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Citation for published version (APA):

Document status and date:
Published: 13/08/2014

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Self-assembled porous media from particle-stabilized emulsions

Stefan Frijters$^{1}$ and Jens Harting$^{1,2}$

$^{1}$Department of Applied Physics, Eindhoven University of Technology, Den Dolech 2, NL-5600MB Eindhoven, The Netherlands
$^{2}$Faculty of Science and Technology, Mesa+ Institute, University of Twente, P.O. Box 217, NL-7500AE Enschede, The Netherlands

(Dated: August 14, 2014)

We propose a new mechanism to create self-assembled porous media with highly tunable geometrical properties and permeabilities: We first allow a particle-stabilized emulsion to form from a mixture of two fluids and colloidal particles. Then, either one fluid phase or the particle layer is solidified, which can be achieved by techniques such as polymerization or freezing. Based on computer simulations we demonstrate that modifying only the particle wettability or concentration results in porous structures with a wide range of pore sizes and a permeability that can be varied by up to three orders of magnitude. We then discuss optimization of these properties for self-assembled filters or reactors and conclude that structures based on so-called “bijels” are most suitable candidates.

PACS numbers: 47.55.Kf, 47.56.+r, 81.16.Dn

Introduction.—Man-made porous media are used in various branches of science and industry, and they form the basis of, for example, many types of reactors, filters, or fuel cells [1, 2]. Each application has its own set of desirable and undesirable properties and as such creating highly tunable porous media with well-defined pore size distributions and permeabilities is of particular interest. It is advantageous to be able to create a catalyst or filter directly at a location that is hard to access, and where fine-grained control over an assembly process is necessarily absent, such as through the use of zeolite nano crystals [3], microemulsions [4], or magnetic self-assembly [5].

This letter follows a different route and discusses how the emulsification process of particle-stabilized emulsions can be tuned to create highly controlled self-assembled porous media [6]. We restrict ourselves to emulsions containing two fluid species and suspended spherical particles and propose two ways to create a porous medium from such an emulsion: Firstly, if one of the fluid phases contains an additional component that can be triggered—be it chemically, photochemically, thermally, or in some other fashion—to solidify (e.g. with the aid of solved polymers [7]), we create “filled” porous media with a relatively small pore fraction. Alternatively, if the solid particles are modified such that they can be linked together, an altogether different “open” geometry is created.

In experiments, this can be achieved using, for example, an additional phase of solved polymers [7, 8], or soft particles that can crosslink and agglomerate [9]. The particles can then form a dense layer that can be considered impenetrable, creating a wall-like structure. Compared to the previous, this type of system has a greatly enhanced porosity. In either of these ways a porous medium can be created in a remote location by supplying the ingredients (and trigger) from far away.

Particle-stabilized emulsions commonly present in one of two forms: the Pickering emulsion (discrete droplets) or the bijel (bicontinuous interfacially jammed emulsion gel), which have very different geometrical and rheological properties [10–12]. We use the knowledge of the simulation of particle-stabilized emulsions gleaned in previous work [13–15] to good effect, and we explore the emulsion parameter space for regions that result in geometries with desirable properties, such as large permeability yet small domain sizes (filters), or large surface-to-volume ratio, porosity, and large permeability (reactors). Examples of geometries created from Pickering emulsions and bijels are shown in Fig. 1.

Method.—We simulate particle-stabilized emulsions [15] by using the LB3D simulation software: a massively parallel implementation of the three-dimensional lattice-Boltzmann (LB) method [16] to treat the fluid components, and molecular dynamics (MD) to treat particle-particle interactions. The immiscibility of the two involved fluids (“oil” and “water”) is modeled as proposed by Shan and Chen [17], who add a local interaction force between the different fluid components present at a lattice site which effectively leads to a surface tension. The (colloidal) particles interact with the fluids through the method proposed by Ladd [18, 19], which discretizes the particles on the fluid lattice, and allows for momentum transfer where fluid attempts to enter a site covered by a particle. This method is extended to allow for multiple fluid components and to set the contact angle of the particles [13, 20].

We use data for different emulsion states which we obtained earlier and the reader is referred to Ref. [15] for details on simulation parameters and the validation of the method. The porous structures are then created in two different ways: To achieve “filled” porous media, we transform all fluid volumes that contain mostly oil-like fluid into solid sites. As the original emulsions are all oil-
in-water emulsions, one is left with a percolating system, which can then either contain a large continuous solid domain (if the source emulsion was a bijel) or smaller discrete solid domains (if the source emulsion was in a Pickering state). The latter case is slightly harder to achieve in experiments, as in the simulations the solid domains are suspended in the fluid without any support. However, in most cases the droplets are close to each other, and therefore such a structure is already close to being stable. It can then be fully stabilized by, e.g., a secondary polymeric structure, embedding the droplets into a foam, or bridging effects [21]. We assume that the effect of the additional stabilizing structure is assumed to be negligible. For the “open” variation, we transform both water and oil regions to pore space, and convert the volume occupied by the stabilizing particles into solid. As the particle coverage of the interface is not complete, we also create solid sites from the inter-particle spaces at the interfaces.

