ASME SETTING THE STANDARD IMECE 2017:

Stony Brook University
College of Engineering & Applied Sciences

Estimating Effective Thermal Conductivity of Hollow Sphere Foam Materials

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11/6/2017

Stony Brook University
Mechanical Engineering

Outline

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1. Introduction

- Hollow sphere foams;
- Applications.

2. Methods

- Theoretical modelling;
- Numerical simulation.

3. Results and discussion

- Effect of shell porosity and multilayer shell;
- Effect of sphere packing and binder shape;
- Effect of Interfacial Thermal resistance (ITR).

4. Conclusion

- Guidelines to designs HSFs.

1. Introduction

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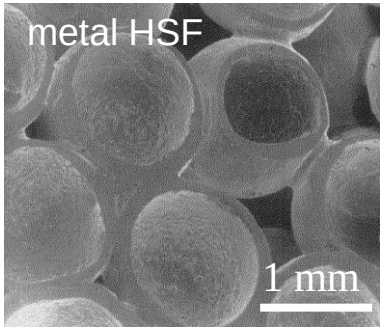
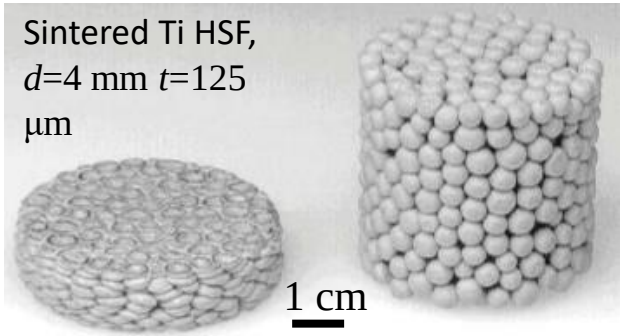
- **Hollow sphere foams (HSF)** are special cellular solids that exhibit low density, large void space, and large specific surface area.

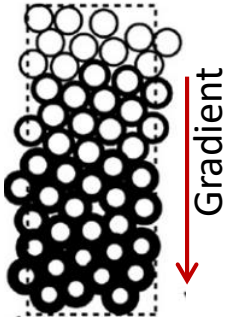
- Macroscale level (~mm)



Curr. Opin. Solid State Mater. Sci. 3.5 (1998): 474-479.



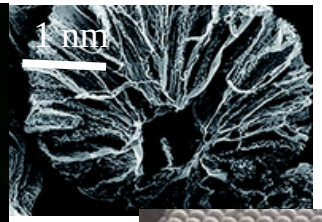
Adv. Eng. Mater. 2.4 (2000): 192-195.



IJMS 52.5 (2010): 680-688.

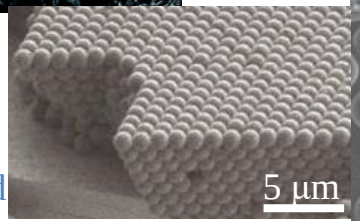
- Mesoscale level (μm~nm)

Nature 127.3211 (1931): 741.

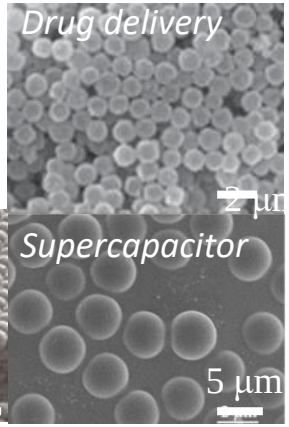


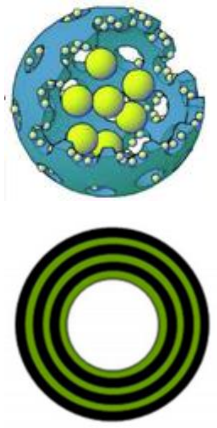
random

ordered



Nature 414.6861 (2001): 289-293.





Adv. Mater. 26.20 (2014): 3176-3205.
Electrochim. Acta 173 (2015): 184-192.

1. Introduction

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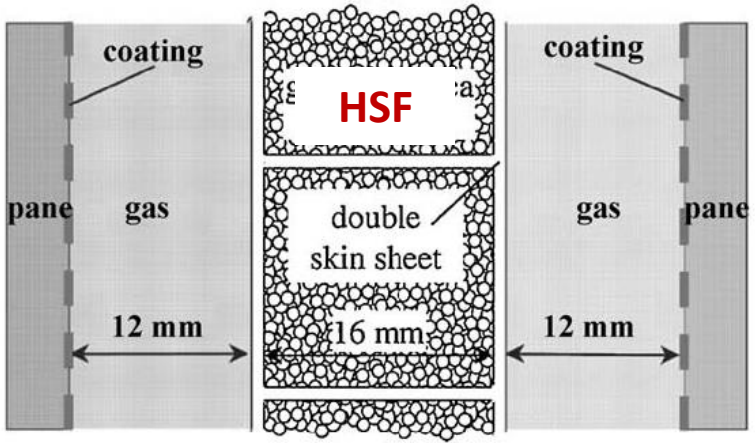
➢ Hollow sphere foams (HSF) Applications

- Heat exchangers, cooling machines;
- Thermal insulation (offshore pipelines => buoyance);
- Catalyst supports.

Energy and Buildings 43 (2011) 761–769

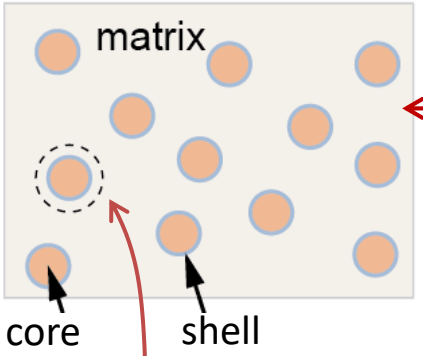


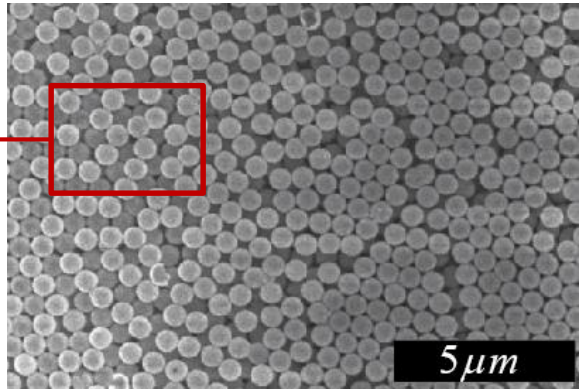
Solar Energy 79 (2005) 131–139

For sphere radius 1μm~10mm, thermal conduction dominates.

2. Methods: theoretical modelling

- **Evaluating the effective thermal conductivity (ETC) of HSF**
- composed of three components - core, shell, and matrix.
- Transfer HSF problem to solid-particle problem, which is well studied.





Langmuir **2012,** *28* (13), 5580-5588.

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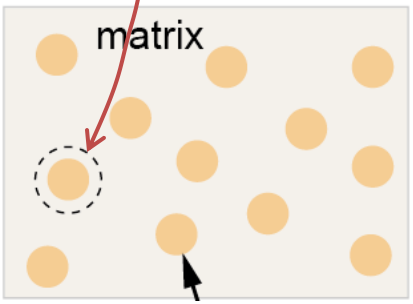


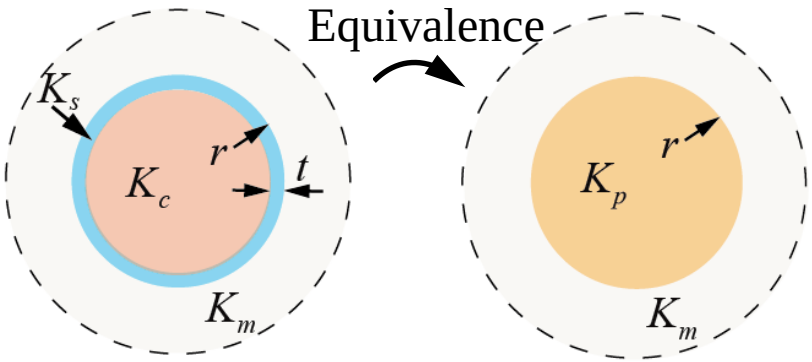
solid particle without shell

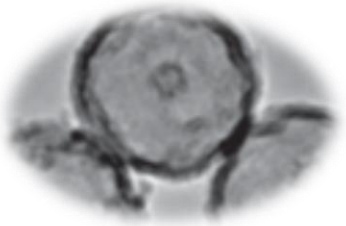
Notice there're many models developed for Solid particle-filled composites.

