Discrete models, continuous models and scale transitions for the drying of porous media

Evangelos Tsotsas

Otto von Guericke University, Magdeburg, Germany

www.tvt.ovgu.de

InterPore 2022

30 May - 2 June 2022, Abu Dhabi & Online

Discrete vs. Continuous models

	Discrete	Continuous
Consideration of microscale (structure, processes)	✓	
Computational efficiency		✓

Double check in discrete: Progress in computers/algorithms, but we would still need continuous models to organize the numerical results

Double check in continuous:

- How good/bad are existing continuous models (CM)?
- Can continuous models be made better by parameter estimation from discrete models?
- Even the best continuous models would not be able to fully reflect the microscale.

CM to be addressed

- Classical drying of porous materials and particles
  in air, or inert gas (convective drying):
  From polymers to ceramics, from foods to electrodes

- Continuous models for this:
  - Characteristic drying curve model, CDC
  - Diffusion model, DM
  - Reaction engineering approach, REA
  - Homogenized one-equation model, HM

Characteristic drying curve model, CDC

$$\frac{1^{st}\,\text{period};\, X \geq X_{cr},\, \eta \geq 1}{\dot{m}_{v,I} = \frac{\tilde{M}_v A}{\tilde{R} T}\beta_g\left(p_v^* - p_\infty\right)}$$

β_g : gas-side mass transfer coefficient

p_v^* : saturation vapor pressure,

i.e. $\varphi_{surf} = 1$

$$\frac{2^{nd}\,\text{period};\, X < X_{cr},\, \eta < 1}{\dot{m}_{v,I} = \dot{\nu}(\eta)\dot{m}_{v,I},\, \eta = \frac{X - X_{eq}}{X_{cr} - X_{eq}}}$$

X : moisture content, dry-based

cr: critical, eq: sorption isotherm

Surface	• 1^{st} period: $\varphi_{surf} = 1$ • 2^{nd} period: may be read as $\varphi_{surf} < 1$
Interior	Arbitrary fitting function ($\dot{\nu}(\eta)$, CDC)
Claim	Admits being empirical

First van Meel, 1958, then many authors

Diffusion model, DM

$$\dot{m}_v = \frac{\tilde{M}_v A}{\tilde{R} T} \beta_g \left(\varphi_{surf}(S) p_v^* - p_{v,\infty} \right)$$

β_g, p_v^*: same as in CDC

S: local saturation

$\varphi_{surf}(S) < 1$, from sorption isotherm

$$\varepsilon \frac{\partial S}{\partial t} = \frac{\partial}{\partial z} \left(D(S) \frac{\partial S}{\partial z} \right)$$

ε: porosity

z: space coordinate, can be 3D

D(S): diffusion coefficient that may depend on saturation (moisture content)

Surface	$\varphi_{surf}(S) < 1$ sorption isotherm
Interior	• Founded for solid matrix diffusion • Otherwise arbitrary fitting
Claim	Gives the impression of theory

Many authors

Reaction engineering approach, REA

$$\dot{m}_v = \frac{\tilde{M}_v A}{\tilde{R}T} \beta_g \left(\varphi(X) p_v^* - p_{v,\infty} \right)$$

$$\varphi(X) = \exp\left(-\tilde{E}(X) / \left(\tilde{R}T \right) \right)$$

$\tilde{E}(X)$: activation energy for moisture release, fitted material „fingerprint"

Lumped REA (LREA): $\tilde{E}(X)$ for surface with global X

Spatial REA (SREA): Local X from other models (DM, HM, …), $\tilde{E}(X)$ for surface AND interior with corresponding local X

Surface	$\varphi(X) < 1$ from $\tilde{E}(X)$
Interior	LREA: None SREA: $\varphi(X) < 1$ from $\tilde{E}(X)$
Claim	Tries to look like theory, but unclear relation to sorption isotherm, activated diffusion etc.

Dong Chen et al., in many publications

Homogenized one-equation model, HM

$$\dot{m}_v = \frac{\tilde{M}_v A}{\tilde{R}T} \beta_g \left(\varphi(X) p_v^* - p_{v,\infty} \right)$$

$$\varepsilon \frac{\partial S}{\partial t} = \frac{\partial}{\partial z}\left[\left(D_l(S) + D_v(S) \right) \frac{\partial S}{\partial z} \right] \Rightarrow$$

$$\varepsilon \frac{\partial S}{\partial t} = \frac{\partial}{\partial z}\left[\left(\frac{k_{abs} k_r}{\mu_l} \left(-\frac{\partial p_c}{\partial S} \right) + \frac{1}{\rho_l} \frac{\tilde{M}_v}{\tilde{R}T} \frac{p p_v^*}{p - p_v} D_{abs} D_r \frac{\partial \varphi(S)}{\partial S} \right) \frac{\partial S}{\partial z} \right]$$

k_{abs}: absolute permeability

k_r: relative permeability of liquid

$\partial p_c / \partial S$: capillary pressure curve

D_{abs}: absolute effective diffusivity of gas

D_r: relative effective diffusivity of gas

$\varphi(S)$: sorption isotherm (local l-v-equilibrium)

Surface	$\varphi_{surf}(S) < 1$ sorption isotherm
Interior	• Founded for capillary transport and gas diffusion • $\varphi(S) < 1$ sorption isotherm • No solid matrix diffusion
Claim	Results from mathematical homogenization

De Vries, Whitaker, and others

Summary of models

	CDC	DM	REA	HM
Surface	• 1^{st} period: $\varphi_{surf} = 1$ • 2^{nd} period: may be read as $\varphi_{surf} < 1$	φ_{surf} (S) < 1 sorption isotherm	φ (X) < 1 from $\tilde{E}(X)$	φ_{surf} (S) < 1 sorption isotherm
Interior	Arbitrary fitting function ($\dot{\nu}(\eta)$, CDC)	• Founded for solid matrix diffusion • Otherwise arbitrary fitting	LREA: None SREA: φ (X) < 1 from $\tilde{E}(X)$	• Founded for capillary transport and gas diffusion • φ(S) < 1 sorption isotherm • No solid matrix diffusion
Claim	Admits being empirical	Gives the impression of theory	Tries to look like theory, but, in fact, it is not	Results from mathematical homogenization

CDC vs. DM

Assume that
- Solid matrix diffusion prevails
- DM is physically founded
- Activated diffusion obeys

