Squirt flow due to interfacial water films in hydrate bearing sediments

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Please note: All our responses to remarks of reviewers are in red and italic.

Dear Anonymous Reviewers,

We appreciate the time, interest and effort you invested to evaluate our manuscript. In the following, we respond to your questions, comments and concerns in order of appearance, to improve our manuscript based on your valued input.

Kind Regards,

Kathleen Sell, Beatriz Quintal, Michael Kersten, and Erik H. Saenger

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Anonymous Referee #1

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The paper presents a model study on absorption based on a squirt flow model in hydrate-bearing sediments. The setup of the model is straight forward and based on visual observations of thin (sub-micron) water films between quartz sand grains and clathrate. The mechanism which creates a pressure gradient and following flow in the water film is described clearly and also the influences of different water film thickness, different grain sizes, presence of isolated water pockets in the hydrate and, the influence of connections between the water films. The shift of the maximum in the dependence of 1/Q on frequency with changing thickness of the water film shows, that a distribution of various film thicknesses would result in high absorption (1/Q) over abroad frequency range. This is what one would expect, because the high absorption of hydrate-

bearing sediments has been observed in the field at seismic frequencies and in the lab at ultrasonic frequencies. The paper provides a valuable contribution towards the understanding of possible absorption mechanisms in hydrate-bearing sediments and should be published soon.

However, to avoid the "misuse" of the model in the interpretation of real measurements the author should clearly state what the restrictions and limits of the model are. The visual observations used for the modelling should also brought in relation to other visual observations (see comment/reference below). The following two main restrictions, at least, should be pointed out to the reader:

The model is based on the observations/results from high-resolution synchrotron-based Xray micro- tomography, where the hydrate is produced with the "gas in excess method". The method used for the hydrate formation is essential to understand the resulting hydrate habit. The "gas in excess method" forms a grain coating hydrate structure (with a water film between hydrate and grains), because the water which is wedding the grains is transformed into hydrate. When hydrate is formed with the "water in excess method" the grains will also be water wet, but these very thin (sub-micron) hydrate films between the grains and the hydrate structure will only occur at very high hydrate saturations (the highest reported values to my knowledge are about 90% from Mallik and the Gulf of Mexico).

Authors: As suggested by the reviewer we added the mandatory information in the Introduction as well as in section 2.

See also Tohidi's paper: "Gas bubbles, when present, act as preferential nucleation sites, but silica glass surfaces are wetted strongly by water and do not promote heterogeneous surface nucleation; a surface water film remains to high clathrate saturations. The fact that hydrates grow within the center of pores, rather than on grain surfaces, is likely to restrict the potential for cementation of sediments, unless a large proportion of the pore space is filled with hydrate."

Tohidi, B., Anderson, R., Clennell, M. B., Burgass, R. W., & Biderkab, A. B. (2001). Visual observation of gas-hydrate formation and dissociation in synthetic porous media by means of glass micromodels. Geology, 29(9), 867-870.1)

This model with sub-micron bound-water films is restricted to very high hydrate saturations (for your model with 250 – 150 m grain size and a water film below 1µm calculated about 99% hydrate saturation) or to gas-bearing reservoirs where the free water, available for hydrate formation, has been completely transformed into hydrate.

Authors: Indeed, the information that for our type of model the assumed GH saturation will be very high <90% was missing. Therefore, this fact has been added to the Introduction section.

The model (e.g. Fig. 7 & Fig. 12) assumes the sand grain as an inclusion in the hydrate matrix (a suspension of quartz grains in hydrate). This neglects the fact that hydrate is a secondary phase forming in the pore space when the sediment already has deposited and forms a grain skeleton with grain-to-grain contacts. Depending on the number and size of these contacts (compaction, overburden) the modulus (mainly the real part of the complex modulus) of the hydrate free grain skeleton will vary. Q is derived from the ratio of imaginary part and the real part of the complex modulus and will, therefore, change when the real part changes due to different number of grain-to-grain contact (coordination number). 2) The specific properties of the sediment grain skeleton and the resulting influence on absorption are not considered.

Authors: It is true that our model is a very simplified approach regarding sedimentary systems with respect to grain contacts and therefore a first step towards more realistic matrices as stated in the conclusion part. We are aiming for SRXCT/HRXCT data input to extend our model approach. But for now we are limited to the simple scenario of unconsolidated sediments.

We added your valuable comment to our Results section.

To study this special squirt-flow mechanism related to the existence of thin water films initially separated from other influences is certainly justified. However, this model can be improved in future to also involve effects from the grain skeleton (e.g. involving Hertz-Mindlin theory) and it can be combined with other absorption mechanisms (see Marin-Moreno's paper).

Authors: Further investigations involve the stepwise extension of this model towards more realistic settings is aimed but hampered by the lack of a segmentation routine capable to cover a full dataset (24GB). Currently a machine learning code is tested on the data to handle this issue.

Anonymous Referee #2

Received and published: 20 November 2017

Review type: Interactive comment

https://doi.org/10.5194/se-2017-106, 2017

Dear authors,

I found your paper intriguing and comprehensive; in my understanding, you provide previously published observational evidence from x-ray tomography to support the claim that a thin water film around sand grains embedded in a gas hydrate matrix is a good conceptual model that captures the high attenuation observed in gas hydrate systems. I believe that the general scope of your paper deserves some attention as squirt flow in hydrates is only recently being considered as the responsible mechanism and Marin-Moreno et al. (2017) is potentially too confusing for scientists to use as it considers the overlap of many mechanisms. So there is definitely a gap in the literature for simple, usable models of the squirt flow of GH and I think your paper is a step towards the right direction. I do however think that the presentation of your work does not do the ideas justice and as a result lessens the potential significance it may have. Below are some of my most serious concerns:

1. I am not entirely familiar with imaging techniques when applied to hydrates so I am not aware how the conceptualisation of your model is affected by the imaging. I realise the experimental imaging results are presented elsewhere but I would still like to see a convincing argument about how the thin water film surrounding a quartz grain within a hydrate is indeed a physically plausible configuration rather than an imaging artifact

Authors: A common image artifact occurring when conducting synchrotron-based tomography is the so-called edge enhancement. Probably, this is the artifact you have in mind. When plotting a histogram over an area where possible edge enhancement occurs the histogram line plot will reveal symmetrical valleys and peaks. Here, this is not the case because we can identify a several voxel wide interface between the GH and quartz. This interface is in the same gray-value range than the water phase identified in the intial (untreated) samples – these samples are completely GH free and we can be sure that the phase identified is water. The observation of the interfacial water layer from the experimental results of Chaouachi et al. (2015) is in accordance with the publication of Tohidi et al. (2001). Additionally several molecular numerical simulations showed that a water layer prefers the interface of GH and quartz grains (Bagherzadeh et al., 2012; Bai et al., 2011; Liang et al., 2011). For the matter of clarification text passages have been added to the manuscript.

2. Your single circular grain model presented in Figure 7 is the exact same model proposed by White, J. (1975) which you cite in passing in your introduction. The only difference here is that your sand grain is in place of a second fluid in White's model. This is nowhere mentioned and I firmly believe it should be.

Authors: Our model might, in principle, resemble White's model from the spherical geometries involved, but it is considerably different. White's model refers to a spherical porous patch embedded in a porous background. Fluid pressure diffusion occurs between those two poroelastic subdomains across the spherical surface. The model that we consider refers to a non-porous solid spherical inclusion separated from the embedding non-porous solid background by a thin liquid shell. In this case, fluid pressure diffusion occurs only within the liquid shell, tangentially to its spherical surfaces.

3. You claim to numerically solve (1), (2) but you show no meshing and mention no restrictions on your domains (is the circular sand grain obeying a free BC, is it fixed etc?)

