Response to Review #1 of
On the Consistency of Scale Among Experiments, Theory, and Simulation
J.E. McClure, A.L. Dye, W. G. Gray, and C. T. Miller

hess-2016-451

1 General

We respond to the comments from Referee #1 beneath comments made. The authors' response is shown as **AU: red**. The changes made are highlighted as **AU: blue**.

2 Referee #1

The paper critiques current models and makes a case for developing models that are consistent across scales based on thermodynamic principles. The nature of the processes these models tackle is kept vague, but some hints suggest that models for subsurface water flow (soil water and groundwater) are the prime target. A theoretical treatment of the Laplace Law is developed to develop equations for microscale capillary pressures, which seems to refer to pressure jumps across fluid-fluid interfaces in single pores. These expressions are more general that the Laplace Law because they apply to equilibrium and non-equilibrium cases. Expressions for average intrinsic phase pressures are also presented.

An experiment is described in which a non-wetting gas phase (nitrogen gas) permeates a 0.5 by 0.5 mm two-dimensional porous medium saturated by a wetting fluid phase (decane). This process and similar ones with different initial and boundary conditions are also modeled numerically. Both the simulated and observed data are used to obtain the 3D equivalent of the decane retention function in which the degree of saturation is a function of both the average fluid pressure and the specific interface area.

Major comments

For a paper on scales I could not help noticing that the time scale is mentioned only once and that there is no clear definition of the spatial scales of interest (microscale and macroscale). No connection is established between these scales and the scale of the representative elementary volume.

AU: The time scale does not affect the form of the equations relied upon in this work. In fact, this work is primarily concerned with equilibrium states, how to best explore the potential states that can exist, and how the state function of capillary pressure can be represented. Time scales are, however, mentioned in the introduction, the background, and the results sections. The reviewer is mistaken that the microscale and macroscale are not connected, as all of the macroscale quantities defined and used in this work are defined completely and explicitly in terms of microscale quantities—thus making the connection that the reviewer claims is missing. We could add explicit definitions of the microscale and the macroscale terminology that we use in this manuscript, and incorporate additional discussion on the scale required to obtain a representative elementary volume.

AU: We have added a paragraph at the beginning of the Background section to explain the differences between the microscale and the macroscale.

The paper uses a few straw man arguments. It is claimed that in experiments, pressures are only measured (or set) at the boundary of the system of interest. With the increased use of microtensiometers this is no longer necessarily the case. In my experience (and with some support in the literature), the microtensiometers tend to confirm that the known pressure at a boundary can be used to calculate the pressure anywhere in the system as long as contact is good and equilibrium has been achieved. The reliance on boundary pressures is not as risky as the authors appear to believe. In the terminology of the analysis of the paper this implies that phase continuity in real-world porous media is often sufficient for the observed pressures to be valid.

AU: We agree with the reviewer that microtensiometers provide a means to measure fluid pressures within a domain, and we can note this in a revised manuscript. We also agree with the reviewer that if both fluids are well connected across an experimental cell and at a true equilibrium state, the boundary condition measurements and microtensiometer observations should be in agreement. We disagree with the reviewer that such observations are adequate for characterizing the state of a porous medium system in a general sense, and the results presented in this manuscript clearly support our view. For example, imbibition is well-known to result in disconnected non-wetting phase regions, which will not be connected to the boundaries; the formation of disconnected pendular rings of wetting phase is also well-known. Only if sufficient observations of the pressures of each of the disconnected regions and their morphological characteristics were available would the state of the system

be adequately characterized.

This does not mean that the associated capillary pressures are inaccessible from experiment. On the contrary, the increased use of x-ray micro-computed tomography (μCT) makes it possible to directly measure the interfacial curvature within 3D experimental systems. This approach has been used for about 20 years and is now used routinely [e.g., 1, 3, 2]. As stressed in the manuscript, the true capillary pressure is the product of the average curvature and the interfacial tension. The average curvature can be determined directly from experimental μCT.

AU: We have added a paragraph at the beginning of section 4.1 to clarify issues associated with pressure.

The authors state that average phase pressures are convenient to work with. I have never read anything in support of this argument. There are no sensors to measure average pressures, so we cannot calibrate models on them, and I have not come across any work that used average pressures in lieu of local pressures and pressure gradients.

AU: Several measures of pressures are important and come directly out of the TCAT theory. These include volume-averaged pressures, interface-averaged pressures, and pressure averaged over a boundary of a system, such as is the case with conventional pressure-saturation experiments. Common existing measurement methods provide averaged quantities due to the size of the instrument. Mechanistic conservation of momentum models include volume-averaged pressures, so from this perspective such quantities are convenient to deal with. Models are developed based on equations that use average pressures and thus must be calibrated and validated in terms of average pressures. It is precisely the distinctions among the different measures of pressures that are a key aspect of the phenomena explored in this work. For theory, models, and data to be mutually useful, they must have a common usage and understanding of pressure. We can highlight these points in a revision of this work.

AU: These issues have now been addressed in text added at the beginning of section 4.1.

I have the impression that the analysis is valid for zero-gravity conditions. This is never stated explicitly, but three elements of the paper suggest it:

- the casual averaging of pressures without acknowledging the immense effect of the geometry of real-world fluid bodies on the average pressure when gravity is non-zero?

- the implicit notion that fluid interfaces and common curves have a non-zero thickness and therefore mass, without the effect of this mass being discussed or even mentioned.
- the extremely small size of the porous medium used in the experiment that indeed makes the effect of gravity negligible. In a paper in which the introduction discusses the importance of consistency of scales for scale ranges that are many orders of magnitude larger and already in the abstract calls for models that are based on rigorous multiscale principles this severely limits the relevance of the paper.

AU: The TCAT theory relied upon in this work includes the effects of gravity in large systems and for interfaces that contain mass; references to this theory are provided. The formulation provided is not affected by the importance of gravity, and all equations hold regardless of the importance of gravity. In this work, gravitational effects were considered to be negligible due to the size of the system, which we will be sure is clearly noted in a revised version.

AU: We have noted that the simulations of the experimental systems neglected gravitational effects, which follows from the very small length scale in the vertical direction. This revision is noted in section 5.2.

The lack or relevance is further reduced by the experimental scale: 0.25 square millimeter is in the sub-Darcian scale for most soils and geologic materials. To call this scale the macroscale seems to betray a fundamental lack of understanding of the concepts of the continuum approach and the representative elementary volume that form the basis that most currently used models are founded on.

AU: The reviewer is mistaken. The actual physical size of a system is not an appropriate measure of whether a system is an REV or not. Karst systems may require 100's of meters for a valid REV, whereas microfluidic systems of the sort relied upon in this work can satisfy the physical and mathematical requirements for an REV at length scales on the order of 500 μm or less quite easily. At the microscale, the laws of continuum mechanics apply for a fluid at length scales that are long compared to the mean free path between molecular collisions. For the particular system investigated, the continuum limit would be easily satisfied with a length scale of 1 μm. A valid macroscale requires a clear separation of length scales with the microscale and the resolution scale needed to characterize the pore morphology and topology. This scale usually translates to systems with a length of at least 10 mean grain diameters on a side. While the systems investigated are physically small, they are close

to an REV in size. The actual physical size cannot be examined in isolation in reaching conclusions about whether a system is an REV. The systems investigated in this study were sufficiently large to show the occurrence of many regions of disconnected phases, which was sufficient to investigate the state function for capillary pressure. We would add some minor discussion about the size of an REV for porous medium systems and reference these comments to the literature.

AU: We have included a paragraph at the beginning of the experimental section 5.2 that explains REV and fluid issues related to the microfluidic work and supported our claims with references to the literature.

Section 4 "Approach" has a non-informative title. It can easily be split in a "Theory" section (modify the title as desired) and a "Materials and Methods" section, thereby making the paper conform to the established structure of scientific papers. The Results and Discussion section is already there.

AU: This appears to be a matter of style preference. Information in the text and cited references provide sufficient background such that experiments used in this work could be reproduced. We note that the HESS guidelines for manuscript preparation do not explicitly require a "Materials and Methods" section. Our manuscript conforms to the structure established in the HESS guidelines. For a serious reviewer to imply that a paper that does not use his or her preferred section headings violates the "established structure of scientific papers" is astonishing.

AU: While we don't agree with the comments of the reviewer, we nonetheless changed the headings as suggested, because it did not degrade the quality of the paper to do so.

Section 4 starts with a treatment of the Laplace Law. One of the authors published an extensive treatment of this law (Hassanizadeh and Gray, 1993, not quoted in the paper). I would like to see included in this paper an explanation of the added value of the current discussion in view of this earlier work, and how this treatment relates to that in the earlier work. There are marked distinctions in notation between the earlier and the current paper which made it hard for me to establish the relation.

AU: A quick search on Google for "capillary pressure porous media" provides over 1M hits. A similar search in Google Scholar provides almost 0.25M hits. We can hazard a guess, with confidence, that many of these papers have made useful contributions to the study of porous media. It is clear that the authors have not seen fit to cite

much of this wealth of information. Even the authors of this paper have been engaged in a good number of papers that deal with porous media physics and capillary pressure. We have chosen not to cite most of these as well because they are tangential to the mission of the current paper. We can say, with confidence, that our work through the years has demonstrated a development in theory and understanding. We have not been stagnant and insisted on sticking with theories and understandings that have become dated or outmoded. Indeed, reports on developments of new theories, experimental tools, experimental techniques, and simulation algorithms do not necessarily provide reports on or references to older methods that the current work supersedes. For the case at hand, the reviewer seems to admire the 1993 paper, and we appreciate that. This 23 year old paper made a contribution at that time. The discussion of the microscale capillary pressure is informative. Frankly, the discussion of the macrocale capillary pressure has been surpassed by understanding gleaned from careful development and application of the TCAT method. This does not negate the contribution of the older paper; neither would a comparable statement about any of the 0.25M citations dealing with capillary pressure in porous media negate their contributions. We can suggest that the reviewer might benefit from looking at more recent contributions in this area of study. We believe that citing one's own work can be self-serving when that work is dated and not particularly pertinent to the issue or issues under discussion in a newer work. We prefer to include references that best serve the hydrologic community that seeks to understand what we are working on and the nature of our contributions. For this reason, we do not cite the 23 year old paper; neither do we provide an extensive review of developments in understanding of capillary pressure, particularly at the macroscale, over the same period. We have a focused set of objectives we wish to address in this manuscript; we employ theoretical, experimental, and computational approaches for doing so. We cite references that are helpful and/or fundamental to fulfilling the objectives of our paper. We see no technically sound reason to cite the paper the reviewer refers to.

The notation used here is explained carefully, and references are given to other works where this notation is explained in detail and used for a variety of applications. Indeed, even when a work involves a more advanced and precise notation than previously used, authors do not have a responsibility to explain and account for the myriad of notations that are used in the same field or in earlier incarnations of work.

AU: No changes were made in response to this comment.

The work culminates in a relationship between capillary pressure, degree of saturation, and specific interfacial area. As long as the latter cannot be measured on 3D samples, the work has no chance of becoming applicable.

AU: We disagree with the reviewer, who seems to be unaware of the considerable amount of active research in this area. Specific interfacial areas are indeed routinely measured in 3D samples now. We present simulations in this work where those quantities are evolved and compare virtually identically with experimental observations. Fast imaging methods are now capable of measuring specific interfacial areas dynamically and nondestructively. The state equation for capillary pressure depends upon a sufficient set of measures of the morphology and topology of the pore space, along with fluid and solid properties. There is no question that specific interfacial area is one of these quantities, as has been well established in the literature. We would like to add that the functional dependence we propose is correct. In itself, that is important. In practice, one does not discard a correct theory in favor of an incorrect one simply because quantities in the correct theory may be difficult to measure. In the present case, the theory is correct, and the results of the combined theoretical, experimental, and computational studies in this paper are moving the theory forward to becoming applied and employed.

AU: No changes were made in response to this comment.

I do not see a path for using this kind of work to arrive at the thermodynamically consistent, scalable models for porous media found in nature, even though the authors claim that goal to be a main motivation for the paper.

AU: The reviewer may not see the path; but it clearly exists. We have cleared most of the brush obstructing it. Many visionary researchers are making progress in obtaining appropriate scalable models for porous media. We can caution that some researchers have claimed to have a model that is "thermodynamically consistent" that, in fact, is not. The work here provides a different and correct direction. In general, we do not think that determinations on whether research should be conducted or presented should be based on the suspicion of one individual (or a few or even many individuals) who claims to have limited vision. The reviewer provides no concrete comments based upon scientific observations but only identifies his/her lack of vision and chooses only to speculate idly.

AU: No changes will be made in regard to this speculation.

Overall assessment

The paper has six objectives that claim to resolve several issues relating to capillary pressure at the micro- and the macroscale and expose limitations of conventional approaches.

The Introduction and its list of objectives raise high expectations about the impact and relevance of this paper for modeling of multiphase flows in soils, aquifers, oil deposits, etc. These expectations are in no way met, either by the theoretical analysis that adds only incrementally to an earlier paper and omits gravity, or by the experiment on 0.25 square mm of an artificial, two-dimensional porous medium with two fluids that have no relevance for hydrology. To make the contrast between this work and real-world hydrology even more glaring, the authors drop the name of Eric Wood, who has worked on continental and global hydrology.

AU: We disagree with the reviewer. On page three we list six objectives, each of which is clearly addressed in the material that follows. Because this manuscript was submitted to be part of a special issue in honor of Professor Wood, it seems appropriate to link this work with the work of Professor Wood. His work and this manuscript deal with issues of scale in hydrologic systems. We believe the treatment and tribute is appropriate. We can add that the theoretical approach that is employed here for small systems can be and has been employed for larger systems, including surface hydrology systems. The overriding common thread is "change of scale." The tools for achieving this are the same, the applications are different.

The presentation of the material is messy:

- the Introduction dwells on subjects not at all covered by the paper and fails to inform the reader about the paper's focus and nature of the work.
  AU: The Introduction purposely links issues of interest to a broader community to the issue of scale as important for porous medium systems. The present form seems appropriate given the nature of the special issue.
- the list of objectives is too long, and vastly overstates what the paper actually delivers.
  AU: The list of objectives is short and each objective is accomplished in the text that follows. It is not clear what the reviewer finds to be overstated or undelivered.
- the paper is not well structured - there is no Materials and Methods section, and the flow of thought is sometimes hard to follow. Some parts are well written, others much less so. A strict adherence to the established format of a scientific paper would help.
  AU: We have adhered to the format established by the guidelines

for manuscript preparation that are available from HESS online.
AU: We have changed the section titles as suggested in this revision.

- not all variables and symbols are explained, and there are inconsistencies in the notation
  AU: This comment is again made without evidence. What inconsistencies? What isn't defined? We have attempted to ensure that each variable is defined. If we have missed any or some, we regret that and would be delighted to address that oversight. We will double check the notation. The reviewer could provide a service by identifying any issues he/she has discovered.
  AU: We have double checked and also examined the reviewer's marked manuscript. All variables are defined.
- the description of the experiment and the computations (what should be the Materials and Methods section) is incomplete.
  AU: Additional details on the experimental methods could be added, although the methods are standard and have been previously published. We don't believe these additions are necessary, and think they would distract from the thrust of the paper and unnecessarily lengthen it. References to experiments and computations are provided. The reviewer seems to be hung up on some preconceived notion of the organization of a scientific contribution that seems to overwhelm his/her ability to assess the actual contents of the contribution. We prefer not to add more details on the experiments and computations as this would be redundant and would add unnecessary clutter to the literature.
  AU: Some additional details have been added to the experimental section to explain issues related to the REV and choice of fluids.

AU: The authors will be happy to go through the manuscript and consider changes that might be appropriate in light of the review comments and our own view of the work. We note that this reviewer made a number of detailed and useful comments in an attached document, and we welcome the opportunity to consider incorporating this information in a revision of this manuscript.

AU: In response to comments made in the marked manuscript but not specifically detailed in these reviewer comments, we have made the following changes: (1) we have substantially revised the abstract; (2) we added two sentences to make the structure of the introduction more clear; (3) modification of the statement on the role of theory was broadened; (4) the role of statistical approaches has been softened; (5) formatting for references has been cleaned up; (6) additional definition of terms where indicated have been added; (7) many minor suggested edits made; (8) additional details were

added on the formulation of specific interfacial areas and common curve lengths; (9) the index set of fluid phases was defined; (10) additional comments on the limitations of pressure transducers for measuring the desired state of a system were added; (11) a reference was added where the reviewer was confused about how to include gravity in Laplace's law; (12) a sentence was added that all equations apply to dynamic conditions as well as static conditions, except for those specifically noted to require equilibrium conditions for which the velocity is zero by definition; (13) the symbol $\overline{\Omega}$ was defined as a closed domain; (14) some additional details were added to the experimental methods section; (15) clarification added in the results regarding capillary pressure; (16) uniqueness was further explained; (17) a reference was added for GAM modeling; (18) units were added to pressure; and (19) clarification was on the state function in the conclusions.

We believe we have been responsive to the concerns of this reviewer. In the cases in which the reviewer was wrong, we have explained why this is the case. We understand that a work of this sort covers a lot of ground and is technical, so we made some changes even when we felt they really weren't necessary.

References

[1] R. I. Al-Raoush and C. Willson. A pore-scale investigation of a multiphase porous media system. *Journal of Contaminant Hydrology*, 77:67–89, 2005.

[2] M. L. Porter, D. Wildenschild, G. Grant, and J. I. Gerhard. Measurement and prediction of the relationship between capillary pressure, saturation, and interfacial area in a NAPL-water-glass bead system. *Water Resources Research*, 46(W08512), 2010.

[3] D. Wildenschild, J. W. Hopmans, C. M. P. Vaz, M. L. Rivers, D. Rikard, and B. S. B. Christensen. Using X-ray computed tomography in hydrology: Systems, resolutions, and limitations. *Journal of Hydrology*, 267(3-4):285–297, 2002.

Response to Review #2 of
On the Consistency of Scale Among Experiments, Theory, and Simulation
J.E. McClure, A.L. Dye, W. G. Gray, and C. T. Miller

hess-2016-451

1 General

We respond to the comments from Referee #2 beneath comments made. The authors' response is shown as **AU: red**. The changes made are highlighted as **AU: blue**.

2 Referee #2

In this manuscript, physically based upscaling of two phase fluid flow in a porous medium is considered by presenting definitions of microscopic and (macroscopic) averaged properties, and investigating this system with experiments and simulations. The manuscript provides nice illustrations of how different experimentally determined pressure differences and local values of capillary pressure are. This is done by a blend of experiments and numerical simulations. While I have no problem with the basic message of the manuscript, the presentation is not as may be expected. Quite some space is reserved for the objectives, a literature overview in the background section, and the presentation of eqs. (1)-(19), which are basically definitions. What remains underexposed, though, is a clear identification of what is new. Certainly, averaging is not, and neither is it for two fluid systems in porous material. Therefore, I propose that this is explicitly mentioned on these sections 2-4.1, as I am not convinced that these sections should be maintained in this manuscript. The aspect of connectivity is given some emphasis (e.g. p.8) and reference is made to McClure et al. Again, I propose that it is clearly identified whether and what is new in this work, as the current text is not clarifying this. Later on, again the experimental and simulation parts appear to be based on work of McClure et al. and it is apparent that this work may duplicate that earlier work. Though the present manuscript is illustrative, I would consider it not fit for publication, if in essence the material is a duplication of earlier work.

AU: The introduction was written to put this work into a broader

context associated with the special issue in honor of Professor Wood. Since this may well be the only manuscript on porous media in the issue, it seems some effort should be expended to make the connection with approaches to other hydrological problems. The objectives are brief, and we don't see anything to cut here. The formulation is included because the focus on individual regions within the porous medium is needed to clearly explain the issues involved with disconnected phases.

There are a number of important differences between the McClure et al. manuscript published in *Physical Review E* and this manuscript. Specifically, the most significant differences with the PRE paper are

(1) this manuscript includes data from drainage in addition to randomly initialized configurations allowing a comparison of a new approach with a traditional approach;
(2) this manuscript considers a system where there is experimental support; and
(3) this work focuses on wetting-phase connectivity rather than non-wetting phase connectivity.

Reference to McClure et. al is necessary to provide additional theoretical details on the random phase initialization, but there is not really a significant topical overlap between the two papers. A sentence or two can be inserted to clearly assert what is the new contribution of the current effort.

AU: The abstract has been substantially revised and the contributions from this work are clearly stated up front.

One of the issues that is quite central to this manuscript is that equilibrium is achieved. Considering the small size of the apparatus, I wonder how this is checked.

AU: We are willing to add additional details to the experimental methods section to explain how these data were collected and how we became convinced that equilibrium conditions existed.

AU: We have added these details to the experimental methods.

On several other statements I also wonder what their justification is. Presumably, this is indicated in the cited references, but as a stand-alone manuscript, important statements need to be justified here.

AU: Not sure what statements this comment refers to.

specific comments: 1. I wonder about some of the English (is the term microfluidic well used;

AU: Yes this is standard terminology that is broadly used. A Google search on "microfluidic" provides over 4M hits (including both microfluidic and microfluidics)

abstract; these instances on p.4 line 11). The abstract contains quite some text, which I would rate as context, that is not necessary for an abstract and must be deleted: lines 1-8 or even 1-11.