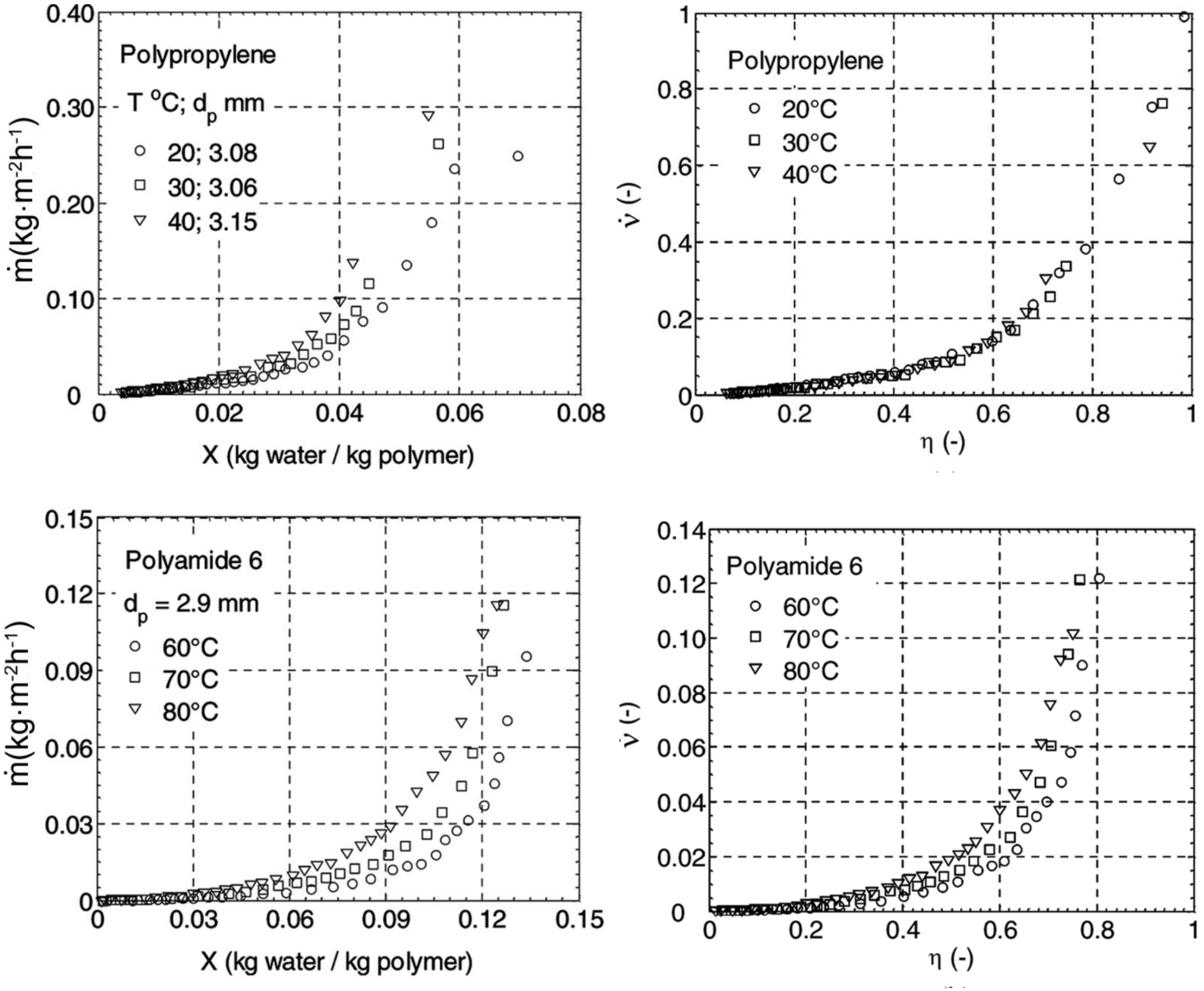
$$D = A \exp\left(-\frac{\tilde{E}}{\tilde{R}T}\right)$$

(depending on T, not depending on X)

- Can CDC still be successful?
- If yes, when? Conditions of equivalence to DM?

Suherman et al., Drying Technol., 2008, 90

CDC for polymer particles



PP:

CDC

succeeds

PA6:

CDC

fails

why?

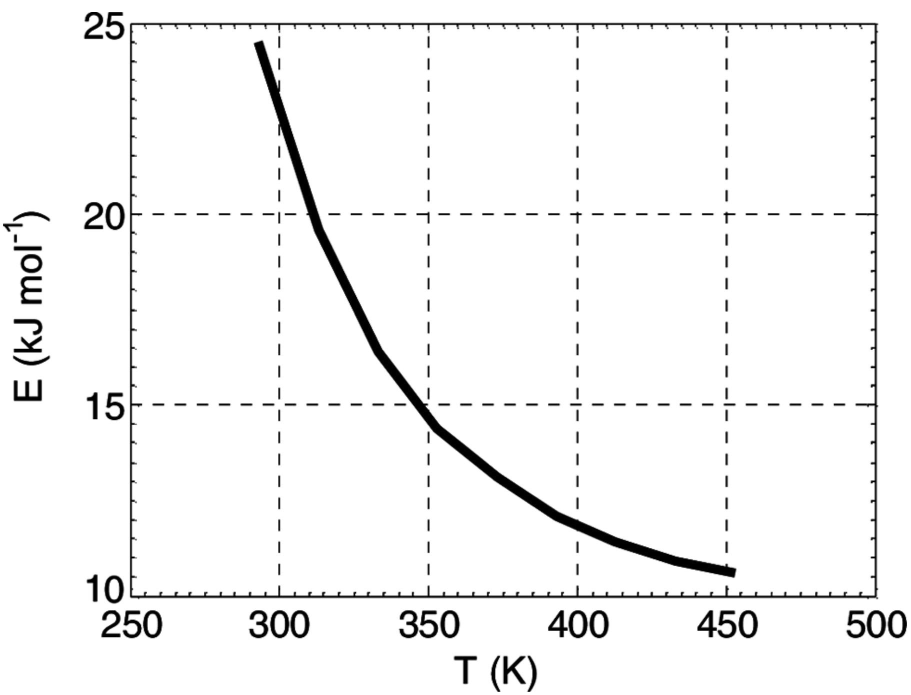
Suherman et al., Drying Technol., 2008, 90

CDC vs. DM

Condition of equivalence CDC-DM

PP: $\tilde{E}$ =24.1 kJ/mol, success

PA6: $\tilde{E}$ = 54.3 kJ/mol, failure



Prediction of CDC performance for biomaterials:

success, medium, failure

No	Material	E(kJ/mol)	T (K)
1	Broccoli	18.5	308-343
2	Cellulose	23.3	287-317
3	Paddy	28.4	383-443
4	Sludge	30.1	353-383
5	Pistachio nut	33.3	313-343
6	Catfish	37.5	303-323
7	Soybean	38.3	293-313
8	Potato	43.3	288-291
9	Bread	48.7	313-343
10	Coconut	81.1	323-343

Suherman et al., Drying Technol., 2008, 90

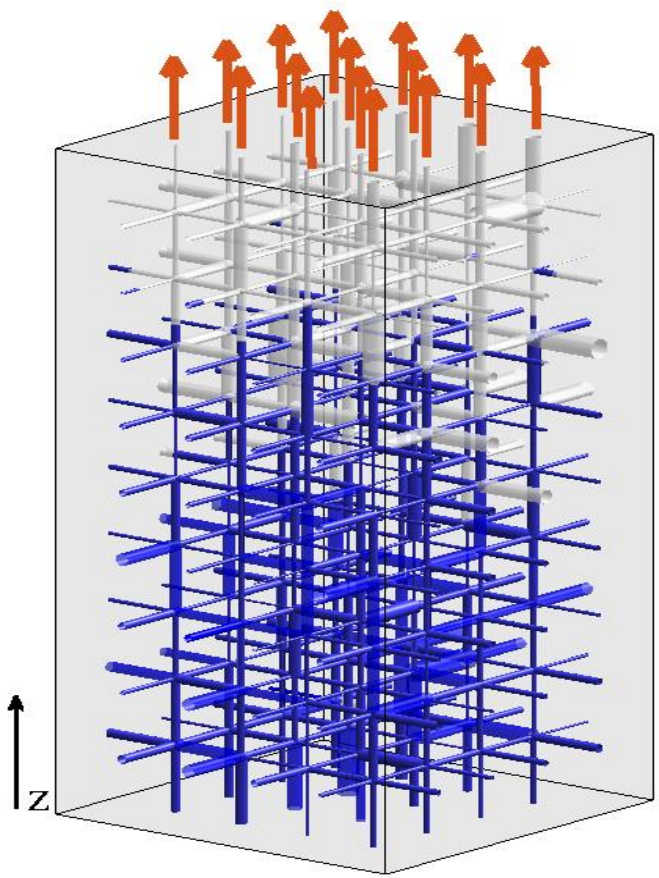
Discrete vs. Continuous models

- Consider a simple case: capillary porous material,
  completely non hygroscopic,
  no water in solid phase,
  slow isothermal drying

- Let us simulate this situation by a discrete model,
  here a pore network model (PNM)

- Let us calculate from the results
  - $\varphi_{surf}(S)$: will it be $\varphi_{surf}(S) = 1$?
  - $\varphi(S)$: will it be $\varphi(S) = 1$?
  - $D_l(S)$, $D_v(S)$ and $D(S)$ of HM: will they be easy to correlate?