Authors: We have added a figure with a mesh for the main model (new Figure 8) and all the necessary BC are explained in the Numerical Methodology section.

4. As I mentioned earlier in comment 2 this model is exactly the same as White's model which has an exact analytic solution. Why does your model of figures 7,14 not have an analytic solution despite the simple domain and, if it does, why are we not seeing it - it is so much easier for someone to replicate your work if they have a formula to use. Does your model agree with White's model if his second fluid becomes really stiff (to the limit of a sand grain)?

Authors: Our model is different than White's model, as explained above. We believe this is clearer after our revision.

5. Although these may be commonplace for people familiar with squirt flow, how do you define "mesoscopic" as a scale here? What are the domains and boundary conditions that go into solving your equations? How does the relative rather than absolute scaling affect the behaviour of your attenuation curves? What I mean here is that if you fixed the GH square in model 7 to have side = 1 you could see the affect of relative saturation of GH and water rather than inserting absolute values. This would be much more illuminating than your figure 8. This problem is also present when you discuss water bridges and your model demonstrates a second peak in the attenuation curves but the reader is left wondering how(if?) does this peak move when the bridge gets longer. There is significant mathematical rigour that is missing from your work

which is not in itself always a bad thing but this impedes the impact and significance it may have.

Authors: Our model is not at the mesoscopic scale, but microscopic. With respect to mathematical rigor, we believe that we gave the necessary information, such as the equations, the parameter values, the model geometry, and the boundary conditions are described in the numerical methodology part.

6. You mention shear dispersion in passing indicating that you have numerically calculated it ("it can be calculated in a similar manner simply by changing the boundary conditions") - is the shear dispersion predicted by this model in any way realistic? I feel that it would be beneficial for your work to show the attenuation and dispersion of shear velocity and discuss the success/limitation of your modelling strategy with respect to shear.

Authors: Unfortunately our code becomes unstable under the boundary condition necessary for a shear test and the results for S-wave attenuation and dispersion at this point are not reliable. The compressional tests to obtain P-wave attenuation and dispersion, on the other hand, have been tested through comparisons with other solutions (e.g., Quintal et al, 2016, Geophysics) and yield stable and reliable results.

And some more minor comments:

- Figure 2 have some labels GH* and I have not been able to see what the * refers

- Figure 3 caption has an unrendered mu character that shows up as a box

- P20L5 needs a space between "effect" and "of"

Authors: These mistakes have been fixed.

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ABSTRACT

Sediments containing gas hydrate dispersed in the pore space are known to show a characteristic seismic anomaly which is a high attenuation along with increasing seismic velocities. Currently, this observation cannot be fully explained albeit squirt-flow type mechanisms ~~at~~ on the microscale have been speculated to be the cause. Recent major findings from in-situ experiments, using the gas in excess and water in excess formation method, and coupled with high-resolution synchrotron-based X-ray micro-tomography, revealed a systematic presence of thin water films between the quartz grains and the encrusting hydrate ~~when formed using the "gas in excess method"~~. ~~In this study, t~~The data ~~was~~ obtained from those experiments ~~and underwent~~are here submitted~~d~~underwent ~~to~~ an image processing procedure to quantify the thicknesses and geometries of the aforementioned interfacial water films. Overall, the water films vary from sub-µm to a few µm in thickness. ~~where and s~~In addition, some of ~~them~~ the water films ~~are interconnected by~~interconnect through water bridges. This geometrical analysis is ~~then~~ used to propose a new conceptual squirt flow model for hydrate bearing sediments. A series of numerical simulations is performed considering variations of the proposed ~~Subsequently the established~~ model ~~acts as a direct model input to obtain~~to study seismic attenuation caused by such thin water films. Our results support previous speculations that squirt flow can explain high attenuation at seismic frequencies in hydrate bearing sediments, but based on a conceptual squirt flow model which is geometrically different than those previously considered.

Keywords: attenuation, squirt flow, interfacial films, dispersion, micro-tomography, gas hydrates, sediments, numerical modeling

1. INTRODUCTION

Important mechanisms of wave attenuation in fluid-saturated porous media from seismic to ultrasonic frequencies, include friction between grain boundaries (Winkler and Nur, 1982), global flow or Biot's mechanism (Biot, 1962), and wave-induced fluid flow at mesoscopic and microscopic scales (e.g., Müller et al., 2010). At the mesoscopic scale, patchy saturation and fractures are the most prominent causes of wave-induced fluid flow (White, 1975; White et al., 1975; Brajanovski et al., 2005; Tisato and Quintal, 2013; Quintal et al., 2014). At the microscopic scale, wave-induced fluid flow is commonly referred to as squirt flow and typically occurs between interconnected microcracks or between grain contacts and stiffer pores (O'Connell and Budiansky, 1977; Murphy et al., 1986; Mavko and Jizba, 1991; Sams et al., 1997; Adelinet et al., 2010; Gurevich et al., 2010). The attenuation caused by global flow as well as that caused by wave-induced fluid flow at microscopic or mesoscopic scales are frequency dependent.~~,~~ ~~-W~~~~but w~~hile the latter can have a strong effect at seismic frequencies (Pimienta et al., 2015; Subramaniyan et al., 2015; Chapman et al., 2016), global flow will only cause significant attenuation in reservoir rocks at ultrasonic frequencies or higher (e.g., Bourbie et al., 1987). The attenuation caused by friction between grain boundaries is, on the other hand, frequency independent and basically depends on the confining pressure and the strain imposed by the propagating wave (Winkler and Nur, 1982). Its effect is expected to be small for the correspondingly small strains caused by seismic waves used in exploration and reservoir geophysics. Furthermore, the attenuation caused by wave-induced fluid flow tends to be linearly superposed to that due to friction between grain boundaries, as shown by Tisato and Quintal (2014).

Gas hydrates (GH) are ice-like structures comprised of gas molecules entrapped by water molecules (Sloan and Koh, 2008). The widespread global occurrence of GH and the fact that 1 m^3 of GH contains up to 164 m^3 of natural gas (CH_4 and CO_2 at standard conditions) draws attention to the idea of using GH as a potential future energy resource (Schicks et al., 2011). Nevertheless, GH-bearing sediments have been discussed not only as a relatively clean hydrocarbon reservoir (Collett and Ladd, 2000), but also in terms of a geohazard that can potentially contribute to global warming associated to hydrate dissociation and subsequent destabilization of GH-cemented deep sea sediments at continental margins (Kvenvolden, 1993; Nixon and Grozic, 2007). Occurrences of GH are restricted to locations providing the required amount of gas and water and the preferred pressure-temperature (p/T) conditions, which are commonly referred to as the so-called gas hydrate stability zones. Usually, GH reservoirs are mainly limited to marine continental margins, deep lakes and permafrost regions (Bohrmann and Torres, 2006).