Model	Equation for ETC prediction
Series model	$\frac{K_{eff}}{K_m}=\frac{K_p/K_m}{K_p/K_m+\phi(1-K_p/K_m)}$, where ϕ is volume fraction of particle filling.
Parallel model	$\frac{K_{eff}}{K_m}=1+\phi(K_p/K_m-1)$
Maxwell model [24]	$\frac{K_{eff}}{K_m}=\frac{(1+2\phi)K_p/K_m+2(1-\phi)}{(1-\phi)K_p/K_m+(\phi+2)}$
Inverse Maxwell model	$\frac{K_{eff}}{K_m}=\frac{2\phi K_p/K_m+(3-2\phi)}{(3-\phi)K_p/K_m+\phi}\cdot\frac{K_p}{K_m}$
Chiew and Glandt model [45]	$\frac{K_{eff}}{K_m}=\frac{1+2\beta\phi+(K_2-3\beta^2)\phi^2}{1-\beta\phi}$ where $\beta=\frac{K_p-K_m}{K_p+2K_m}$, K_2 is a function of ϕ. with fitting parameters suggested in [45]: $\frac{K_{eff}}{K_m}=\frac{1+2\beta\phi+(2\beta^3-0.1\beta)\phi^2+0.05\exp(4.5\beta)\cdot\phi^3}{1-\beta\phi}$.

2. Methods: theoretical modelling

- **Equivalent hollow sphere as an effective solid particle**





J. Appl. Phys. **1997,** *81* (10), 6692-6699.

Based on effective media theory,

$$K_p/K_s = \frac{3+(K_c/K_s-1)(1+2v)}{3+(K_c/K_s-1)(1-v)},$$

K_p is the thermal conductivity of the equivalent particle, and $v = \frac{r^3}{(r+t)^3}$.

Rev. Mod. Phys. 41.1 (1969): 48.

Interfacial thermal resistance (ITR)

$$\kappa_1 \frac{\partial T^1}{\partial n} = \kappa_2 \frac{\partial T^2}{\partial n} = \beta(T^1 - T^2),$$

$$R_{Bd} = \beta^{-1} = \lim_{\substack{t\to 0 \\ K_s \to 0}} (t/K_s)$$

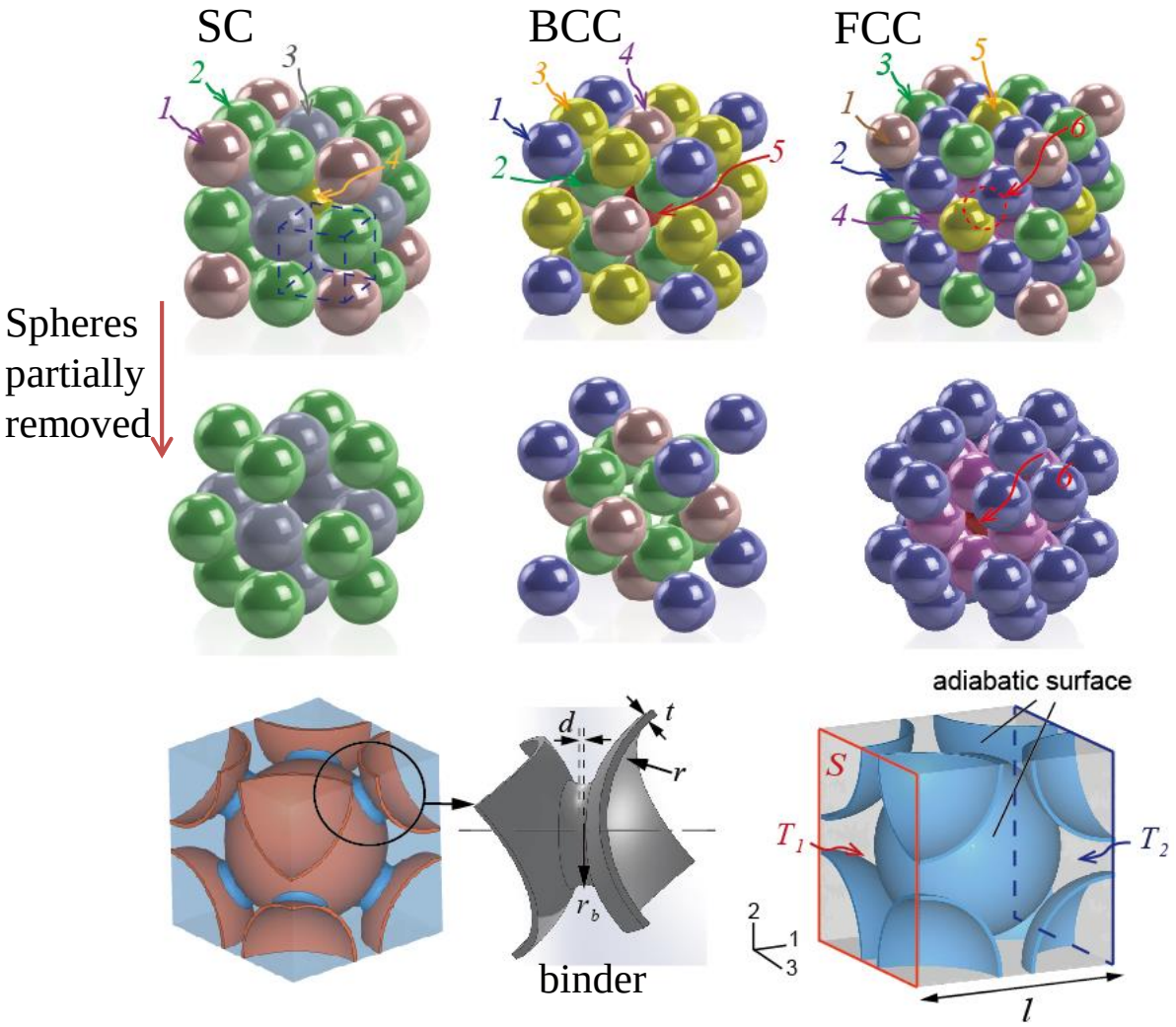
$$K_{ITC} = \frac{K_c}{1+\alpha K_c/K_m}, \quad \alpha = R_{Bd} K_m / r$$

dimensionless parameter

$$K_p^{ITC}/K_m = \frac{3+(s_c-1)(1+2v)}{s_m[3+(s_c-1)(1-v)]+\alpha[3+(s_c-1)(1+2v)]} \cdot s_c = K_c/K_s, s_m = K_m/K_s$$

2. Methods: numerical simulation

- **FEM simulation**



Governing Equation

steady heat transfer problem

$$\nabla^2 T = 0$$

$$\vec{q} = -\mathbf{k}\nabla T$$

for cubic symmetric problem, **k** is a constant.

B.C.

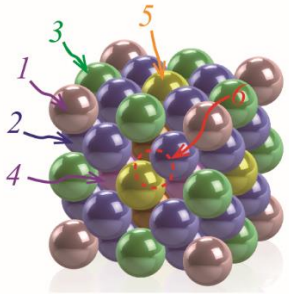
specified temperature difference along the [100] direction T_1-T_2.