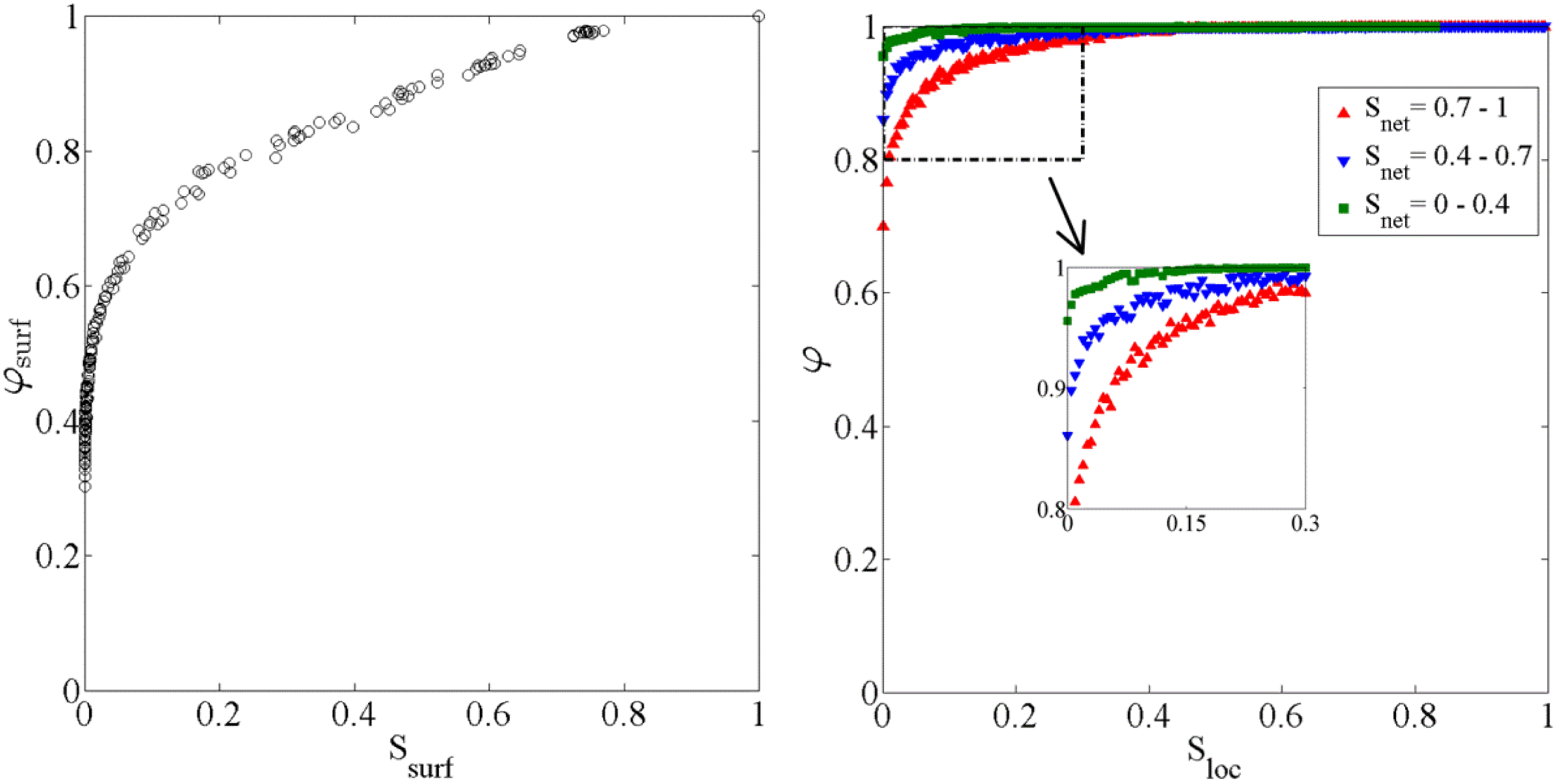
Pore network model, PNM



Network kind	Regular cubic, 3D
Network size	25 x 25 x 51
Boundary layer	25 x 25 x 10
Mean throat radius	250 μm
Standard deviation	25 μm
Throat length	1 mm
Porosity	0.594
Temperature	20°C
Liquid	Water
Gas	Air
Repetitions	15

Moghaddam et al., Water Resources Res., 2017, 10422

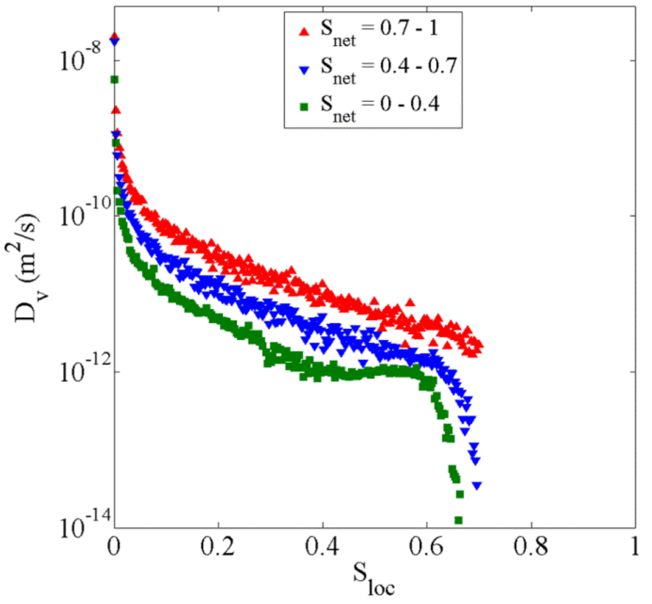
Scale transition

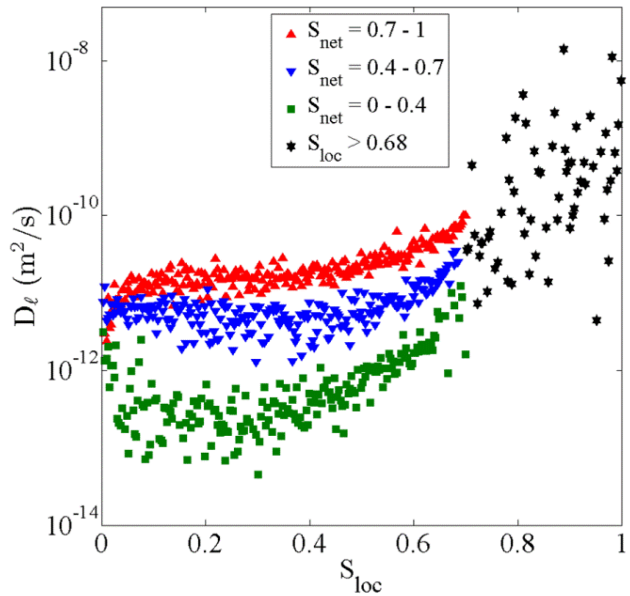


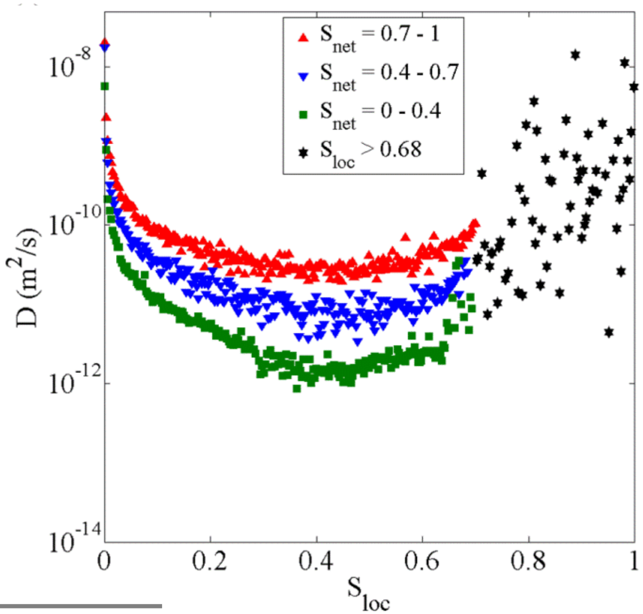
- $\varphi_{surf}(S) < 1!$ $\varphi(S) < 1!$ $\varphi_{surf}(S) \neq \varphi(S)!$
- $\varphi_{surf}(S)$ and $\varphi(S)$ are non-equilibrium functions (or closures)