AU: The abstract could indeed be shortened, but we wanted to ensure, given the special nature of this issue in honor of Eric Wood, that the abstract is sufficiently informative. We would do as the editor wished with regard to this point, but our preference for the reason cited is to leave this longer version pretty much as is.

AU: We shortened the abstract substantially and removed material that was not central to the work performed here.

In addition, the reduction of water content to below the irreducible saturation is mentioned: As the authors make a call for rigorous definitions, I think this contradiction in the text is inappropriate.

AU: We will make it clear in a revised version that the standard terminology is indeed a misnomer.

AU: We added a statement regarding this common misnomer in the computational section and in the abstract added the adjective so-called to alert the reader to this point early on as well.

Of course, in a special issue focused on Eric Wood, there is a temptation to give some thoughts on his career. However, in this manuscript, those thoughts look quite artificial and unnatural. I would omit those parts of the text.

AU: The fact that this paper is intended to be part of a special issue in honor of Eric Wood was our motivation for a broad introduction that sought commonalities between Professor Wood's work and this particular, focused piece of work. Although one might argue that the contexts of upscaling in this work and in Prof. Wood's work are different, we assert that the upscaling techniques that can be used are the same. The fact that experimental and computational efforts to support the theoretical results in the two contexts will be different does not detract from the fact that upscaling, in any context, requires support. Again, we are willing to respond to the editor's recommendation on this point, but we prefer to leave this

portion in tact in light of the nature of the special issue.

AU: We have generally left these comments stand and believe it is appropriate to do so. The connection with our work is much closer than might be apparent without these comments.

2. Averaging (p.4) is older. For instance De Josselin de Jong (around 1955)

AU: We do not know of another source in which the averages computed in this work, and necessary to make the points about the role of connectivity, have been formulated. This material should stay in our view and is necessary for understanding.

AU: This formulation is central to the work, is unique because it is based upon connected components, and has been retained.

3. p.5 line 2: I would add: does not ONLY depend....

AU: Actually, the statement is correct as stands. Capillary pressure is the product of interfacial tension and the mean curvature of the fluid-fluid interface—fluid pressures do not enter the expression. Only at equilibrium is the capillary pressure equal to the pressure difference on either side of the interface. We believe these points are clear in the manuscript.

AU: No changes made.

4. I do understand neither the notation nor the meaning of (2) or the term "extent measure". Please clarify.

AU: We find this comment confusing. Previously, the reviewer opined that this was a standard formulation that wasn't new, and now she/he seems confused about fundamental components of modern averaging theory. We can add some additional references here to help readers who lack the appropriate background but are trying to understand the details of what is written. The indicator function is identified and described in Eqn (2) concisely and correctly. Similarly, the meaning of extent measures is defined right beneath their formulation in Eqn(3).

AU: Slight changes have been made to define the specific interfacial area and specific common curve length.

5. page 8: the term averaged phase pressures is used. I think that it is not appropriately, especially for this manuscript, to be vague about "over what is averaged".

AU: The purpose of including the formulation is to define precisely every quantity that is used. There is no ambiguity as every symbol is defined completely and in detail, with averages explicitly denoted in terms of their smaller scale precursors.

AU: No changes have been made regarding this comment.

6. in Fig.1, the black circles represent solid phase particles. Are these in fact porous cylinders as I understand from p.9 line 15? I think this info should be made very explicit, to address whether or not this experiment is true 2D or in fact 3D (with additional complications that will be obvious).

AU: The caption of Figure 1 clearly stated what the reviewer surmised to be the case, including a note of the portion of the domain accessible to fluid flow.

AU: No change needed.

One complication that may not be left undiscussed is that of boundary effects (at front and rear plates). In the same context, I do not understand p.11 line 4-5: why the "depth" (in Fig.1: vertical, horizontal,...) of the real apparatus and of the model differ.

AU: The two principal radii of curvature are R_1 and R_2. Since the depth of the micromodel sample is fixed, R_2 is fixed, and variations in the mean curvature are due solely to changes in R_1 . The depth of the simulation domain was increased to improve the numerical accuracy, noting that this approach was sufficient to resolve the behavior of R_1.

AU: No change made.

7. Is the instrument new? I ask because it is not clear whether the experiments, their interpretation and such are new and in what sense (see p.10 line 17-18).

AU: The experimental work reported here is new.

8. you create random initial conditions below irreducible saturation (p.11). Only now, it is indicated clearly what makes it irreducible: because it is not connected to the wetting phase reservoir. I think that this needs to be mentioned earlier. Also, explain why it is relevant: these situations cannot develop in reality (for the experimental set up) as it is a state below irreducible. You mention (p.11) that below irreducible saturation, where sub-regions are unconnected, this leads to history dependence. I would think that the same is true in the random initial conditions simulations. Where you inject your "blocks", is simulating history.

AU: We agree that the use of the expression "irreducible saturation" is a bad historical misnomer. This name arose from the form of $p^c - s^{\overline{\overline{w}}}$ curves and the experimental methods used to obtain them. In fact, saturations below the "irreducible saturation" exist and can be achieved experimentally. Encouraging abandonment of this unfortunate, yet deeply ingrained, terminology is a huge task. The term, "history dependent" is employed, perhaps in a traditionally inappropriate way, to indicate that the microscale state of the system cannot be characterized by the macroscale variables p^c and $s^{\overline{\overline{w}}}$. If we consider the relationship $p^c(s^{\overline{\overline{w}}})$, we observe "history dependence," as it is traditionally explained, is a consequence of the fact that for a given s^w there are many possible microstates; and all of these do not produce the same value of p^c. These microstates can be achieved by operating an experimental apparatus under different scenarios changes of the boundary conditions. However, if we include interfacial area, ϵ^{wn}, in the theoretical construct, then the relationship $p^c(s^{\overline{\overline{w}}}, \epsilon^{wn})$ is able to characterize the possible microstates more effectively, independent of experimental operating strategies and histories, which does remove "history dependence."

AU: As previously noted, we have pointed out in the computational section that irreducible saturation is indeed a misnomer.

On the Consistency of Scale Among Experiments, Theory, and Simulation

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Abstract. The career of Professor Eric F. Wood has focused on the resolution of problems of scale in hydrologic systems. Within this context, we consider an evolving approach known as the thermodynamically constrained averaging theory (TCAT), which has broad applicability to hydrology. ~~Specifically, w~~We consider the case of modeling of two-fluid-phase flow in porous media, and we focus on issues of scale as they relate to various measures of pressure, capillary pressure, and state equations needed to produce solvable models. ~~Two-fluid flow processes in the subsurface are fundamentally important for a wide range of hydrologic processes, including the transport of water and air in the vadose zone and geological carbon sequestration. Mathematical models that describe these complex processes have long relied on empirical approaches that neglect important aspects of the system behavior. New data sources make it possible to access the true geometry of geologic materials and directly measure previously inaccessible quantities. This information can be exploited to support a new generation of theoretical models that are constructed based on rigorous multiscale principles for thermodynamics and continuum mechanics. The challenges to constructing a mature model are shown to involve issues of scale, consistency requirements, appropriate representation of operative physical mechanisms at the target scale of the model, and a robust structure to support model evaluation, validation, and refinement.~~ We apply TCAT to perform physics-based data assimilation to understand how the internal behavior influences the macroscale state of two-fluid porous medium systems. ~~Examples of a~~A microfluidic experimental method and a lattice Boltzmann simulation method are used to examine a key deficiency associated with standard approaches. In a hydrologic process such as evaporation, the water content will ultimately be reduced below the so-called irreducible wetting phase saturation determined from experiments. This is problematic since the derived closure relationships cannot predict the associated capillary pressures for these states. ~~In this work, w~~We demonstrate that the irreducible wetting-phase saturation is an artifact of the experimental design, caused by the fact that the boundary pressure difference does not approximate the true capillary pressure. Using averaging methods, we ~~measure~~compute the true capillary pressure for fluid configurations at and below the irreducible wetting phase saturation. Results of our analysis include a state function for the capillary pressure expressed as a function of fluid saturation and interfacial area.

1 Introduction

Hydrologic systems are typically investigated using some combination of experimental, computational, and theoretical approaches. Each of these classes of approaches has played a central role in advancing knowledge. The years spanning the career of Eric F. Wood have witnessed a remarkable development in the ability to study experimentally the elements that comprise the hydrologic universe. The subsurface is a porous medium system that receives experimental attention designed to identify the small-scale fluid distributions within the solid matrix, intermediate scale behavior through laboratory study, and also the response of an aquifer to imposed forces (e.g., Wildenschild and Sheppard, 2013; Dye et al., 2015; Alizadeh and Piri, 2014; Knödel et al., 2007). Turbulence in surface flows and its impact in rivers, estuaries, and oceans for flow, sediment transport, and dissolved species transport is examined using a broad range of experimental techniques (e.g., Bradshaw, 1971; Chanson, 2009; D'Asaro, 2014; Bernard and Wallace, 2002). Atmospheric experiments designed to support theoretical models of turbulence, typically using lidar systems, and to gain insight into turbulence structures have also generated large quantities of data (Sathe and Mann, 2013; Collins et al., 2015; Fuentes et al., 2014). Other studies involve examination of snow pack, desertification, and changes in land usage (Deems et al., 2013; Hermann and Sop, 2016; Lillesand et al., 2015; Nickerson et al., 2013).

Complementing the advancing ability of experimental study is the development of simulation tools for various aspects of hydrologic systems that make use of advanced computer technology (e.g., Miller et al., 2013; Flint et al., 2013; Kauffeldt et al., 2016; Paiva et al., 2011; Dietrich et al., 2013; Zhou and Li, 2011; Miller et al., 1998; Bauer et al., 2015; Dudhia, 2014). These models of watersheds, rivers and estuaries, and subsurface regions usually make use of traditional equations with the advances occurring through the ability of modern computer architecture to handle larger problems using parallel computing and more elegant, efficient graphical user interfaces.

A third element of advancing modeling of water resources systems is the development of theory that accounts for physical processes. On one hand, forming theoretical advances for mechanistic models based upon conservation equations can be viewed as the standard challenges of accounting more completely for conserved quantities and of developing closure relations for dissipative processes. However, the need to pose ~~these~~ closure relations at scales that are consistent with ~~the scales~~those at which the problems have been formulated creates a need for a variety of constitutive proposals. Furthermore, consistency of models requires that equation formulations be consistent across scales such that variables developed at a smaller scale can inform the equations employed at a larger scale. Overall, these considerations lead to identifying scale and scaling behavior in both time and space as important challenges in posing models (Wood, 1995; Wang et al., 2006; Skøien et al., 2003; Pechlivanidis et al., 2011; Gleeson and Paszkowski, 2014; Gentine et al., 2012; Blöschl, 2001).

~~In an era of unprecedented data generation, a specter haunts the scientific landscape: the pervasive application of statistical methods to misinterpret complex physical phenomena. In the face of this challenge, multiscale averaging theory offers a glimmer of hope. Opportunities to apply theoretical methods for physics-based data assimilation have never been more evident.~~ In an era of unprecedented data generation, opportunities to use multiscale averaging theory to develop physics-based data assimilation strategies based have never been more evident. The challenge of performing meaningful theoretical, experimental,

and computational analyses is constrained by the need to ensure that the length and time scales of quantities arising in each approach can be related. The scales of experimental data, variables appearing in equations, and computed quantities must be the same if they are to be compared in any meaningful way. As a prerequisite for this to happen, data generated by any of the methods must be consistent across the range of scales considered (Ly et al., 2013; Kauffeldt et al., 2013).

While the desire for ~~consistency~~consistencies across scales and approaches is conceptually simple to understand, it has proven to be a difficult practical objective to meet. ~~in practice~~ The change in scale of conservation and balance equations can be accomplished rather easily. The problem with applying these equations lies in the aforementioned need to average some intensive variables, the requirement that closure conditions be proposed at the larger scale, and the need to account for the dynamics of new quantities that arise in the change of scale. Without accounting for all of these items properly, models are doomed to fail. An essential element in ensuring success is the averaging of thermodynamic relations to the larger scale (Gray and Miller, 2013). This provides linkage of variables across scales and also ensures that all physical processes are properly accounted for. For modeling rainfall-runoff processes, Wood et al. (1988) proposed the use of a representative elementary area as a portion of a watershed over which averaging can occur to develop a model. This idea was extended and applied by Blöschl et al. (1995). Subsequently, Reggiani et al. (1998) proposed treating a hydrologic system as a collection of interconnected lumped elements. The lumping was accomplished by integration over individual portions of the system with distinct properties, e.g., aquifers, streams, channels. This effort did not include integration of thermodynamic relations, and as a result did not properly account for the impact of gravitational potential in driving flow between system elements. An effort to address this shortcoming by a somewhat ad hoc introduction of gravitational forces (Reggiani et al., 1999) was only partially successful. Averaging of thermodynamic relations to lumped elements has since been presented (Gray and Miller, 2009).

~~Similar challenges~~Challenges in assuring consistency across scales have ~~confronted~~also been confronted in the modeling of porous medium systems. Special challenges have been encountered for two-fluid-phase flow, where upscaling leads to the introduction of quantities such as specific interfacial area, which is the area where two phases meet normalized by the volume of the region, and specific common curve length, which is length of a curve where three phases meet normalized by the volume of the region. Modeling of multiscale porous medium systems ~~can also benefit from~~must also employ thermodynamics that is scale-consistent and included naturally as a part of the process. ~~As a result of~~Because of the inability to overcome these challenges, most efforts to model multiscale, multiphase porous medium systems do not have thermodynamic constraints and full-scale consistency that ~~is sought~~ would be expected in mature models. The thermodynamically constrained averaging theory (TCAT) approach is relatively refined and ~~does~~ provides means to model ~~effectively~~ systems that are inherently multiscale in nature and also to link disparate length scales, while representing the essential physics naturally and hierarchically with varying levels of sophistication. However, realizing these scale-consistent attributes requires new approaches, new equations of state, novel parameterizations, and, as with any new model, evaluation and validation.

2 Objectives

The overall goal of this work is to examine issues of scale consistency for two-fluid-phase porous medium systems. The specific objectives of this work are:

- to review efforts to resolve critical issues of scale for two-fluid-phase flow in porous media;
- to formulate microscale and macroscale descriptions of state variables important for traditional and evolving descriptions of capillary pressure;
- to determine state variables for capillary pressure using both experimental and computational approaches;
- to compare a traditional state equation approximation approaches with a carefully formulated approach based in multi-scale TCAT theory;
- to demonstrate the limitations of traditional state equation approaches for capillary pressure; and
- to examine the uniqueness of alternative state equation formulations.

3 Background

Two spatial scales are of primary interest for the porous medium problems of focus herein: the microscale, which is often referred to as the pore scale; and the macroscale, which is often referred to as the porous medium continuum scale. At the microscale, the geometry of all phase distributions are fully resolved in space and in time, which makes it possible to locate interfaces where two phases meet and common curves where three phases meet. The equations governing the conservation of mass, momentum, and energy, the balance of entropy, and equilibrium thermodynamic relations are well established at the microscale. Microscale experimental work and modeling are active areas of research because of their relevance to understanding operative processes in complex porous medium systems that were previously impossible to observe. The macroscale is a scale for which a point is associated with some averaged properties of an averaging region comprising all phases, interfaces, and common curves present in the system. Notions such as volume fraction and specific interfacial area arise when a system is represented at the macroscale in terms of averaged measures of the state of the system. These additional measures are quantities that must be determined in the model solution process. Because of historical limitations on both computational and observational data, the macroscale has been the traditional scale at which models of natural porous media systems have been formulated and solved Closure relations at this scale are needed to yield well-posed models. Traditionally, these closure relations have been posited empirically and parameter estimation has been accomplished based upon relatively simple laboratory experiments. In general, traditional macroscale models, while the dominant class of model, suffer from several limitations related to the way in which such models are formulated and closed (Gray and Miller, 2014). A precise coupling between these disparate length scales has usually been ignored.

As efforts to model and link hydrologic elements in models advance, the ability to address scales effectively will become essential. For porous media, methods such as averaging, mixture theory, percolation theory, and homogenization have been employed to transform governing system equations from smaller to larger length scales (Hornung, 1997; Panfilov, 2000; Cushman, 1997). The goal of such approaches is to transform small-scale data to a larger scale such that it can be used to inform models that have been obtained by consistent transformation of conservation and balance equations across scales.

Averaging procedures have been used for analysis of porous media for approximately 50 years (e.g., Bear, 1972; Anderson and Jackson, 1967; Whitaker, 1986, 1999; Marle, 1967). The methods of averaging can be applied to single-fluid-phase systems as well as to multiphase systems. Success in the development of averaging equations for single-fluid-phase porous media to obtain equations such as Darcy's Law has been achieved (e.g., Bachmat and Bear, 1964; Whitaker, 1967; Gray and O'Neill, 1976). These instances did not so much derive a flow equation as show that a ~~desired~~ commonly used flow equation could be obtained using averaging theorems and appropriate assumptions. Thus, these early efforts did not contribute significantly to objective development of flow equations that seek to capture important physical processes. They do serve to provide a systematic framework for developing larger scale equations. Work for two or more fluid phases in porous media has proven to be more difficult and has not been as illuminating.

The problems associated with trying to model multiple fluid phases in porous media include: (1) difficulties in properly accounting for interface properties, (2) lack of definition of macroscale intensive thermodynamic variables, (3) failure to account for system kinematics, and (4) challenges representing other important physical phenomena explicitly, such as contact angles and common curve behavior. These four difficulties sometimes impact the system description in combination.

Multiple-fluid-phase porous media differ from a single-fluid-phase porous medium system by the presence of the interface between the fluids. This interface is different from a fluid-solid interface because of its dynamics. The total amount of solid surface is roughly constant, or is slowly varying, for most natural solid materials. The fluid-fluid specific interfacial area changes in response to flow in the system and redistribution of phases. The time scale of this change is between that of the pore diameter divided by flow velocity and that of pore diameter divided by solid phase movement. These specific interfacial areas are important for their extent, surface tension, and curvature. They are the location where capillary forces are present. Thus, a physically consistent model must account for mass, momentum, and energy conservation at the interfaces; a model concerned only with phase behavior cannot ~~be successful~~represent capillary pressure in a mechanistically high-fidelity fashion (Gray et al., 2015). This ~~failure~~shortcoming is evidenced, in part, by multi-valuedness when capillary pressure is proposed to be a function only of saturation (Albers, 2014).

Intensive variables that are introduced at the macroscale without consideration of microscale precursor values are also poorly defined. For example, a range of procedures for averaging microscale temperature can be employed that will lead to different macroscale values unless the microscale temperature is constant over the averaging region. Thus, mere speculation that a macroscale value exists fails to identify how or if this value is related to unique microscale variables and most certainly does not relate the macroscale variable to microscale quantities. The absence of a theoretical relation makes it impossible to reliably relate microscale measurements to larger scale representations (Essex et al., 2007; Maugin, 1999). Further confusion arises when pressure is proposed directly at the macroscale. Microscale capillary pressure is related to the curvature of the interface

between fluid phases and does not depend on the pressures in the two phases themselves. At equilibrium, microscale capillary pressure becomes equal to the difference between phase pressures at the interface. Proposed representations of macroscale capillary pressure~~proposals~~ often specify that the capillary pressure is equal to the difference in some directly presumed quantities known as macroscale pressures of phases. ~~and thus~~These representations ignore both interface curvature and the fact that only when evaluated at the interface is the phase pressure ~~important~~useful for describing equilibrium capillary pressure. This is especially problematic when boundary pressures in an experimental cell are used to compute a so called "capillary pressure." Note that under these common experimental conditions, regions of entrapped non-wetting phase are not in contact with the non-wetting fluid that is observed on the boundary of the system.

The importance of kinematics is recognized, at least implicitly, in modeling many systems at reduced dimensionality or when averaging over a region the system occupies. For example, in the derivation of vertically integrated shallow water flow equations, a kinematic condition on the top surface is imposed based on the condition that no fluid crosses that surface (Vreugdenhil, 1995). Macroscale kinematic equations for interfaces between fluids in the absence of porous media have been proposed in the context of boiling (Kocamustafaogullari and Ishii, 1995; Ishii et al., 2005). Despite the fact that interface reconfiguration has an important role in determining the properties and behavior of a multifluid porous medium system, attention to this feature is extremely limited (Gray and Miller, 2013; Gray et al., 2015). In some cases, models of two-fluid-phase flow in porous media have been proposed that do not account for either system kinematics ~~and also do not properly account~~or for interfacial stress (e.g. Niessner et al., 2011). Both are necessary components of physically realistic, high fidelity models.

The mixed success in posing appropriate theoretical models, making use of relevant data, and harnessing effective computer power to advance understanding of hydrologic systems is attributable to the inherent difficulty of each of these scientific activities. For progress to be made in enhancing understanding, a significant hurdle must be navigated that requires consistency among these three approaches and within each approach individually. We have found that by performing complementary microscale experimental and computational studies, we have formed a basis for being able to upscale data spatially with insights into the operative time scales for the system (Gray et al., 2015). The small-scale data supports our quest for larger scale closure relations and eliminates confusion about concepts such as capillary pressure as a state function and dynamic processes that cause changes in the value of capillary pressure. Key to being able to develop faithful models are consistent scale change of thermodynamic relations and implementation of appropriate kinematic relations. The approach of combining sound theory, modern experimental techniques, and advanced computational techniques to the study of environmental systems has applicability not only for the porous media systems emphasized here but also for large scale systems with interacting atmospheric, surface, and subsurface elements.