ETC is evaluated with Fourier's law:

$$K_{eff} = \frac{\iint_S q\,ds}{(T_1 - T_2)\cdot l}.$$

2. Methods: numerical modelling

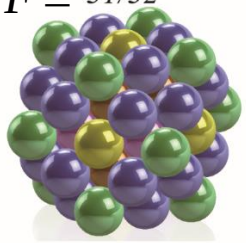
FCC



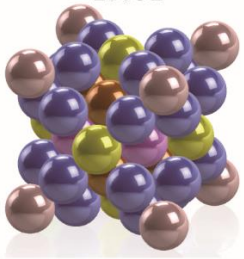
32 particles in one RVE
Different color represents different particle
Initial packing fraction: φ=0.707

Number	1	2	3	4	5	6
Effective	1/8	1/2	1/4	1	1/2	1
amount	8	24	12	12	6	1
total	1	12	3	12	3	1

$F =$ 31/32



29/32



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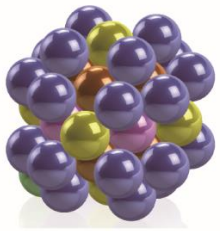
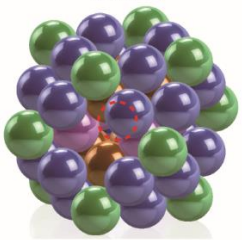
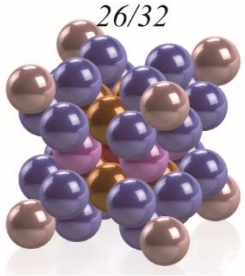


27/32



→ 14 different packing arrangements

26/32



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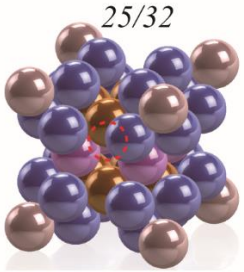

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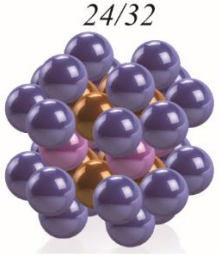

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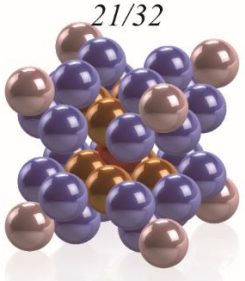

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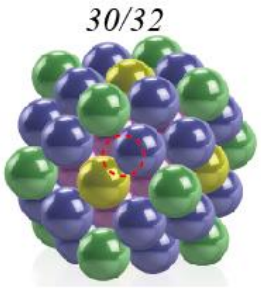

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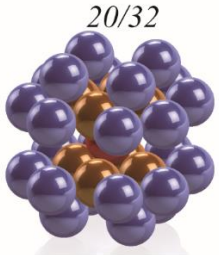

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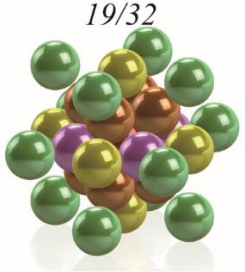

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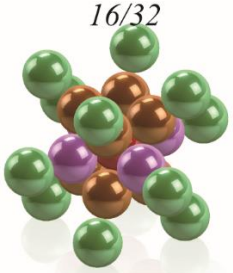

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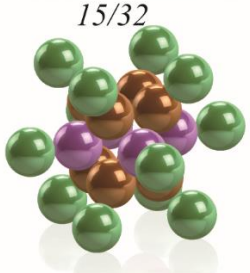

3. Results

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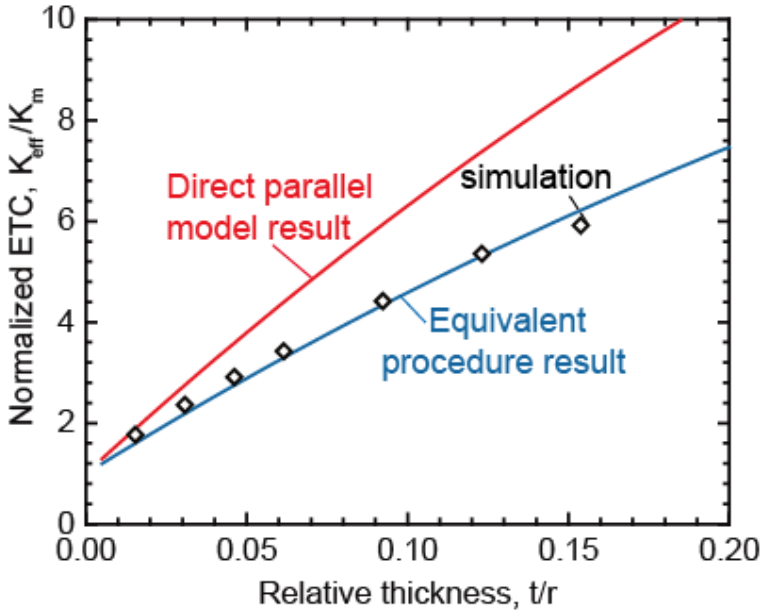
- **Verification of the theoretical model**

  -compare with a "rule of mixture" model and numerical simulations,

  -the proposed equivalent model gives much better consistency.



Shell
- glass (0.8W/m·K),

Matrix and core
- air (0.0257W/m·K)

$K_c/K_s = K_m/K_s = 1/30$

Size r~100 μm

Binder r_b=0.15r

d_b=0.1r

Direct model or "rule of mixture"

$$K_{eff} = \bar{\kappa}_s + \bar{\kappa}_m$$

$$\bar{\kappa}_s = \kappa_s\left(\rho^*/\rho_s\right), \bar{\kappa}_m = \kappa_m\left(1-\rho^*/\rho_s\right)$$

Equivalent procedure

$$K_p/K_s = \frac{3+(K_c/K_s-1)(1+2v)}{3+(K_c/K_s-1)(1-v)},$$

$$K_{eff}/K_m = 1+\phi(K_p/K_m-1).$$

3. Results

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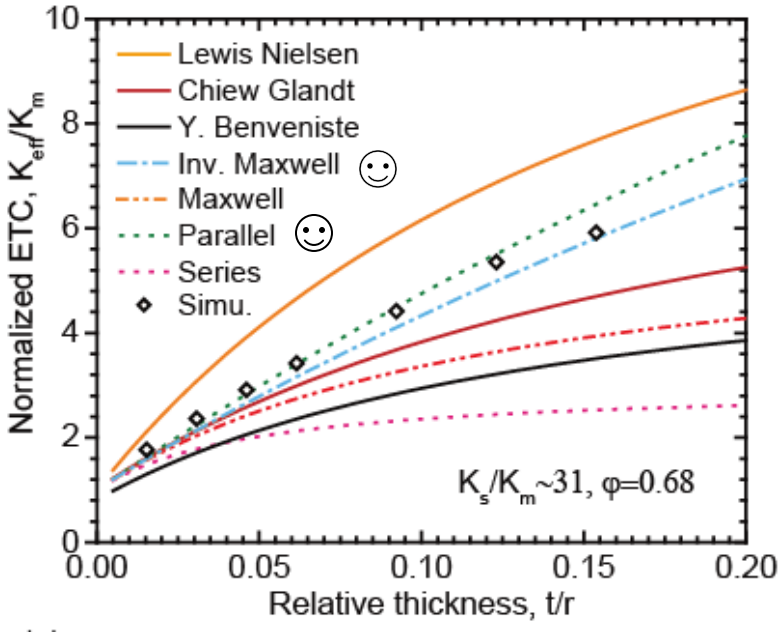
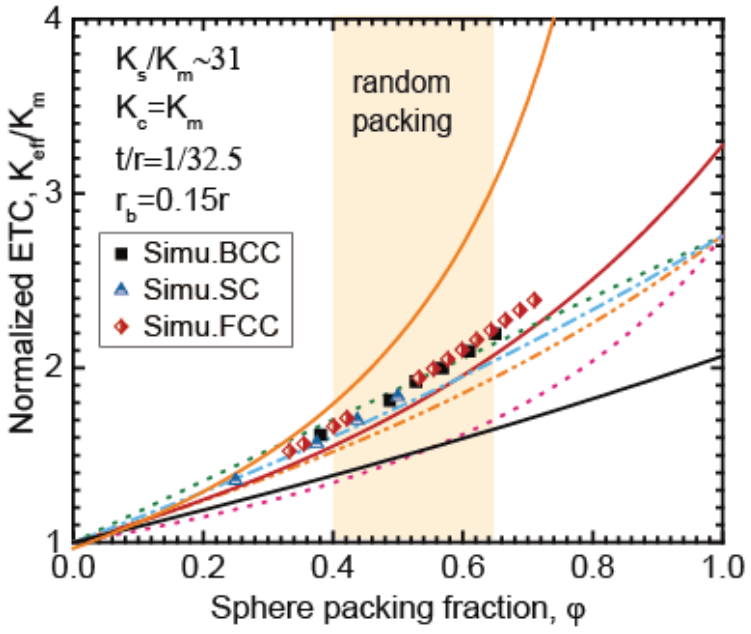
- **Verification of the theoretical model**
  - Parallel model and Inverse Maxwell model gives the best result.
  - Sphere packing fraction is the main factor that controls ETC, while packing patterns has negligible effect.