In the search for GH reservoirs, the attenuation of seismic waves caused by the pore fluids might be an important survey tool (e.g. Bellefleur et al. 2007). However, little effort has been directed toward studying its effects for unconsolidated sediments hosting GH in a rather dispersed manner. GH forming in the pore space of unconsolidated sediments at given p/T-conditions alters the effective elastic and effective transport properties of the hosting sediment. It is known that the presence of GH in the sediment not only reduces the porosity and causes

significant changes on its permeability, but also results in higher P- and S-wave velocities due to stiffening of the hosting matrix (Dvorkin et al., 2003; Guerin & Goldberg, 2005; Yun et al., 2005; Priest et al., 2006; Waite et al., 2009). In other words, the bulk and shear moduli increase due to the GH matrix-supporting effect within the sedimentary frame (Ecker et al., 1998). Additionally, the presence of GH causes higher attenuation of the seismic waves (Bellefleur et al. 2007; Dewangan et al. 2014) which was in particular observed for sediments containing dispersed GH in the pore space (Guerin and Goldberg, 2002; Dvorkin and Uden, 2004). This ~~identified~~ anomalous seismic behavior in terms of increased attenuation and velocities (Guerin and Goldberg, 2002; Dvorkin and Uden, 2004) cannot be fully explained, although wave-induced fluid flow at the microscopic and mesoscopic scales have ~~has~~ been speculated to cause them (Priest et al., 2006; Gerner et al. 2007). Gerner et al. (2007) conducted numerical P-wave velocity simulations in highly permeable sedimentary layers, similar to hydrate-bearing sediments, and identified interlayer flow at the mesoscopic scale (White et al., 1975) as a potential mechanism of attenuation. Other authors have considered classical squirt flow models (O'Connell and Budiansky, 1977; Murphy et al., 1986) as the main source of attenuation in hydrate-bearing sediments (Dvorkin and Uden, 2004; Guerin & Goldberg, 2005; Priest et al., 2006; Waite et al., 2009; Marin-Moreno et al., 2017).

Quantifying GH saturation levels through geophysical exploration techniques is, however, not straightforward as there are still open questions on GH formation, its microstructure and distribution in the natural settings. Additionally, the recovery of unaltered natural GH samples is hampered due to their fast decomposition under ambient conditions. Therefore, various researchers have attempted to mimic the natural environment of GH-bearing sedimentary matrices in laboratory experiments (Berge et al., 1999; Ecker et al., 2000; Dvorkin et al., 2003; Yun et al., 2005; Spangenberg and Kulenkampff, 2006; Priest et al., 2006, 2009; Best et al., 2010, 2013; Hu et al., 2010; Li et al., 2011; Zhang et al., 2011; Dai et al., 2012; Schicks et al., 2013). The results of this collective effort established a number of conceptual models for the role of GH embedded in its sedimentary matrix (Figure 1). Nevertheless, these approximations turned out to be still not satisfactory. Although it has been suggested that all hydrate habits known from laboratory investigation involving synthetic samples occur also in nature (Spangenberg et al. 2015), none of those simplified models can yield accurate predictions of GH saturations from field electric resistivity or seismic data alone (Waite et al., 2009; Dai et al., 2012).

Chaouachi et al. (2015) performed in-situ experiments based on ~~the gas in excess method~~ different formation mechanisms, including the "~~gas in excess~~water in excess" and the "gas in excess" method, to form gas hydrates in various sedimentary matrices. The in-situ experiments~~an dcoupled coupled~~ with high-resolution synchrotron-based X-ray micro-tomography (SRXCT) yielded ~~in~~ 3D images of sub-µm spatial resolution ~~for quartz sands bearing GH~~. Using the "gas in excess" ~~In this study, we introduce an alternative conceptual model for GH formed with the "gas in excess method". Using this formation~~ method, the water present in the samples weds the grain surfaces~~,~~ and transforms into GH at the required pressure/temperature conditions. When hydrate is formed with the "water in excess method" the grains will also be water wet, but these very thin (sub-micron) hydrate films between the grains and the hydrate structure will only occur at very high GH saturations. ~~Furthermore, the~~

~~GH appears to form a rather coating structure surrounding the grain. Our study's objective basesbased on findings from in situ experiments coupled with high resolution synchrotron-based X-ray micro-tomography (Chaouachi et al., 2015; Sell et al., 2016).~~ The resulting 3D micro-tomography data ~~for quartz sands bearing GH~~ revealed the systematic presence of ~~thin~~ interfacial water films~~,~~ between the pore-filling GH and the grains, independently of which formation method was used (gas in excess or water in excess method)~~,~~. The observed interfacial water films are occasionally interconnected via water bridges but also~~, as well as~~ water pockets are embedded in the GH.

~~Here we submit~~For this study, the ~~3D micro-tomography~~SRXCT data presented by Chaouachi et al. (2015) underwent ~~to~~ an image processing workflow in order to quantify the thicknesses of the thin interfacial water films. Based on the obtained results, we introduce a conceptual model for GH-bearing sediments to numerically study squirt flow. Our~~We perform~~ numerical simulations ~~of squirt flow in the proposed conceptual model to study the related~~allow for the dispersion of the ~~stiffness~~ P-wave modulus and the ~~corresponding~~ frequency-dependent P-wave attenuation. The results demonstrate the high levels of seismic attenuation/dispersion that ~~such features~~a range of variations of our conceptual model can cause. Additionally, our results~~and~~ support the suggestions that the estimation of GH saturation, for GH occurring in a rather dispersed manner, could be accomplished by using ~~P- and S-~~seismic wave attenuation as a tool for indirect geophysical quantification (Guerin and Goldberg, 2002; Priest et al. 2006; Best et al. 2013; Marin-Moreno et al., 2017).

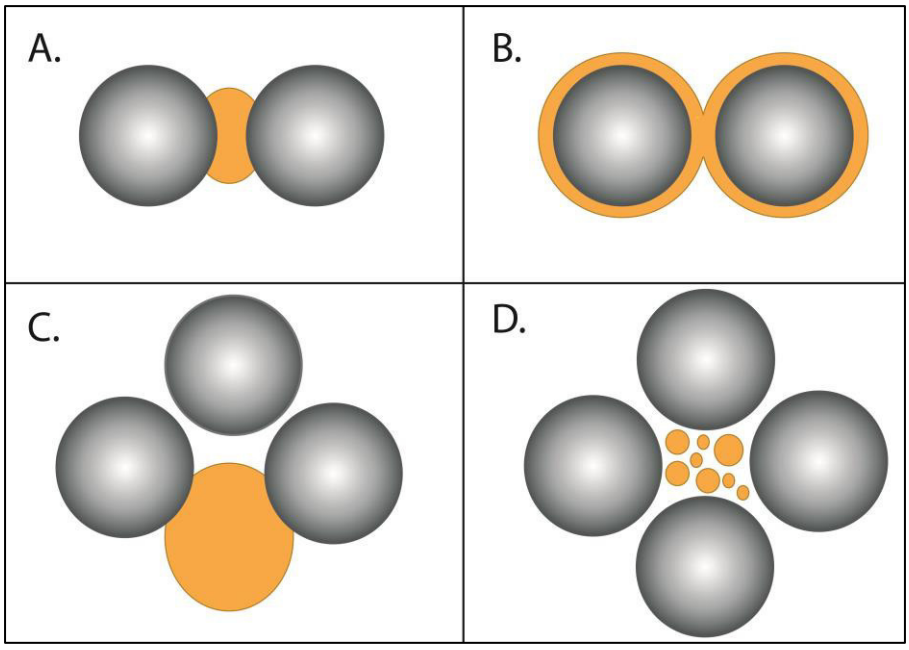


Figure 1. Review of the established conceptual models (Grains = grey and GH = orange), with (A) cementation – GH cements the grains, (B) encrustation – GH coats the grains, (C) matrix-supporting – GH is part of the sediment matrix, and (D) pore-filling – GH employs the pore space forming crystallites of varying size (modified after Dai et al., 2004).

2. THE INTERFACIAL WATER FILMS

Chaouachi et al. (2015) conducted various in-situ experiments coupled with synchrotron-based tomography at the TOMCAT beamline of the Paul Scherrer Institute in Villigen, Switzerland. The aim was to study the formation process and distribution of gas hydrates in various matrices, such as pure quartz sand and glass beads, as well as mixtures of quartz sand with clay minerals. These in-situ experiments have been ~~realized~~ conducted using an experimental setup ~~under elevated~~that allowed for high pressures and low~~ered~~ temperatures. Further details are given by Chaouachi et al. (2015), Falenty et al. (2015), and Sell et al. (2016).