4 Theory

An important aspect of the issues of concern in this work is related to the various ways in which capillary pressure can be measured and the consequences of using traditional approaches that observe fluid pressures on the boundary of an experimental cell and approximate the capillary pressure based upon the difference between the non-wetting phase pressure and the wetting

phase pressure. However, even alternative approaches such as those based upon measurements using microtensiometers cannot resolve the issues of concern identified in this work. The differences among approaches are important, and commonly used approaches are flawed. In the formulation that follows, we show how microscale pressures can be averaged in a variety of ways as well as the relationship of these averaged pressures to the true capillary pressure. We note that averaging of pressures is inherent in the formulation of macroscale models; and indeed measurement devices themselves provide averages over a length scale depending upon the device. The issues related to averaging cannot be avoided.

Direct upscaling can be performed based on microscale information, providing an opportunity to explore aspects of macroscale system behavior that have previously been overlooked. Underpinning this exploration is the precise definition of macroscale quantities. TCAT models are derived from first-principles starting from the microscale. At the macroscale, important quantities such as phase pressures, specific interfacial areas, curvatures, and other averaged quantities are defined unambiguously based on the microscale state (e.g. Gray and Miller, 2014). For two-fluid-phase flow we consider the wetting phase (w), the non-wetting phase (n), and the solid phase (s) within a domain Ω. Each phase occupies part of the domain, Ω_α, where $\alpha = \{w, n, s\}$. The intersection between any two phases is an interface. The three interfaces are denoted by Ω_{wn} Ω_{ws}, and Ω_{ns}. Finally, the common curve Ω_{wns} is defined by the juncture of all three phases. The TCAT two-phase model is developed based on averaging with the complete set of entities, with the index set $\mathcal{J} = \{w, n, s, wn, ws, ns, wns\} = \mathcal{J}_P \cup \mathcal{J}_I \cup \mathcal{J}_C$ chosen to include all three phases $\mathcal{J}_P = \{w, n, s\}$, the interfaces $\mathcal{J}_I = \{wn, ws, ns\}$, and the common curve $\mathcal{J}_C = \{wns\}$. Based on this, the pore space is defined as the union of the domains for the two fluids $\mathcal{D}_f = \Omega_w \cup \Omega_n$.

Macroscale quantities can be determined explicitly from microscale information based on averages. In this work, the form for averages is

$$\left\langle P \right\rangle_{\alpha,\beta} = \frac{\int_{\Omega_\alpha} P d\mathbf{r}}{\int_{\Omega_\beta} d\mathbf{r}} \,, \tag{1}$$

where P is the microscale quantity being averaged. The domains for integration can be the full domain Ω, the entity domains Ω_α for $\alpha \in \mathcal{J}$, or their boundary Γ_α. The boundary of an entity can be further sub-divided into an internal component $\Gamma_{\alpha i}$ and an external component $\Gamma_{\alpha e}$, which together yield $\Gamma_\alpha = \Gamma_{\alpha i} \cup \Gamma_{\alpha e}$. The external boundary is simply $\Gamma_{\alpha e} = \Omega_\alpha \cap \Gamma$.

The volume fractions, specific interfacial areas, and specific common curve length are each extent measures that can be formulated as

$$\epsilon^{\overline{\overline{\alpha}}} = \left\langle 1 \right\rangle_{\Omega_\alpha,\Omega} \,. \tag{2}$$

The volume fractions correspond to $\alpha \in \mathcal{J}_P$; specific interfacial areas correspond to averaging over a two-dimensional interface for $\alpha \in \mathcal{J}_I$; and the specific common curve length corresponds to averaging over a one-dimensional common curve for $\alpha = wns$. The system porosity, ϵ, is directly related to the solid phase volume fraction by

$$\epsilon = 1 - \epsilon^{\overline{\overline{s}}} \,. \tag{3}$$

The wetting phase saturation, $s^{\overline{\overline{w}}}$, can also be expressed in terms of the extent measures,

$$s^{\overline{\overline{w}}} = \frac{\epsilon^{\overline{\overline{w}}}}{1 - \epsilon^{\overline{\overline{s}}}} = \frac{\epsilon^{\overline{\overline{w}}}}{\epsilon} \,. \tag{4}$$

At the macroscale, various averages arise for the fluid pressures. For flow processes, the relevant quantity is an intrinsic average of the microscale fluid pressure, p_α, expressed as

$$p^\alpha = \left\langle p_\alpha \right\rangle_{\Omega_\alpha, \Omega_\alpha} \tag{5}$$

for $\alpha \in \mathcal{J}_f$, which is the index set of fluid phases. In most laboratory experiments phase pressures are measured at the boundary~~, since it is not practical to insert pressure transducers within the sample~~. Pressure transducers can be placed within a domain at pre-selected locations, which still does not provide a dense, non-intrusive measure of fluid pressure at all locations, including along interfaces. The associated average pressure for the intersection of the boundary of the phase with the exterior of the domain is

$$p_\alpha^\Gamma = \left\langle p_\alpha \right\rangle_{\Gamma_{\alpha e}, \Gamma_{\alpha e}} , \tag{6}$$

for $\alpha \in \mathcal{J}_f$.

The capillary pressure of the two-fluid-phase system depends on the curvature of the interface between the fluids. The curvature of the boundary of phase β is defined at the microscale as

$$J_\beta = \nabla' \cdot \mathbf{n}_\beta , \tag{7}$$

where $\nabla' = (\mathbf{I} - \mathbf{n}_\beta \mathbf{n}_\beta) \cdot \nabla$ is the microscale divergence operator restricted to a surface, and $\mathbf{n}_\beta$ is the outward normal vector from the β phase. Since the internal boundary is an interface, the curvature of a phase boundary is also the curvature of the interface between phases for locations within the domain. At the microscale, the capillary pressure is defined at the interface between fluid phases as

$$p_{wn} = -\gamma_{wn} J_w , \tag{8}$$

where γ_{wn} is the interfacial tension of the wn interface. Laplace's law is a microscale balance of forces acting on an interface that relates the capillary pressure to the difference between the microscale phase pressures evaluated at the interface with

$$p_n - p_w = -\gamma_{wn} J_w . \tag{9}$$

It is important to understand that Laplace's law applies at points on the wn interface only at equilibrium; the definition of capillary pressure given by Eq. 8 applies even when the system is not at equilibrium. Additionally, if the mass per area of the interface is non-zero, Laplace's law must be modified to account for gravitational effects (Gray and Miller, 2014). Care must be taken when extending this relationship to the macroscale, as is shown below.

Since the capillary pressure is defined for the interface between the two fluids, Ω_{wn}, we consider an average of the microscale curvature based on this entity

$$J_w^{wn} = \left\langle J_w \right\rangle_{\Omega_{wn}, \Omega_{wn}} = -\left\langle J_n \right\rangle_{\Omega_{wn}, \Omega_{wn}} . \tag{10}$$

Similarly, the macroscale capillary pressure is

$$p^{wn} = -\left\langle \gamma_{wn} J_w \right\rangle_{\Omega_{wn},\Omega_{wn}} . \tag{11}$$

The case of a constant interfacial tension at the microscale allows for

$$p^{wn} = -\gamma^{wn} J_w^{wn} . \tag{12}$$

In the context of Eq. 9 a third pressure of interest for two-fluid-phase systems is the interface-averaged pressure

$$p_\alpha^{wn} = \left\langle p_\alpha \right\rangle_{\Omega_{wn},\Omega_{wn}} , \tag{13}$$

for $\alpha \in \mathcal{J}_f$. A macroscale version of Laplace's law can then be written as

$$p_n^{wn} - p_w^{wn} = -\gamma^{wn} J_w^{wn} . \tag{14}$$

At equilibrium, Laplace's microscale law will hold everywhere on Ω_{wn}. This implies that Eq. 14 must also be satisfied at equilibrium for the case of a constant interfacial tension. However, measurements of p_w^{wn} and p_n^{wn} must be performed at the interface Ω_{wn}. This is not practical, and perhaps not even useful since neither quantity appears in macroscale models. At the macroscale, it is most convenient to work in terms of averaged phase pressures p^w and p^n. ~~Since~~Because p^α and p_α^{wn} are not equivalent, the way in which Eq. 14 can be used is in question. In this work, we explore this dilemma, giving special consideration to the connectivity of the wetting phase.

In previously published work, we have considered the impact of non-wetting phase connectivity in detail (McClure et al., 2016b). The connectivity-based analysis presented in that work can be used to re-cast Eq. 14 in terms of the connected wetting phase regions. These ~~connected wetting phase~~ regions are identified by sub-dividing Ω_w into N_w sub-regions that do not intersect. The sub-regions cannot touch each other, meaning that $\overline{\Omega}_{w_i} \cap \overline{\Omega}_{w_j} = \emptyset$ for all $i \neq j$ with $i, j \in \{1, 2, \ldots N_w\}$ where the overbar on Ω denotes a closed domain that includes explicitly the boundary. Interfacial sub-regions are formed from the intersection $\Omega_{w_i n} = \Omega_{wn} \cap \overline{\Omega}_{w_i}$. When the non-wetting phase is fully connected, an approximate version of Laplace's law can be derived as

$$p^n - p^{w_i} = -\gamma^{wn} J_w^{w_i n} , \tag{15}$$

for $i \in \{1, 2, \ldots, N_w\}$. This expression relates the average phase pressures within each region of wetting phase to the curvature of the adjoining interface. The average phase pressures are defined as

$$p^{w_i} = \left\langle p_w \right\rangle_{\Omega_{w_i},\Omega_{w_i}} , \tag{16}$$

and the average curvature as

$$J_w^{w_i n} = \left\langle J_w \right\rangle_{\Omega_{w_i n},\Omega_{w_i n}} . \tag{17}$$

The quantities p^{w_i} and $J_w^{w_i n}$ are averaged quantities, but they are not macroscale quantities. The macroscale pressure of the wetting phase can be determined as

$$p^w = \frac{1}{\epsilon^{\overline{\overline{w}}}} \sum_{i=1}^{N_w} \epsilon^{\overline{\overline{w_i}}} p^{w_i} \,, \tag{18}$$

and the macroscale capillary pressure is

$$p^{wn} = -\frac{\gamma^{wn}}{\epsilon^{\overline{\overline{wn}}}} \sum_{i=1}^{N_w} \epsilon^{\overline{\overline{w_i n}}} J_w^{w_i n} \,. \tag{19}$$

For the case where multiple disconnected sub-regions are present for either phase, the relationship between $p^n - p^w$ and p^{wn} is therefore quite complex from a geometric standpoint. Associated challenges for the measurement of phase pressures impact our understanding of the system behavior at the macroscale, hindering our ability to develop effective models.

~~From the~~The definitions of pressures provided ~~it is clear~~demonstrate that several different pressures are of interest for two-fluid systems. In general these pressures will not be equivalent. Thus care is needed in analyzing the system state and in proposing relations among pressures. ~~In general~~Typically only the pressure defined by Eq. 6 is ~~typically~~ measured in traditional laboratory experiments, and this is often true even with state-of-the-science experiments that include high-resolution imaging. On the other hand, computational approaches provide a means to compute all of the defined pressures, yielding a basis to deduce a more complete understanding of the macroscale behavior of the system than would be accessible using approaches that are only able to control and observe fluid pressures on the boundaries of the domain. Further, the formulation detailed above applies for dynamic conditions as well as equilibrium or steady state conditions except where specifically noted. For dynamic conditions, the averaged quantities are computed at some instant in time.

5 Materials and Methods

5.1 Experimental Design

An experimental approach was sought to investigate the distribution of capillary pressure in a porous medium system. To meet the objectives of this work, we needed directly to observe capillary pressure at high resolution, which requires computation of the average curvature of the fluid-fluid interface as a function of the averaging region. Because we wished to observe systems at true equilibrium and knew from recent experience that extended periods of time are necessary to obtain such a state (Gray et al., 2015), we elected to rely upon a microfluidic approach for which we could verify true equilibrium states were achieved. Microfluidic devices are physically small but can be made sufficiently large to satisfy the conditions for being a valid macroscale REV. This is so because the systems are well above the microscale continuum limit and then only need to satisfy the conditions for the size being a representative sampling of the pore morphology and topology of the media. The size needed for an REV has been investigated previously for two-fluid-phase flow. Typically in three-dimensions a few thousand spheres is needed to produce essentially invariant information for quantities such as saturations, interfacial areas, and capillary pressure. This translates to slightly over 10 mean grain diameters in each dimension. Microfluidic cells can be fashioned to

meet this requirement. Even though hydrologic problems motivate this work, the fundamental nature of the capillary pressure state function can be investigated with any pair of immiscible fluids. Minimizing the mutual solubilities of each fluid in the companion fluid is an important design characteristic that can simplify the experimental work without loss of generality. Thus physically small microfluidic systems that did not include water were used in this work, which might on the surface appear to be far removed from the motivating hydrologic systems of concern.

~~Two-fluid flow experiments~~Experiments involving two-fluid flow through porous media are typically conducted using a setup similar to the one shown in Fig. 1. A porous material, in this case a two-dimensional micromodel cell, is connected to two fluid reservoirs at opposite ends of the sample. The two fluids are referred to as wetting (w) and non-wetting (n) based on the relative affinity of the fluids toward the solid phase (s, the black region of Fig. 1). The two-dimensional micromodel was fabricated using photolithography techniques. The 500 μm $\times$ 525 μm $\times$ 4.4 μm porous medium cell of the micromodel contained a distribution of cylinders, with a porosity of 0.54. The short dimension of the cell was oriented in the vertical dimension such that flow was essentially horizontal. The boundary reservoirs were used to inject fluid into the sample, resulting in the displacement of one fluid by the other. As depicted in Figure 1, one inlet of the cell was connected to a wetting-fluid-phase (decane) reservoir and the other to a non-wetting-fluid-phase (nitrogen gas) reservoir, with the other four boundaries being solid. A displacement experiment was performed in the micromodel depicted in Fig. 1 using the experimental methods detailed in Dye et al. (2015). This approach provides observations of equilibrium configurations of the two-fluid-phase system. The displacement experiment began by fully saturating the porous medium cell with decane through the inlet reservoir located at one end of the cell. Primary drainage was then carried out by incrementally increasing the pressure of the nitrogen reservoir, located on the opposite end of the cell. After each pressure step, the system was allowed to equilibrate. The final equilibrium state for a given pressure boundary condition was determined based ~~on~~ on an invariance of the average mean curvature of the wn interface, J_w^{wn}, as determined from image analysis. After the system reached an equilibrium state, the pressure in each reservoir, measured with pressure tranducers, and an image of the cell were recorded before another incremental change in pressure step was applied. The drainage process was terminated prior to nitrogen breakthrough into the decane reservoir.

The solid geometry used in our microfluidic experiments was designed to allow for high capillary pressure at the end of primary drainage. At the wetting-fluid-phase reservoir, a layer of evenly spaced homogeneous cylinders was placed such that the gap between cylinders was uniformly small. This allowed for a large pressure difference between the fluid reservoirs, since the non-wetting fluid phase did not penetrate the wetting-fluid-phase reservoir over a wide range of pressure differences.

5.2 Computational Approach

The experimental microfluidics setup described in the previous section provides a way to perform traditional two-fluid-flow experiments and observe the internal dynamics of interface kinematics and equilbrium distributions. Microscale phase configurations can be observed directly, and averaged geometric measures can be obtained from this data. While boundary pressure values are known, the experiment does not provide a way to measure the microscale pressure field. Accurate computer simulation of the experiment can provide this information and can also be used to generate additional fluid configurations that may not be accessible experimentally. In particular, configurations below the so-called irreducible wetting phase saturation

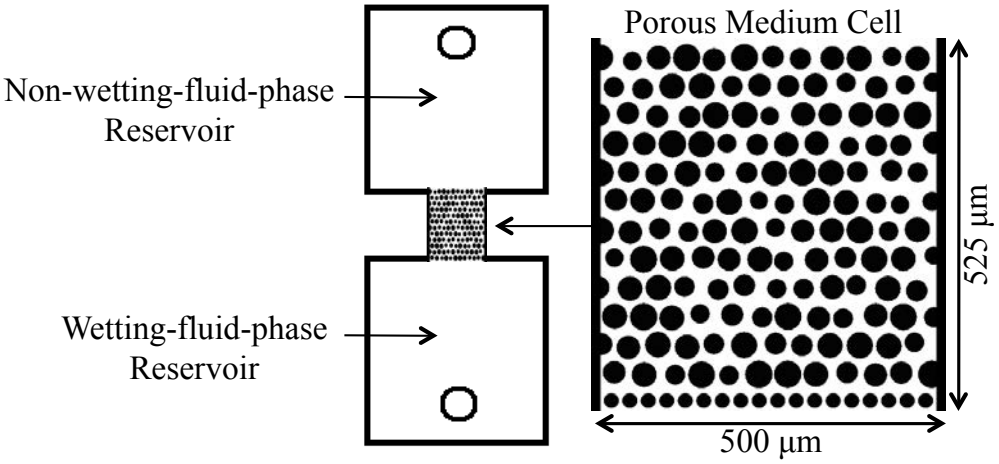

Figure 1. A depiction of the two-dimensional micromodel that was used in the displacement experiment. The solid is represented by black and the regions accessible to fluid flow by white within the porous medium cell.

will be considered. The common identification of a saturation as “irreducible" is a misnomer because wetting phase saturations beneath this value can be achieved through, for example, evaporation or by initializing a saturation below this value in an experimental setup. In this work, simulation is applied in two contexts: (1) to simulate the microscale pressure field based on experimentally-observed fluid configurations; and (2) to simulate two-fluid equilibrium configurations based on random initial conditions. Success with the first set of simulations in matching the experiments provides confidence that the results of the second set of computations represent physically reasonable configurations. Here we summarize each of the approaches.

Simulations are performed using a “color" lattice Boltzmann method (LBM). Our implementation has been described in detail in the literature (see McClure et al., 2014a, b). The approach relies on a multi-relaxation time (MRT) scheme to model the momentum transport. In the limit of low Mach number, the implementation recovers the Navier-Stokes equations with additional contributions to the stress tensor in the vicinity of the interfaces. The interfacial stresses between fluids result from capillary forces, which play a dominant role in many two-fluid porous medium systems. The formulation relies on separate lattice Boltzmann equations (LBEs) to recover the mass transport for each fluid. This decouples the density from the pressure to allow for the simulation of incompressible fluids. Our implementation has been applied to simulate two-fluid-phase flows in a variety of porous medium geometries, recovering the correct scaling for common curve dynamics (McClure et al., 2016a), and it has also been used to closely predict experimental fluid configurations (Dye et al., 2015; Gray et al., 2015). The effect of gravity was ignored in the simulation of the experimental systems due to the very small length scale in the vertical dimension.

The implementation allows us to initialize fluid configurations directly from experimental images. Segmented images are generated from grey-scale camera data. These images were used to specify the initial position of the phases in the simulations with high resolution. The micromodel cell was computationally resolved within a domain that is $20 \times 500 \times \times 500$. The lattice spacing for the simulation was $\delta x = 1$ μm. ~~Note that additional resolution was used to resolve the depth of the micromodel~~

~~cell.~~Note that the depth of the micromodel was resolved in the simulation. The physical depth of the simulation cell (20 μm) was larger than the depth of the micromodel cell (4.4 μm). This was done so that the curvature in the depth of the cell could be resolved accurately. Due to geometric constraints, the curvature associated with the micromodel depth cannot vary. The curvature of the interface between the two fluids can be written as

$$J_w = -\left(\frac{1}{R_1} + \frac{1}{R_2}\right) , \tag{20}$$

where R_1 is the radius of curvature in the horizontal plane and R_2 is associated with the micomodel depth. Only R_1 can vary independently. In the simulation, the fixed value of R_2 was 10 μm. In the experiment, the fixed value of R_2 was 2.2 μm. With R_2 known in both cases, the simulated curvatures were mapped to the experimental system. In the experimental system, pressure transducers were used to measure the phase pressures in the boundary reservoirs. These measurements were used to inform pressure boundary conditions within the simulation. Since boundary conditions were enforced explicitly within the simulation, the boundary pressures match the experimentally measured values exactly. The fluid configurations can vary independently based on these conditions. Simulations were performed until the interfacial curvature stabilized, since prior work has demonstrated the important fact that the curvature equilibrates more slowly ~~compared to~~than other macroscale quantities, such as fluid saturation Gray et al. (2015).

A set of simulations was also performed based on random initial conditions. The approach used to generate random fluid configurations and associated equilibrium states is described in detail by McClure et al. (2016b). The solid configuration for the flow cell was identical for both sets of simulations. Blocks of fluid were inserted into the system at random until a desired fluid saturation was obtained. This allowed for the generation of fluid configurations at wetting phase saturations that were below the experimentally-determined, so-called irreducible wetting-phase saturation. Periodic boundary conditions were then enforced, and the simulation was performed to produce an equilibrium configuration as determined by the average curvature of the interface between fluids. Based on the final fluid configurations, connectivity-based analysis was performed to infer macroscale capillary pressure, saturation, and interfacial area for a dense set of equilibrium states.