3. Results - theoretical

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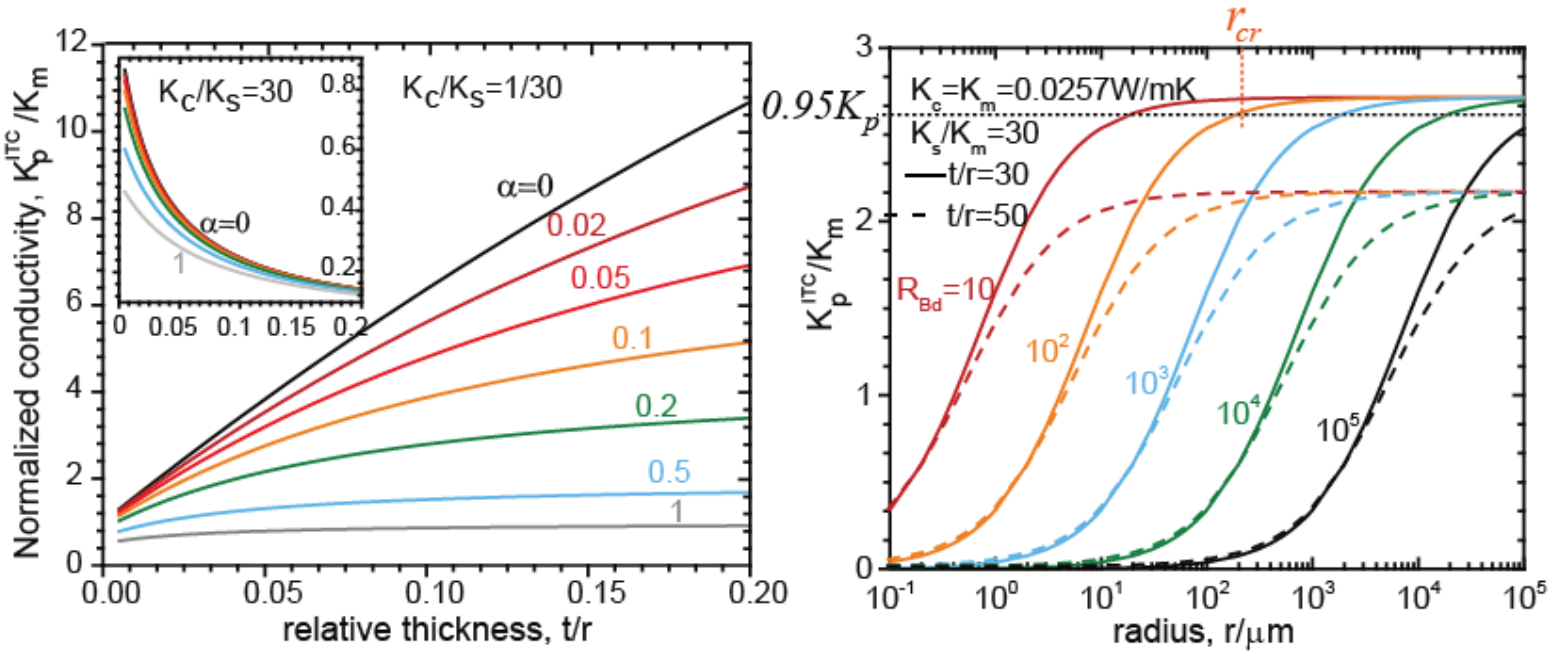
- **Effect of interfacial thermal resistance (ITR)**



$$\alpha = R_{Bd} K_m / r$$

- ETC is sensitive to ITR when shells have good conductivity;
- Exists a critical size r_{cr}, larger than which the ITR can be ignored.

$$r_{cr} \approx 20 R_{Bd} K_p$$

3. Results - theoretical

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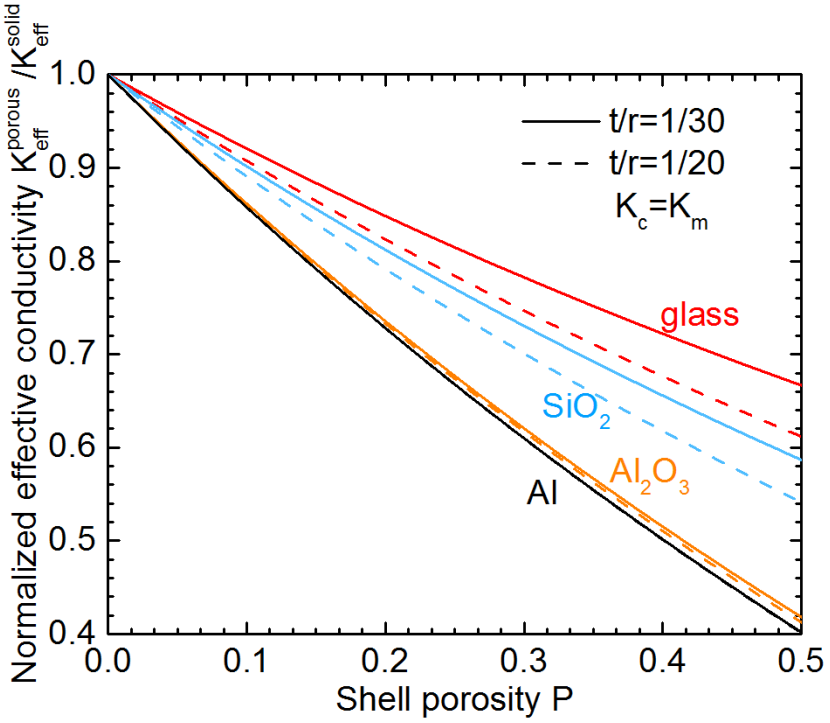
- **Introducing porosity in the shell**

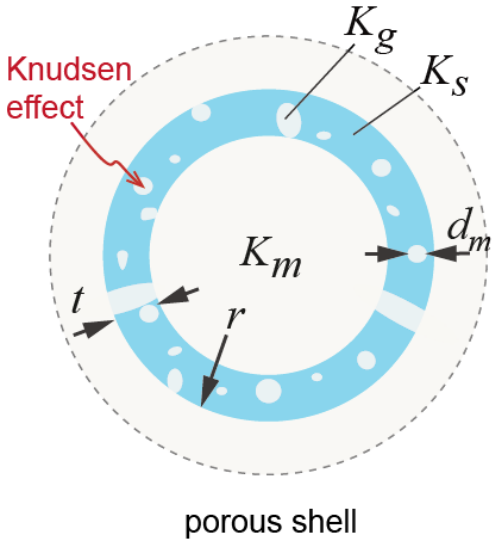
  -Modelled with two steps, 1) equivalent of the porous shell and 2) using the proposed model;

  -Conductivity reduces greatly by partially removing the shell material.

$$\frac{K_{eff}^{shell}}{K_m} = \frac{(1+2P)K_m/K_s + 2(1-P)}{(1-P)K_m/K_s + (P+2)}$$

P is porosity of shell





3. Results - theoretical

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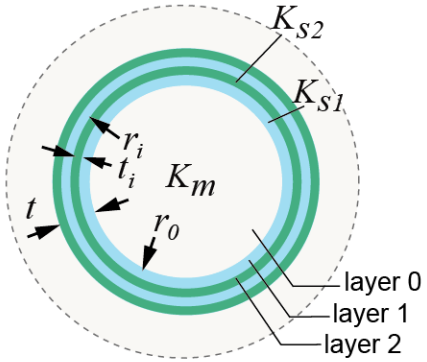
- **Multilayer shells - supercapacitor**

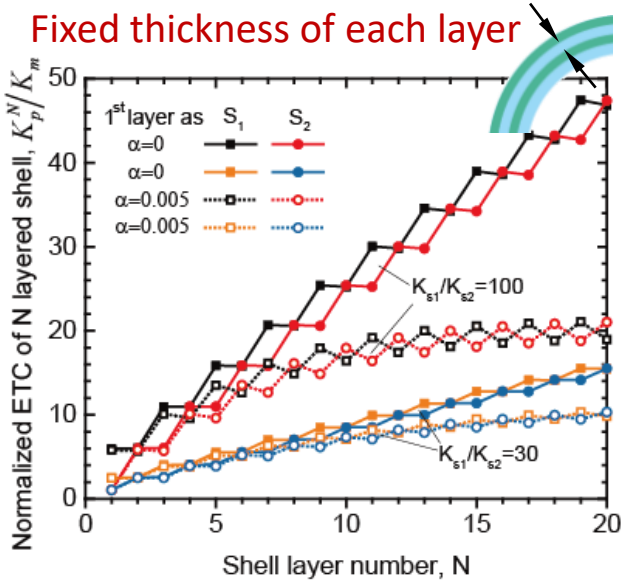
-the normalized ETC of a hollow sphere with *i* to *i*+1 layer included can be written in a recursive relation:

$$\frac{K_{eff}^{i+1}}{K_m} = f\left(\frac{K_{eff}^{i}}{K_{s_j}}, \frac{K_m}{K_{s_j}}, \alpha_i, \frac{t_i}{r_i}\right) \qquad 0 < i < N$$

