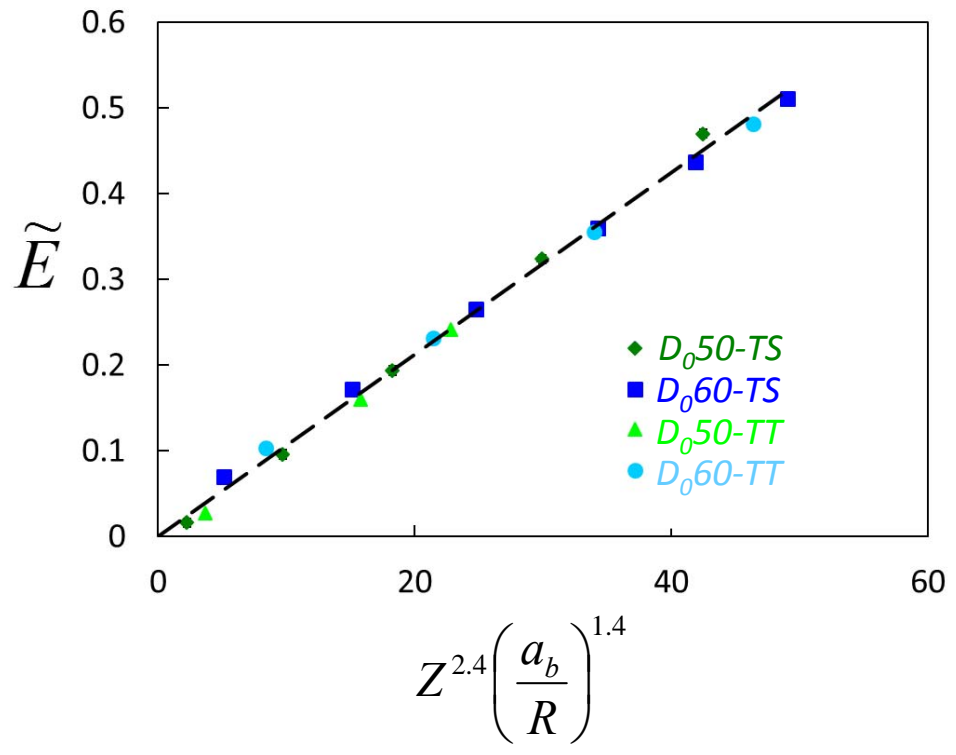
$$E \propto Z^m \left( \frac{a}{R} \right)^{1.4}$$