5.3 Results and Discussion

Phase connectivity presents a critical challenge for the theory and simulation of two-fluid-phase flow. When all or part of a phase forms a fully-connected pathway through a porous medium, flow can occur without the movement of interfaces. However, the case where phase sub-regions are not connected is a source of history-dependent behavior in traditional models. Traditional models ~~predict~~make use of the capillary pressure proposed as a function of the fluid saturation only, $p^c(s^{\overline{\overline{w}}})$. However, this relationship is not unique. Furthermore, key features of the relationship are an artifact of the experimental design. For example, the irreducible wetting phase saturation, $s_I^{\overline{\overline{w}}}$, can play an important role.

To calculate p^w as it is defined from Eq. 5, the microscale pressure field must be known throughout the domain. Simulation provides a means to study how the pressure varies within the system and to obtain averages within all phase sub-regions. Based on Eq. 16, values of p^{w_i}, $J_w^{w_i n}$ and $\epsilon^{\overline{\overline{w_i}}}$ can be determined for each connected region of the wetting phase Ω_{w_i} for $i \in \{1, 2, \ldots, N_w\}$. Two sets of simulations were performed, including (1) a set of 24 configurations initialized directly from

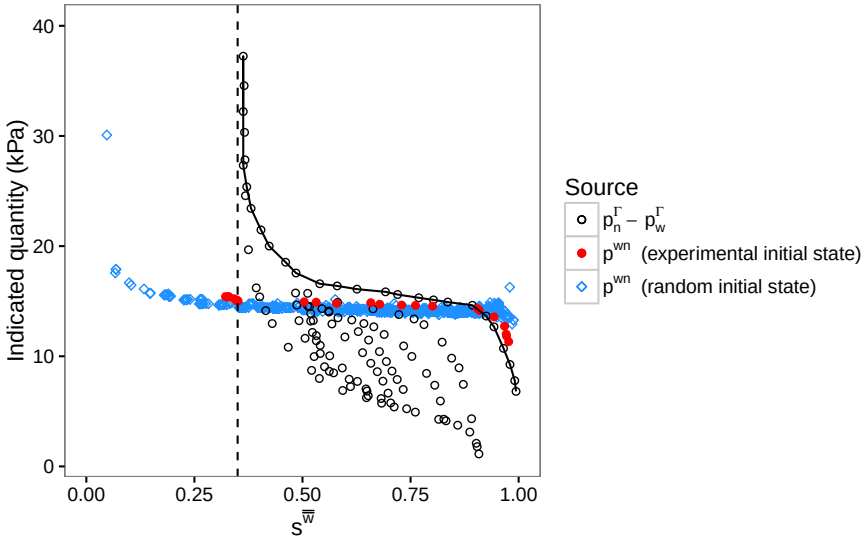

Figure 2. Comparison between the experimentally measured boundary pressure difference $p_n^\Gamma - p_w^\Gamma$ and the capillary pressure p^{wn} for the micromodel geometry. The solid line represents the boundary pressure along primary drainage.

experimentally-observed configurations along primary drainage; and (2) a set of 48 configurations with random initial conditions as discussed in Section 5.2. The ~~final~~equilibrium fluid arrangements were analyzed to determine the true capillary pressure, p^{wn}, by analyzing the curvature of the fluid-fluid interface, fluid saturation, $s^{\overline{w}}$, and specific interfacial area, $\epsilon^{\overline{wn}}$. The data was aggregated to produce a dense set of equilibrium configurations.

Pressure transducers located in each of the two fluid reservoirs were used to measure experimental boundary pressures for each fluid. The resulting values of $p_n^\Gamma - p_w^\Gamma$ are plotted in Fig. 2. Average capillary pressure values calculated from the simulations are presented along with this experimental data. The solid line represents the boundary pressure difference during primary drainage. The boundary pressures for simulations initialized from experimental data matched the experimentally measured values of $p_n^\Gamma - p_w^\Gamma$ exactly. Boundary measurements taken during simulation are also presented for imbibition and scanning curve sequences. The values of $p_n^\Gamma - p_w^\Gamma$ plotted in Fig. 2 represent a comprehensive set of experimental measurements that would typically be identified as capillary pressure values. This provides a basis for comparison with measurements of the true capillary pressure based on the configuration of the interfaces. In general, agreement between $p_n^\Gamma - p_w^\Gamma$ and p^{wn} should not be expected. Only when both the w and n fluids are fully connected and when the system is at equilibrium will the boundary pressure difference balance the internal average capillary pressure. The difference between the boundary measurement and the internal average capillary pressure due to the phases being disconnected is evident by comparing the experimental data from primary drainage and the simulation points initialized from the associated fluid configurations. Pressure boundary conditions for the simulations were set to match the measured values of p_n^Γ and p_w^Γ. As $s^{\overline{w}}$ decreases, there is an increasing gap between

$p_n^\Gamma - p_w^\Gamma$ and the average capillary pressure p^{wn}. This gap is attributed to the formation of disconnected wetting phase regions during drainage, an effect that is most significant as the so-called irreducible wetting phase saturation is approached.

In the experimental system, ~~the~~an irreducible wetting phase saturation was clearly observed as $s_I^{\overline{\overline{w}}} = 0.35$. This value is marked with a vertical dashed line in Fig. 2. This irreducible wetting phase saturation corresponds to the lowest experimentally accessible wetting phase saturation, since fluid configurations with $s^{\overline{\overline{w}}} < s_I^{\overline{\overline{w}}}$ cannot be obtained from the experimental setup and operating conditions. The underlying reason for this is related to the connectivity of the wetting phase. This can be understood from Fig. 3, which shows the phase configuration observed experimentally at the end of primary drainage. Within a connected region of wetting phase, the microscale pressure, p_w, will tend to be nearly constant. However, the wetting phase pressure can vary from one region to another. The connected components of the wetting phase are shown in Fig. 3 (b). At equilibrium, the measured difference in boundary pressures $p_n^\Gamma - p_w^\Gamma$ must balance with the capillary pressure of the interface sub-region between the two phase components. Note that the non-wetting phase is fully connected in Fig. 3 (a). The implication is that $p_n^\Gamma = p^n$ at equilibrium. However, p_w^Γ only reflects the pressure of the wetting phase reservoir. The sub-regions of the wetting phase that remain after primary drainage are plotted in color in Fig. 3 (b). The part of Ω_w that is connected to the wetting phase reservoir is shown in light green in Fig. 3 (b). When the irreducible wetting phase saturation is reached the portion of Ω_w that connects to the reservoir no longer fills any of the porespace within the micromodel. The irreducible wetting-phase saturation is associated with the trapped wetting phase regions only. Changing the pressure difference between the fluid reservoirs to increase $p_n^\Gamma - p_w^\Gamma$ does not change the capillary pressure in these regions. This leads to arbitrarily high measurements, claimed to be "capillary pressure" measurements, which are actually a difference in reservoir pressures rather than a measure of interface curvature. This also misconstrues the reduction in wetting phase saturation that occurs. The true average capillary pressure, as defined in Eq. 12, is much lower. Furthermore, the wetting-phase saturation can be further reduced as a consequence of other processes, such as evaporation. It is irreducible only within the context of the experimental design.

In light of this result, it is useful to consider alternative means to generate two-fluid configurations in porous media. For example, suppose a fluid configuration were encountered with $s^{\overline{\overline{w}}} = 0.2$, a value lower than the irreducible saturation. How can we determine the macroscale capillary pressure? From a traditional macroscale parameterization approach, the experimentally proposed relation $p^{wn}(s^{\overline{\overline{w}}})$ is of absolutely no use, since capillary pressure is undefined for $s^{\overline{\overline{w}}} < s_I^{\overline{\overline{w}}}$. From the microscale perspective, it is clearly possible to produce fluid configurations for which $s^{\overline{\overline{w}}} < s_I^{\overline{\overline{w}}}$ (for any system), and to measure the associated capillary pressure based on Eq. 12. For randomly initialized phase configurations, many such systems are produced. Simulations performed based on these initial geometries lead to equilibrium capillary pressure measurements shown in Fig. 2. While the classic "J curve" shape is still present, the experimentally-determined value $s_I^{\overline{\overline{w}}}$ offers no guidance regarding this form.

Comparing capillary pressures measured from random initial conditions with those measured from experimental initial conditions provides additional insight. First, the true capillary pressure measurements based on Eq. 8 are remarkably consistent, particularly when considering the values of p^{wn} obtained as $s^{\overline{\overline{w}}} \to s_I^{\overline{\overline{w}}}$. Compared to randomly initialized data, configurations from primary drainage have a higher average capillary pressure. This is expected, since along primary drainage p^{wn} is determined by the pore-throat sizes. These represent the highest capillary pressures that are typically observed. We note that primary

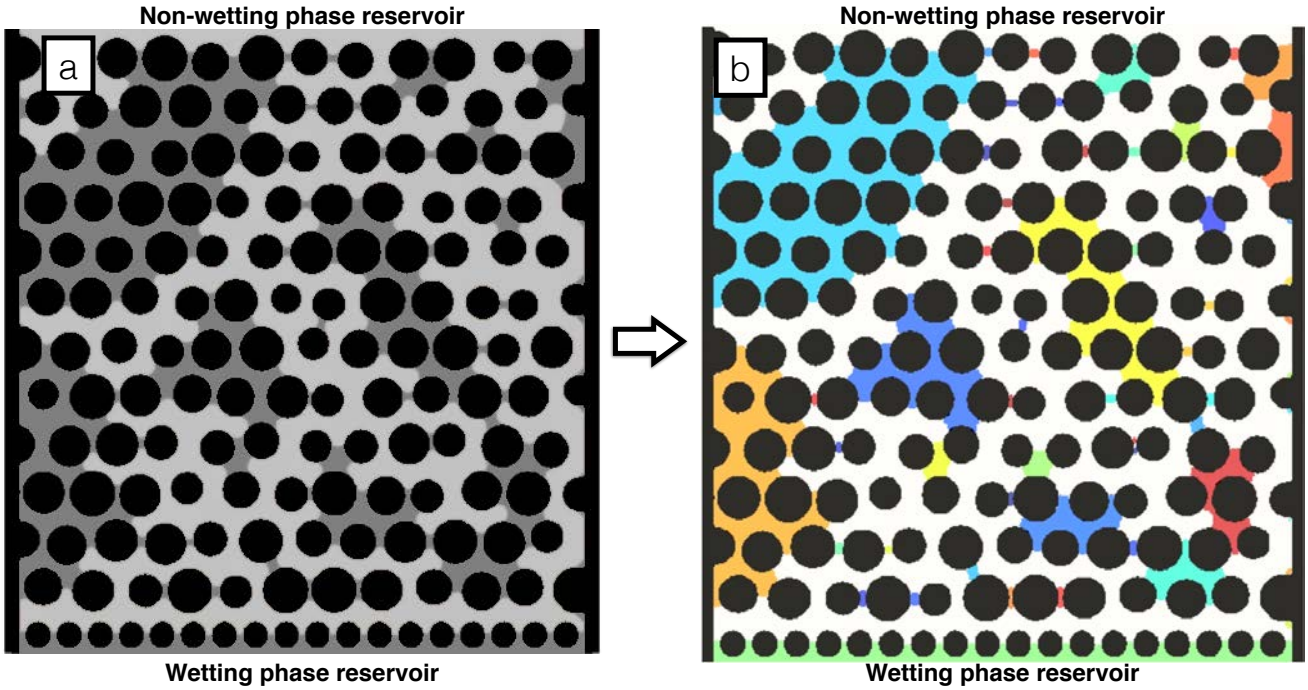

Figure 3. Phase connectivity has a direct impact on the meaning of the macroscale experimental measurements: (a) experimentally observed phase configuration corresponding to irreducible wetting phase saturation; and (b) connected components analysis shows all wetting phase that remains in the system is disconnected from the wetting phase reservoir. The black denotes the solid phase, the gray and various colors denote the wetting phase, and the white denotes the non-wetting phase.

drainage does not specify the maximum possible capillary pressure, since bubbles of non-wetting phase may form that have a smaller radius of curvature than the minimum throat width.

Since the boundary pressure difference $p_n^\Gamma - p_w^\Gamma$ cannot be substituted for the capillary pressure, a key question is how this impacts capillary pressure hysteresis. When $p_n^\Gamma - p_w^\Gamma$ is used to erroneously infer the capillary pressure, the relationship between capillary pressure and saturation appears as the black circles in Fig. 2. When the true capillary pressure is used to plot the same data the shape of the relationship between capillary pressure and saturation is distinctly different. Capillary pressures are obtained at all fluid saturations, and no irreducible wetting-phase saturation is observed. Due to the fact that the true capillary pressure includes the effects of disconnected phase regions, moderate capillary pressures are observed. This is because the extrema for the boundary pressure measurements are not constrained by the internal geometry. We note that the relationship $p^{wn}(s^{\overline{\overline{w}}})$ remains non-unique, since capillary pressure is not a one-to-one relationship with wetting-phase saturation. The higher-dimensional form $p^{wn}(s^{\overline{\overline{w}}}, \epsilon^{\overline{\overline{wn}}})$ is therefore considered in Fig. 4. Using a generalized additive model (GAM) (Wood, 2008), a best-fit surface was generated to approximate the simulated data, incorporating data points derived from both random

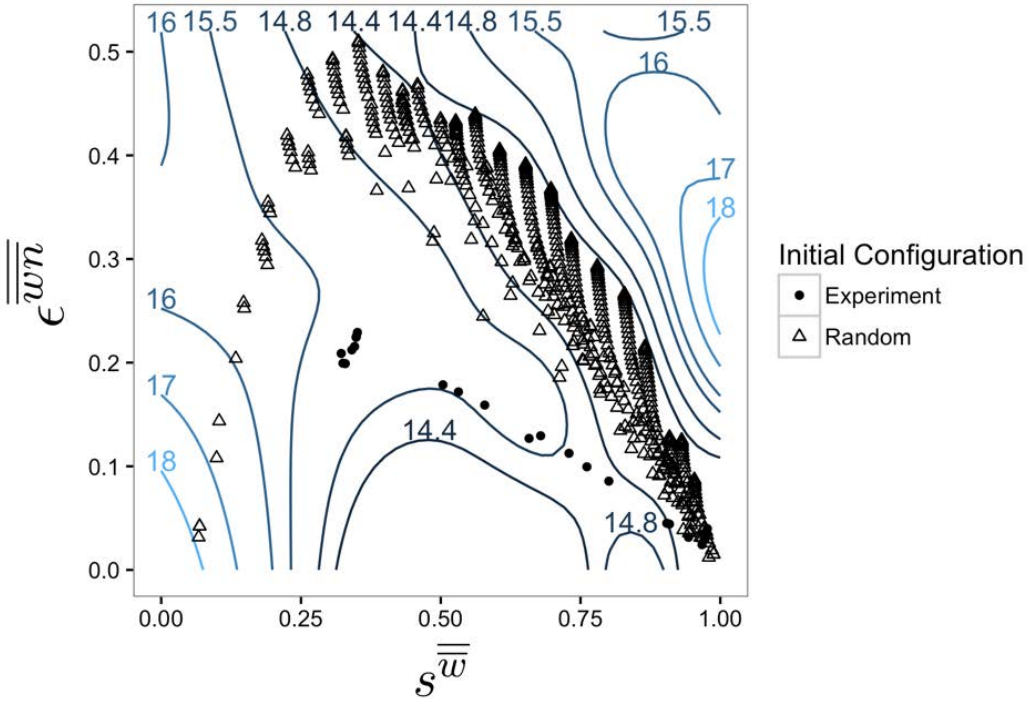

Figure 4. Contour plot showing the relationship $p^{wn}(s^{\overline{w}}, \epsilon^{\overline{\overline{wn}}}$, with ~~the black curves representing constant value of~~ contours showing the capillary pressure p^{wn} (kPa). Data points used to construct the surface are also shown, including randomly initialized fluid configurations ~~(blue)~~ and experimentally initialized configurations from primary drainage ~~(red)~~.

and experimentally-observed initial conditions. The black lines in Fig. 4 show the iso-contours of the capillary pressure surface ~~(p^{wn} is constant along each contour)~~. It is clear that primary drainage leads to states with lower interfacial area as compared to randomly initialized configurations. Both sets of points lie along a consistent surface. The extent to which the relationships $p^{wn}(s^{\overline{\overline{w}}})$ and $p^{wn}(s^{\overline{\overline{w}}}, \epsilon^{\overline{\overline{wn}}})$ describe the data points measured from microscale configurations is quantitatively assessed by evaluating the residuals for the GAM approximation. The residuals are shown in Fig. 5. The traditionally used relationship $p^{wn}(s^{\overline{\overline{w}}})$ is able to explain only 60.6% of the variance in the data. When the effect of interfacial area is included, $p^{wn}(s^{\overline{\overline{w}}}, \epsilon^{\overline{\overline{wn}}})$, 77.1% of the variance is explained. Based on previous work for three-dimensional porous media, it is anticipated that higher fidelity approximations can be produced by including the effects of other topological invariants, such as the average Gaussian curvature or Euler characteristic (McClure et al., 2016b).

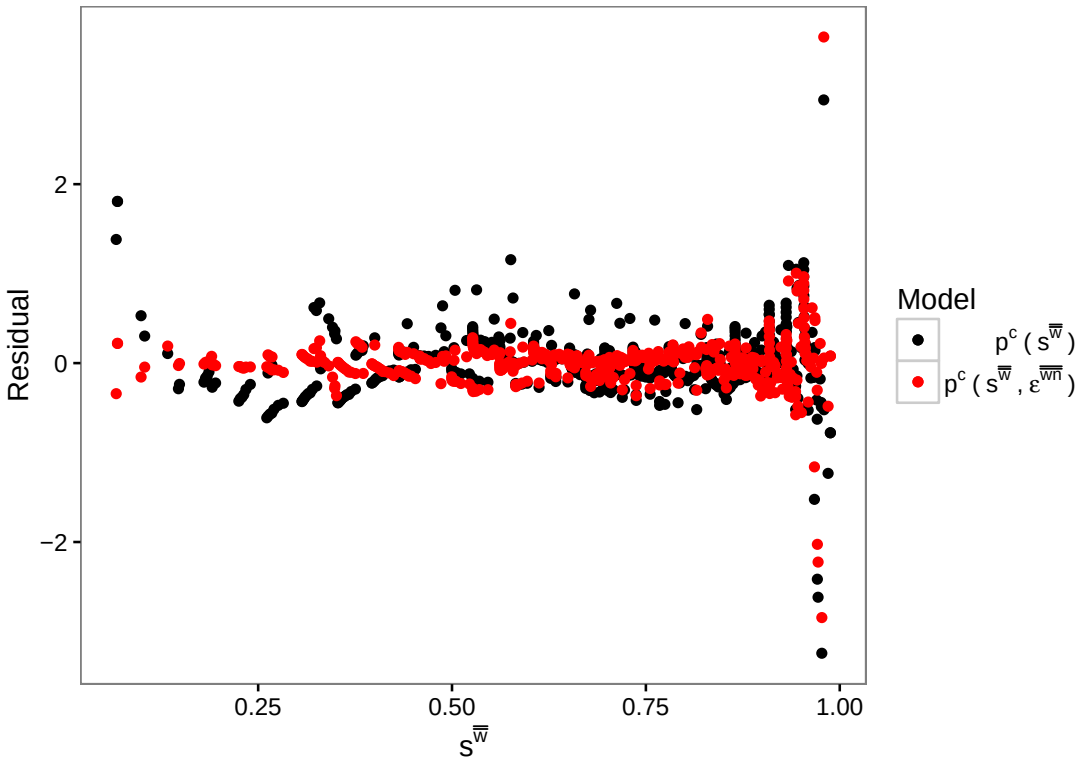

Figure 5. Comparison of the residual errors for the GAM fits that approximate $p^{wn}(s^{\overline{w}})$ and $p^{wn}(s^{\overline{w}}, \epsilon^{\overline{wn}})$.

6 Conclusions

In this work, we show that the ability to quantitatively analyze the internal structure of two-fluid porous medium systems has a profound impact on macroscale understanding. We considered the behavior of the capillary pressure based on traditional laboratory boundary measurements and compare this to the true average capillary pressure, a state function, determined by directly averaging the curvature of the interface between fluids. We demonstrate that the difference between the phase pressures as measured from the boundary cannot be used to deduce the capillary pressure of the system. In particular, the high capillary pressure measured for irreducible wetting phase saturation is an artifact of the experimental design. Four important conclusions result.

First, the true capillary pressure measured at traditionally identified irreducible wetting-phase saturation is significantly lower than predicted from boundary pressure measurements. This can be understood based on the underlying phase connectivity. At irreducible wetting-phase saturation, the wetting-phase reservoir pressure no longer reflects the internal pressure of the system since the reservoir does not connect to the remaining wetting phase inside the system.

Second, randomly generated fluid configurations provide a way to access states where the wetting-phase saturation is below the irreducible wetting phase saturation. By carrying out direct averaging based on these states, the capillary pressure

state function can be ~~studied~~computed over the full range of possible saturation values, including configurations that are inaccessible from traditional experiments. We note that modified experimental designs could be used to accomplish the same ~~objective~~studies.

Third, we show that the equilibrium relationship ~~between~~among capillary pressure, fluid saturation and interfacial area is consistent between randomly initialized configurations used only in computation and experimentally initialized configurations. Combining the two data sets, generalized additive models were used to approximate the surface relating ~~the three quantities~~ p^c, $s^{\overline{\overline{w}}}$, and $\epsilon^{\overline{\overline{wn}}}$. At fixed saturation, states evolved from primary drainage have higher capillary pressure and lower interfacial area than equilibrium states that evolve from randomly generated states. Our results are particularly significant for systems where low wetting-phase ~~configurations~~saturations are important, such as evaporation in the vadose zone.