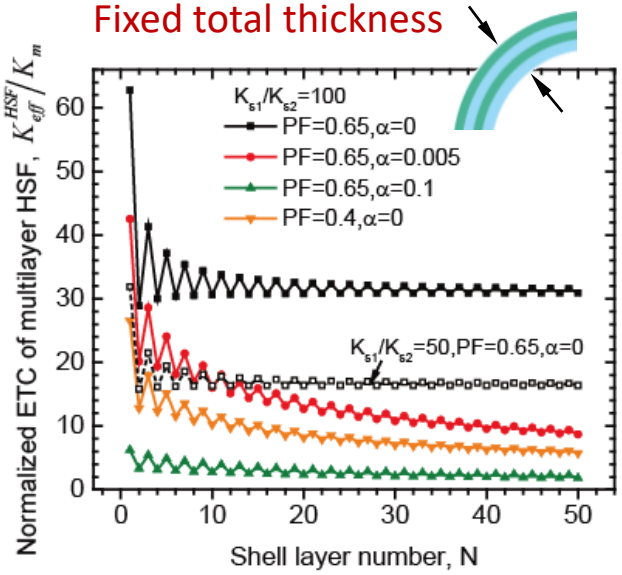
$$\sum_{i=1}^{N} t_i = t \quad \text{and} \quad \begin{cases} j = 1, \text{ odd } i \\ j = 2, \text{even } i \end{cases}$$



Fixed thickness of each layer



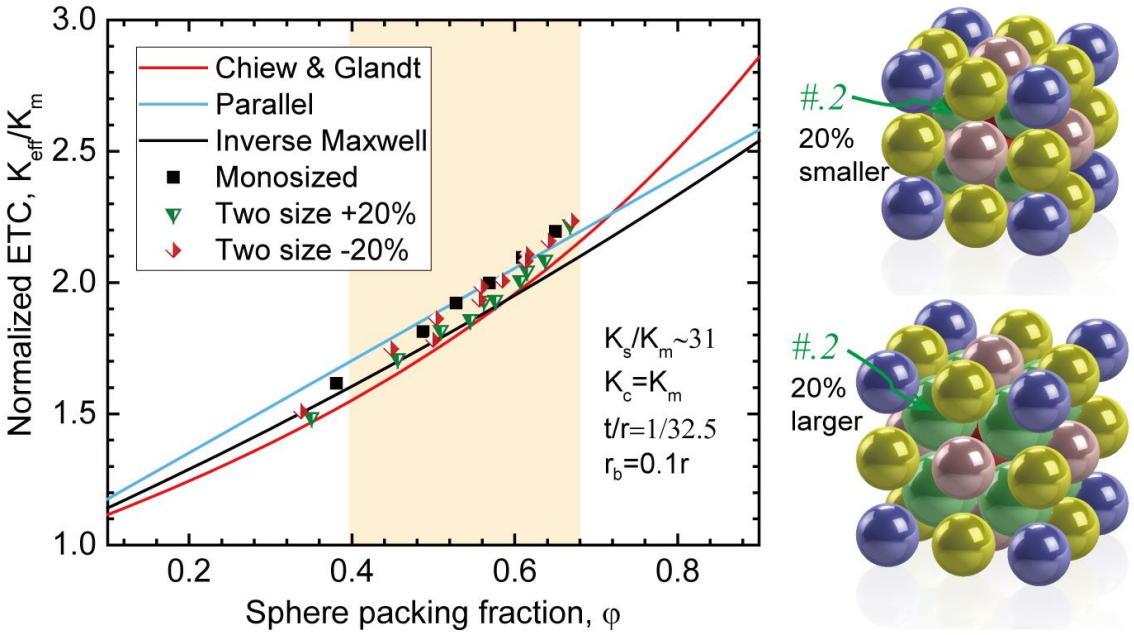
Fixed total thickness



-a proper total layer number and material sequence can be designed to tune the ETC of multilayer shell foams.

3. Results - theory and simulations

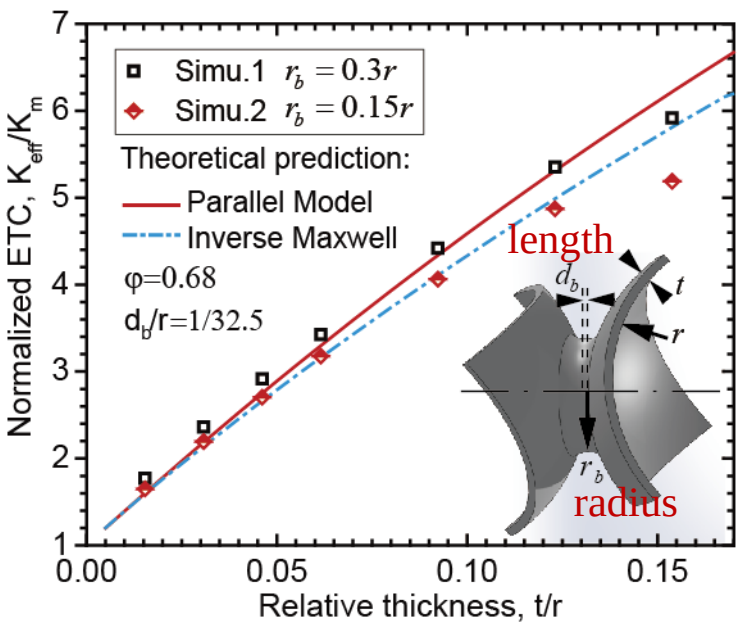
- **How about foams with size distributions?**

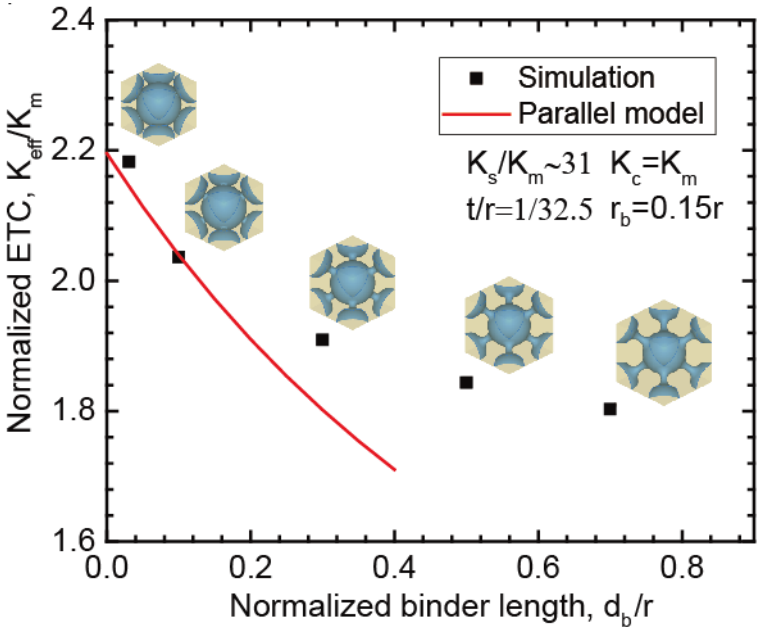


Sphere size distribution also have weak influence on the ETC, suggesting that packing fraction is the main parameter that controls the ETC.

