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Wigner Research Centre for Physics
Institute for Solid State Physics and Optics
Department of Experimental Solid State Physics
Structure Research Laboratory

Phase-field Modeling of Biomorphic Solidification

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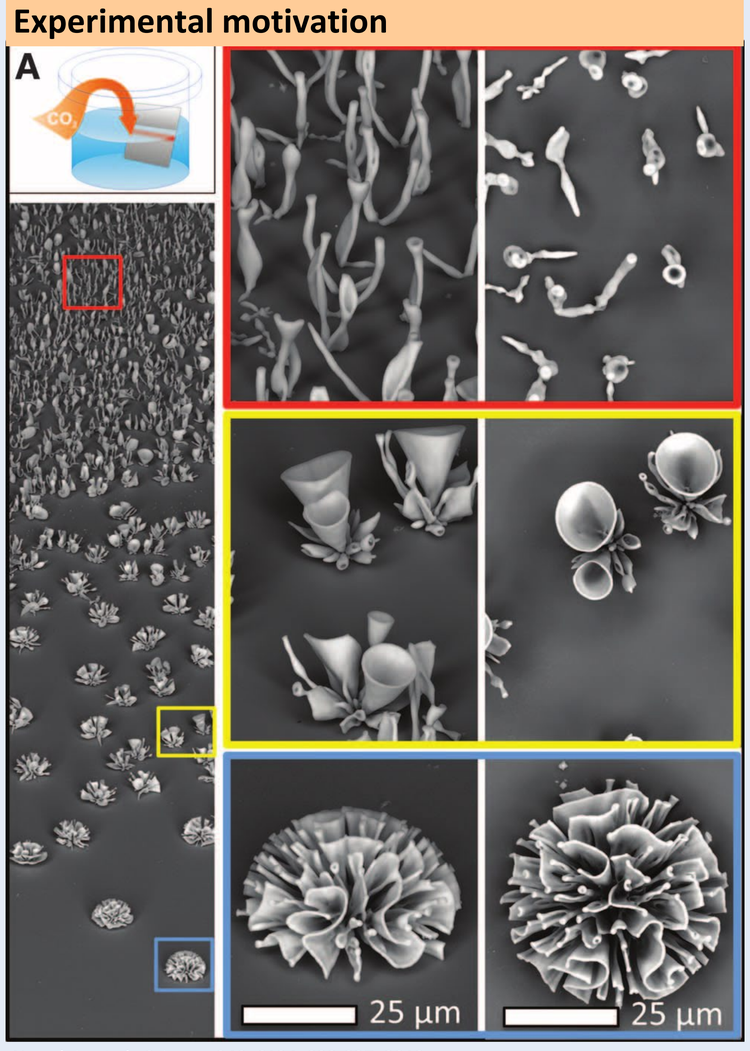
Introduction

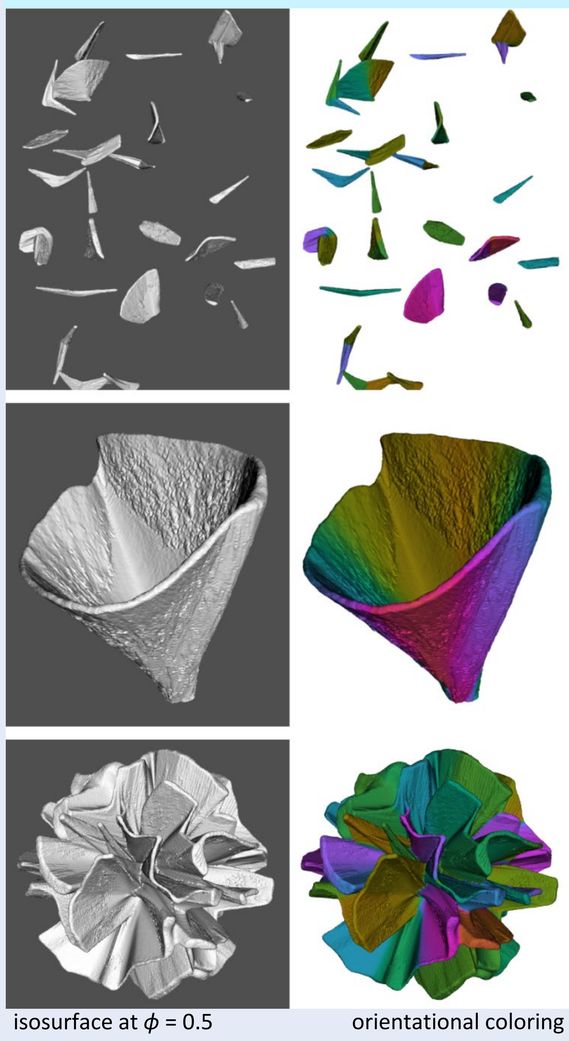
The nanocrystalline, inorganic composites known as "biomorphs" form micron-scale structures such as helices, sheets, funnels, coral-like, and arboresque patterns made of alkaline earth metal (Ca, Sr, or Ba) carbonates assembled into high-aspect-ratio nanorod structures covered by silica, when precipitating from solution on solid substrate[1,2]. While reaction-diffusion models recovered essential features of such 2D and 3D aggregation processes[3], we explore here whether the orientation field-based phase-field models[4] developed for polycrystalline solidification could describe various aspects of the formation of biomorphic structures. This model relates solidification morphology to thermodynamics, interfacial properties and chemical diffusion.