Author contributions. All authors participated in the writing of this manuscript. WGG and CTM contributed to the introduction, background, and theory, ALD contributed to the microfluidics, and JEM contributed to lattice Boltzmann modeling. All authors contributed to the discussion and conclusions from this work.

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References

Albers, B.: Modeling the hysteretic behavior of the capillary pressure in partially saturated porous media: a review, Acta Mechanica, 225, 2163–2189, 2014.

Alizadeh, A. H. and Piri, M.: The effect of saturation history on three-phase relative permeability: An experimental study, Water Resources Research, 50, 1636–1664, 2014.

Anderson, T. B. and Jackson, R.: A fluid mechanical description of fluidized beds, Industrial and Engineering Chemistry Fundamentals, 6, 527–539, 1967.

Bachmat, Y. and Bear, J.: The General Equations of Hydrodynamic Dispersion in Homogeneous, Isotropic, Porous Mediums, Journal of Geophysical Research, 69, 2561–2567, 1964.

Bauer, P., Thorpe, A., and Brunet, G.: The quiet revolution of numerical weather prediction, Nature, 525, 47–55, 2015.

Bear, J.: Dynamics of Fluids in Porous Media, Elsevier, New York, 1972.

Bernard, P. S. and Wallace, J. M.: Turbulent Flow, John Wiley & Sons, 2002.

Blöschl, G.: Scaling in Hydrology, Hydrological Processes, 15, 709–711, 2001.

Blöschl, G., Grayson, R. B., and Sivapalan, M.: On the representative elementary area (rea) concept and its utility for distributed rainfall-runoff modelling, Hydrological Processes, 9, 313–330, 1995.

Bradshaw, P.: An Introduction to Turbulence and its Measurement, Pergamon Press, 1971.

Chanson, H.: Current knowledge in hydraulic jumps and related phenomena. A survey of experimental results, European Journal of Mechanics B Fluids, 28, 191–210, 2009.

Collins, R., Triplett, C., Barjatya, A., Lehmacher, G., and Fritts, D.: Using lidar and rockets to explore turbulence in the atmosphere, SPIE Newsroom, doi:10.1117/2.1201505.005922, 2015.

Cushman, J. H.: The Physics of Fluids in Hierarchical Porous Media: Angstroms to Miles, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997.

D'Asaro, E. A.: Turbulence in the Upper-Ocean Mixed Layer, Annual Review of Marine Science, 6, 101–115, 2014.

Deems, J. S., Painter, T. H., and Finnegan, D. C.: Lidar measurement of snow depth: a review, Journal of Glaciology, 59, 467–479, 2013.

Dietrich, J. C., Dawson, C. N., Proft, J. M., Howard, M. T., Wells, G., Fleming, J. G., Luettich Jr., R. A., Westerink, J. J., Cobell, Z., Vitse, M., Lander, H., Blanton, B. O., Szpilka, C. M., and Atkinson, J. H.: Real-time forecasting and visualization of hurricane waves and storm surges using SWAN+ADCIRC and FigureGen, in: Computational Challenges in the Geosciences, edited by Dawson, C. and Gerritsen, M., vol. 156 of The IMA Volumes in Mathematics and Its Applications, Springer Science & Business Media, New York, 2013.

Dudhia, J.: A history of mesoscale model development, Asia-Pacific Journal of Atmospheric Science, 50, 121–131, 2014.

Dye, A. L., McClure, J. E., Gray, W. G., and Miller, C. T.: Multiscale modeling of porous medium systems, in: Handbook of Porous Media, edited by Vafai, K., chap. 1, pp. 3–45, CRC Press, third edn., 2015.

Essex, C., McKitrick, R., and Andresen, B.: Does a Global Temperature Exist?, Journal of Non-Equilibrium Thermodynamics, 32, 1–27, 2007.

Flint, L. E., Flint, A. L., Thorne, J. H., and Boynton, R.: Fine-scale hydrologic modeling for regional landscape application: the California Basin characterization model development and performance, Ecological Processes, 2, http://www.ecologicalprocesses.com/content/2/1/25, 2013.

Fuentes, F. C., Iungo, G. V., and Porté-Agel, F.: 3D turbulence measurements using three synchronous wind lidars: Validation against sonic anemometry, Journal of Atmospheric and Oceanic Technology, 31, 1549–1556, 2014.

Gentine, P., Troy, T. J., Lintner, B. R., and Findell, K. L.: Scaling in Surface Hydrology: Progress and Challenges, Journal of Contemporary Water Research & Education, 147, 28–40, 2012.

Gleeson, T. and Paszkowski, D.: Perceptions of scale in hydrology: What do you mean by regional scale?, Hydrological Sciences Journal, doi:10.1080/02626667.2013.797581, 2014.

Gray, W. G. and Miller, C. T.: Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 7. Single-phase megascale flow models, Advances in Water Resources, 32, 1121–1142, doi:10.1016/j.advwatres.2009.05.010, 2009.

Gray, W. G. and Miller, C. T.: A generalization of averaging theorems for porous medium analysis, Advances in Water Resources, 62, 227–237, doi:10.1016/j.advwatres.2013.06.006, 2013.

Gray, W. G. and Miller, C. T.: Introduction to the Thermodynamically Constrained Averaging Theory for Porous Media Systems, Springer-Verlag, 2014.

Gray, W. G. and O'Neill, K.: On the development of Darcy's law for the general equations for flow in porous media, Water Resources Research, 12, 148–154, 1976.

Gray, W. G., Dye, A. L., McClure, J. E., Pyrak-Nolte, L. J., and Miller, C. T.: On the dynamics and kinematics of two-fluid-phase flow in porous media, Water Resources Research, 51, 5365–5381, 2015.

Hermann, S. M. and Sop, T. K.: The map is not the territory: How satellite remote sensing and ground evidence have re-shaped the image of Sahelian desertification, in: The End of Desertification? Disputing Enviornmental Change in the Drylands, edited by Behnke, R. and Mortimore, M., Springer Earth System Sciences, pp. 117–145, Springer, 2016.

Hornung, U.: Homogenization and Porous Media, no. 6 in Interdisciplinary Applied Mathematics, Springer, 1997.

Ishii, M., Kim, S., and Kelly, J.: Development of Interfacial Area Transport Equation, Nuclear Engineering and Technology, 37, 525–536, 2005.

Kauffeldt, A., Halldin, S., Rodhe, A., Xu, C.-Y., and Westerberg, I. K.: Disinformative data in large-scale hydrological modelling, Hydrology and Earth System Sciences, 17, 2845–2857, 2013.

Kauffeldt, A., Wetterhall, F., Pappenberger, F., Salamon, P., and Thielen, J.: Technical review of large-scale hydrological models for implementation in operational flood forecasting schemes on continental level, Environmental Modelling and Software, 75, 68–76, 2016.

Knödel, K., Lange, G., and Voigt, H.-J.: Environmental Geology: Handbook of Field Methods and Case Studies, Springer Berlin Heidelberg New York, 2007.

Kocamustafaogullari, G. and Ishii, M.: Foundation of the interfacial area transport equation and its closure relations, International Journal of Heat and Mass Transfer, 38, 481–493, 1995.

Lillesand, T. M., Kiefer, R. W., and Chipman, J. W.: Remote Sensing and Image Interpretation, Wiley, seventh edn., 2015.

Ly, S., Charles, C., and Degré, A.: Different methods for spatial interpolation of rainfall data for operational hydrology and hydrological modeling at watershed scale. A review, Biotechnology, Agronomy, Society and Environment, 17, 392–406, 2013.

Marle, C.: Ècoulements monophasiques en milieu poreux, Revue de L'Institut Français du Pétrole, 22, 1471–1509, 1967.

Maugin, G. A.: The Thermomechanics of Nonlinear Irreversible Behaviors: An Introduction, World Scientific Press, Singapore, 1999.

McClure, J. E., Berrill, M. A., Gray, W. G. and Miller, C. T.: Tracking Interface and Common Curve Dynamics for Two-Fluid Flow in Porous Media, Journal of Fluid Mechanics, 796, 211–232, 2016a.

McClure, J. E., Berrill, M. A., Gray, W. G. and Miller, C. T.: Influence of phase connectivity on the relationship among capillary pressure, fluid saturation, and interfacial area in two-fluid-phase porous medium systems, Physical Review E, (Accepted), 2016b.

McClure, J. E., Prins, J. F., and Miller, C. T.: A Novel Heterogeneous Algorithm to Simulate Multiphase Flow in Porous Media on Multicore CPU-GPU Systems, Computer Physics Communications, 185, 1865–1874, doi:http://dx.doi.org/10.1016/j.cpc.2014.03.012, 2014a.

McClure, J. E., Wang, H., Prins, J. F., Miller, C. T., and Feng, W.: Petascale Application of a Coupled CPU-GPU Algorithm for Simulation and Analysis of Multiphase Flow Solutions in Porous Medium Systems, in: 28th IEEE International Parallel& Distributed Processing Symposium, Phoenix, Arizona, 2014b.

Miller, C. T., Christakos, G., Imhoff, P. T., McBride, J. F., Pedit, J. A., and Trangenstein, J. A.: Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches, Advances in Water Resources, 21, 77–120, 1998.

Miller, C. T., Dawson, C. N., Farthing, M. W., Hou, T. Y., Huang, J. F., Kees, C. E., Kelley, C. T., and Langtangen, H. P.: Numerical simulation of water resources problems: Models, methods, and trends, Advances in Water Resources, 51, 405–437, doi:10.1016/j.advwatres.2012.05.008, 2013.

Miller, C. T., Christakos, G., Imhoff, P. T., McBride, J. F., Pedit, J. A., and Trangenstein, J. A.: Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches, Advances in Water Resources, 21, 77–120, 1998.

Nickerson, C., Harper, M., Henrie, C. J., Mayberry, R., Shimmin, S., Smith, B., and Smith, J. H.: Sources of Data Providing Land Use and Land Cover Estimates for the U. S., Tech. rep., Interagency Council on Agricultural and Rural Statistics, subcommittee of the Interagency Council on Statistical Policy, https://www.data.gov/media/2013/10/attachments/ICARS%20Land%20Use%20and%20Cover%20data.pdf, 2013.

Niessner, J., Berg, S., and Hassanizadeh, S. M.: Comparison of Two-Phase Darcy's Law with a Thermodynamically Consistent Approach, Transport in Porous Media, 88, 133–148, doi:10.1007/s11242-011-9730-0, 2011.

Paiva, R. C. D., Collischonn, W., and Tucci, C. E. M.: Large scale hydrologic and hydrodynamic modeling using limited data and a GIS based approach, Journal of Hydrology, 406, 170–181, 2011.

Panfilov, M.: Macroscale Models of Flow Through Highly Heterogeneous Porous Media, Springer, 2000.

Pechlivanidis, I. G., Jackson, B. M., McIntyre, N. R., and Wheater, H. S.: Catchment scale hydrological modelling: A review of model types, calibration approaches and uncertainty analysis methods in the context of recent developments in technology and applications, Global NEST Journal, 13, 193–214, 2011.

Reggiani, P., Sivapalan, M., and Hassanizadeh, S. M.: A Unifying Framework for Watershed Thermodynamics: Balance Equations for Mass, Momentum, Energy and Entropy, and the Second Law of Thermodynamics, Advances in Water Resources, 22, 367–398, 1998.

Reggiani, P., Hassanizadeh, S. M., Sivapalan, M., and Gray, W. G.: A Unifying Framework for Watershed Thermodynamics: Constitutive Relationships, Advances in Water Resources, 23, 15–39, 1999.

Sathe, A. and Mann, J.: A review of turbulence measurements using ground-based wind ladars, Atmospheric Measurement Techniques, 6, 3147–3167, 2013.

Skøien, J. O., Blöschl, G., and Western, A. W.: Characteristic space scales and timescales in hydrology, Water Resources Research, 39, 11–1–11–19, 2003.

Vreugdenhil, C. B.: Numerical Methods for Shallow-Water Flow, no. 13 in Water Science and Technology Library, Springer, 1995.

Wang, A., Zeng, X., Shen, S. S. P., Zeng, Q.-C., and Dickinson, R. E.: Time Scales of Land Surface Hydrology, Journal of Hydrometeorology, 7, 868–879, 2006.

Whitaker, S.: Diffusion and Dispersion in Porous Media, American Institute of Chemical Engineers Journal, 13, 420–427, 1967.

Whitaker, S.: Flow in Porous Media I: A Theoretical Derivation of Darcy's Law, Transport in Porous Media, 1, 3–25, 1986.

Whitaker, S.: The Method of Volume Averaging, Kluwer Academic Publishers, Dordrecht, 1999.

Wildenschild, D. and Sheppard, A. P.: X-ray imaging and analysis techniques for quantifying pore-scale structure and processes in subsurface porous medium systems, Advances in Water Resources, 51, 217–246, 2013.

Wood, E. F.: Scaling behaviour of hydrological fluxes and variables: Empirical studies using a hydrological model and remote sensing data, Hydrological Processes, 9, 331–346, 1995.

Wood, E. F., Sivapalan, M., Beven, K., and Band, L.: Effects of spatial variability and scale with implications to hydrologic modeling, Journal of Hydrology, 102, 29–47, 1988.

Wood, S.N. : Fast stable direct fitting and smoothness selection for generalized additive models, Journal of the Royal Statistical Society Series B-Statistical Methodology, 70, 495–518, 2008

Zhou, Y. and Li, W.: A review of regional groundwater flow modeling, Geoscience Frontiers, 2, 205–214, 2011.

On the Consistency of Scale Among Experiments, Theory, and Simulation

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Abstract. The career of Professor Eric F. Wood has focused on the resolution of problems of scale in hydrologic systems. Within this context, we consider an evolving approach known as the thermodynamically constrained averaging theory (TCAT), which has broad applicability to hydrology. ~~Specifically, w~~We consider the case of modeling of two-fluid-phase flow in porous media, and we focus on issues of scale as they relate to various measures of pressure, capillary pressure, and state equations needed to produce solvable models. ~~Two-fluid flow processes in the subsurface are fundamentally important for a wide range of hydrologic processes, including the transport of water and air in the vadose zone and geological carbon sequestration. Mathematical models that describe these complex processes have long relied on empirical approaches that neglect important aspects of the system behavior. New data sources make it possible to access the true geometry of geologic materials and directly measure previously inaccessible quantities. This information can be exploited to support a new generation of theoretical models that are constructed based on rigorous multiscale principles for thermodynamics and continuum mechanics. The challenges to constructing a mature model are shown to involve issues of scale, consistency requirements, appropriate representation of operative physical mechanisms at the target scale of the model, and a robust structure to support model evaluation, validation, and refinement.~~ We apply TCAT to perform physics-based data assimilation to understand how the internal behavior influences the macroscale state of two-fluid porous medium systems. ~~Examples of a~~A microfluidic experimental method and a lattice Boltzmann simulation method are used to examine a key deficiency associated with standard approaches. In a hydrologic process such as evaporation, the water content will ultimately be reduced below the so-called irreducible wetting phase saturation determined from experiments. This is problematic since the derived closure relationships cannot predict the associated capillary pressures for these states. ~~In this work, w~~We demonstrate that the irreducible wetting-phase saturation is an artifact of the experimental design, caused by the fact that the boundary pressure difference does not approximate the true capillary pressure. Using averaging methods, we ~~measure~~compute the true capillary pressure for fluid configurations at and below the irreducible wetting phase saturation. Results of our analysis include a state function for the capillary pressure expressed as a function of fluid saturation and interfacial area.

1 Introduction

Hydrologic systems are typically investigated using some combination of experimental, computational, and theoretical approaches. Each of these classes of approaches has played a central role in advancing knowledge. The years spanning the career of Eric F. Wood have witnessed a remarkable development in the ability to study experimentally the elements that comprise the hydrologic universe. The subsurface is a porous medium system that receives experimental attention designed to identify the small-scale fluid distributions within the solid matrix, intermediate scale behavior through laboratory study, and also the response of an aquifer to imposed forces (e.g., Wildenschild and Sheppard, 2013; Dye et al., 2015; Alizadeh and Piri, 2014; Knödel et al., 2007). Turbulence in surface flows and its impact in rivers, estuaries, and oceans for flow, sediment transport, and dissolved species transport is examined using a broad range of experimental techniques (e.g., Bradshaw, 1971; Chanson, 2009; D'Asaro, 2014; Bernard and Wallace, 2002). Atmospheric experiments designed to support theoretical models of turbulence, typically using lidar systems, and to gain insight into turbulence structures have also generated large quantities of data (Sathe and Mann, 2013; Collins et al., 2015; Fuentes et al., 2014). Other studies involve examination of snow pack, desertification, and changes in land usage (Deems et al., 2013; Hermann and Sop, 2016; Lillesand et al., 2015; Nickerson et al., 2013).

Complementing the advancing ability of experimental study is the development of simulation tools for various aspects of hydrologic systems that make use of advanced computer technology (e.g., Miller et al., 2013; Flint et al., 2013; Kauffeldt et al., 2016; Paiva et al., 2011; Dietrich et al., 2013; Zhou and Li, 2011; Miller et al., 1998; Bauer et al., 2015; Dudhia, 2014). These models of watersheds, rivers and estuaries, and subsurface regions usually make use of traditional equations with the advances occurring through the ability of modern computer architecture to handle larger problems using parallel computing and more elegant, efficient graphical user interfaces.

A third element of advancing modeling of water resources systems is the development of theory that accounts for physical processes. On one hand, forming theoretical advances for mechanistic models based upon conservation equations can be viewed as the standard challenges of accounting more completely for conserved quantities and of developing closure relations for dissipative processes. However, the need to pose ~~these~~ closure relations at scales that are consistent with ~~the scales~~those at which the problems have been formulated creates a need for a variety of constitutive proposals. Furthermore, consistency of models requires that equation formulations be consistent across scales such that variables developed at a smaller scale can inform the equations employed at a larger scale. Overall, these considerations lead to identifying scale and scaling behavior in both time and space as important challenges in posing models (Wood, 1995; Wang et al., 2006; Skøien et al., 2003; Pechlivanidis et al., 2011; Gleeson and Paszkowski, 2014; Gentine et al., 2012; Blöschl, 2001).

~~In an era of unprecedented data generation, a specter haunts the scientific landscape: the pervasive application of statistical methods to misinterpret complex physical phenomena. In the face of this challenge, multiscale averaging theory offers a glimmer of hope. Opportunities to apply theoretical methods for physics-based data assimilation have never been more evident.~~ In an era of unprecedented data generation, opportunities to use multiscale averaging theory to develop physics-based data assimilation strategies based have never been more evident. The challenge of performing meaningful theoretical, experimental,

and computational analyses is constrained by the need to ensure that the length and time scales of quantities arising in each approach can be related. The scales of experimental data, variables appearing in equations, and computed quantities must be the same if they are to be compared in any meaningful way. As a prerequisite for this to happen, data generated by any of the methods must be consistent across the range of scales considered (Ly et al., 2013; Kauffeldt et al., 2013).

While the desire for ~~consistency~~consistencies across scales and approaches is conceptually simple to understand, it has proven to be a difficult practical objective to meet. ~~in practice~~ The change in scale of conservation and balance equations can be accomplished rather easily. The problem with applying these equations lies in the aforementioned need to average some intensive variables, the requirement that closure conditions be proposed at the larger scale, and the need to account for the dynamics of new quantities that arise in the change of scale. Without accounting for all of these items properly, models are doomed to fail. An essential element in ensuring success is the averaging of thermodynamic relations to the larger scale (Gray and Miller, 2013). This provides linkage of variables across scales and also ensures that all physical processes are properly accounted for. For modeling rainfall-runoff processes, Wood et al. (1988) proposed the use of a representative elementary area as a portion of a watershed over which averaging can occur to develop a model. This idea was extended and applied by Blöschl et al. (1995). Subsequently, Reggiani et al. (1998) proposed treating a hydrologic system as a collection of interconnected lumped elements. The lumping was accomplished by integration over individual portions of the system with distinct properties, e.g., aquifers, streams, channels. This effort did not include integration of thermodynamic relations, and as a result did not properly account for the impact of gravitational potential in driving flow between system elements. An effort to address this shortcoming by a somewhat ad hoc introduction of gravitational forces (Reggiani et al., 1999) was only partially successful. Averaging of thermodynamic relations to lumped elements has since been presented (Gray and Miller, 2009).

~~Similar challenges~~Challenges in assuring consistency across scales have ~~confronted~~also been confronted in the modeling of porous medium systems. Special challenges have been encountered for two-fluid-phase flow, where upscaling leads to the introduction of quantities such as specific interfacial area, which is the area where two phases meet normalized by the volume of the region, and specific common curve length, which is length of a curve where three phases meet normalized by the volume of the region. Modeling of multiscale porous medium systems ~~can also benefit from~~must also employ thermodynamics that is scale-consistent and included naturally as a part of the process. ~~As a result of~~Because of the inability to overcome these challenges, most efforts to model multiscale, multiphase porous medium systems do not have thermodynamic constraints and full-scale consistency that ~~is sought~~ would be expected in mature models. The thermodynamically constrained averaging theory (TCAT) approach is relatively refined and ~~does~~ provides means to model ~~effectively~~ systems that are inherently multiscale in nature and also to link disparate length scales, while representing the essential physics naturally and hierarchically with varying levels of sophistication. However, realizing these scale-consistent attributes requires new approaches, new equations of state, novel parameterizations, and, as with any new model, evaluation and validation.