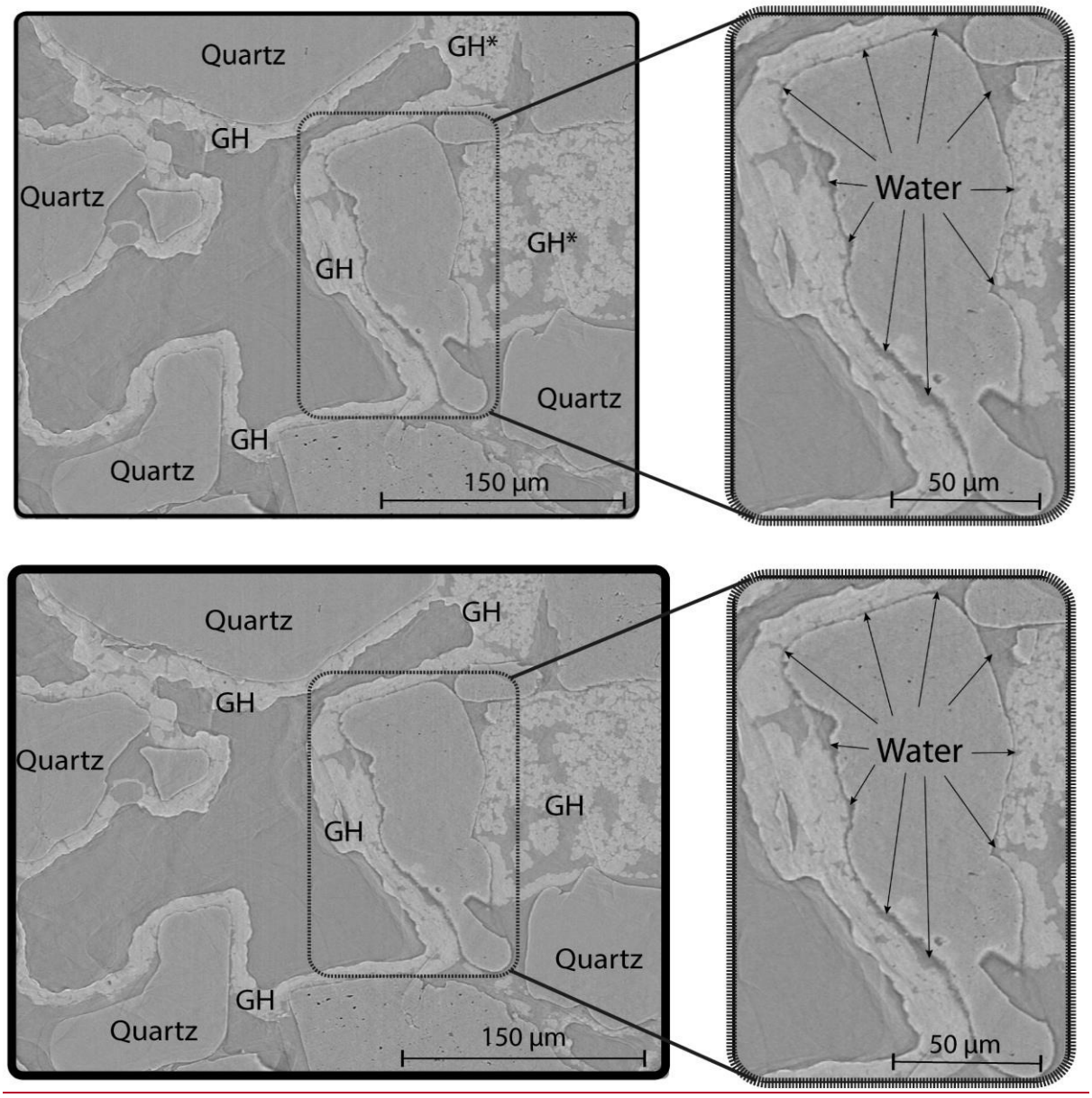


Figure 2. (Left) Overview of an unfiltered 2D slice in y,z-direction of quartz sand containing GH. Note that due to its unfiltered state, this image contains artifacts, such as streaks and slight edge enhancement. Phases can be identified on the base of grey scale differences.

~~In~~ For this study, the ~~3D micro-tomography~~SRXCT data obtained from the mentioned in-situ experiments~~, are used~~ focused~~the focus lies~~ on samples containing pure natural quartz sand

sieved at 200–300 µm grain size. ~~Details on the sedimentology and mineralogy of the host sediment are provided by~~ Chuvilin et al. (2011) provides details on the sedimentology and mineralogy of the host sediment. We use a reconstruction process (Marone and Stampanoni, 2012) that yields an image matrix of 2560 × 2560 × 2160 voxels, with ~~an~~ isometric voxel sizes of 0.74 and 0.38 µm at 10-fold and 20-fold optical magnification, respectively. The reconstructed tomograms revealed discernible grey value differences between the three relevant phases of the sample: solid grains, hydrate, and water (Figure 2). ~~The I~~ image analysis ~~was has been accomplished T~~to reduce image artifacts, such as inhomogeneity in grey scale values, streaks and edge enhancement, we ~~by~~ apply~~ing~~ a systematic image enhancement workflow comprising different image filter combinations in 2D and 3D (Sell et al., 2016). ~~One of the most interesting observations made was a~~Chaouachi et al. (2015) observed ~~A~~a systematic appearance of an ~~thin~~ interfacial water film separating the quartz grains from the GH phase ~~(Chaouachi et al., 2015). This fluid interface was observed~~ in samples where GH was formed ~~in quartz sand samples~~ directly from the juvenile state not involving GH dissociation, as well as where GH was formed from ~~gas-enriched water~~the gas in excess method. This observation is in accordance with the publication of Tohidi et al. (2001). Additionally several molecular numerical simulations showed that a water layer prefers the interface of GH and quartz grains (Bagherzadeh et al., 2012; Bai et al., 2011; Liang et al., 2011). Identifying the water films and quantifying its thickness was one scope of this study to adapt our conceptual model.