Compliance of the contact used in DEM contact law

- Homogeneous microstructures: scaling law for  $E$

Best fit on DEM results  
 gives  $m = 2.4$

$$E \propto Z^{2.4} \left( \frac{a}{R} \right)^{1.4}$$



- Homogeneous microstructures: scaling law for  $K_{IC}$

Revisiting Green's analytical work

D. J. Green and D. Hardy, J. Mater. Sci. Lett., 15, 1167–1168, 1996.

Force  $N$  at first contact ahead of crack tip

$$N \propto K_I R^{3/2}$$

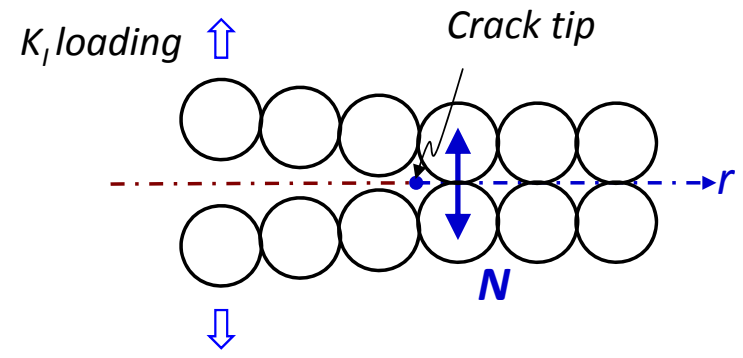
Introducing dependance on  $Z$

$$N \propto \frac{K_I R^{3/2}}{Z^p}$$

With  $N = N_c = \sigma_c \pi a^2$  and  $\sigma_c$  used in DEM model

➔

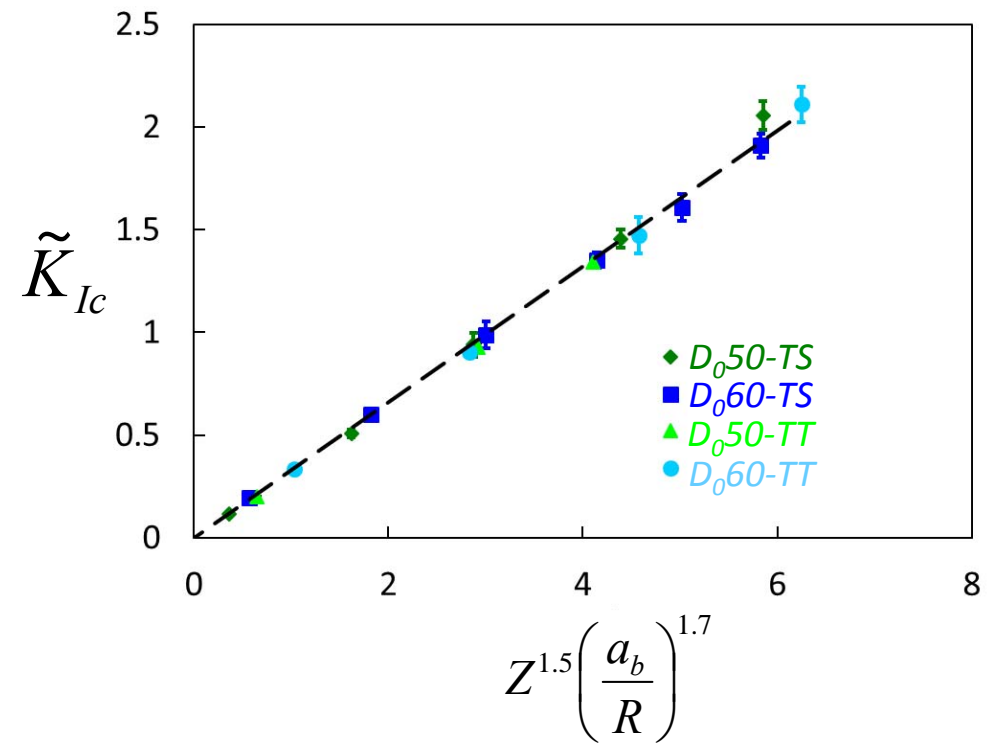
$$K_{Ic} \propto Z^p \left( \frac{a}{R} \right)^{1.7}$$



- Homogeneous microstructures: scaling law for  $K_{Ic}$

Best fit on DEM results  
 gives  $p = 1.5$

$$K_{Ic} \propto Z^{1.5} \left( \frac{a}{R} \right)^{1.7}$$

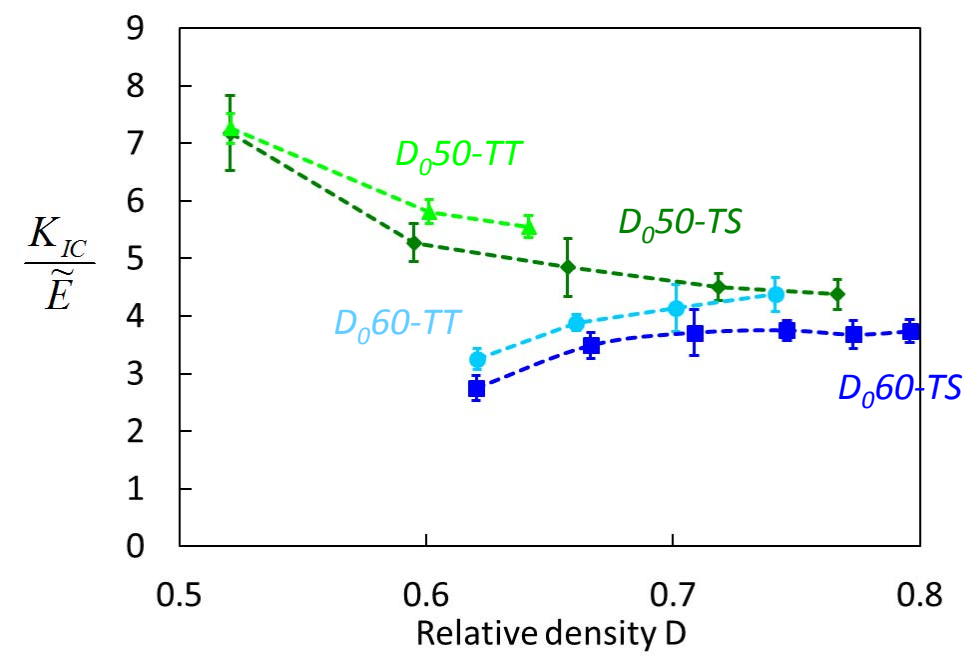


• Homogeneous microstructures: strain tolerance

$$E \propto Z^{2.4} \left(\frac{a}{R}\right)^{1.4} \qquad K_{Ic} \propto Z^{1.5} \left(\frac{a}{R}\right)^{1.7}$$