2 Objectives

The overall goal of this work is to examine issues of scale consistency for two-fluid-phase porous medium systems. The specific objectives of this work are:

- to review efforts to resolve critical issues of scale for two-fluid-phase flow in porous media;
- to formulate microscale and macroscale descriptions of state variables important for traditional and evolving descriptions of capillary pressure;
- to determine state variables for capillary pressure using both experimental and computational approaches;
- to compare a traditional state equation approximation approaches with a carefully formulated approach based in multi-scale TCAT theory;
- to demonstrate the limitations of traditional state equation approaches for capillary pressure; and
- to examine the uniqueness of alternative state equation formulations.

3 Background

Two spatial scales are of primary interest for the porous medium problems of focus herein: the microscale, which is often referred to as the pore scale; and the macroscale, which is often referred to as the porous medium continuum scale. At the microscale, the geometry of all phase distributions are fully resolved in space and in time, which makes it possible to locate interfaces where two phases meet and common curves where three phases meet. The equations governing the conservation of mass, momentum, and energy, the balance of entropy, and equilibrium thermodynamic relations are well established at the microscale. Microscale experimental work and modeling are active areas of research because of their relevance to understanding operative processes in complex porous medium systems that were previously impossible to observe. The macroscale is a scale for which a point is associated with some averaged properties of an averaging region comprising all phases, interfaces, and common curves present in the system. Notions such as volume fraction and specific interfacial area arise when a system is represented at the macroscale in terms of averaged measures of the state of the system. These additional measures are quantities that must be determined in the model solution process. Because of historical limitations on both computational and observational data, the macroscale has been the traditional scale at which models of natural porous media systems have been formulated and solved Closure relations at this scale are needed to yield well-posed models. Traditionally, these closure relations have been posited empirically and parameter estimation has been accomplished based upon relatively simple laboratory experiments. In general, traditional macroscale models, while the dominant class of model, suffer from several limitations related to the way in which such models are formulated and closed (Gray and Miller, 2014). A precise coupling between these disparate length scales has usually been ignored.

As efforts to model and link hydrologic elements in models advance, the ability to address scales effectively will become essential. For porous media, methods such as averaging, mixture theory, percolation theory, and homogenization have been employed to transform governing system equations from smaller to larger length scales (Hornung, 1997; Panfilov, 2000; Cushman, 1997). The goal of such approaches is to transform small-scale data to a larger scale such that it can be used to inform models that have been obtained by consistent transformation of conservation and balance equations across scales.

Averaging procedures have been used for analysis of porous media for approximately 50 years (e.g., Bear, 1972; Anderson and Jackson, 1967; Whitaker, 1986, 1999; Marle, 1967). The methods of averaging can be applied to single-fluid-phase systems as well as to multiphase systems. Success in the development of averaging equations for single-fluid-phase porous media to obtain equations such as Darcy's Law has been achieved (e.g., Bachmat and Bear, 1964; Whitaker, 1967; Gray and O'Neill, 1976). These instances did not so much derive a flow equation as show that a ~~desired~~ commonly used flow equation could be obtained using averaging theorems and appropriate assumptions. Thus, these early efforts did not contribute significantly to objective development of flow equations that seek to capture important physical processes. They do serve to provide a systematic framework for developing larger scale equations. Work for two or more fluid phases in porous media has proven to be more difficult and has not been as illuminating.

The problems associated with trying to model multiple fluid phases in porous media include: (1) difficulties in properly accounting for interface properties, (2) lack of definition of macroscale intensive thermodynamic variables, (3) failure to account for system kinematics, and (4) challenges representing other important physical phenomena explicitly, such as contact angles and common curve behavior. These four difficulties sometimes impact the system description in combination.

Multiple-fluid-phase porous media differ from a single-fluid-phase porous medium system by the presence of the interface between the fluids. This interface is different from a fluid-solid interface because of its dynamics. The total amount of solid surface is roughly constant, or is slowly varying, for most natural solid materials. The fluid-fluid specific interfacial area changes in response to flow in the system and redistribution of phases. The time scale of this change is between that of the pore diameter divided by flow velocity and that of pore diameter divided by solid phase movement. These specific interfacial areas are important for their extent, surface tension, and curvature. They are the location where capillary forces are present. Thus, a physically consistent model must account for mass, momentum, and energy conservation at the interfaces; a model concerned only with phase behavior cannot ~~be successful~~represent capillary pressure in a mechanistically high-fidelity fashion (Gray et al., 2015). This ~~failure~~shortcoming is evidenced, in part, by multi-valuedness when capillary pressure is proposed to be a function only of saturation (Albers, 2014).

Intensive variables that are introduced at the macroscale without consideration of microscale precursor values are also poorly defined. For example, a range of procedures for averaging microscale temperature can be employed that will lead to different macroscale values unless the microscale temperature is constant over the averaging region. Thus, mere speculation that a macroscale value exists fails to identify how or if this value is related to unique microscale variables and most certainly does not relate the macroscale variable to microscale quantities. The absence of a theoretical relation makes it impossible to reliably relate microscale measurements to larger scale representations (Essex et al., 2007; Maugin, 1999). Further confusion arises when pressure is proposed directly at the macroscale. Microscale capillary pressure is related to the curvature of the interface

between fluid phases and does not depend on the pressures in the two phases themselves. At equilibrium, microscale capillary pressure becomes equal to the difference between phase pressures at the interface. Proposed representations of macroscale capillary pressure~~proposals~~ often specify that the capillary pressure is equal to the difference in some directly presumed quantities known as macroscale pressures of phases. ~~and thus~~These representations ignore both interface curvature and the fact that only when evaluated at the interface is the phase pressure ~~important~~useful for describing equilibrium capillary pressure. This is especially problematic when boundary pressures in an experimental cell are used to compute a so called "capillary pressure." Note that under these common experimental conditions, regions of entrapped non-wetting phase are not in contact with the non-wetting fluid that is observed on the boundary of the system.

The importance of kinematics is recognized, at least implicitly, in modeling many systems at reduced dimensionality or when averaging over a region the system occupies. For example, in the derivation of vertically integrated shallow water flow equations, a kinematic condition on the top surface is imposed based on the condition that no fluid crosses that surface (Vreugdenhil, 1995). Macroscale kinematic equations for interfaces between fluids in the absence of porous media have been proposed in the context of boiling (Kocamustafaogullari and Ishii, 1995; Ishii et al., 2005). Despite the fact that interface reconfiguration has an important role in determining the properties and behavior of a multifluid porous medium system, attention to this feature is extremely limited (Gray and Miller, 2013; Gray et al., 2015). In some cases, models of two-fluid-phase flow in porous media have been proposed that do not account for either system kinematics ~~and also do not properly account~~or for interfacial stress (e.g. Niessner et al., 2011). Both are necessary components of physically realistic, high fidelity models.

The mixed success in posing appropriate theoretical models, making use of relevant data, and harnessing effective computer power to advance understanding of hydrologic systems is attributable to the inherent difficulty of each of these scientific activities. For progress to be made in enhancing understanding, a significant hurdle must be navigated that requires consistency among these three approaches and within each approach individually. We have found that by performing complementary microscale experimental and computational studies, we have formed a basis for being able to upscale data spatially with insights into the operative time scales for the system (Gray et al., 2015). The small-scale data supports our quest for larger scale closure relations and eliminates confusion about concepts such as capillary pressure as a state function and dynamic processes that cause changes in the value of capillary pressure. Key to being able to develop faithful models are consistent scale change of thermodynamic relations and implementation of appropriate kinematic relations. The approach of combining sound theory, modern experimental techniques, and advanced computational techniques to the study of environmental systems has applicability not only for the porous media systems emphasized here but also for large scale systems with interacting atmospheric, surface, and subsurface elements.

4 Theory

An important aspect of the issues of concern in this work is related to the various ways in which capillary pressure can be measured and the consequences of using traditional approaches that observe fluid pressures on the boundary of an experimental cell and approximate the capillary pressure based upon the difference between the non-wetting phase pressure and the wetting

phase pressure. However, even alternative approaches such as those based upon measurements using microtensiometers cannot resolve the issues of concern identified in this work. The differences among approaches are important, and commonly used approaches are flawed. In the formulation that follows, we show how microscale pressures can be averaged in a variety of ways as well as the relationship of these averaged pressures to the true capillary pressure. We note that averaging of pressures is inherent in the formulation of macroscale models; and indeed measurement devices themselves provide averages over a length scale depending upon the device. The issues related to averaging cannot be avoided.

Direct upscaling can be performed based on microscale information, providing an opportunity to explore aspects of macroscale system behavior that have previously been overlooked. Underpinning this exploration is the precise definition of macroscale quantities. TCAT models are derived from first-principles starting from the microscale. At the macroscale, important quantities such as phase pressures, specific interfacial areas, curvatures, and other averaged quantities are defined unambiguously based on the microscale state (e.g. Gray and Miller, 2014). For two-fluid-phase flow we consider the wetting phase (w), the non-wetting phase (n), and the solid phase (s) within a domain Ω. Each phase occupies part of the domain, Ω_α, where $\alpha = \{w, n, s\}$. The intersection between any two phases is an interface. The three interfaces are denoted by Ω_{wn} Ω_{ws}, and Ω_{ns}. Finally, the common curve Ω_{wns} is defined by the juncture of all three phases. The TCAT two-phase model is developed based on averaging with the complete set of entities, with the index set $\mathcal{J} = \{w, n, s, wn, ws, ns, wns\} = \mathcal{J}_P \cup \mathcal{J}_I \cup \mathcal{J}_C$ chosen to include all three phases $\mathcal{J}_P = \{w, n, s\}$, the interfaces $\mathcal{J}_I = \{wn, ws, ns\}$, and the common curve $\mathcal{J}_C = \{wns\}$. Based on this, the pore space is defined as the union of the domains for the two fluids $\mathcal{D}_f = \Omega_w \cup \Omega_n$.

Macroscale quantities can be determined explicitly from microscale information based on averages. In this work, the form for averages is

$$\left\langle P \right\rangle_{\alpha,\beta} = \frac{\int_{\Omega_\alpha} P d\mathbf{r}}{\int_{\Omega_\beta} d\mathbf{r}} \,, \tag{1}$$

where P is the microscale quantity being averaged. The domains for integration can be the full domain Ω, the entity domains Ω_α for $\alpha \in \mathcal{J}$, or their boundary Γ_α. The boundary of an entity can be further sub-divided into an internal component $\Gamma_{\alpha i}$ and an external component $\Gamma_{\alpha e}$, which together yield $\Gamma_\alpha = \Gamma_{\alpha i} \cup \Gamma_{\alpha e}$. The external boundary is simply $\Gamma_{\alpha e} = \Omega_\alpha \cap \Gamma$.

The volume fractions, specific interfacial areas, and specific common curve length are each extent measures that can be formulated as

$$\epsilon^{\overline{\overline{\alpha}}} = \left\langle 1 \right\rangle_{\Omega_\alpha,\Omega} \,. \tag{2}$$

The volume fractions correspond to $\alpha \in \mathcal{J}_P$; specific interfacial areas correspond to averaging over a two-dimensional interface for $\alpha \in \mathcal{J}_I$; and the specific common curve length corresponds to averaging over a one-dimensional common curve for $\alpha = wns$. The system porosity, ϵ, is directly related to the solid phase volume fraction by

$$\epsilon = 1 - \epsilon^{\overline{\overline{s}}} \,. \tag{3}$$

The wetting phase saturation, $s^{\overline{\overline{w}}}$, can also be expressed in terms of the extent measures,

$$s^{\overline{\overline{w}}} = \frac{\epsilon^{\overline{\overline{w}}}}{1 - \epsilon^{\overline{\overline{s}}}} = \frac{\epsilon^{\overline{\overline{w}}}}{\epsilon} \,. \tag{4}$$

At the macroscale, various averages arise for the fluid pressures. For flow processes, the relevant quantity is an intrinsic average of the microscale fluid pressure, p_α, expressed as

$$p^\alpha = \left\langle p_\alpha \right\rangle_{\Omega_\alpha, \Omega_\alpha} \tag{5}$$

for $\alpha \in \mathcal{J}_f$, which is the index set of fluid phases. In most laboratory experiments phase pressures are measured at the boundary~~, since it is not practical to insert pressure transducers within the sample~~. Pressure transducers can be placed within a domain at pre-selected locations, which still does not provide a dense, non-intrusive measure of fluid pressure at all locations, including along interfaces. The associated average pressure for the intersection of the boundary of the phase with the exterior of the domain is

$$p_\alpha^\Gamma = \left\langle p_\alpha \right\rangle_{\Gamma_{\alpha e}, \Gamma_{\alpha e}} , \tag{6}$$

for $\alpha \in \mathcal{J}_f$.

The capillary pressure of the two-fluid-phase system depends on the curvature of the interface between the fluids. The curvature of the boundary of phase β is defined at the microscale as

$$J_\beta = \nabla' \cdot \mathbf{n}_\beta , \tag{7}$$

where $\nabla' = (\mathbf{I} - \mathbf{n}_\beta \mathbf{n}_\beta) \cdot \nabla$ is the microscale divergence operator restricted to a surface, and $\mathbf{n}_\beta$ is the outward normal vector from the β phase. Since the internal boundary is an interface, the curvature of a phase boundary is also the curvature of the interface between phases for locations within the domain. At the microscale, the capillary pressure is defined at the interface between fluid phases as

$$p_{wn} = -\gamma_{wn} J_w , \tag{8}$$

where γ_{wn} is the interfacial tension of the wn interface. Laplace's law is a microscale balance of forces acting on an interface that relates the capillary pressure to the difference between the microscale phase pressures evaluated at the interface with

$$p_n - p_w = -\gamma_{wn} J_w . \tag{9}$$

It is important to understand that Laplace's law applies at points on the wn interface only at equilibrium; the definition of capillary pressure given by Eq. 8 applies even when the system is not at equilibrium. Additionally, if the mass per area of the interface is non-zero, Laplace's law must be modified to account for gravitational effects (Gray and Miller, 2014). Care must be taken when extending this relationship to the macroscale, as is shown below.

Since the capillary pressure is defined for the interface between the two fluids, Ω_{wn}, we consider an average of the microscale curvature based on this entity

$$J_w^{wn} = \left\langle J_w \right\rangle_{\Omega_{wn}, \Omega_{wn}} = -\left\langle J_n \right\rangle_{\Omega_{wn}, \Omega_{wn}} . \tag{10}$$

Similarly, the macroscale capillary pressure is

$$p^{wn} = -\left\langle \gamma_{wn} J_w \right\rangle_{\Omega_{wn},\Omega_{wn}} . \tag{11}$$

The case of a constant interfacial tension at the microscale allows for

$$p^{wn} = -\gamma^{wn} J_w^{wn} . \tag{12}$$

In the context of Eq. 9 a third pressure of interest for two-fluid-phase systems is the interface-averaged pressure

$$p_\alpha^{wn} = \left\langle p_\alpha \right\rangle_{\Omega_{wn},\Omega_{wn}} , \tag{13}$$

for $\alpha \in \mathcal{J}_f$. A macroscale version of Laplace's law can then be written as

$$p_n^{wn} - p_w^{wn} = -\gamma^{wn} J_w^{wn} . \tag{14}$$

At equilibrium, Laplace's microscale law will hold everywhere on Ω_{wn}. This implies that Eq. 14 must also be satisfied at equilibrium for the case of a constant interfacial tension. However, measurements of p_w^{wn} and p_n^{wn} must be performed at the interface Ω_{wn}. This is not practical, and perhaps not even useful since neither quantity appears in macroscale models. At the macroscale, it is most convenient to work in terms of averaged phase pressures p^w and p^n. ~~Since~~Because p^α and p_α^{wn} are not equivalent, the way in which Eq. 14 can be used is in question. In this work, we explore this dilemma, giving special consideration to the connectivity of the wetting phase.

In previously published work, we have considered the impact of non-wetting phase connectivity in detail (McClure et al., 2016b). The connectivity-based analysis presented in that work can be used to re-cast Eq. 14 in terms of the connected wetting phase regions. These ~~connected wetting phase~~ regions are identified by sub-dividing Ω_w into N_w sub-regions that do not intersect. The sub-regions cannot touch each other, meaning that $\overline{\Omega}_{w_i} \cap \overline{\Omega}_{w_j} = \emptyset$ for all $i \neq j$ with $i, j \in \{1, 2, \ldots N_w\}$ where the overbar on Ω denotes a closed domain that includes explicitly the boundary. Interfacial sub-regions are formed from the intersection $\Omega_{w_i n} = \Omega_{wn} \cap \overline{\Omega}_{w_i}$. When the non-wetting phase is fully connected, an approximate version of Laplace's law can be derived as

$$p^n - p^{w_i} = -\gamma^{wn} J_w^{w_i n} , \tag{15}$$

for $i \in \{1, 2, \ldots, N_w\}$. This expression relates the average phase pressures within each region of wetting phase to the curvature of the adjoining interface. The average phase pressures are defined as

$$p^{w_i} = \left\langle p_w \right\rangle_{\Omega_{w_i},\Omega_{w_i}} , \tag{16}$$

and the average curvature as

$$J_w^{w_i n} = \left\langle J_w \right\rangle_{\Omega_{w_i n},\Omega_{w_i n}} . \tag{17}$$

The quantities p^{w_i} and $J_w^{w_i n}$ are averaged quantities, but they are not macroscale quantities. The macroscale pressure of the wetting phase can be determined as

$$p^w = \frac{1}{\epsilon^{\overline{\overline{w}}}} \sum_{i=1}^{N_w} \epsilon^{\overline{\overline{w_i}}} p^{w_i} \,, \tag{18}$$

and the macroscale capillary pressure is

$$p^{wn} = -\frac{\gamma^{wn}}{\epsilon^{\overline{\overline{wn}}}} \sum_{i=1}^{N_w} \epsilon^{\overline{\overline{w_i n}}} J_w^{w_i n} \,. \tag{19}$$

For the case where multiple disconnected sub-regions are present for either phase, the relationship between $p^n - p^w$ and p^{wn} is therefore quite complex from a geometric standpoint. Associated challenges for the measurement of phase pressures impact our understanding of the system behavior at the macroscale, hindering our ability to develop effective models.

~~From the~~The definitions of pressures provided ~~it is clear~~demonstrate that several different pressures are of interest for two-fluid systems. In general these pressures will not be equivalent. Thus care is needed in analyzing the system state and in proposing relations among pressures. ~~In general~~Typically only the pressure defined by Eq. 6 is ~~typically~~ measured in traditional laboratory experiments, and this is often true even with state-of-the-science experiments that include high-resolution imaging. On the other hand, computational approaches provide a means to compute all of the defined pressures, yielding a basis to deduce a more complete understanding of the macroscale behavior of the system than would be accessible using approaches that are only able to control and observe fluid pressures on the boundaries of the domain. Further, the formulation detailed above applies for dynamic conditions as well as equilibrium or steady state conditions except where specifically noted. For dynamic conditions, the averaged quantities are computed at some instant in time.

5 Materials and Methods

5.1 Experimental Design

An experimental approach was sought to investigate the distribution of capillary pressure in a porous medium system. To meet the objectives of this work, we needed directly to observe capillary pressure at high resolution, which requires computation of the average curvature of the fluid-fluid interface as a function of the averaging region. Because we wished to observe systems at true equilibrium and knew from recent experience that extended periods of time are necessary to obtain such a state (Gray et al., 2015), we elected to rely upon a microfluidic approach for which we could verify true equilibrium states were achieved. Microfluidic devices are physically small but can be made sufficiently large to satisfy the conditions for being a valid macroscale REV. This is so because the systems are well above the microscale continuum limit and then only need to satisfy the conditions for the size being a representative sampling of the pore morphology and topology of the media. The size needed for an REV has been investigated previously for two-fluid-phase flow. Typically in three-dimensions a few thousand spheres is needed to produce essentially invariant information for quantities such as saturations, interfacial areas, and capillary pressure. This translates to slightly over 10 mean grain diameters in each dimension. Microfluidic cells can be fashioned to

meet this requirement. Even though hydrologic problems motivate this work, the fundamental nature of the capillary pressure state function can be investigated with any pair of immiscible fluids. Minimizing the mutual solubilities of each fluid in the companion fluid is an important design characteristic that can simplify the experimental work without loss of generality. Thus physically small microfluidic systems that did not include water were used in this work, which might on the surface appear to be far removed from the motivating hydrologic systems of concern.