Moghaddam et al., Water Resources Res., 2017, 10422

Scale transition







D_v, D_l and

$D = D_v + D_l$

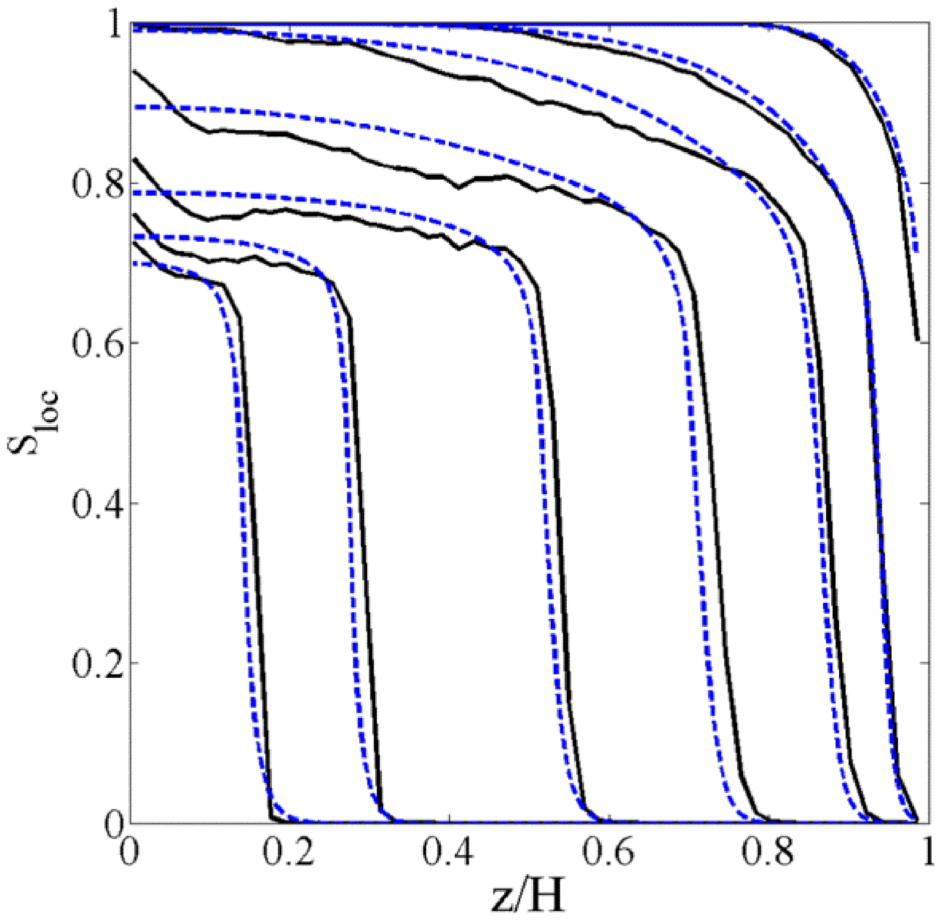
depend on the level of global saturation

⇨

Not unique, strongly changing, difficult to correlate

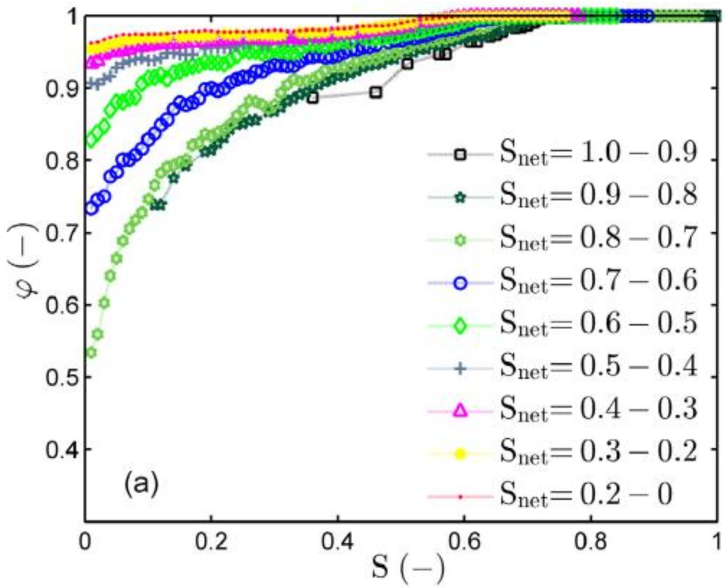
Moghaddam et al., Water Resources Res., 2017, 10422

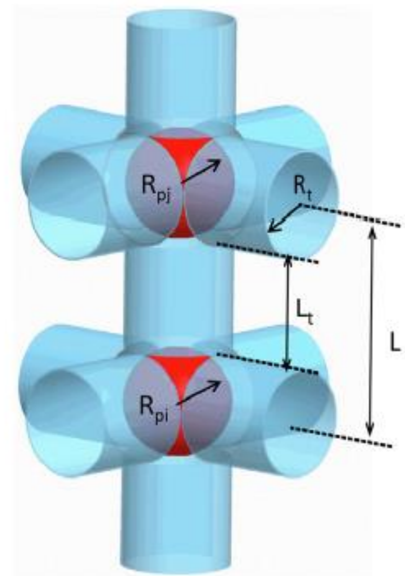
HM (continuous) vs. PNM (discrete)

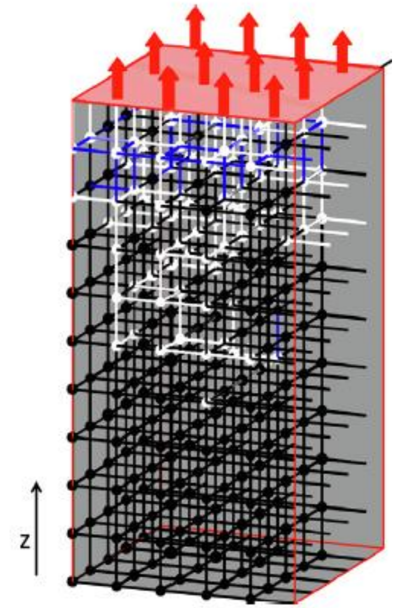


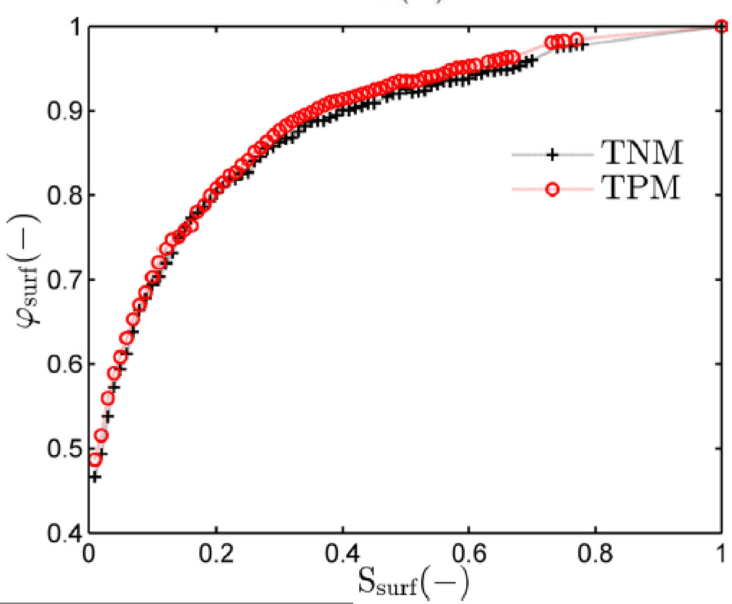
It is not an easy task,
but we can improve
the standard
continuous model (HM)
by parameter estimation
from a discrete model (PNM),
here also standard
(throat-node model, TNM)