$$\frac{K_{Ic}}{E} \propto \frac{(a/R)^{0.3}}{Z^{0.9}}$$

Strain tolerance



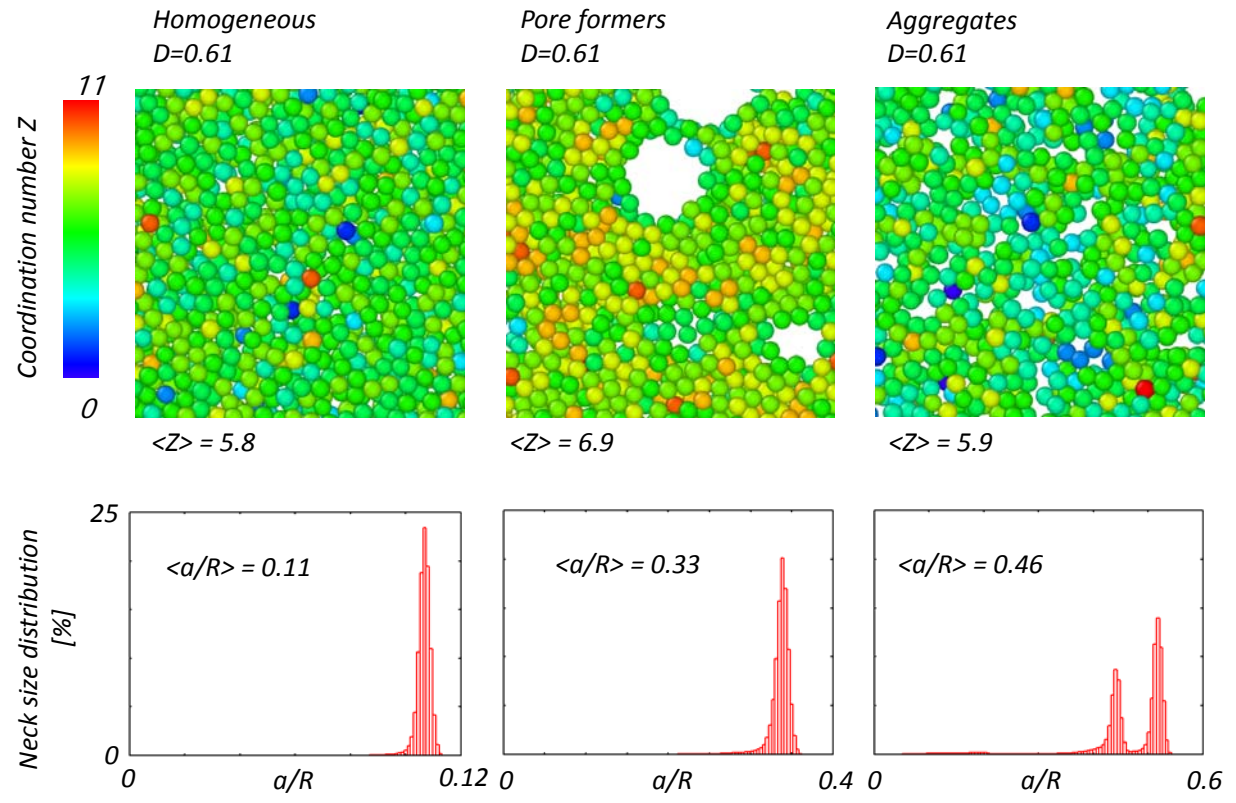
- Promoting larger neck sizes has limited efficiency in improving strain tolerance
- Simple efficient method to improve strain tolerance = reduce Z using low green densities