Experimental motivation



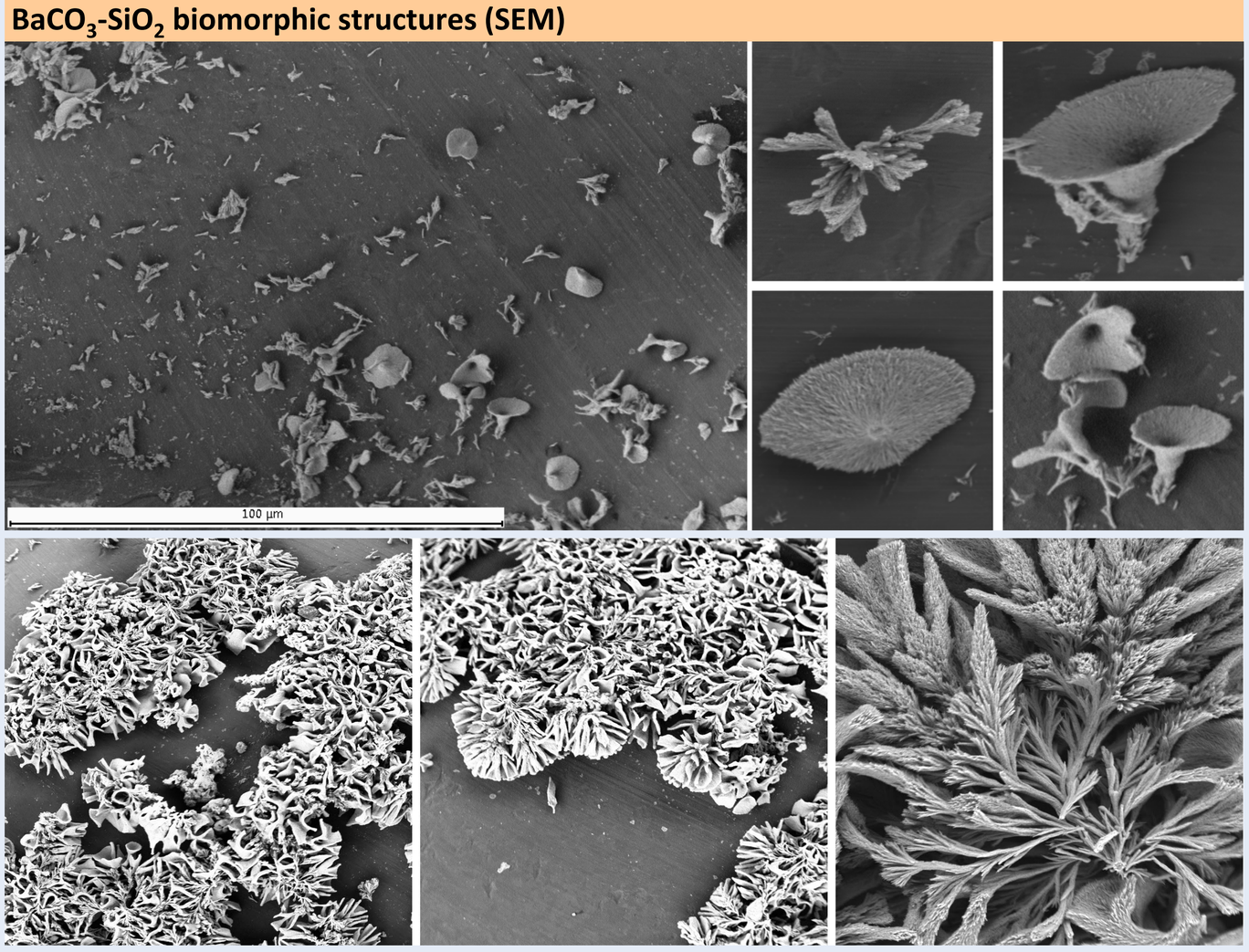
Noorduin et al., Science, 340, 6134, 832-837, 2013