Throat-pore model (TPM)







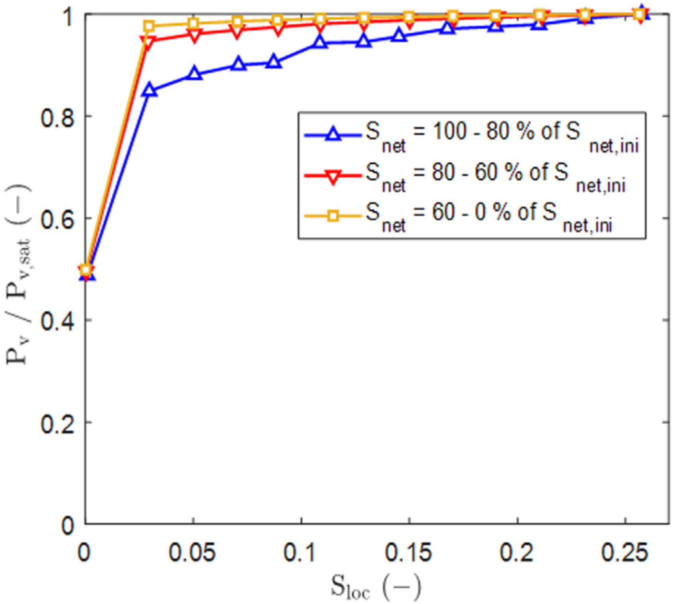


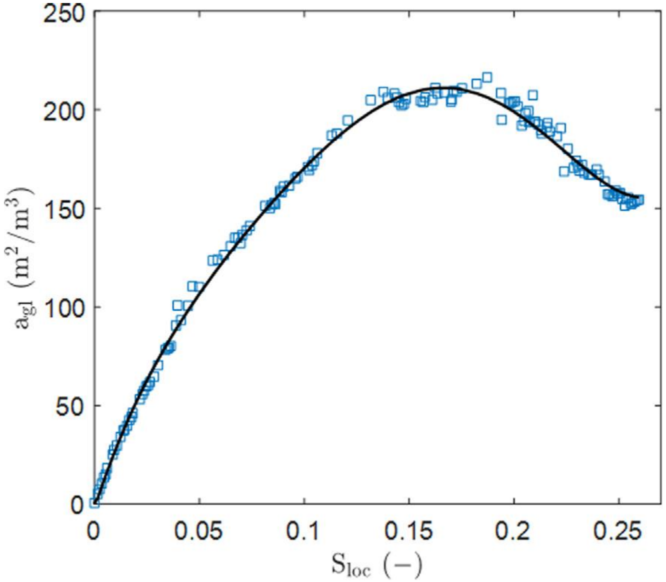
Left, top: Mean values of internal NLE function (φ) obtained from TPM drying simulations as function of local saturation (S) for different network saturation (S_{net}) intervals.

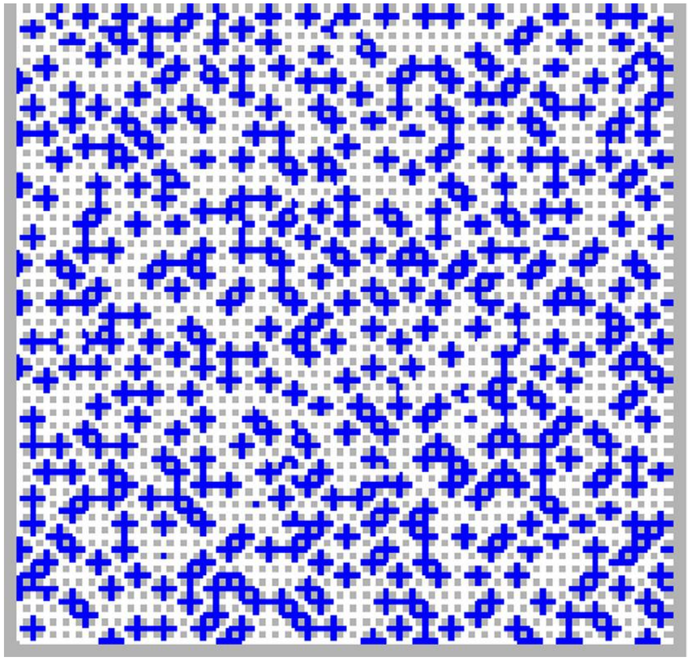
Left, down: Mean values of external NLE function (φ_{surf}) versus the network surface saturation (S_{surf}) obtained from PNM simulations for the TNM and the TPM.

Lu et al., Chem. Eng. Sci., 2020, 115723

PNM to Two-equation CM



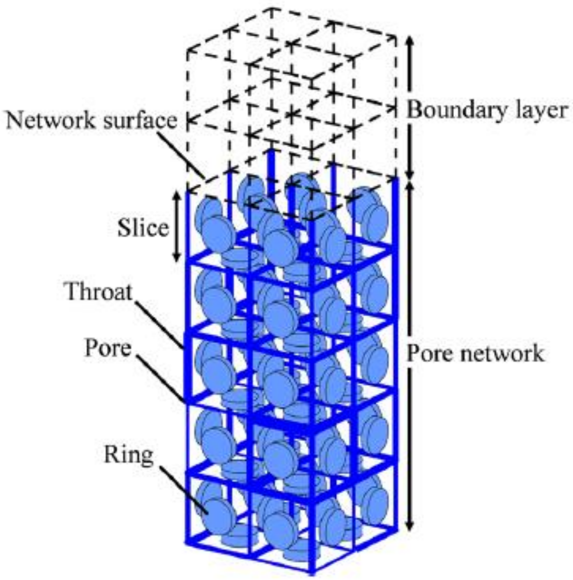


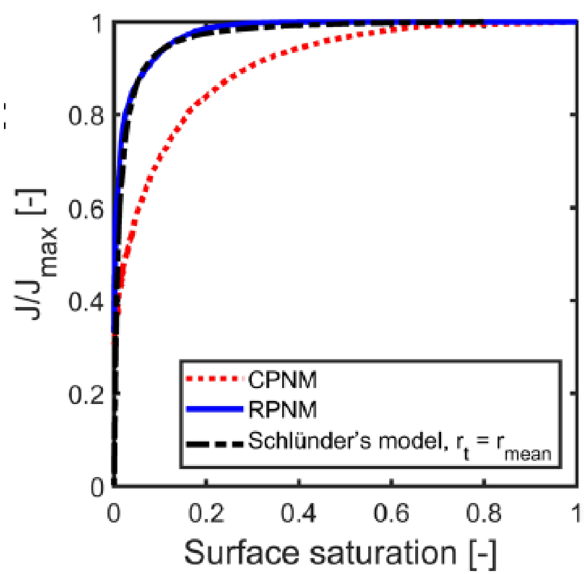


- Isolated liquid clusters
- Weak surface NLE
- Weak fitting of $D_v(S_{loc})$
- Internal gas-liquid area, Hertz-Knudsen-Schrage evaporation, no further NLE