~~Two-fluid flow experiments~~Experiments involving two-fluid flow through porous media are typically conducted using a setup similar to the one shown in Fig. 1. A porous material, in this case a two-dimensional micromodel cell, is connected to two fluid reservoirs at opposite ends of the sample. The two fluids are referred to as wetting (w) and non-wetting (n) based on the relative affinity of the fluids toward the solid phase (s, the black region of Fig. 1). The two-dimensional micromodel was fabricated using photolithography techniques. The 500 μm $\times$ 525 μm $\times$ 4.4 μm porous medium cell of the micromodel contained a distribution of cylinders, with a porosity of 0.54. The short dimension of the cell was oriented in the vertical dimension such that flow was essentially horizontal. The boundary reservoirs were used to inject fluid into the sample, resulting in the displacement of one fluid by the other. As depicted in Figure 1, one inlet of the cell was connected to a wetting-fluid-phase (decane) reservoir and the other to a non-wetting-fluid-phase (nitrogen gas) reservoir, with the other four boundaries being solid. A displacement experiment was performed in the micromodel depicted in Fig. 1 using the experimental methods detailed in Dye et al. (2015). This approach provides observations of equilibrium configurations of the two-fluid-phase system. The displacement experiment began by fully saturating the porous medium cell with decane through the inlet reservoir located at one end of the cell. Primary drainage was then carried out by incrementally increasing the pressure of the nitrogen reservoir, located on the opposite end of the cell. After each pressure step, the system was allowed to equilibrate. The final equilibrium state for a given pressure boundary condition was determined based ~~on~~ on an invariance of the average mean curvature of the wn interface, J_w^{wn}, as determined from image analysis. After the system reached an equilibrium state, the pressure in each reservoir, measured with pressure tranducers, and an image of the cell were recorded before another incremental change in pressure step was applied. The drainage process was terminated prior to nitrogen breakthrough into the decane reservoir.

The solid geometry used in our microfluidic experiments was designed to allow for high capillary pressure at the end of primary drainage. At the wetting-fluid-phase reservoir, a layer of evenly spaced homogeneous cylinders was placed such that the gap between cylinders was uniformly small. This allowed for a large pressure difference between the fluid reservoirs, since the non-wetting fluid phase did not penetrate the wetting-fluid-phase reservoir over a wide range of pressure differences.

5.2 Computational Approach

The experimental microfluidics setup described in the previous section provides a way to perform traditional two-fluid-flow experiments and observe the internal dynamics of interface kinematics and equilbrium distributions. Microscale phase configurations can be observed directly, and averaged geometric measures can be obtained from this data. While boundary pressure values are known, the experiment does not provide a way to measure the microscale pressure field. Accurate computer simulation of the experiment can provide this information and can also be used to generate additional fluid configurations that may not be accessible experimentally. In particular, configurations below the so-called irreducible wetting phase saturation

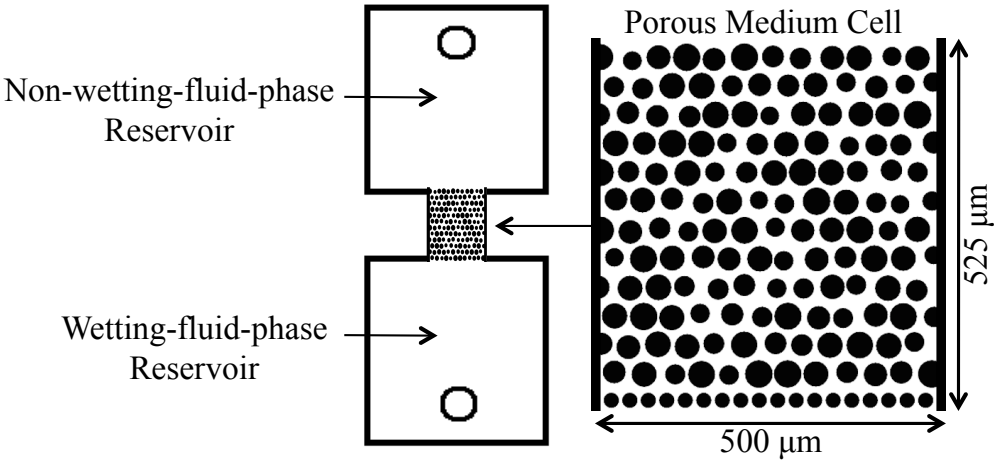

Figure 1. A depiction of the two-dimensional micromodel that was used in the displacement experiment. The solid is represented by black and the regions accessible to fluid flow by white within the porous medium cell.

will be considered. The common identification of a saturation as “irreducible" is a misnomer because wetting phase saturations beneath this value can be achieved through, for example, evaporation or by initializing a saturation below this value in an experimental setup. In this work, simulation is applied in two contexts: (1) to simulate the microscale pressure field based on experimentally-observed fluid configurations; and (2) to simulate two-fluid equilibrium configurations based on random initial conditions. Success with the first set of simulations in matching the experiments provides confidence that the results of the second set of computations represent physically reasonable configurations. Here we summarize each of the approaches.

Simulations are performed using a “color" lattice Boltzmann method (LBM). Our implementation has been described in detail in the literature (see McClure et al., 2014a, b). The approach relies on a multi-relaxation time (MRT) scheme to model the momentum transport. In the limit of low Mach number, the implementation recovers the Navier-Stokes equations with additional contributions to the stress tensor in the vicinity of the interfaces. The interfacial stresses between fluids result from capillary forces, which play a dominant role in many two-fluid porous medium systems. The formulation relies on separate lattice Boltzmann equations (LBEs) to recover the mass transport for each fluid. This decouples the density from the pressure to allow for the simulation of incompressible fluids. Our implementation has been applied to simulate two-fluid-phase flows in a variety of porous medium geometries, recovering the correct scaling for common curve dynamics (McClure et al., 2016a), and it has also been used to closely predict experimental fluid configurations (Dye et al., 2015; Gray et al., 2015). The effect of gravity was ignored in the simulation of the experimental systems due to the very small length scale in the vertical dimension.

The implementation allows us to initialize fluid configurations directly from experimental images. Segmented images are generated from grey-scale camera data. These images were used to specify the initial position of the phases in the simulations with high resolution. The micromodel cell was computationally resolved within a domain that is $20 \times 500 \times \times 500$. The lattice spacing for the simulation was $\delta x = 1$ μm. ~~Note that additional resolution was used to resolve the depth of the micromodel~~

~~cell.~~Note that the depth of the micromodel was resolved in the simulation. The physical depth of the simulation cell (20 μm) was larger than the depth of the micromodel cell (4.4 μm). This was done so that the curvature in the depth of the cell could be resolved accurately. Due to geometric constraints, the curvature associated with the micromodel depth cannot vary. The curvature of the interface between the two fluids can be written as

$$J_w = -\left(\frac{1}{R_1} + \frac{1}{R_2}\right) , \tag{20}$$

where R_1 is the radius of curvature in the horizontal plane and R_2 is associated with the micomodel depth. Only R_1 can vary independently. In the simulation, the fixed value of R_2 was 10 μm. In the experiment, the fixed value of R_2 was 2.2 μm. With R_2 known in both cases, the simulated curvatures were mapped to the experimental system. In the experimental system, pressure transducers were used to measure the phase pressures in the boundary reservoirs. These measurements were used to inform pressure boundary conditions within the simulation. Since boundary conditions were enforced explicitly within the simulation, the boundary pressures match the experimentally measured values exactly. The fluid configurations can vary independently based on these conditions. Simulations were performed until the interfacial curvature stabilized, since prior work has demonstrated the important fact that the curvature equilibrates more slowly ~~compared to~~than other macroscale quantities, such as fluid saturation Gray et al. (2015).

A set of simulations was also performed based on random initial conditions. The approach used to generate random fluid configurations and associated equilibrium states is described in detail by McClure et al. (2016b). The solid configuration for the flow cell was identical for both sets of simulations. Blocks of fluid were inserted into the system at random until a desired fluid saturation was obtained. This allowed for the generation of fluid configurations at wetting phase saturations that were below the experimentally-determined, so-called irreducible wetting-phase saturation. Periodic boundary conditions were then enforced, and the simulation was performed to produce an equilibrium configuration as determined by the average curvature of the interface between fluids. Based on the final fluid configurations, connectivity-based analysis was performed to infer macroscale capillary pressure, saturation, and interfacial area for a dense set of equilibrium states.

5.3 Results and Discussion

Phase connectivity presents a critical challenge for the theory and simulation of two-fluid-phase flow. When all or part of a phase forms a fully-connected pathway through a porous medium, flow can occur without the movement of interfaces. However, the case where phase sub-regions are not connected is a source of history-dependent behavior in traditional models. Traditional models ~~predict~~make use of the capillary pressure proposed as a function of the fluid saturation only, $p^c(s^{\overline{\overline{w}}})$. However, this relationship is not unique. Furthermore, key features of the relationship are an artifact of the experimental design. For example, the irreducible wetting phase saturation, $s_I^{\overline{\overline{w}}}$, can play an important role.

To calculate p^w as it is defined from Eq. 5, the microscale pressure field must be known throughout the domain. Simulation provides a means to study how the pressure varies within the system and to obtain averages within all phase sub-regions. Based on Eq. 16, values of p^{w_i}, $J_w^{w_i n}$ and $\epsilon^{\overline{\overline{w_i}}}$ can be determined for each connected region of the wetting phase Ω_{w_i} for $i \in \{1, 2, \ldots, N_w\}$. Two sets of simulations were performed, including (1) a set of 24 configurations initialized directly from

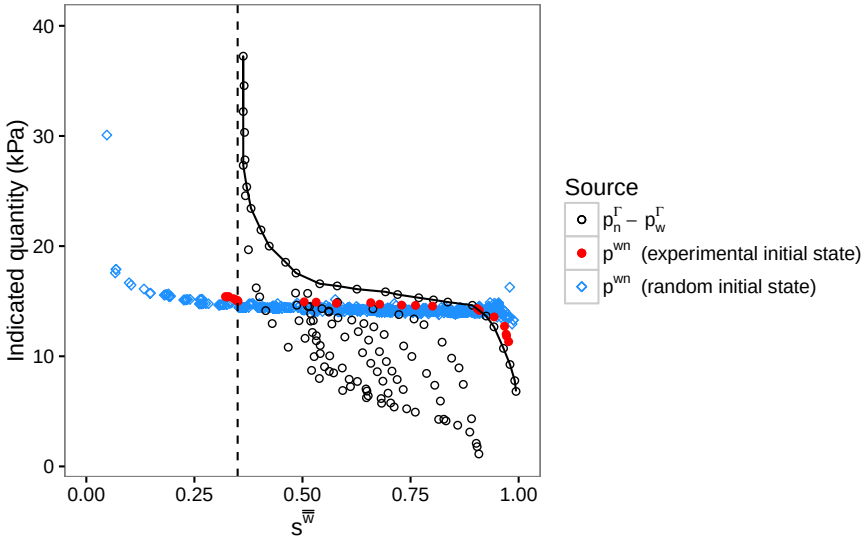

Figure 2. Comparison between the experimentally measured boundary pressure difference $p_n^\Gamma - p_w^\Gamma$ and the capillary pressure p^{wn} for the micromodel geometry. The solid line represents the boundary pressure along primary drainage.

experimentally-observed configurations along primary drainage; and (2) a set of 48 configurations with random initial conditions as discussed in Section 5.2. The ~~final~~equilibrium fluid arrangements were analyzed to determine the true capillary pressure, p^{wn}, by analyzing the curvature of the fluid-fluid interface, fluid saturation, $s^{\overline{\overline{w}}}$, and specific interfacial area, $\epsilon^{\overline{\overline{wn}}}$. The data was aggregated to produce a dense set of equilibrium configurations.

Pressure transducers located in each of the two fluid reservoirs were used to measure experimental boundary pressures for each fluid. The resulting values of $p_n^\Gamma - p_w^\Gamma$ are plotted in Fig. 2. Average capillary pressure values calculated from the simulations are presented along with this experimental data. The solid line represents the boundary pressure difference during primary drainage. The boundary pressures for simulations initialized from experimental data matched the experimentally measured values of $p_n^\Gamma - p_w^\Gamma$ exactly. Boundary measurements taken during simulation are also presented for imbibition and scanning curve sequences. The values of $p_n^\Gamma - p_w^\Gamma$ plotted in Fig. 2 represent a comprehensive set of experimental measurements that would typically be identified as capillary pressure values. This provides a basis for comparison with measurements of the true capillary pressure based on the configuration of the interfaces. In general, agreement between $p_n^\Gamma - p_w^\Gamma$ and p^{wn} should not be expected. Only when both the w and n fluids are fully connected and when the system is at equilibrium will the boundary pressure difference balance the internal average capillary pressure. The difference between the boundary measurement and the internal average capillary pressure due to the phases being disconnected is evident by comparing the experimental data from primary drainage and the simulation points initialized from the associated fluid configurations. Pressure boundary conditions for the simulations were set to match the measured values of p_n^Γ and p_w^Γ. As $s^{\overline{\overline{w}}}$ decreases, there is an increasing gap between

$p_n^\Gamma - p_w^\Gamma$ and the average capillary pressure p^{wn}. This gap is attributed to the formation of disconnected wetting phase regions during drainage, an effect that is most significant as the so-called irreducible wetting phase saturation is approached.

In the experimental system, ~~the~~an irreducible wetting phase saturation was clearly observed as $s_I^{\overline{\overline{w}}} = 0.35$. This value is marked with a vertical dashed line in Fig. 2. This irreducible wetting phase saturation corresponds to the lowest experimentally accessible wetting phase saturation, since fluid configurations with $s^{\overline{\overline{w}}} < s_I^{\overline{\overline{w}}}$ cannot be obtained from the experimental setup and operating conditions. The underlying reason for this is related to the connectivity of the wetting phase. This can be understood from Fig. 3, which shows the phase configuration observed experimentally at the end of primary drainage. Within a connected region of wetting phase, the microscale pressure, p_w, will tend to be nearly constant. However, the wetting phase pressure can vary from one region to another. The connected components of the wetting phase are shown in Fig. 3 (b). At equilibrium, the measured difference in boundary pressures $p_n^\Gamma - p_w^\Gamma$ must balance with the capillary pressure of the interface sub-region between the two phase components. Note that the non-wetting phase is fully connected in Fig. 3 (a). The implication is that $p_n^\Gamma = p^n$ at equilibrium. However, p_w^Γ only reflects the pressure of the wetting phase reservoir. The sub-regions of the wetting phase that remain after primary drainage are plotted in color in Fig. 3 (b). The part of Ω_w that is connected to the wetting phase reservoir is shown in light green in Fig. 3 (b). When the irreducible wetting phase saturation is reached the portion of Ω_w that connects to the reservoir no longer fills any of the porespace within the micromodel. The irreducible wetting-phase saturation is associated with the trapped wetting phase regions only. Changing the pressure difference between the fluid reservoirs to increase $p_n^\Gamma - p_w^\Gamma$ does not change the capillary pressure in these regions. This leads to arbitrarily high measurements, claimed to be "capillary pressure" measurements, which are actually a difference in reservoir pressures rather than a measure of interface curvature. This also misconstrues the reduction in wetting phase saturation that occurs. The true average capillary pressure, as defined in Eq. 12, is much lower. Furthermore, the wetting-phase saturation can be further reduced as a consequence of other processes, such as evaporation. It is irreducible only within the context of the experimental design.

In light of this result, it is useful to consider alternative means to generate two-fluid configurations in porous media. For example, suppose a fluid configuration were encountered with $s^{\overline{\overline{w}}} = 0.2$, a value lower than the irreducible saturation. How can we determine the macroscale capillary pressure? From a traditional macroscale parameterization approach, the experimentally proposed relation $p^{wn}(s^{\overline{\overline{w}}})$ is of absolutely no use, since capillary pressure is undefined for $s^{\overline{\overline{w}}} < s_I^{\overline{\overline{w}}}$. From the microscale perspective, it is clearly possible to produce fluid configurations for which $s^{\overline{\overline{w}}} < s_I^{\overline{\overline{w}}}$ (for any system), and to measure the associated capillary pressure based on Eq. 12. For randomly initialized phase configurations, many such systems are produced. Simulations performed based on these initial geometries lead to equilibrium capillary pressure measurements shown in Fig. 2. While the classic "J curve" shape is still present, the experimentally-determined value $s_I^{\overline{\overline{w}}}$ offers no guidance regarding this form.

Comparing capillary pressures measured from random initial conditions with those measured from experimental initial conditions provides additional insight. First, the true capillary pressure measurements based on Eq. 8 are remarkably consistent, particularly when considering the values of p^{wn} obtained as $s^{\overline{\overline{w}}} \to s_I^{\overline{\overline{w}}}$. Compared to randomly initialized data, configurations from primary drainage have a higher average capillary pressure. This is expected, since along primary drainage p^{wn} is determined by the pore-throat sizes. These represent the highest capillary pressures that are typically observed. We note that primary

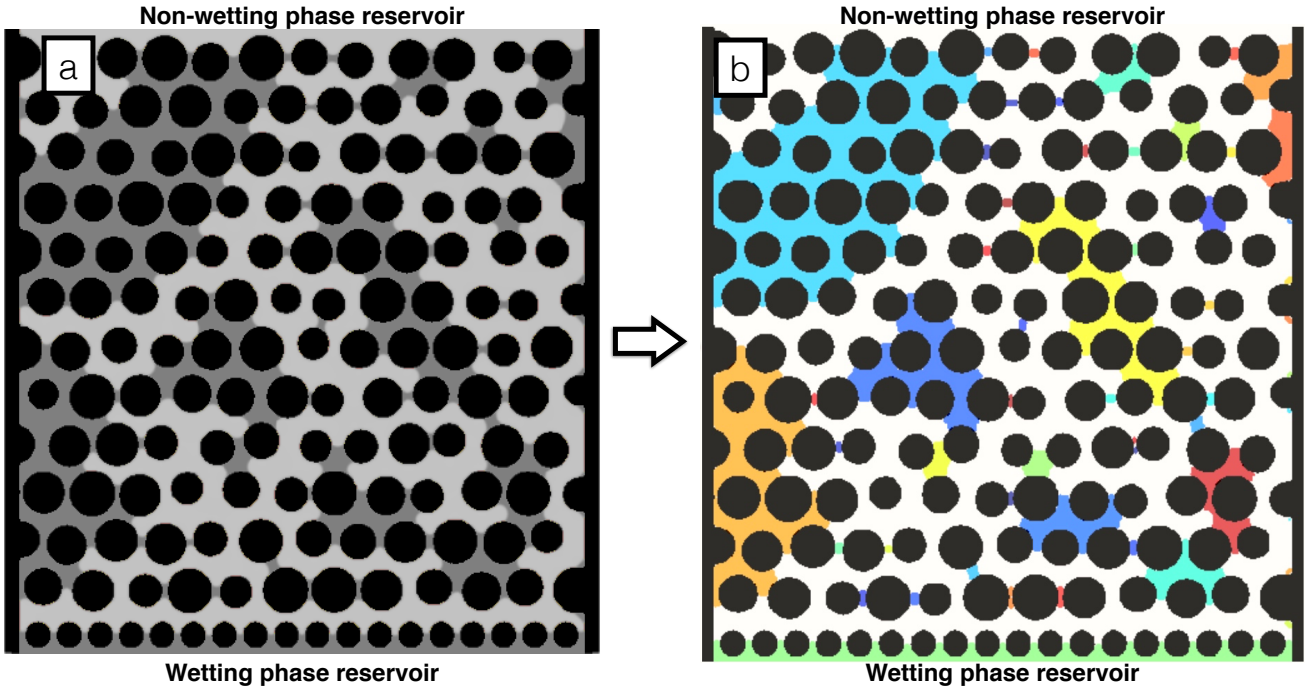

Figure 3. Phase connectivity has a direct impact on the meaning of the macroscale experimental measurements: (a) experimentally observed phase configuration corresponding to irreducible wetting phase saturation; and (b) connected components analysis shows all wetting phase that remains in the system is disconnected from the wetting phase reservoir. The black denotes the solid phase, the gray and various colors denote the wetting phase, and the white denotes the non-wetting phase.

drainage does not specify the maximum possible capillary pressure, since bubbles of non-wetting phase may form that have a smaller radius of curvature than the minimum throat width.