3. Results - theory and simulations

- **How does binder shape affects ETC?**

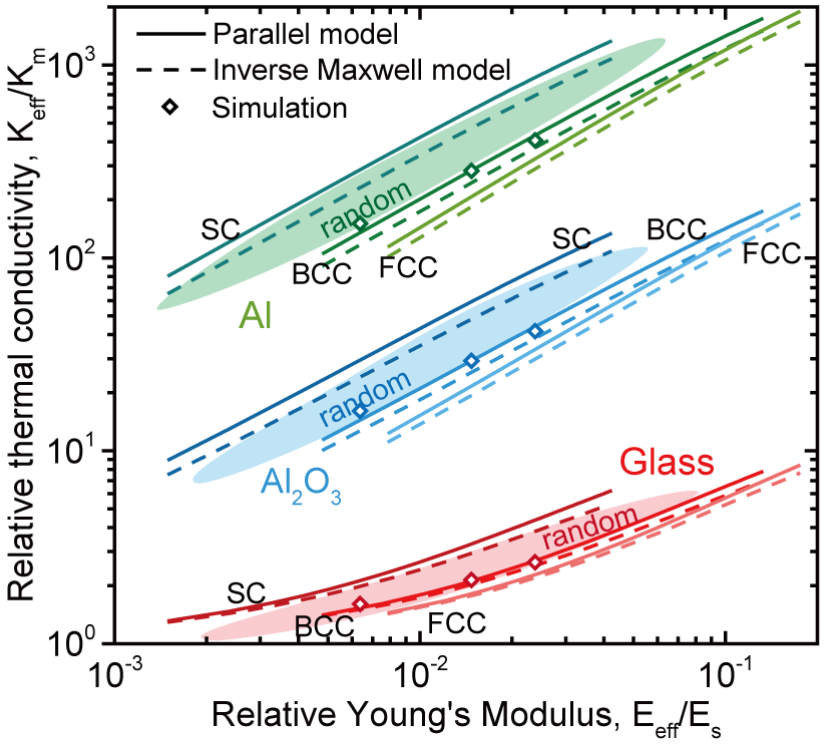




Binder radius r_b has relative small influence;
While the binder length d_b have a more noticeable influence.

3. Results and discussion:

- **Materials property chart**
- Relative thermal conductivity vs relative Young's modulus;
- Using Gibson's fitting equation for mechanical prediction;
- Wide design space.



Mater. Sci. and Eng. A **2003,** *347* (1), 70-85.

$$E_{eff} = [3.85\times10^{-3}\theta^2 - 0.294\theta + 8.33]\times\left(\frac{t}{r}\right)^{1.4\times10^{-2}\theta - 1.39}$$

$$\tan\theta = r_b/h_b$$

t/r=0.01~0.2

4. Conclusion:

- We've proposed an equivalence model that gives accurate prediction of the ETC of HSFs;
- The model considers the effects of porous shells, multi-layered shells, and interfacial thermal resistance;
- Two size effects, the Knudsen effect and the interfacial thermal resistance effect, are further evaluated, extending the model to nanoscale foams.

Guidelines for designing HSFs:

- A small size is essential to achieve extremely thermal insulation materials.
- Lower packing fractions, larger shell porosity, longer binder length and higher interfacial thermal resistance lead to lower ETC;
- Packing patterns, binder radius, and sphere size distribution have weak influence.

Thank you for your attention!

Acknowledgement:

IMECE 2017

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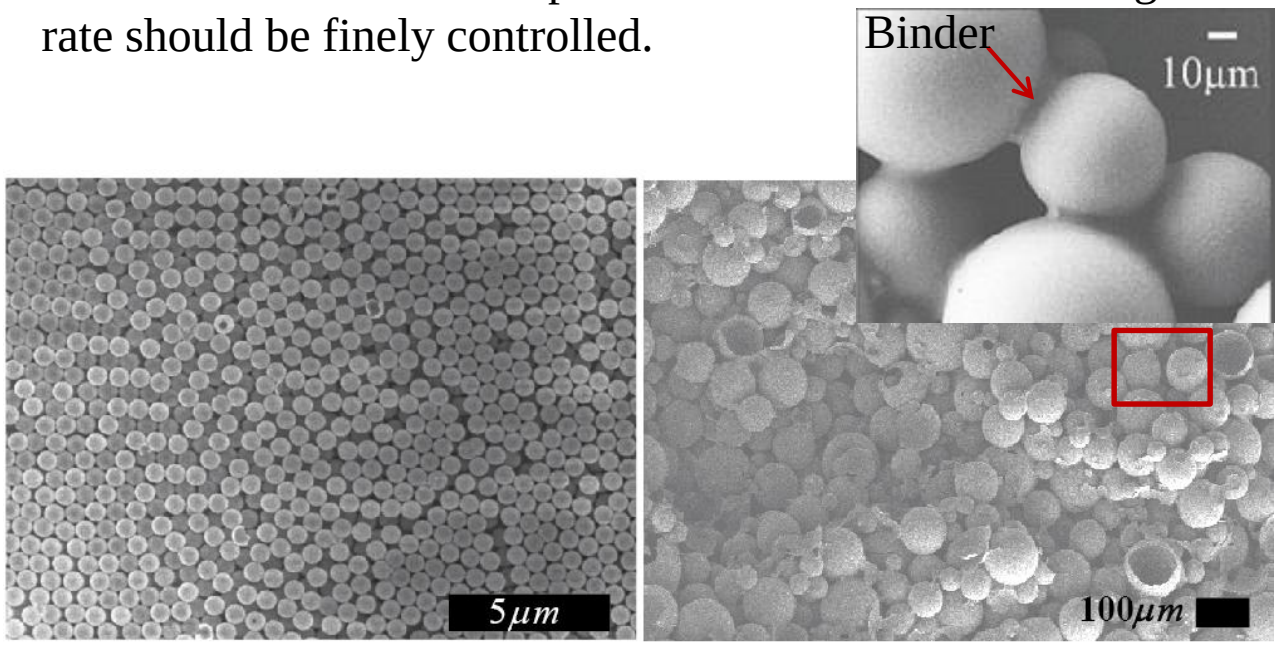
Supporting material

1. Introduction

- **Problem description**
- Heat transfer in HSF is of particular interest when cooling or heating rate should be finely controlled.



thermal radiation can be estimated using the unit cell method[31], which gives $K^r = 8F_E^* \sigma r \bar{T}^3$, where $\bar{T}$ is the mean temperature, σ is the Stefan-Boltzmann constant, F_E^* is radiation exchange factor ($F_E^* = 1/(P^{-1} - 1)$), and P is porosity. For porous materials F_E^*=0.2~0.6, when cell length ~100 μm, $\bar{T}$ ~300K, K^r is estimated as 0.8~2.4×10^{-4} W/m·K.

3. Results - theoretical

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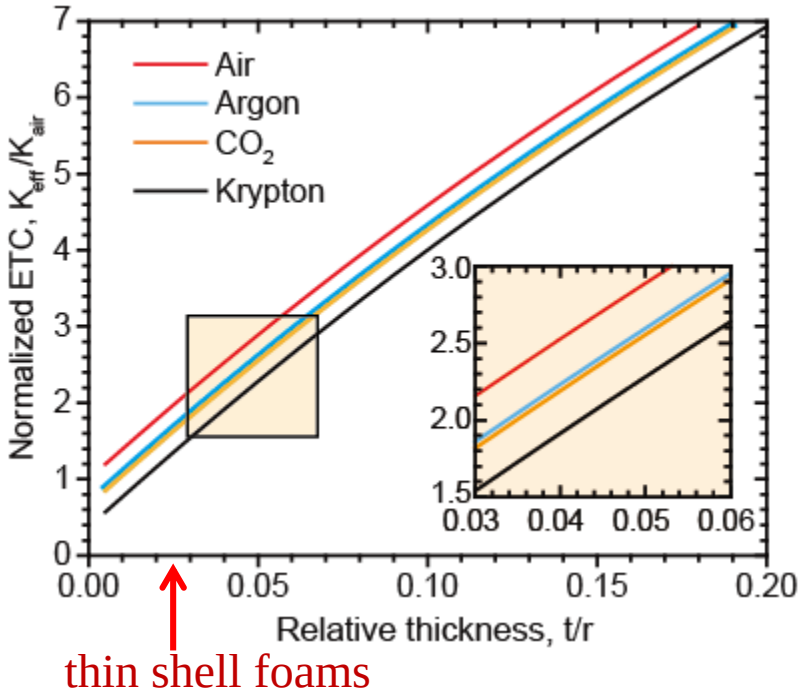
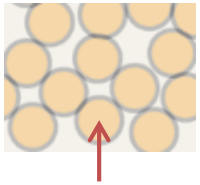
- **Using low thermal conductivity gas filling?**