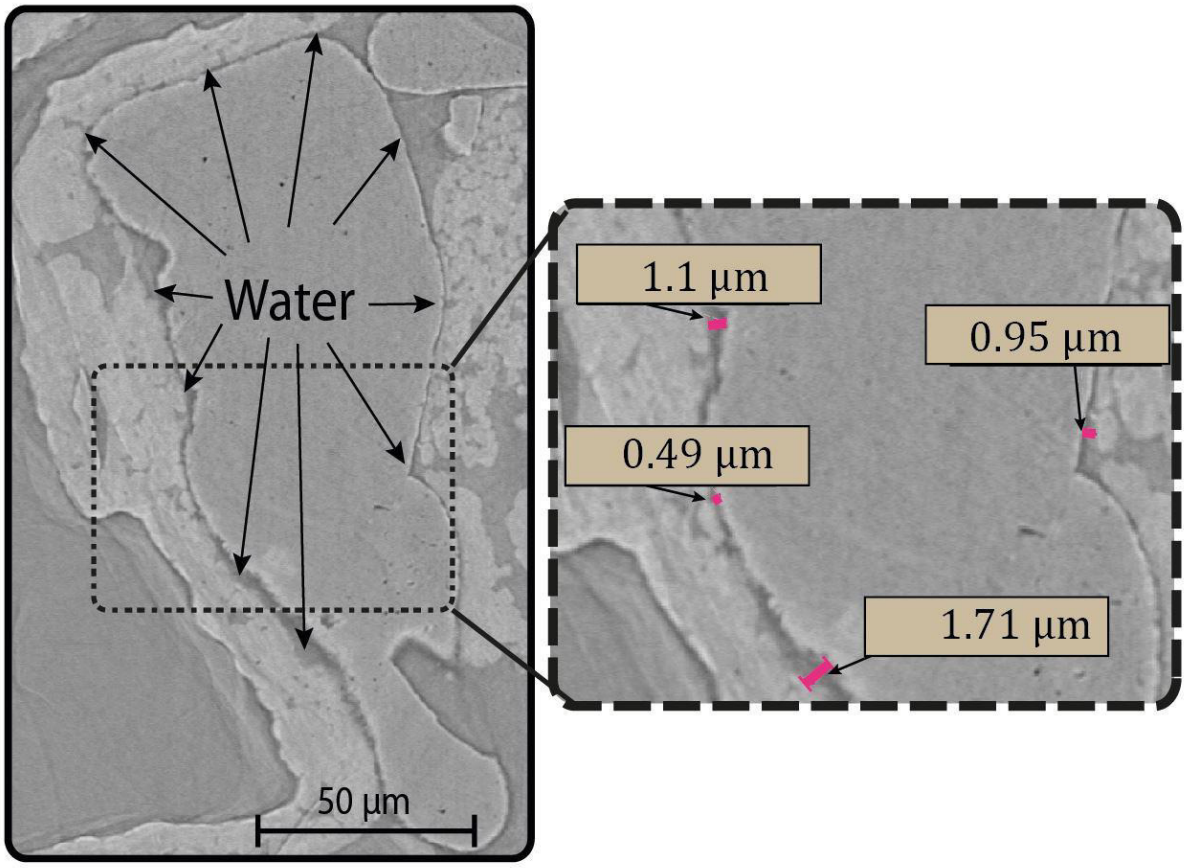


Figure 3. Raw (unfiltered) 2D image in y,z-direction at a spatial resolution of 0.38 m. The zoom depicts the measurement of a thin interfacial water film varying in thickness from 0.49 ~~–~~µm to 1.71 µm.

The broad range of grey scale values of the filtered images ~~can be~~were classified using watershed segmentation combined with region growing tools of the software packages of Avizo Fire 7 (FEI, France) and Fiji. ~~The full workflow has been described by Sell et al. (2016). Basically, f~~~~F~~~~or~~In the present study,~~is work~~ we determined the thickness variation and geometry of the water film~~ has been determined~~ (Figure 3)~~, an information needed to define our conceptual model to investigate on attenuation in GH-bearing sedimentary matrices (Figure 6)~~. Following the image enhancement and segmentation process described by~~in~~ Sell et al. (2016), the segmented data illustrate the characteristics and appearance of the phases distributed in the samples (Figure 4). Moreover, the high resolution of the data enables us to obt~~g~~ain 3D images in which particular details, ~~like~~such as water bridges connecting two interfacial water films, are detectable (Figure 5). With information collected from the 3D data,~~T~~ our ~~newly introduced~~proposed ~~he multi-phase~~ conceptual model ~~–~~involves ~~initially idealized~~ round-shaped grains covered by a homogenous ~~thin~~ water film which is in turn ~~and can be adjusted (i) to include grains~~ embedded in non-porous hydrate. The conceptual model ~~or porous hydrate,~~ can be adjusted ~~(ii)~~ to include water bridges connecting the water films (Figure 6~~ and 12~~) and/or ~~(iii)~~ isolated water pockets within the hydrate and separated from the water films.

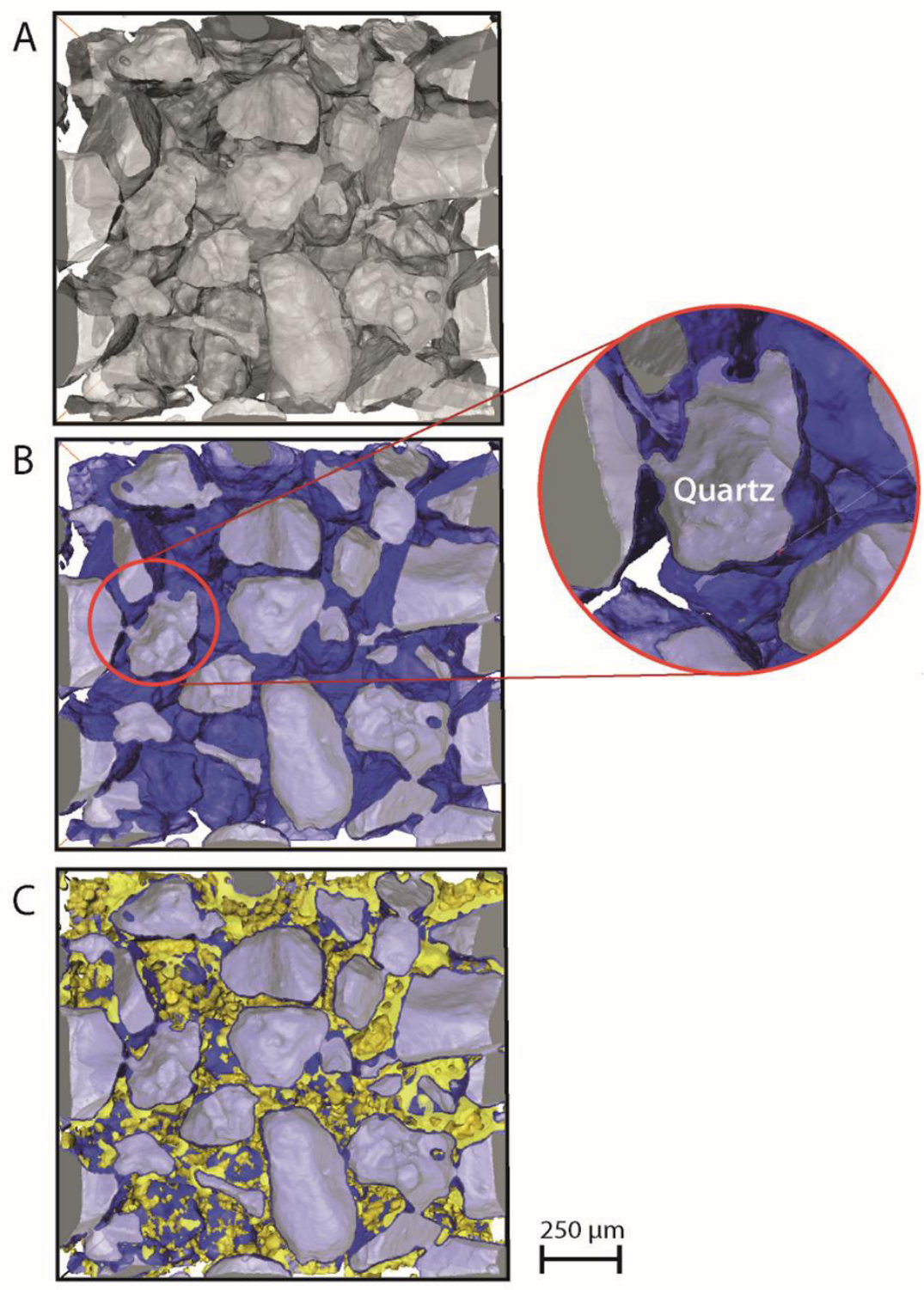


Figure 4. Volume-rendered phases in a representative image sample. For a better visualization, the phases are introduced step-by-step, with (A) grains (grey), (B) grains and interfacial water films (blue), and (C) grains, water film and hydrate (yellow). A zoom in (B) shows an interfacial water film measured at 1 – 4 voxels equivalent to 0.38 – 1.52 µm thickness, respectively.