We define three geometrical properties of interest: Firstly, the effective porosity $\phi = \frac{V_{\text{pore}}^{\text{eff}}}{V_{\text{pore}} + V_{\text{solid}}}$. Secondly, we define the effective surface-to-volume ratio $\zeta = \frac{A_{\text{eff}}}{V_{\text{fluid}}^{\text{eff}}}$, where $A_{\text{eff}}$ is the total solid area facing a pore that contributes to percolation. This quantity is relevant when studying these solid geometries in the context of, e.g., a catalytic reactor. Finally, we follow a method for measuring domain sizes in emulsions as shown in other works [13, 15] and compute the spherically averaged structure factor to determine the averaged lateral domain size $\Lambda$ as a measure of the characteristic domain sizes of the porous media.

Darcy’s law relates the velocity $\langle v \rangle$ at which a fluid with kinematic viscosity $\eta$ flows through a porous medium to a pressure gradient $\nabla P$ applied over the medium. The permeability $\kappa$ appears in this law as a proportionality constant: $\kappa = \eta \langle v \rangle$. Unlike the geometrical quantities discussed above, we do not calculate the permeability of a geometry statically. Instead, we again use the lattice Boltzmann method, following Narváez et al. [22, 23], and relate this result to theoretical expectations.

**Results.**—We control the structure of the emulsion and the resulting porous medium by modifying two parameters: the particle volume fraction $\Xi$ and the wettability of the stabilizing particles, expressed as a contact angle $\theta_p$. Details on their effects can be found in [13] and [15], but we include two salient facts here: Firstly, the average domain size is inversely proportional to $\Xi$ (more particles can collectively stabilize a larger interface, allowing for smaller structures [24]). Secondly, in the case of the oil-water ratio of 5/9 that is used here, hydrophilic particles favor Pickering emulsions and hydrophobic particles favor bijels.

The porosity is trivially higher for open geometries as compared to filled ones based on the same emulsion state. For open geometries bijels have a higher effective porosity than Pickering emulsions because the insides of Pickering droplets do not participate in percolation. The surface-to-volume ratio increases with increasing $\Xi$ in all cases, because the average domains become smaller. For filled geometries, $\zeta$ decreases as particles become more hydrophobic: i.e. porous media based on Pickering emulsions have a higher effective surface-to-volume ratio as compared to bijels. However, for open geometries, there exists a minimum for neutrally wetting particles, as particle detachment in the case of extreme hydrophobicity leads to a large increase in available surface area based on the contribution of the surface area of these particles. We have measured the permeability of the porous media, and conclude that the highest permeabilities are reached by low values of $\Xi$ and high values of $\theta_p$. The particle volume fraction mainly affects the coarseness of the domains, while the contact angle of the particles controls the state of the emulsion: as such we can say that coarse bijels result in the most permeable porous media.

To combine these results in a more quantitative fashion, we use the Blake-Kozeny model, which represents the pore network of the porous medium as a bundle of non-homogeneous tubes with an equivalent radius $R_e$ and an effective length $L'$ that is larger than the length $L$ of the

![FIG. 1. (Color online) Examples of filled (a, c) and open (b, d) geometries created from particle-stabilized emulsions in the Pickering (a, b) and bijel (c, d) states. For clarity, only a slice is rendered as a 3D volume (grey), while the rest of the porous medium is depicted as a block with the solid and fluid at the edge of the domain shown as red and blue, respectively.](image)
porous medium [25]. The square of the ratio of these two lengths is known as the tortuosity \( \tau \), which is a measure for how twisted the pore network of the porous medium is. The average velocity in these capillary tubes is given by the Hagen-Poiseuille law

\[
\langle v \rangle = \frac{R_i^2 \Delta P}{8 \eta L}.
\]

This law can be combined with Darcy's law and the hydraulic radius \( R_h = R_i/2 = V_{\text{pore}}/A_{\text{eff}} \) to arrive at

\[
\kappa = \phi \frac{R_i^2}{8 \tau} = \frac{\phi V_{\text{pore}}}{2 \tau (A_{\text{eff}})^2} = \frac{\phi}{2 \tau \zeta^2},
\]

which expresses the permeability in terms of the porosity and the surface-to-volume ratio. Based on the structure of the source emulsions we expect \( \tau \approx 1 \). An example of the measured permeability and the theoretical prediction is shown in Fig. 2; they compare very well until extremely hydrophobic particles are used. At that point the domains coarsen so much that the assumption \( \tau \approx 1 \) is no longer valid. The figure also shows that variations of the permeability of three orders of magnitude are possible, without even changing the ratio of the fluids or the number of particles. Furthermore, we observe that for open geometries, the domains that were originally filled with oil contribute only weakly to the total permeability of the porous medium. This is caused by the fact that these domains are connected to the rest of the percolating pores by narrow pore necks only.