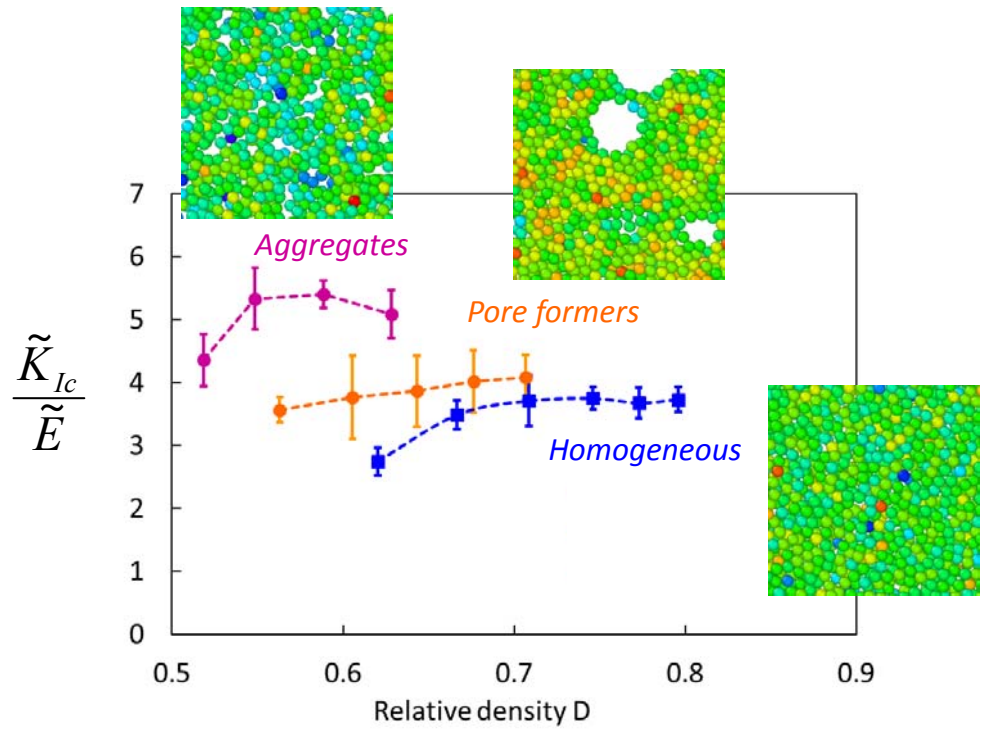




- Heterogeneous microstructures



• Heterogeneous microstructures: strain tolerance

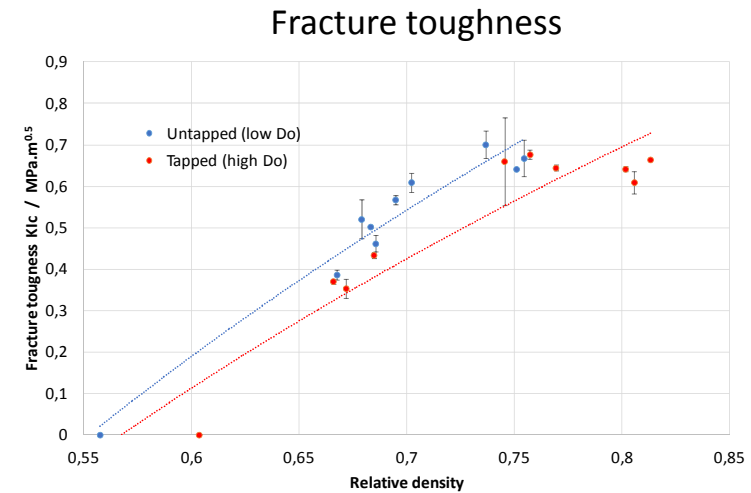
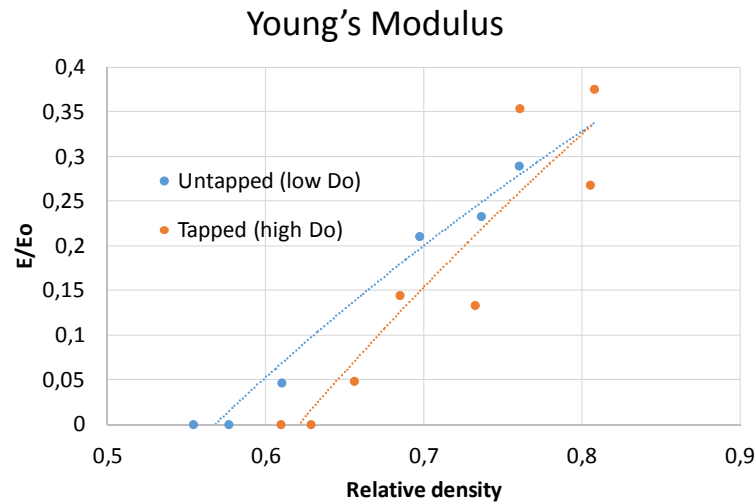