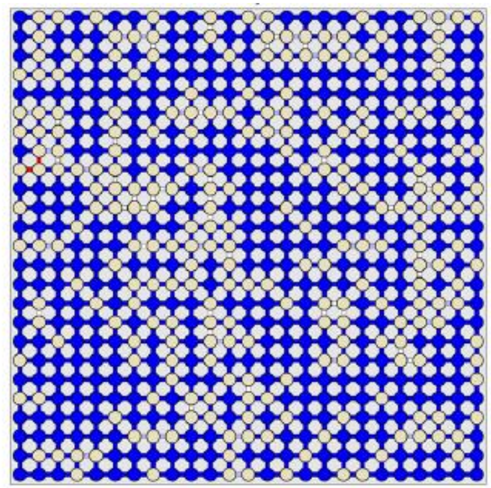
Ahmad et al., Chem. Eng. Sci., 2020, 115957

Secondary capillary structures and surface wetting



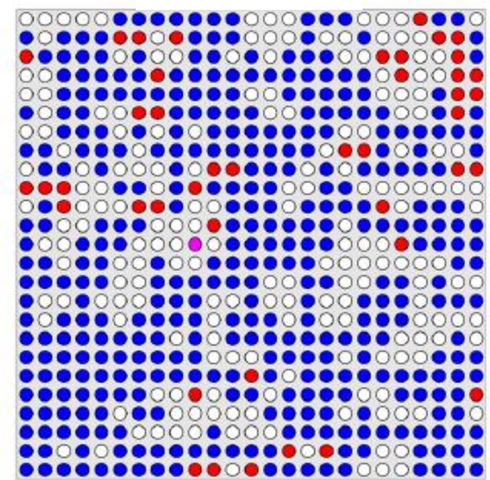


RPNM



0.60, 0.58

CPNM



0.60, 0.99

CPNM: without, RPNM: with rings

Left: S_{surf}, Right: S_{net}

RPNM: High S_{surf} to low S_{net}

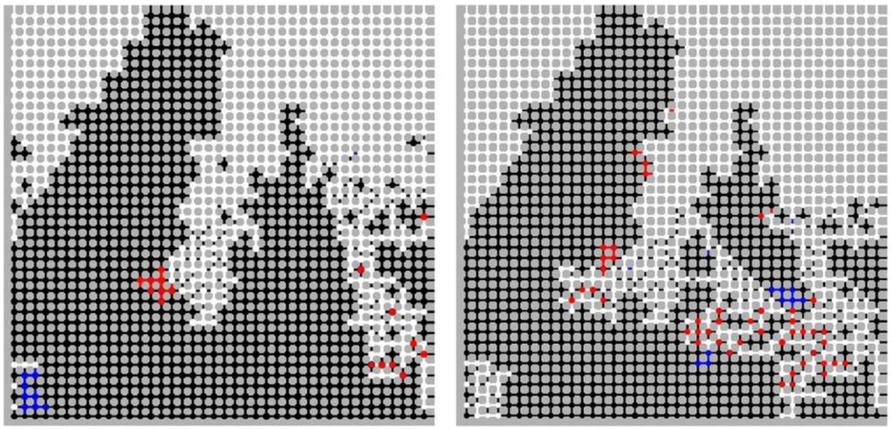
One liquid cluster (all blue)