Our PF simulations



isosurface at $\phi = 0.5$ orientational coloring

$BaCO_3$-SiO_2 biomorphic structures (SEM)



Phase-field model

Order parameters

phase-field: $\phi \in [0, 1]$ ($\phi = 0$: liquid, $\phi = 1$: solid)
concentration field: $c \in [0, 1]$
orientation field: $\mathbf{q} = (q_x, q_y, q_z, q_w)$ unit quaternion, $\Sigma_i q_i = 0$

Free energy functional

$$F = \int d^3r \left\{ \frac{\epsilon_\phi^2 T}{2} |\nabla\phi|^2 + WTg(\phi) + [1-p(\phi)] f_S(c) + p(\phi) f_L(c) + 2HT(1-p(\phi)) \left[\sum\nolimits_i (\nabla q_i)^2 \right]^{1/2} \right\}$$

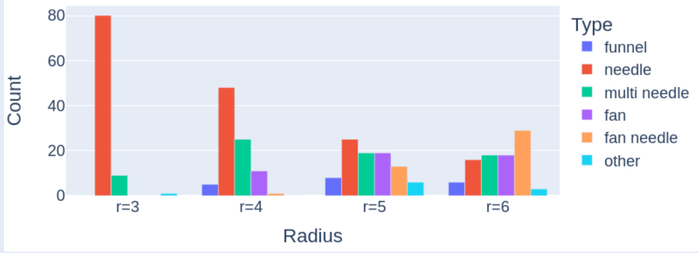
Equations of motion

$$\dot{\phi} = -M_\phi \frac{\partial F}{\partial \phi} + \xi_\phi = M_\phi \left\{ \nabla \left(\frac{\partial I}{\partial \nabla \phi} - \frac{\partial I}{\partial \phi} \right) \right\} + \xi_\phi$$

$$\dot{c} = \nabla M_c \nabla \left(\frac{\partial F}{\partial c} - \xi_j \right) = \nabla \left\{ \frac{V_m}{RT} Dc(1-c) \nabla \left[\frac{\partial I}{\partial \phi} - \nabla \frac{\partial I}{\partial \nabla \phi} - \xi_j \right] \right\}$$

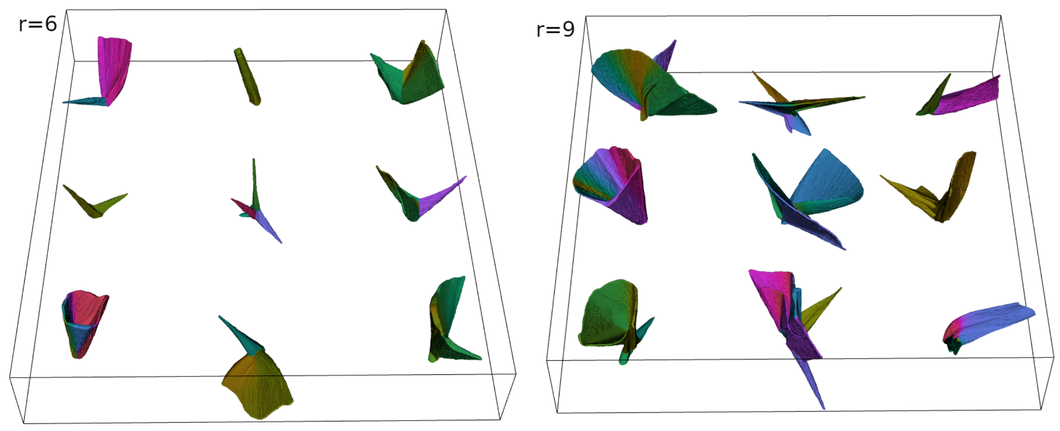
$$\dot{q}_i = -M_q \frac{\partial F}{\partial q_i} + \xi_i = M_q \left\{ \nabla \left(\frac{\partial I}{\partial \nabla q_i} - \frac{\partial I}{\partial q_i} \right) \right\} + \xi_i$$