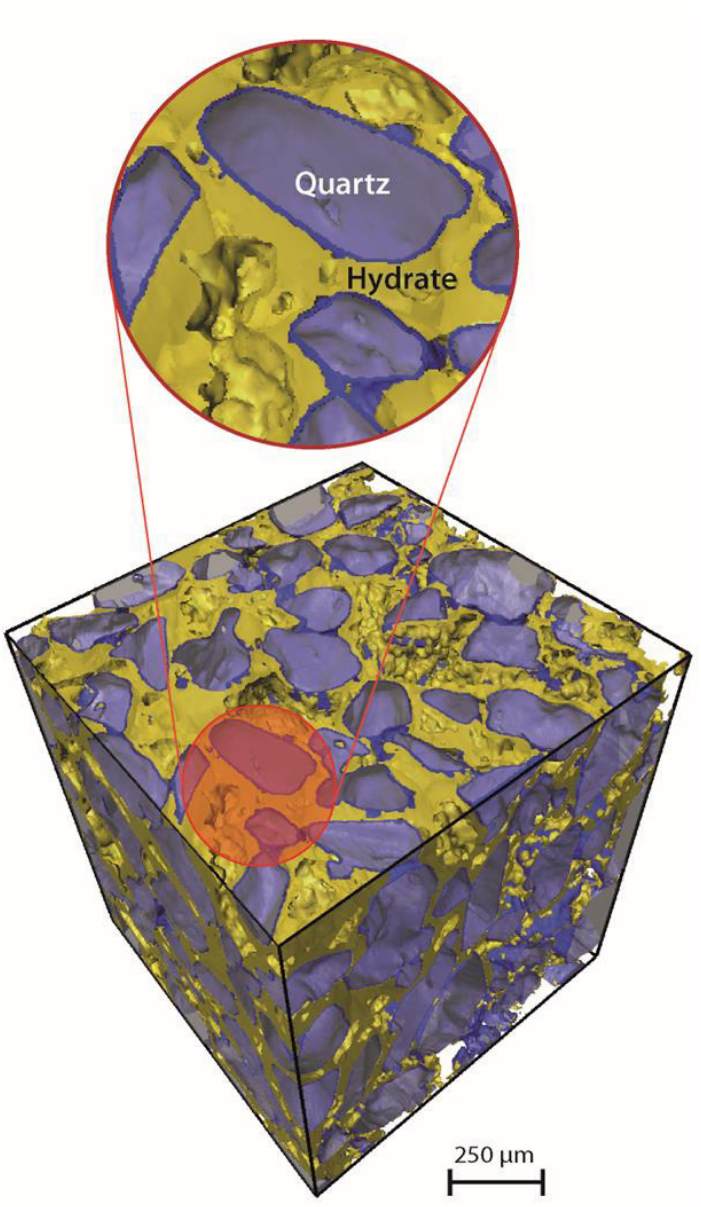


Figure 5. Volume-rendered image of a representative Region of interest (ROI) of 600 × 600 × 600 voxels at 0.38 µm spatial resolution. The zoom-in depicts quartz grains fully separated from the pore-filling hydrate by thin interfacial water films, with two quartz grains having their water films interconnected by a water bridge.

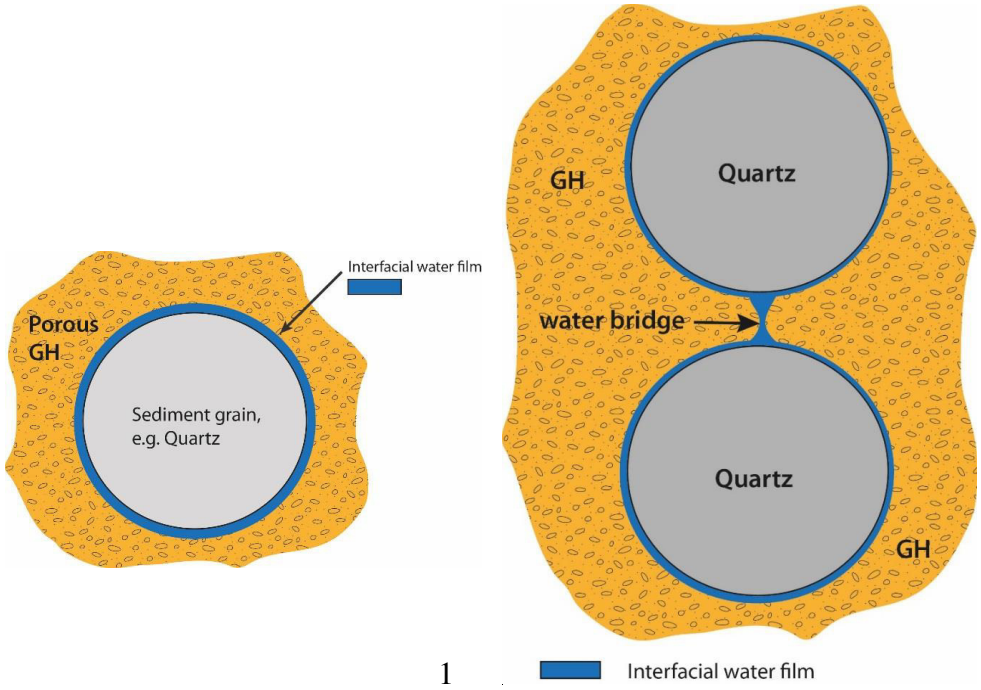


Figure 6. Schemes of (A) a new concept model for GH encrusting quartz grains separated by a thin interfacial water film and (B) connected by a water bridge.

3. NUMERICAL METHODOLOGY

3.1 Mathematical formulation

To estimate frequency-dependent attenuation in the GH systems described above we employ a hydromechanical approach (Quintal et al., 2016) based on the conservation of momentum

$$\nabla \cdot \boldsymbol{\sigma} = 0, \tag{1}$$

with the components σ_{kl} of the stress tensor $\boldsymbol{\sigma}$ defined according to the general stress-strain relations in the frequency domain

$$\sigma_{kl} = 2\mu\varepsilon_{kl} + \left(K - \frac{2}{3}\mu\right)e\delta_{kl} + 2\eta\omega i\varepsilon_{kl} - \frac{2}{3}\eta\omega i e\delta_{kl}, \tag{2}$$

where ε_{kl} denotes the components of the strain tensor, e denotes the cubical dilatation given by the trace of the strain tensor, ω is the angular frequency, and i represents the unit imaginary number. The indexes k, l = 1, 2, 3 refer to the three Cartesian directions x_1, x_2, x_3 or x, y, z and δ_{kl} is the Kronecker delta (δ_{kl} = 1 for $k = l$ and δ_{kl} = 0 for $k \neq l$). The material parameters μ, K, and η are the shear modulus, the bulk modulus, and the shear viscosity, respectively.

Using this general mathematical formulation (equations 1 and 2), a heterogeneous medium can be described as having an isotropic, linear elastic solid frame and fluid-filled cavities or pores, to which a specific choice of material parameters can be assigned. ~~The same unknowns and material parameters describe the behaviors of the solid and the fluid phases. For example, an unknown u describes the solid displacement in the domains of the model representing an elastic~~

~~solid and also describes the fluid displacement in the domains representing a viscous fluid. In fact, e~~Equation 2 reduces to Hooke's law by setting the shear viscosity η to zero in the solid domains. In these regions, μ and K denote the shear and bulk moduli of the corresponding elastic solid~~, and the shear viscosity η is zero~~. In the fluid-filled~~model~~ domains ~~representing a compressible viscous fluid~~, the shear modulus μ is set to zero while K and η denote the bulk modulus and shear viscosity of the fluid. In this domains~~and~~ the combined equations 1 and 2 reduce to the quasi-static, linearized Navier-Stokes' equations for the laminar flow of a Newtonian fluid (e.g., Jaeger et al., 2007). ~~In these fluid-filled regions, K and η denote the bulk modulus and shear viscosity of the fluid.~~

When the aforementioned heterogeneous medium is deformed, fluid pressure differences between neighbor regions induce fluid flow or, more accurately, fluid pressure diffusion, which in turn results in energy loss caused by viscous dissipation (Quintal et al., 2016). At the microscopic scale, this attenuation mechanism is commonly referred to as squirt flow (e.g., O'Connell and Budiansky, 1977; Murphy et al., 1986) and is the sole cause of attenuation in our simulations, as we neglected the inertial terms in equations 1 and 2.