Aggregates perform better for two main reasons:

- Lower Z compared to pore former
- Pores with irregular shape are less efficient in terms of elasticity than spherical pores



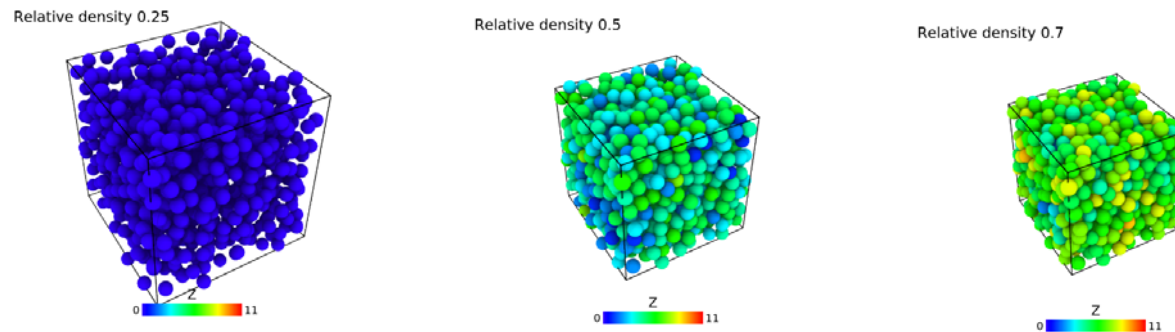
- Toward experimental validation ?



- Trend that low green densities perform better is confirmed
- Large uncertainties in  $Z$  and  $a/R$  for  $D > 0.7$  → not possible to test the scaling laws obtained numerically
- Next: heterogeneous microstructures ?

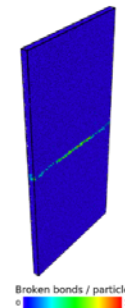
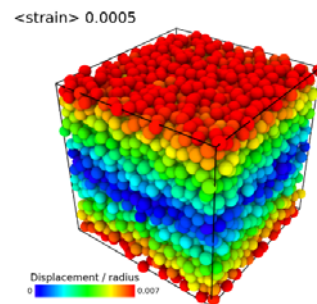
- Methods: from particles to mechanical properties

- Realistic microstructure: compaction + sintering



- Elasticity and toughness: bond contact law + fracture criteria, **no fitting parameters**

$$E, \nu$$



$$K_{Ic} = \sigma_f Y \sqrt{\pi a}$$

• Methods: from particles to mechanical properties

- Realistic microstructure: compaction + sintering
- Elasticity and toughness: bond contact law + fracture criteria, **no fitting parameters**

*D. Jauffres et al., 2012, MSMSE 20, 045009  
 D. Jauffres et al., 2012, Acta Mat 60, 4685-4694*

• Results: design of strain tolerant microstructures

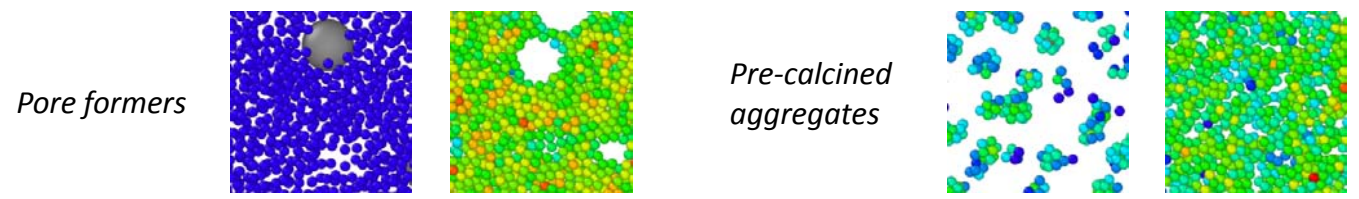
- Scaling laws for Young's modulus and fracture toughness

$$E \propto Z^{2.4} \left( \frac{a}{R} \right)^{1.4}$$

$$K_{Ic} \propto Z^{1.5} \left( \frac{a}{R} \right)^{1.7}$$

$$\frac{K_{Ic}}{E} \propto \frac{(a/R)^{0.3}}{Z^{0.9}}$$

- Introduction of heterogeneity via macroporosity improves strain tolerance



- Prospect: experimental validation

*D. Jauffres et al., 2017, Acta Mat, under review*