Much faster global kinetics

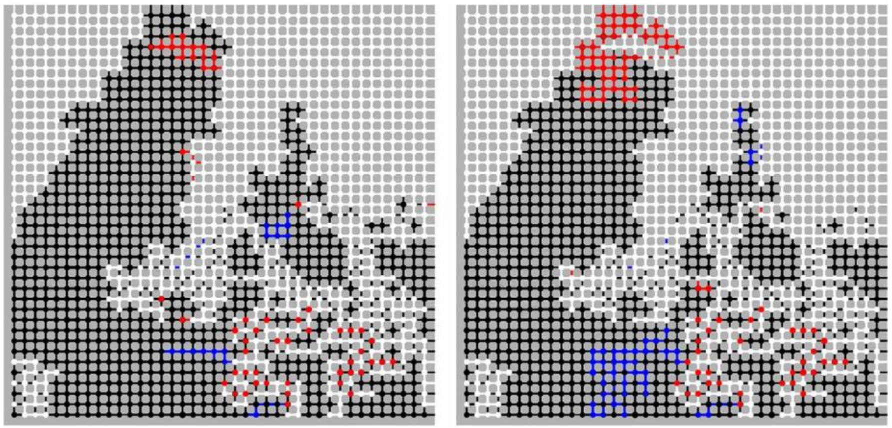
NLE-like function on surface

Mahmood et al., Transport Porous Media, 2021, 351

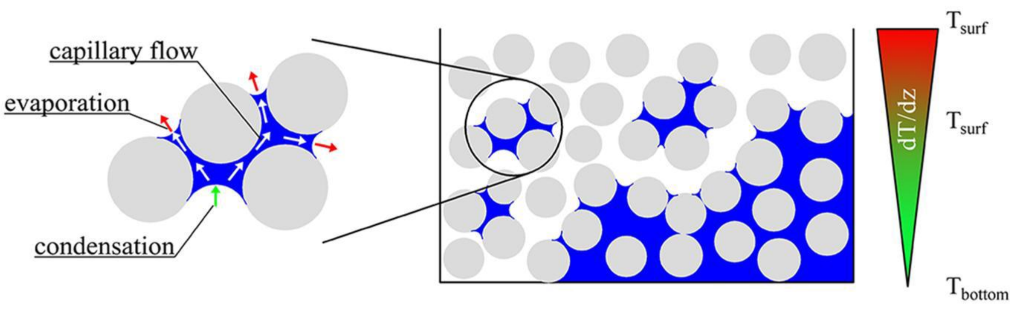
Local recondensation in drying material



(a) S = 0.59 (b) S = 0.50



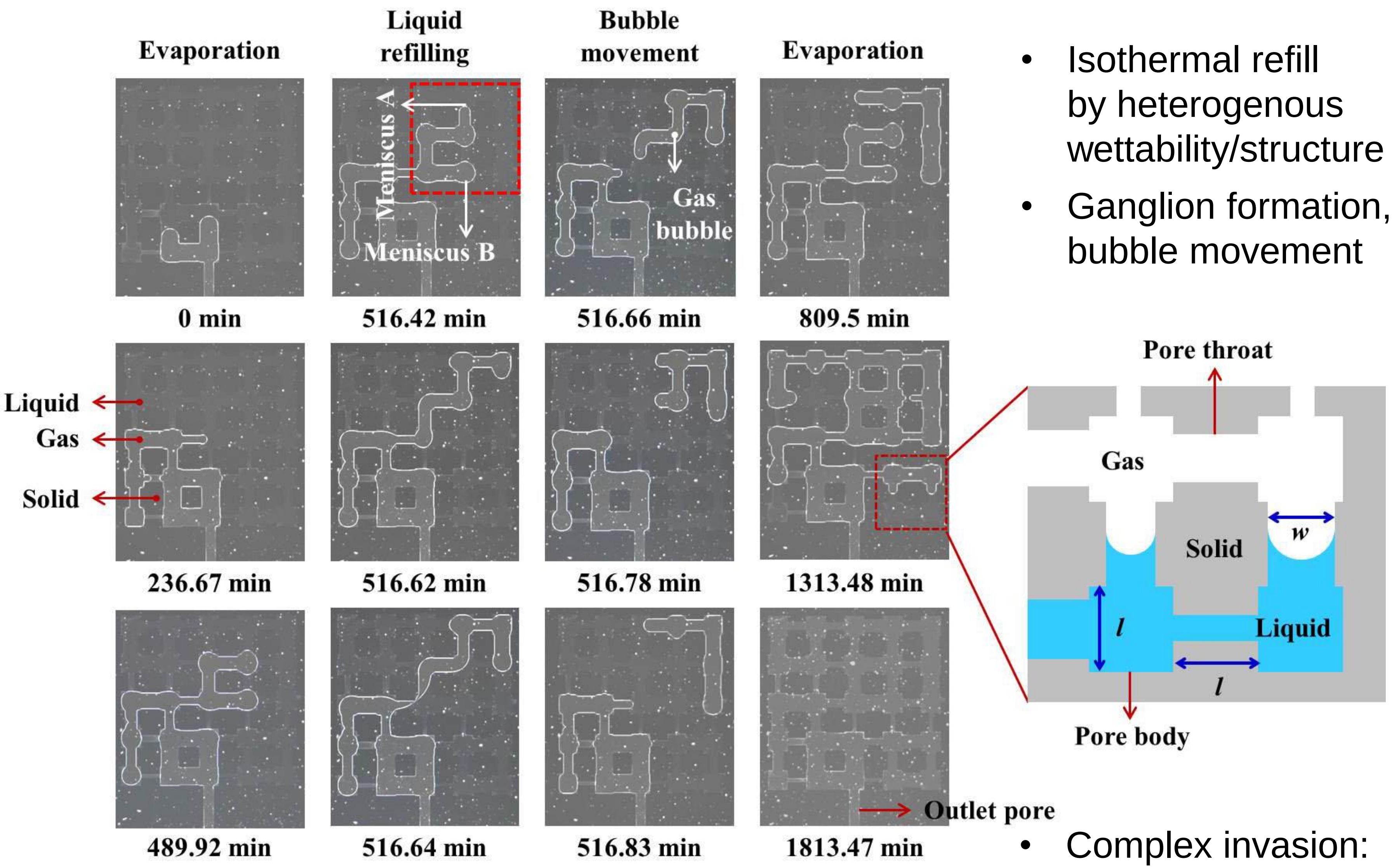
(c) S = 0.46 (d) S = 0.43



- Superheated steam drying: Vapor flow & heat transfer
- Local recondensation is not considered in CMs
- In PNM two schemes: Condensation fully treated, condensation partially treated

Hiep et al., Drying Technol., 2017, 1584

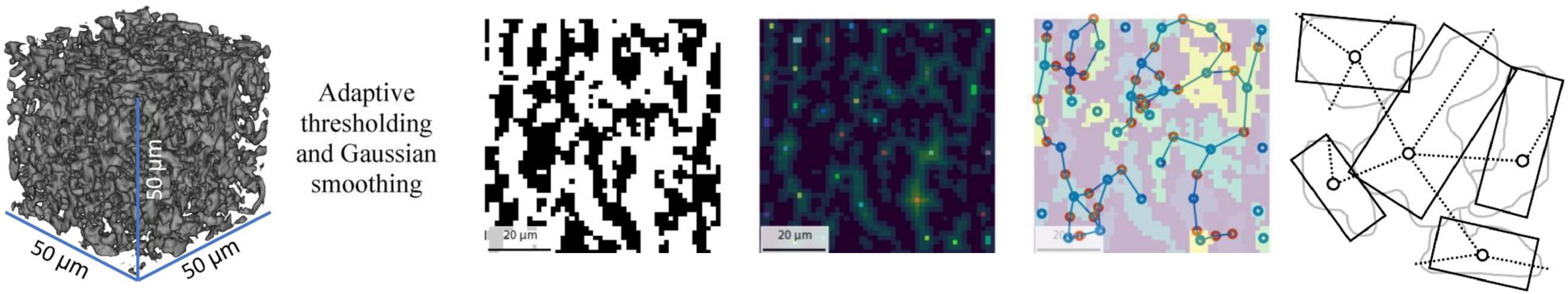
Local capillary instability

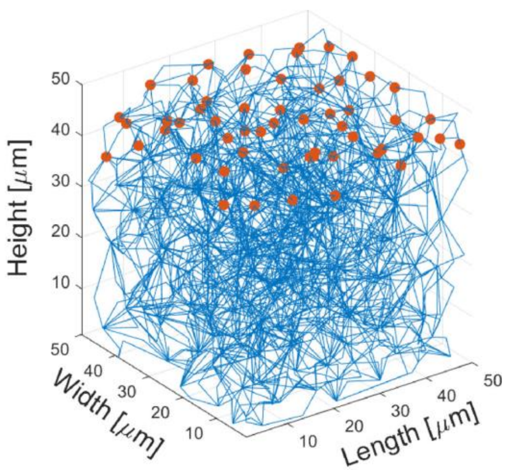


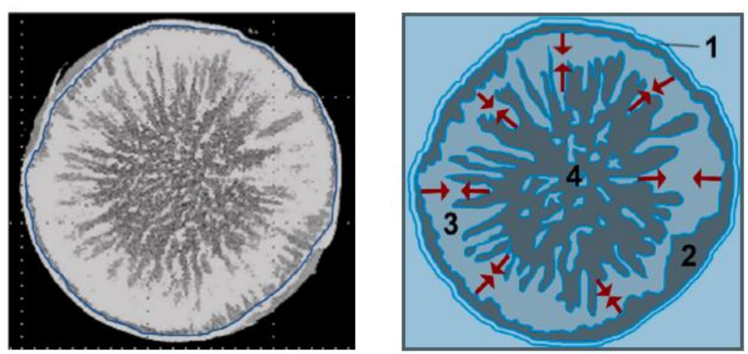
- Isothermal refill by heterogenous wettability/structure
- Ganglion formation, bubble movement
- Complex invasion: capillary valve, inertia

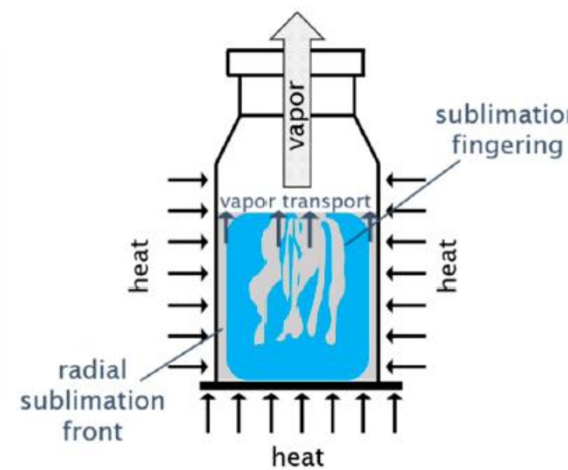
Zhang et al., Phys. Rev. Fluids, 2020, 104305