3.2 Finite element modeling

Our 2D problem is equivalent to a 3D case under plain strain conditions, which means no strain outside the modeling plane is allowed to develop. For the corresponding simulations, we consider the directions x and y, to be in the modeling plane and direction z to be the one in which no displacement or displacement gradients can occur.

The numerical solution is based on a finite-element approach in the frequency domain. We employ an unstructured triangular mesh, which allows for an efficient discretization of slender heterogeneities having large aspect ratios, such as the thin interfacial water films, by strongly varying the sizes of the triangular elements (e.g., Quintal et al., 2014). A few elements across the thin interfacial water film are necessary to accurately capture the viscous dissipation in this region, while much larger elements are sufficient in the solid elastic domains. The sizes of smallest and largest elements in our meshes differ by 3 orders of magnitude.

To assess the P-wave attenuation and modulus dispersion caused by squirt-flow, we subject a rectangular numerical model to an oscillatory test. A sinusoidal downward displacement is applied homogeneously at the top boundary of the numerical model. At the bottom, the displacement in the (y) vertical direction is set to zero. At the lateral boundaries of the model, the displacement in the (x) horizontal direction is set to zero. From this test, we obtain the stress and strain fields, averaged over the entire model domain. The mean stress and strain are used to compute the complex-valued and frequency-dependent P-wave modulus corresponding to a wave propagating in the vertical direction. The real part of the P-wave modulus H is used to illustrate the P-wave modulus dispersion while the ratio between its imaginary and real parts is used to quantify the P-wave attenuation $1/Q_P$. The S-wave attenuation and dispersion can be evaluated in a similar manner ~~simply~~ by changing the boundary conditions to those of a simple-shear test (e.g., Quintal et al., 2012, 2014).

~~Our 3D problem is solved s~~Similar~~ly~~ to the 2D problem, the solution to our 3D problem ~~using~~bases is based on the application of an unstructured mesh~~, but~~ with tetrahedral elements. ~~Again, t~~The element sizes in our 3D meshes also vary by about 3 orders of magnitude.

4. NUMERICAL RESULTS

Many sources of squirt flow might coexist in unconsolidated sediments hosting GH, such as those resembling the conventional squirt flow models introduced by O'Connell and Budiansky (1977) for interconnected microcracks and by Murphy et al. (1986) for microcracks or grain contacts connected to spherical pores. Marin-Moreno et al. (2017) describes an integrated approach that combines the effects of some squirt flow models and other attenuation mechanisms. Here our objective diverges from that. We instead aim at studying the squirt flow phenomenon and the resulting frequency-dependent attenuation associated with a specific model, which is geometrically different from the mentioned conventional squirt flow models and is based on the thin interfacial water films. We thus neglect all other potentials sources of attenuation.

4.1 Attenuation mechanism in a thin interfacial water film

Our 2D numerical model domain corresponds to a fundamental block of a periodic distribution of unconsolidated circular quartz grains dispersed in a continuous GH background and separated from the latter by a thin interfacial water film (Figure 7). ~~Aim of this basic model is to have a first estimate of the possible attenuation effect by a thin interfacial water film.~~ The subdomain representing the thin interfacial water film is described by the corresponding properties of this viscous fluid, while the other subdomains are described by properties of two different elastic solids, quartz and GH. These properties are given in Table 1 and the numerical mesh is shown in Figure 8.

~~Based on the material properties given in Table 1, w~~We consider thicknesses of the interfacial water film ranging from 0.1 μm to 1 μm as well as two grain diameters 150 and 250 μm for the 2D model. These values were chosen considering the sizes of the quartz grains used in the laboratory experiment from which the SRXCT data were obtained, which ranged from 150 to 300 μm, and the thicknesses of the interfacial water films observed in the data, ranging from 0.38 μm to 1.5 μm. Note that the thinnest interfacial water films observed were limited by the highest achieved spatial resolution of 0.38 μm. Despite this limitation ~~of spatial resolution~~, ~~the~~ water film thicknesses below 0.38 μm have also been considered for our numerical analysis ~~as well~~.

The numerical results are expressed as the real part of the P-wave modulus and the P-wave attenuation $1/Q_P$ (Figure 9 ~~8~~). We observe that a decrease in the thickness of the interfacial water film causes the attenuation and dispersion curves to shift to lower frequencies. In fact, high attenuation values ($1/Q$ ~ 0.1) are observed at seismic frequencies (~100 Hz) when the

interfacial water film is as thin as 0.1 μm and the grain diameter is as large as 250 μm. Decreasing the grain diameter~~, on the other hand,~~ causes a shift to higher frequencies of the attenuation and dispersion curves.

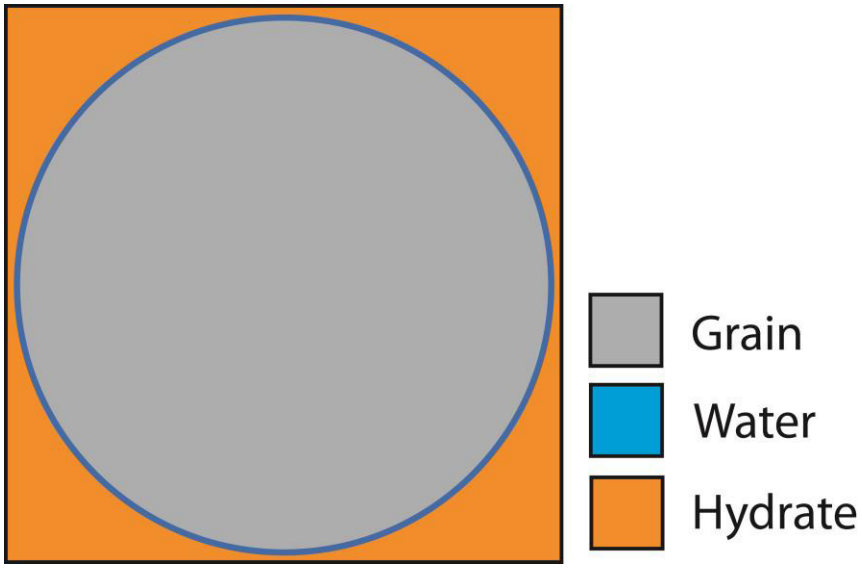


Figure 7. Fundamental block of an idealized periodic medium representing ~~-~~sediment grains which are separated from the embedding GH background by a thin interfacial water film.

Table 1. Material properties used in the numerical simulations. ~~*~~The properties of quartz are based on the work of Bass (1995) and those of hydrate on Helgerud (2003).

Material parameter	Quartz~~*~~	Hydrate~~*~~	Water
Shear modulus μ	44.3 GPa	13.57 GPa	0
Bulk modulus K	37.8 GPa	8.76 GPa	2.4 GPa
Shear viscosity η	0	0	0.003 Pa×s

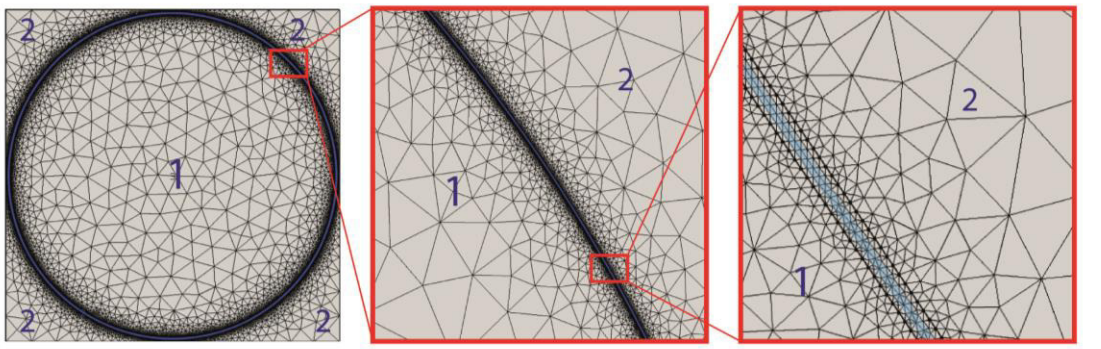


Figure 8. The triangular mesh used for the numerical model shown in Figure 7. To distinguish between the phases: Quartz is denoted with # 1,GH is denoted with # 2 and the interfacial water film is depicted in a light-blue color.