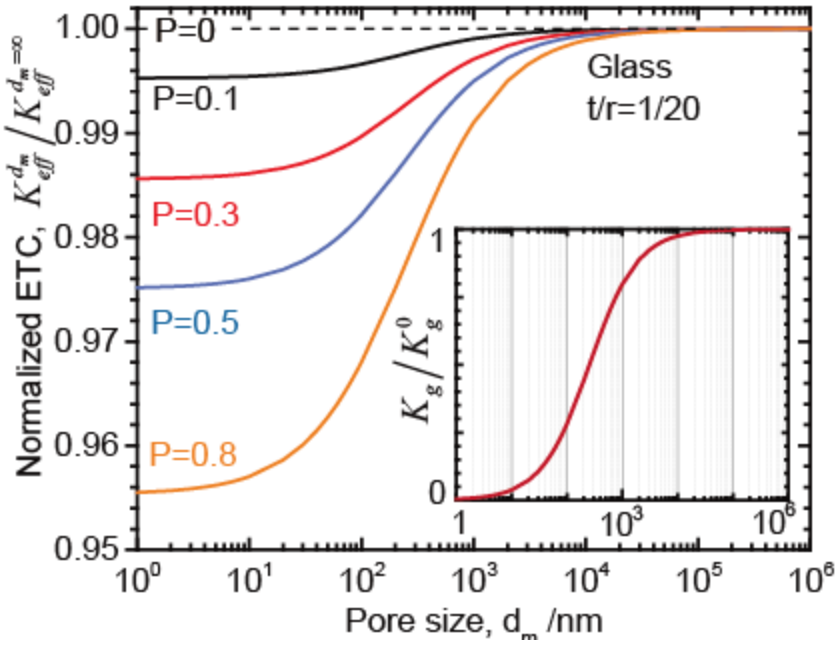


Air 25.7mW/m·K
Argon 17.9 mW/m·K
Krypton 9.5 mW/m·K
CO_2 16.8 mW/m·K

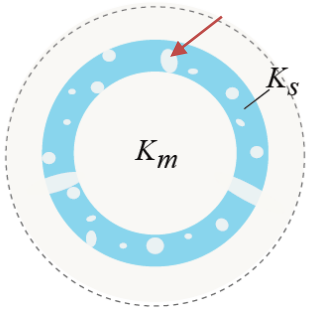
Use low thermal conductivity filling gas for thin shell foams!

3. Results - theoretical

- **Knudsen effect in the pores of porous foams**



Knudsen effect



Knudsen effect

a reduction of thermal conductivity in gases when the size of the cavity encompassing the gas becomes comparable to the mean free path.

The ETC reduction induced by Knudsen effect of inside the porous shell is small, because the pores in the shell have both a small volume fraction and a small K_g^0/K_s. K_g^0 is thermal conductivity of a free gas.

Theoretical prediction of effective thermal conductivity:

- **Dimensional analysis result**

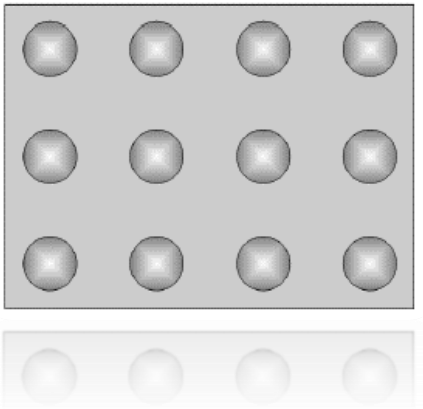
  -for foam material

$$\kappa_{eff} = \overline{\kappa}_s + \overline{\kappa}_g + \overline{\kappa}_c + \overline{\kappa}_r$$

$$\overline{\kappa}_s = \eta\kappa_s\left(\rho^*/\rho_s\right)^{\alpha}, \overline{\kappa}_g = \eta'\kappa_g\left(1-\rho^*/\rho_s\right)$$

- **Effective thermal conductivity models**

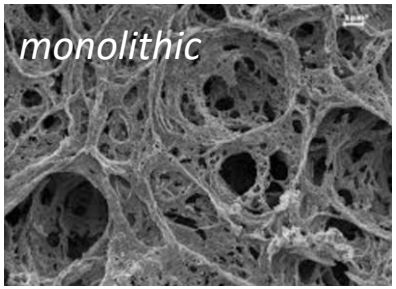
MODEL	EFFECTIVE THERMAL CONDUCTIVITY MODELS
SERIES MODEL	$\frac{K_{eff}}{K_m} = \frac{K_p/K_m}{K_p/K_m + \phi(1-K_p/K_m)}$, ϕ is volume faction of particle filling.
PARALLEL MODEL	$\frac{K_{eff}}{K_m} = 1+\phi(K_p/K_m - 1)$,
MAXWELL MODEL[17]	$\frac{K_{eff}}{K_m} = \frac{(1+2\phi)K_p/K_m + 2(1-\phi)}{(1-\phi)K_p/K_m + (\phi+2)}$,
INVERSE MAXWELL MODEL	$\frac{K_{eff}}{K_m} = \frac{(1+2\phi)K_p/K_m + 3}{(2-\phi)K_p/K_m + \phi}\cdot\frac{K_p}{K_m}$,
CHIEW AND GLANDT MODEL[38]	$\frac{K_{eff}}{K_m} = \frac{1+2\beta\phi+(K_2-3\beta^2)\phi^2}{1-\beta\phi}$ where $\beta = \frac{K_p-K_m}{K_p+2K_m}$, K_2 is a function of ϕ. with fitting parameters: $\frac{K_{eff}}{K_m} = \frac{1+2\beta\phi+(2\beta^3-0.1\beta)\phi^2+0.05\exp(4.5\beta)\cdot\phi^3}{1-\beta\phi}$,
Y. BENVENISTE MODEL[21]	$\frac{K_{eff}}{K_m} = \frac{2\alpha(1-\phi)+[(1+2\phi)+K_p/K_m(2-2\phi)]}{\alpha(2+\phi)+[(1-\phi)+K_p/K_m(2+2\phi)]}$, For perfect interface, $\alpha\to 0$ $\frac{K_{eff}}{K_m} = \frac{(1+2\phi)+K_p/K_m(2-2\phi)}{(1-\phi)+K_p/K_m(2+2\phi)}$,
LEWIS-NIELSEN MODEL[24]	$K_{eff} = \frac{1+AB\phi}{1-B\psi\phi}$, A is shape factor, for sphere A=1.5, $B = \frac{K_p/K_m-1}{K_p/K_m+A}$, $\psi = 1+\frac{1-\phi_m}{\phi_m^2}\phi$, ϕ_m is the maximum filler volume fraction.

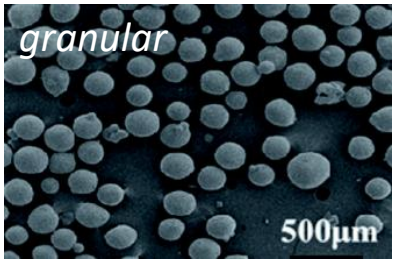


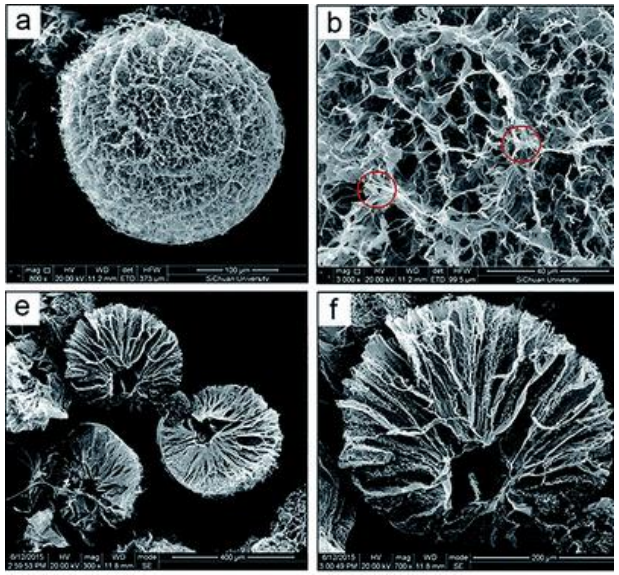
Nearly all models are for Solid particles filled materials, Not for hollow spheres filled Materials.