Structured fronts, even in freeze drying



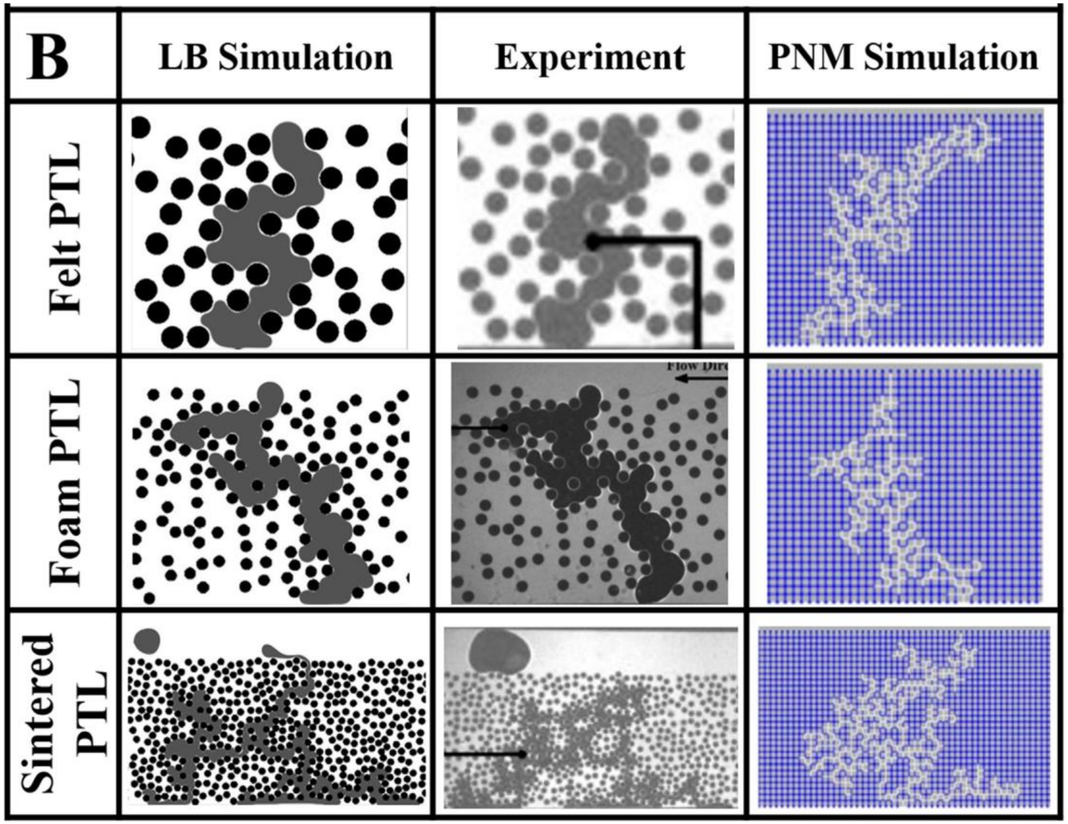






Vorhauer-Huget et al., Processes, 2020, 1091; Thomik, et al., Drying Technol., 10.1080/07373937.2021.1966030

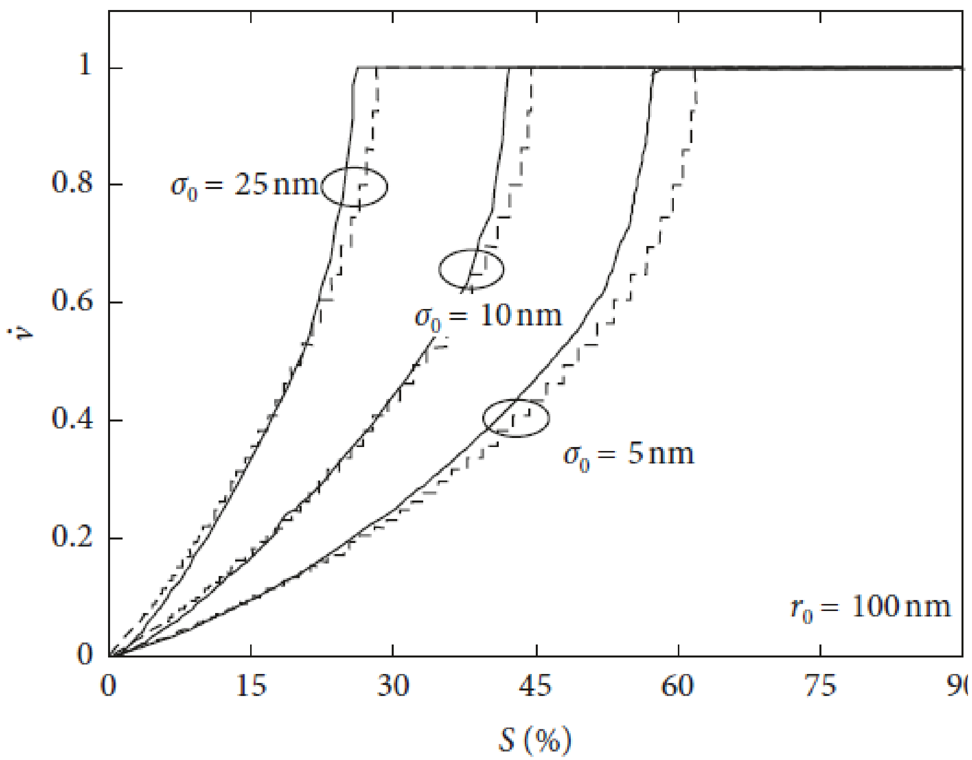
Thin media, influence of structure

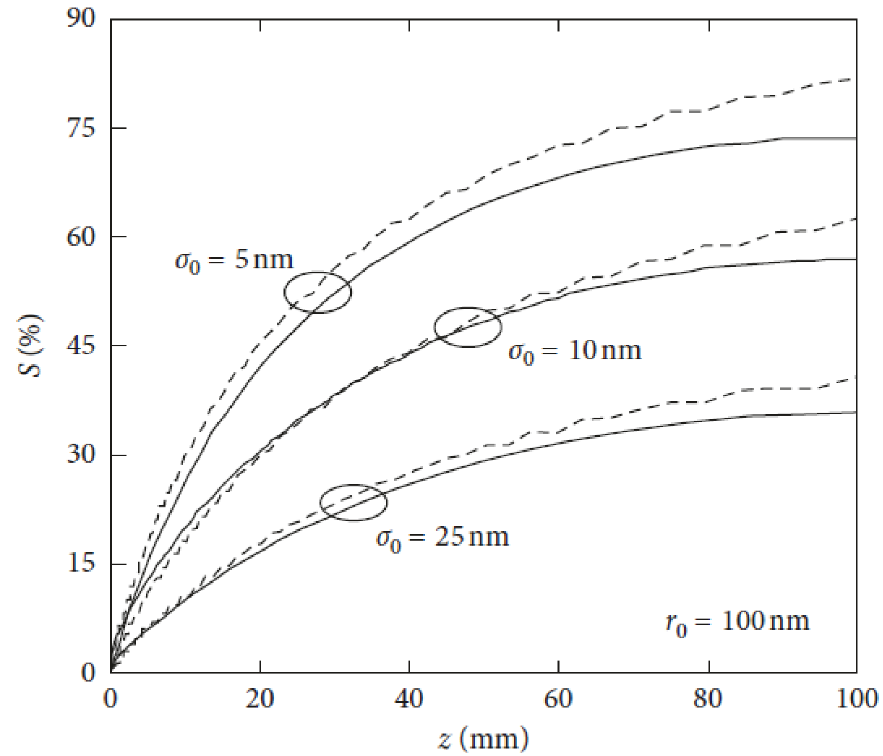


- No drying: Emerging oxygen in water on electrolyser anode
- Smaller scale than PNM: Shen-Chen LBM
- Simplified scheme of circles in 2D for three materials to mimick the influence of structure

Paliwal et al., J. Hydrogen Energy, 2021, 22747

Influence of structure on drying: The classics





——— : CM, -----: Discrete model, no PNM: Bundle of capillaries

For 200 mm thick plate

Drying kinetics depends on the variance of pore size distribution

High variance: Surface stays (much) longer wet

Metzger, T., Drying Technol., 2005, 1797; Vu, Intern. J. Chem. Eng., 2019, 9043670

Final remarks

- Drying of porous media is highly complex
- Global models can serve dryer design, but not more
- Classical CM results from brute homogenization
- Properties and closures are complex and non-unique
- Discrete models may contribute better properties and closures, or even lead to new and better CMs, preserving more microscale information
- Still, many microscale structural features, processes and events are localized and hard to transfer

Thanks and feel free to visit us at: www.tvt.ovgu.de