![FIG. 2. (Color online) Measured (points) and predicted (lines) permeability \( \kappa \) based on Eq. 2 for various filled geometries as a function of the particle contact angle \( \theta_p \), with the assumption \( \tau = 1 \). A value close to one is expected because of the structure of the source emulsions. Measurements and predictions show good agreement up to the case of extremely hydrophobic particles (large \( \theta_p \)).](image1)

We now combine the information presented above in a brief look at how to optimize a self-assembled porous medium to be used as a filter. For an efficient filter, we assume the permeability needs to be maximized to obtain optimal throughput, while the domain sizes need to be small; this corresponds to a system with narrow pore necks that block contaminants, such as small solid particles. Fig. 3 directly shows the relation between the domain sizes and the permeability of the geometries under consideration. The data points can be divided into two main branches, corresponding to open and filled geometries. Particles with extreme contact angles are likely to detach from the fluid-fluid interface and the effect of their size as individual solid domains is included in the measured average domain size \( \Lambda \) [15]. As such, the leftmost (open) branch is expected to underrepresent the true value of the domain sizes (this is not captured in the error bars for reasons of clarity of the plot). However, based on the magnitude of these errors (which has been studied but not explicitly reported here), this does not affect our analysis and the two-branch structure is expected to be qualitatively correct. We conclude that open bijels serve best as a basis for a self-assembled filter.

Alternatively, we can investigate how a porous medium with optimal properties for catalysis or other chemical reactions can be created. We propose that maximization of both permeability (to ensure high throughput) and available surface area (to ensure high reactivity) is important for this purpose. In particular, we define an efficiency \( \Upsilon = \kappa \zeta \phi \) to be maximized. We plot the permeability against the available surface area in Fig. 4 and add isolines for \( \Upsilon \), which give an indication of the most efficient combinations of parameters; the optimization process moves at right angles to the isolines. Again, the open geometries based on bijels are clearly the most suitable, and in this case it is also preferred to have as few particles as possible: the increased coarseness of the emulsion
surface-to-volume ratio for open geometries; this extra surface area is mostly located in pore domains that only weakly contribute to percolation. However, this effect is small enough as to not affect the optimization strategy.

Conclusion. — We demonstrated the applicability of a new mechanism to generate self-assembled porous media based on partly solidified particle-stabilized emulsions. By solely modifying the concentration of particles and their wettability we were able to generate porous structures with highly tunable pore sizes and permeabilities varying over three orders of magnitude. The lattice Boltzmann method has proven to be an efficient method to first simulate the formation of the emulsions, and later to calculate the permeability of the resulting porous medium. As such it could be applied as an alternative tool to optimize novel self-assembled filters or reactors. For filters, optimization was achieved by maximizing permeability (to maximize throughput) while minimizing the pore size (to be able to block smaller particles). For a self-assembled reactor, we defined an efficiency as being the product of the permeability (to ensure high throughput) and available surface area (to ensure high reactivity). We conclude that in both cases open geometries are preferred, in particular those based on a bijel.

Acknowledgments. — Financial support is acknowledged from FOM/Shell (09iPOG14) and NWO/STW (Vidi grant 10787 of J. Harting). We thank the Jülich Supercomputing Centre and the High Performance Computing Center Stuttgart for the CPU time which was allocated through large scale GSC and PRACE grants.

FIG. 4. (Color online) The permeability \( \kappa \) of open geometries is combined with the available surface area to obtain an efficiency \( \Upsilon = \kappa \zeta \phi \). The particle contact angle is expressed through the color gradient from blue (\( \theta_p = 50^\circ \), Pickering emulsion, bottom right) to red (\( \theta_p = 130^\circ \), bijel, at the end of all three branches). Also shown are isolines for the efficiency \( \Xi \) split off into different branches in the bijel regime. Their best efficiencies are similar, and larger than those of Pickering emulsions, and of filled bijels (not shown).

\[
\zeta \phi = A_{\text{eff}} / V_{\text{sim}}
\]

leads to such an increase in permeability that the loss of surface area is negated in terms of efficiency. Particle detachment also leads to an additional contribution to the