Applications:

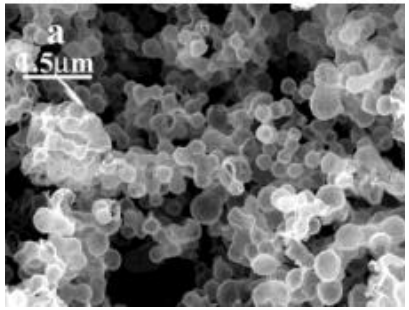
- **mesoscale level** (10~100nm)

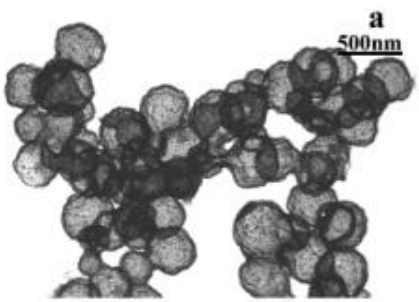


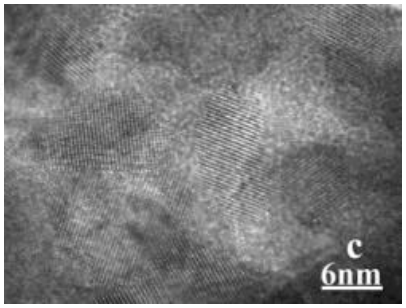




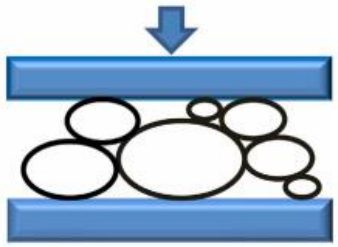
Highly Sensitive WO_3 Hollow-Sphere Gas Sensors





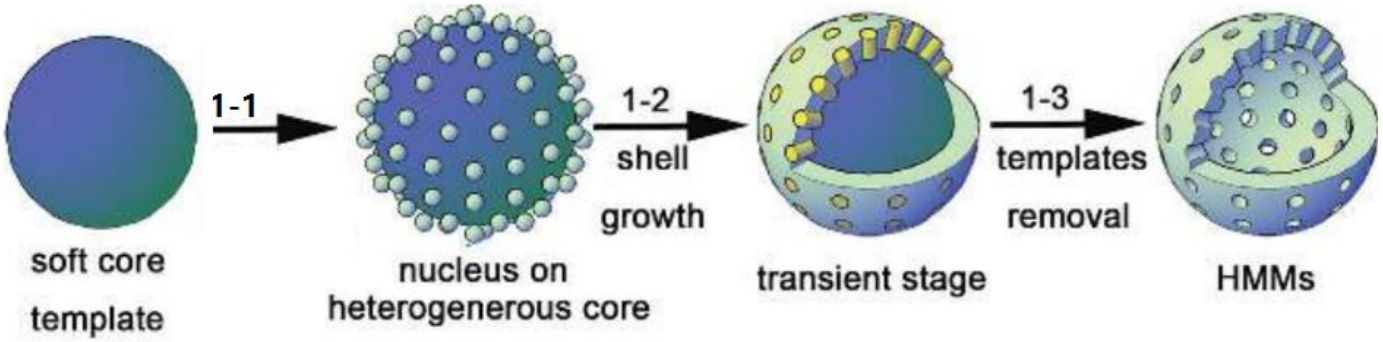


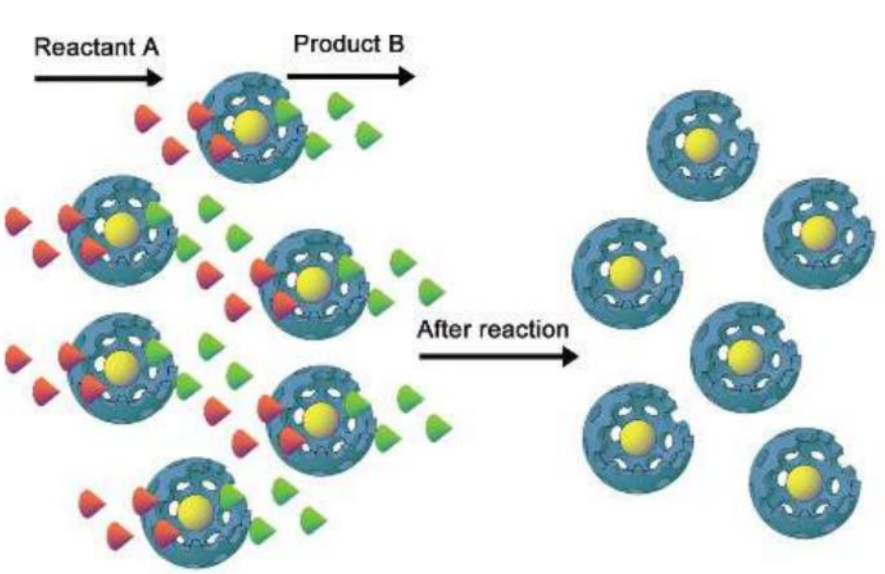
pressure Sensors

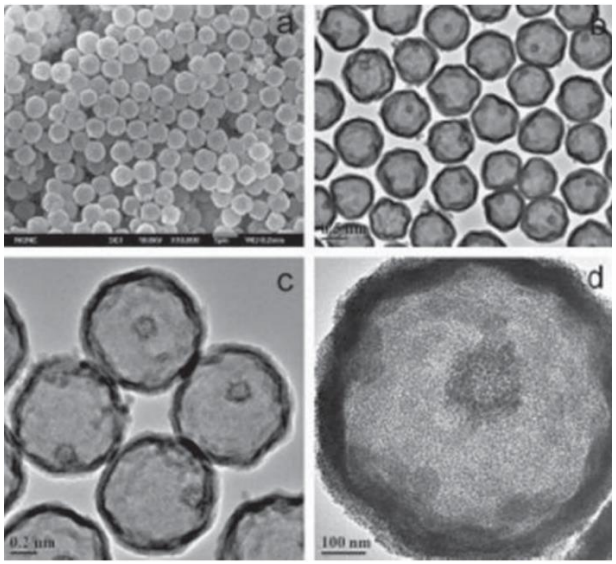


Applications:

- **mesoscale level** (mesoscale hollow-structured materials)







Hollow-Structured Mesoporous Materials

Applications:

- **mesoscale level** (mesoscale hollow-structured materials)

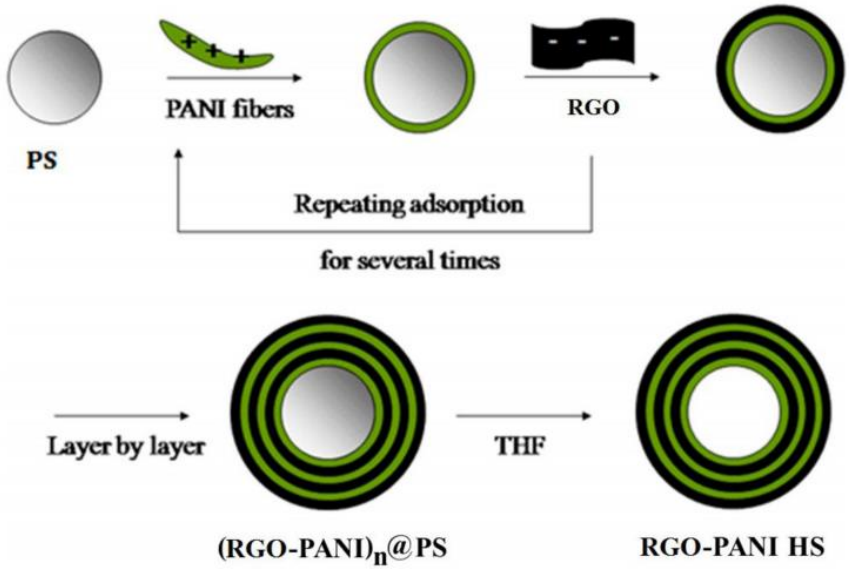
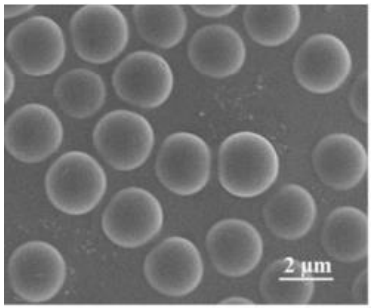
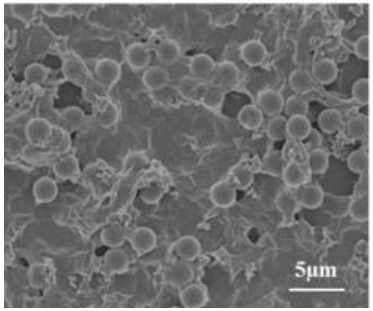


Fig. 1. The illustration of the fabrication procedure of the graphene–PANI hollow spheres (RGO-PANI HS).





Supercapacitor

Shell Spherical Colloids with Movable Cores