Statistics of structures (simulations)

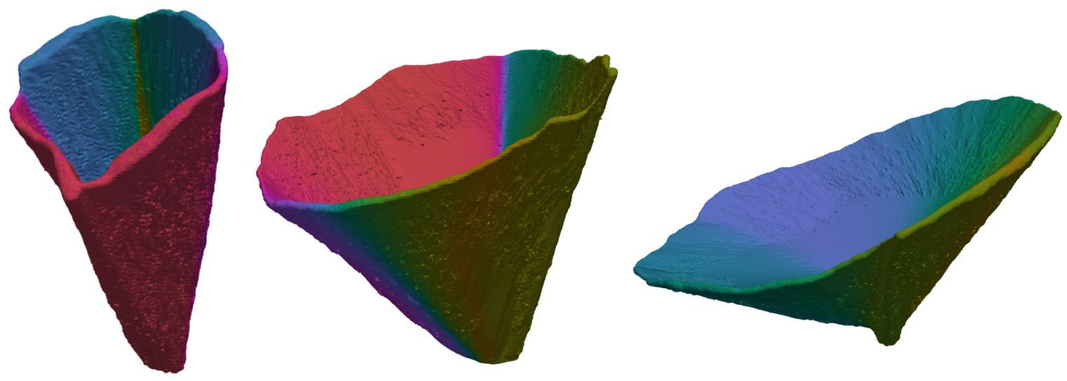


Solidification starts with circular seeds of pixelwise random orientation. Frequency of structures from 90 simulations for each seed size (radius).

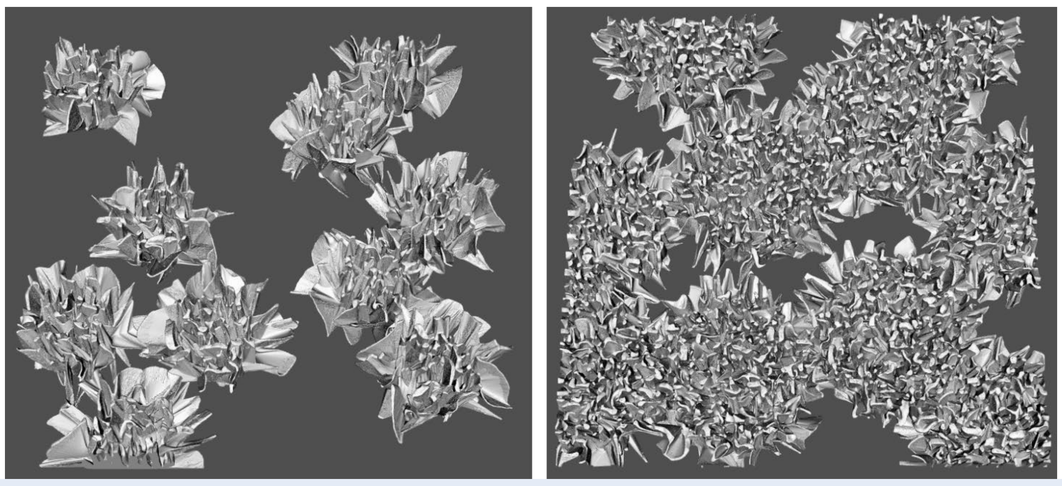
Catalogue of structures (simulations)



Funnels



Thicket-like structures



References

[1]: J. M. Garcia-Ruiz et al. Science 302, 1194, 2003
[2]: W.L. Noorduin, et al. Science 340, 832, 2013
[3]: C.N. Kaplan et al. Science 355, 1395, 2017
[4]: L. Gránásy, L. Rátkai, et al. Metall. Mater. Trans. A 45, 1694, 2014

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