Since the boundary pressure difference $p_n^\Gamma - p_w^\Gamma$ cannot be substituted for the capillary pressure, a key question is how this impacts capillary pressure hysteresis. When $p_n^\Gamma - p_w^\Gamma$ is used to erroneously infer the capillary pressure, the relationship between capillary pressure and saturation appears as the black circles in Fig. 2. When the true capillary pressure is used to plot the same data the shape of the relationship between capillary pressure and saturation is distinctly different. Capillary pressures are obtained at all fluid saturations, and no irreducible wetting-phase saturation is observed. Due to the fact that the true capillary pressure includes the effects of disconnected phase regions, moderate capillary pressures are observed. This is because the extrema for the boundary pressure measurements are not constrained by the internal geometry. We note that the relationship $p^{wn}(s^{\overline{\overline{w}}})$ remains non-unique, since capillary pressure is not a one-to-one relationship with wetting-phase saturation. The higher-dimensional form $p^{wn}(s^{\overline{\overline{w}}}, \epsilon^{\overline{\overline{wn}}})$ is therefore considered in Fig. 4. Using a generalized additive model (GAM) (Wood, 2008), a best-fit surface was generated to approximate the simulated data, incorporating data points derived from both random

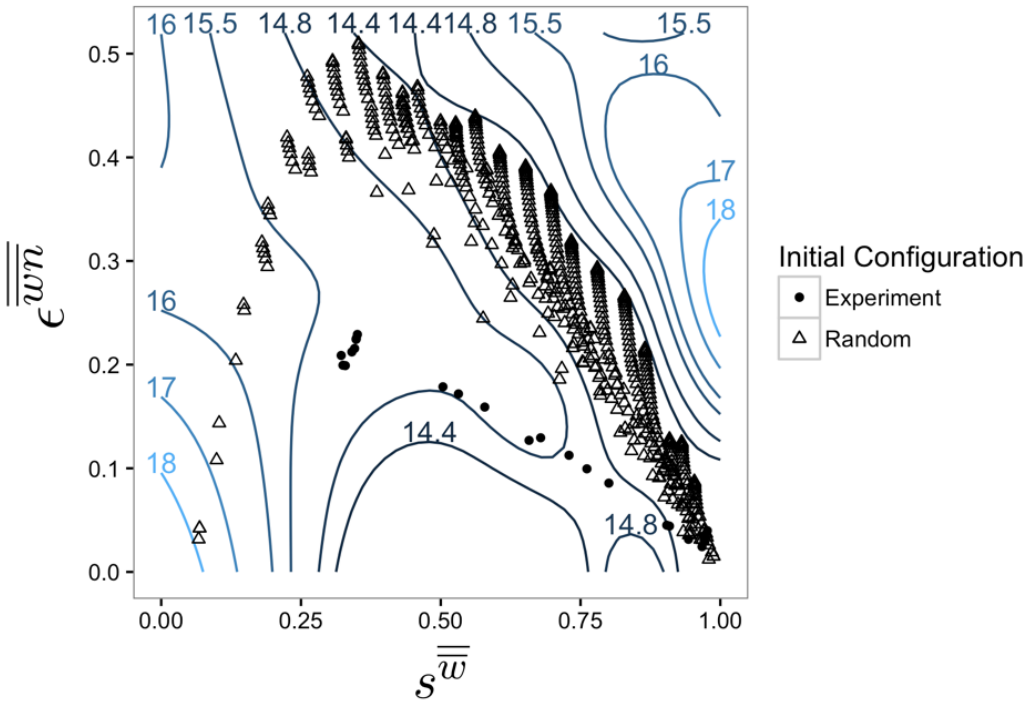

Figure 4. Contour plot showing the relationship $p^{wn}(s^{\overline{w}}, \epsilon^{\overline{\overline{wn}}}$, with ~~the black curves representing constant value of~~ contours showing the capillary pressure p^{wn} (kPa). Data points used to construct the surface are also shown, including randomly initialized fluid configurations ~~(blue)~~ and experimentally initialized configurations from primary drainage ~~(red)~~.

and experimentally-observed initial conditions. The black lines in Fig. 4 show the iso-contours of the capillary pressure surface ~~(p^{wn} is constant along each contour)~~. It is clear that primary drainage leads to states with lower interfacial area as compared to randomly initialized configurations. Both sets of points lie along a consistent surface. The extent to which the relationships $p^{wn}(s^{\overline{\overline{w}}})$ and $p^{wn}(s^{\overline{\overline{w}}}, \epsilon^{\overline{\overline{wn}}})$ describe the data points measured from microscale configurations is quantitatively assessed by evaluating the residuals for the GAM approximation. The residuals are shown in Fig. 5. The traditionally used relationship $p^{wn}(s^{\overline{\overline{w}}})$ is able to explain only 60.6% of the variance in the data. When the effect of interfacial area is included, $p^{wn}(s^{\overline{\overline{w}}}, \epsilon^{\overline{\overline{wn}}})$, 77.1% of the variance is explained. Based on previous work for three-dimensional porous media, it is anticipated that higher fidelity approximations can be produced by including the effects of other topological invariants, such as the average Gaussian curvature or Euler characteristic (McClure et al., 2016b).

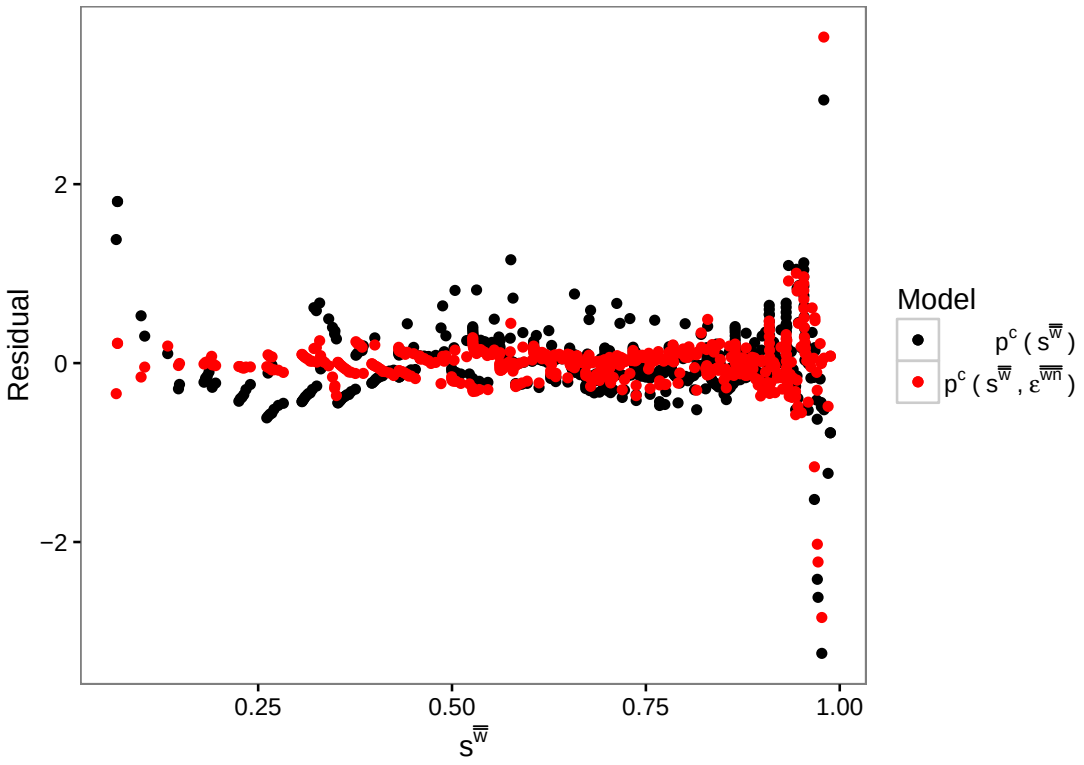

Figure 5. Comparison of the residual errors for the GAM fits that approximate $p^{wn}(s^{\overline{w}})$ and $p^{wn}(s^{\overline{w}}, \epsilon^{\overline{wn}})$.

6 Conclusions

In this work, we show that the ability to quantitatively analyze the internal structure of two-fluid porous medium systems has a profound impact on macroscale understanding. We considered the behavior of the capillary pressure based on traditional laboratory boundary measurements and compare this to the true average capillary pressure, a state function, determined by directly averaging the curvature of the interface between fluids. We demonstrate that the difference between the phase pressures as measured from the boundary cannot be used to deduce the capillary pressure of the system. In particular, the high capillary pressure measured for irreducible wetting phase saturation is an artifact of the experimental design. Four important conclusions result.

First, the true capillary pressure measured at traditionally identified irreducible wetting-phase saturation is significantly lower than predicted from boundary pressure measurements. This can be understood based on the underlying phase connectivity. At irreducible wetting-phase saturation, the wetting-phase reservoir pressure no longer reflects the internal pressure of the system since the reservoir does not connect to the remaining wetting phase inside the system.

Second, randomly generated fluid configurations provide a way to access states where the wetting-phase saturation is below the irreducible wetting phase saturation. By carrying out direct averaging based on these states, the capillary pressure

state function can be ~~studied~~computed over the full range of possible saturation values, including configurations that are inaccessible from traditional experiments. We note that modified experimental designs could be used to accomplish the same ~~objective~~studies.

Third, we show that the equilibrium relationship ~~between~~among capillary pressure, fluid saturation and interfacial area is consistent between randomly initialized configurations used only in computation and experimentally initialized configurations. Combining the two data sets, generalized additive models were used to approximate the surface relating ~~the three quantities~~ p^c, $s^{\overline{\overline{w}}}$, and $\epsilon^{\overline{\overline{wn}}}$. At fixed saturation, states evolved from primary drainage have higher capillary pressure and lower interfacial area than equilibrium states that evolve from randomly generated states. Our results are particularly significant for systems where low wetting-phase ~~configurations~~saturations are important, such as evaporation in the vadose zone.

Author contributions. All authors participated in the writing of this manuscript. WGG and CTM contributed to the introduction, background, and theory, ALD contributed to the microfluidics, and JEM contributed to lattice Boltzmann modeling. All authors contributed to the discussion and conclusions from this work.

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References

Albers, B.: Modeling the hysteretic behavior of the capillary pressure in partially saturated porous media: a review, Acta Mechanica, 225, 2163–2189, 2014.

Alizadeh, A. H. and Piri, M.: The effect of saturation history on three-phase relative permeability: An experimental study, Water Resources Research, 50, 1636–1664, 2014.

Anderson, T. B. and Jackson, R.: A fluid mechanical description of fluidized beds, Industrial and Engineering Chemistry Fundamentals, 6, 527–539, 1967.

Bachmat, Y. and Bear, J.: The General Equations of Hydrodynamic Dispersion in Homogeneous, Isotropic, Porous Mediums, Journal of Geophysical Research, 69, 2561–2567, 1964.

Bauer, P., Thorpe, A., and Brunet, G.: The quiet revolution of numerical weather prediction, Nature, 525, 47–55, 2015.

Bear, J.: Dynamics of Fluids in Porous Media, Elsevier, New York, 1972.

Bernard, P. S. and Wallace, J. M.: Turbulent Flow, John Wiley & Sons, 2002.

Blöschl, G.: Scaling in Hydrology, Hydrological Processes, 15, 709–711, 2001.

Blöschl, G., Grayson, R. B., and Sivapalan, M.: On the representative elementary area (rea) concept and its utility for distributed rainfall-runoff modelling, Hydrological Processes, 9, 313–330, 1995.

Bradshaw, P.: An Introduction to Turbulence and its Measurement, Pergamon Press, 1971.

Chanson, H.: Current knowledge in hydraulic jumps and related phenomena. A survey of experimental results, European Journal of Mechanics B Fluids, 28, 191–210, 2009.

Collins, R., Triplett, C., Barjatya, A., Lehmacher, G., and Fritts, D.: Using lidar and rockets to explore turbulence in the atmosphere, SPIE Newsroom, doi:10.1117/2.1201505.005922, 2015.

Cushman, J. H.: The Physics of Fluids in Hierarchical Porous Media: Angstroms to Miles, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997.

D'Asaro, E. A.: Turbulence in the Upper-Ocean Mixed Layer, Annual Review of Marine Science, 6, 101–115, 2014.

Deems, J. S., Painter, T. H., and Finnegan, D. C.: Lidar measurement of snow depth: a review, Journal of Glaciology, 59, 467–479, 2013.

Dietrich, J. C., Dawson, C. N., Proft, J. M., Howard, M. T., Wells, G., Fleming, J. G., Luettich Jr., R. A., Westerink, J. J., Cobell, Z., Vitse, M., Lander, H., Blanton, B. O., Szpilka, C. M., and Atkinson, J. H.: Real-time forecasting and visualization of hurricane waves and storm surges using SWAN+ADCIRC and FigureGen, in: Computational Challenges in the Geosciences, edited by Dawson, C. and Gerritsen, M., vol. 156 of The IMA Volumes in Mathematics and Its Applications, Springer Science & Business Media, New York, 2013.

Dudhia, J.: A history of mesoscale model development, Asia-Pacific Journal of Atmospheric Science, 50, 121–131, 2014.

Dye, A. L., McClure, J. E., Gray, W. G., and Miller, C. T.: Multiscale modeling of porous medium systems, in: Handbook of Porous Media, edited by Vafai, K., chap. 1, pp. 3–45, CRC Press, third edn., 2015.

Essex, C., McKitrick, R., and Andresen, B.: Does a Global Temperature Exist?, Journal of Non-Equilibrium Thermodynamics, 32, 1–27, 2007.

Flint, L. E., Flint, A. L., Thorne, J. H., and Boynton, R.: Fine-scale hydrologic modeling for regional landscape application: the California Basin characterization model development and performance, Ecological Processes, 2, http://www.ecologicalprocesses.com/content/2/1/25, 2013.

Fuentes, F. C., Iungo, G. V., and Porté-Agel, F.: 3D turbulence measurements using three synchronous wind lidars: Validation against sonic anemometry, Journal of Atmospheric and Oceanic Technology, 31, 1549–1556, 2014.

Gentine, P., Troy, T. J., Lintner, B. R., and Findell, K. L.: Scaling in Surface Hydrology: Progress and Challenges, Journal of Contemporary Water Research & Education, 147, 28–40, 2012.

Gleeson, T. and Paszkowski, D.: Perceptions of scale in hydrology: What do you mean by regional scale?, Hydrological Sciences Journal, doi:10.1080/02626667.2013.797581, 2014.

Gray, W. G. and Miller, C. T.: Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 7. Single-phase megascale flow models, Advances in Water Resources, 32, 1121–1142, doi:10.1016/j.advwatres.2009.05.010, 2009.

Gray, W. G. and Miller, C. T.: A generalization of averaging theorems for porous medium analysis, Advances in Water Resources, 62, 227–237, doi:10.1016/j.advwatres.2013.06.006, 2013.

Gray, W. G. and Miller, C. T.: Introduction to the Thermodynamically Constrained Averaging Theory for Porous Media Systems, Springer-Verlag, 2014.

Gray, W. G. and O'Neill, K.: On the development of Darcy's law for the general equations for flow in porous media, Water Resources Research, 12, 148–154, 1976.

Gray, W. G., Dye, A. L., McClure, J. E., Pyrak-Nolte, L. J., and Miller, C. T.: On the dynamics and kinematics of two-fluid-phase flow in porous media, Water Resources Research, 51, 5365–5381, 2015.

Hermann, S. M. and Sop, T. K.: The map is not the territory: How satellite remote sensing and ground evidence have re-shaped the image of Sahelian desertification, in: The End of Desertification? Disputing Enviornmental Change in the Drylands, edited by Behnke, R. and Mortimore, M., Springer Earth System Sciences, pp. 117–145, Springer, 2016.

Hornung, U.: Homogenization and Porous Media, no. 6 in Interdisciplinary Applied Mathematics, Springer, 1997.

Ishii, M., Kim, S., and Kelly, J.: Development of Interfacial Area Transport Equation, Nuclear Engineering and Technology, 37, 525–536, 2005.

Kauffeldt, A., Halldin, S., Rodhe, A., Xu, C.-Y., and Westerberg, I. K.: Disinformative data in large-scale hydrological modelling, Hydrology and Earth System Sciences, 17, 2845–2857, 2013.

Kauffeldt, A., Wetterhall, F., Pappenberger, F., Salamon, P., and Thielen, J.: Technical review of large-scale hydrological models for implementation in operational flood forecasting schemes on continental level, Environmental Modelling and Software, 75, 68–76, 2016.

Knödel, K., Lange, G., and Voigt, H.-J.: Environmental Geology: Handbook of Field Methods and Case Studies, Springer Berlin Heidelberg New York, 2007.

Kocamustafaogullari, G. and Ishii, M.: Foundation of the interfacial area transport equation and its closure relations, International Journal of Heat and Mass Transfer, 38, 481–493, 1995.

Lillesand, T. M., Kiefer, R. W., and Chipman, J. W.: Remote Sensing and Image Interpretation, Wiley, seventh edn., 2015.

Ly, S., Charles, C., and Degré, A.: Different methods for spatial interpolation of rainfall data for operational hydrology and hydrological modeling at watershed scale. A review, Biotechnology, Agronomy, Society and Environment, 17, 392–406, 2013.

Marle, C.: Ècoulements monophasiques en milieu poreux, Revue de L'Institut Français du Pétrole, 22, 1471–1509, 1967.

Maugin, G. A.: The Thermomechanics of Nonlinear Irreversible Behaviors: An Introduction, World Scientific Press, Singapore, 1999.

McClure, J. E., Berrill, M. A., Gray, W. G. and Miller, C. T.: Tracking Interface and Common Curve Dynamics for Two-Fluid Flow in Porous Media, Journal of Fluid Mechanics, 796, 211–232, 2016a.

McClure, J. E., Berrill, M. A., Gray, W. G. and Miller, C. T.: Influence of phase connectivity on the relationship among capillary pressure, fluid saturation, and interfacial area in two-fluid-phase porous medium systems, Physical Review E, (Accepted), 2016b.

McClure, J. E., Prins, J. F., and Miller, C. T.: A Novel Heterogeneous Algorithm to Simulate Multiphase Flow in Porous Media on Multicore CPU-GPU Systems, Computer Physics Communications, 185, 1865–1874, doi:http://dx.doi.org/10.1016/j.cpc.2014.03.012, 2014a.

McClure, J. E., Wang, H., Prins, J. F., Miller, C. T., and Feng, W.: Petascale Application of a Coupled CPU-GPU Algorithm for Simulation and Analysis of Multiphase Flow Solutions in Porous Medium Systems, in: 28th IEEE International Parallel& Distributed Processing Symposium, Phoenix, Arizona, 2014b.

Miller, C. T., Christakos, G., Imhoff, P. T., McBride, J. F., Pedit, J. A., and Trangenstein, J. A.: Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches, Advances in Water Resources, 21, 77–120, 1998.

Miller, C. T., Dawson, C. N., Farthing, M. W., Hou, T. Y., Huang, J. F., Kees, C. E., Kelley, C. T., and Langtangen, H. P.: Numerical simulation of water resources problems: Models, methods, and trends, Advances in Water Resources, 51, 405–437, doi:10.1016/j.advwatres.2012.05.008, 2013.

Miller, C. T., Christakos, G., Imhoff, P. T., McBride, J. F., Pedit, J. A., and Trangenstein, J. A.: Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches, Advances in Water Resources, 21, 77–120, 1998.

Nickerson, C., Harper, M., Henrie, C. J., Mayberry, R., Shimmin, S., Smith, B., and Smith, J. H.: Sources of Data Providing Land Use and Land Cover Estimates for the U. S., Tech. rep., Interagency Council on Agricultural and Rural Statistics, subcommittee of the Interagency Council on Statistical Policy, https://www.data.gov/media/2013/10/attachments/ICARS%20Land%20Use%20and%20Cover%20data.pdf, 2013.

Niessner, J., Berg, S., and Hassanizadeh, S. M.: Comparison of Two-Phase Darcy's Law with a Thermodynamically Consistent Approach, Transport in Porous Media, 88, 133–148, doi:10.1007/s11242-011-9730-0, 2011.

Paiva, R. C. D., Collischonn, W., and Tucci, C. E. M.: Large scale hydrologic and hydrodynamic modeling using limited data and a GIS based approach, Journal of Hydrology, 406, 170–181, 2011.

Panfilov, M.: Macroscale Models of Flow Through Highly Heterogeneous Porous Media, Springer, 2000.

Pechlivanidis, I. G., Jackson, B. M., McIntyre, N. R., and Wheater, H. S.: Catchment scale hydrological modelling: A review of model types, calibration approaches and uncertainty analysis methods in the context of recent developments in technology and applications, Global NEST Journal, 13, 193–214, 2011.

Reggiani, P., Sivapalan, M., and Hassanizadeh, S. M.: A Unifying Framework for Watershed Thermodynamics: Balance Equations for Mass, Momentum, Energy and Entropy, and the Second Law of Thermodynamics, Advances in Water Resources, 22, 367–398, 1998.

Reggiani, P., Hassanizadeh, S. M., Sivapalan, M., and Gray, W. G.: A Unifying Framework for Watershed Thermodynamics: Constitutive Relationships, Advances in Water Resources, 23, 15–39, 1999.

Sathe, A. and Mann, J.: A review of turbulence measurements using ground-based wind ladars, Atmospheric Measurement Techniques, 6, 3147–3167, 2013.

Skøien, J. O., Blöschl, G., and Western, A. W.: Characteristic space scales and timescales in hydrology, Water Resources Research, 39, 11–1–11–19, 2003.

Vreugdenhil, C. B.: Numerical Methods for Shallow-Water Flow, no. 13 in Water Science and Technology Library, Springer, 1995.

Wang, A., Zeng, X., Shen, S. S. P., Zeng, Q.-C., and Dickinson, R. E.: Time Scales of Land Surface Hydrology, Journal of Hydrometeorology, 7, 868–879, 2006.

Whitaker, S.: Diffusion and Dispersion in Porous Media, American Institute of Chemical Engineers Journal, 13, 420–427, 1967.

Whitaker, S.: Flow in Porous Media I: A Theoretical Derivation of Darcy's Law, Transport in Porous Media, 1, 3–25, 1986.

Whitaker, S.: The Method of Volume Averaging, Kluwer Academic Publishers, Dordrecht, 1999.

Wildenschild, D. and Sheppard, A. P.: X-ray imaging and analysis techniques for quantifying pore-scale structure and processes in subsurface porous medium systems, Advances in Water Resources, 51, 217–246, 2013.

Wood, E. F.: Scaling behaviour of hydrological fluxes and variables: Empirical studies using a hydrological model and remote sensing data, Hydrological Processes, 9, 331–346, 1995.

Wood, E. F., Sivapalan, M., Beven, K., and Band, L.: Effects of spatial variability and scale with implications to hydrologic modeling, Journal of Hydrology, 102, 29–47, 1988.

Wood, S.N. : Fast stable direct fitting and smoothness selection for generalized additive models, Journal of the Royal Statistical Society Series B-Statistical Methodology, 70, 495–518, 2008

Zhou, Y. and Li, W.: A review of regional groundwater flow modeling, Geoscience Frontiers, 2, 205–214, 2011.