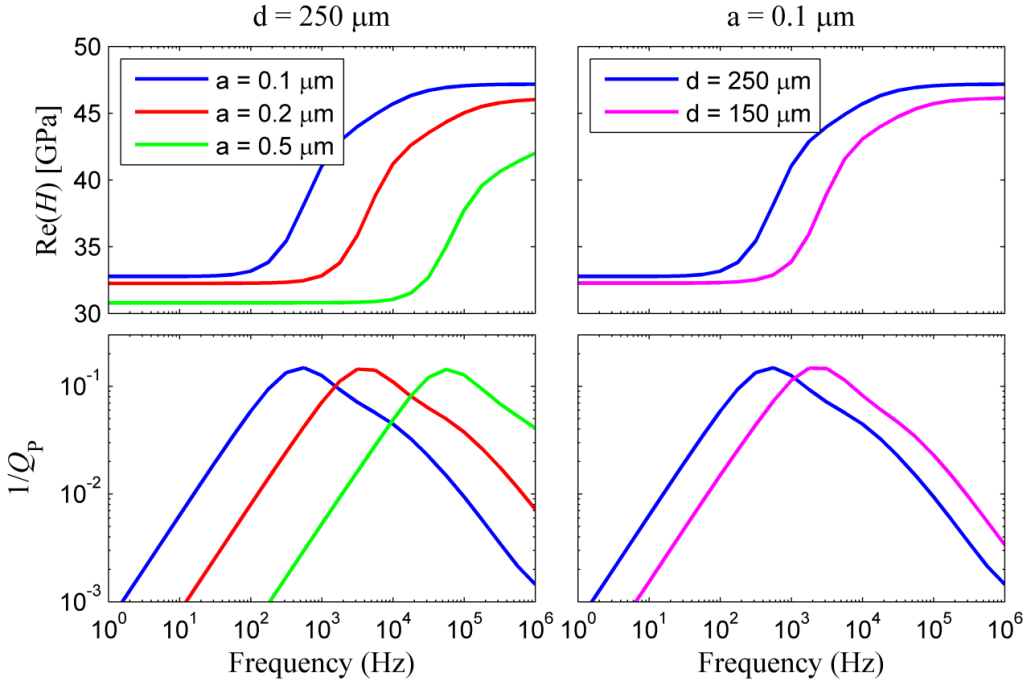
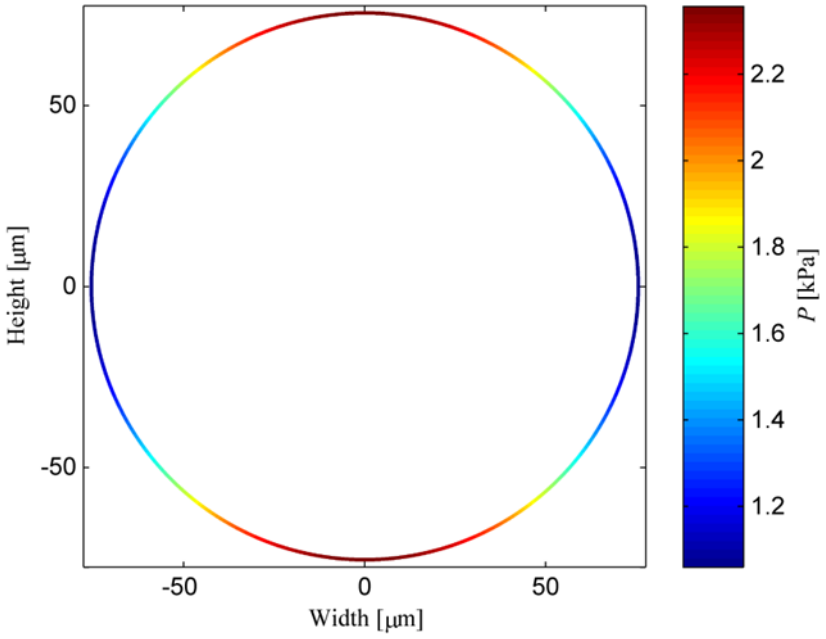


Figure 9 8. Real part of P-wave modulus, H, and corresponding P-wave attenuation, $1/Q_P$, as functions of frequency, for the model shown in Figure 7, considering the grain diameter d and thickness a of the interfacial water film, which are indicated in the legends and plot titles.

The geometry of the introduced model (Figure 7) is different than the classical squirt-flow geometries involving interconnected plane cracks or a plane crack connected to a pore of low aspect ratio. To better understand how dissipation occurs for this type of geometry, we initially focus on the fluid pressure field P (Figure 10 9) in the circular interfacial water film at the characteristic frequency. The vertical compression of the model illustrated in Figure 7 causes a larger deformation of the interfacial water film at the top and bottom ~~of its circular geometry~~parts than on the lateral parts~~sides~~. This observation is comparable to horizontal cracks that are more deformed by a vertical compression than vertical cracks in a classical squirt flow model. Here, the heterogeneous deformation causes fluid pressure to increase. The

most deformed parts which are the top and the bottom, exhibit the highest fluid pressure, as shown in Figure 10~~9~~. The pressure gradient present in this heterogeneous pressure field induces fluid to be displaced from the regions of higher pressure (top and bottom) towards the regions of lower pressure (left and right~~sides~~). ~~Exemplarily, t~~The components of the fluid velocity field in the x and y directions V_x and V_y (Figure 1~~1~~0) and ~~its~~ the corresponding local attenuation field $1/q$ (Figure 1~~1~~2) are depicted ~~in~~only the ~~representative~~ top-right quadrant of the model. Considering the symmetry of this process in the four quadrants of the circular interfacial water film (Figure 10~~9~~) it is ~~reasonable~~ sufficient to show only one quadrant ~~out of four~~.

In Figure 1~~1~~0 we observe the text-book (e.g., Jaeger et al., 2007) parabolic profile of the fluid velocity across the interfacial water film, with larger fluid velocity in the center of the film, governed by Navier-Stokes equations. This fluid velocity is associated with an energy dissipation caused by viscous friction, shown in Figure 1~~1~~2. At the boundaries of the interfacial water film, larger viscous friction explains the lower fluid velocity and larger energy dissipation, in comparison to the center of the film. The attenuation is strongly reduced towards the center of the film by a few orders of magnitude. ~~Now l~~Looking at how these fields change along the interfacial water film, we observe that the maximal velocity and attenuation (compare Figures 1~~1~~0 and 12~~1~~) coincide with the maximal pressure gradient (Figure 10~~9~~). ~~Whereas~~ On the other hand, in the middle of the higher pressure and lower pressure regions, the pressure gradient is minimal causing the fluid velocity and attenuation to drop drastically.



Figure~~ 10~~9. Fluid pressure P for the model shown in Figure 7, considering a grain diameter d = 150 μm and thickness of the interfacial water film a = 1 μm. The oscillation frequency is equal to the characteristic frequency (1.8×10^6 Hz).

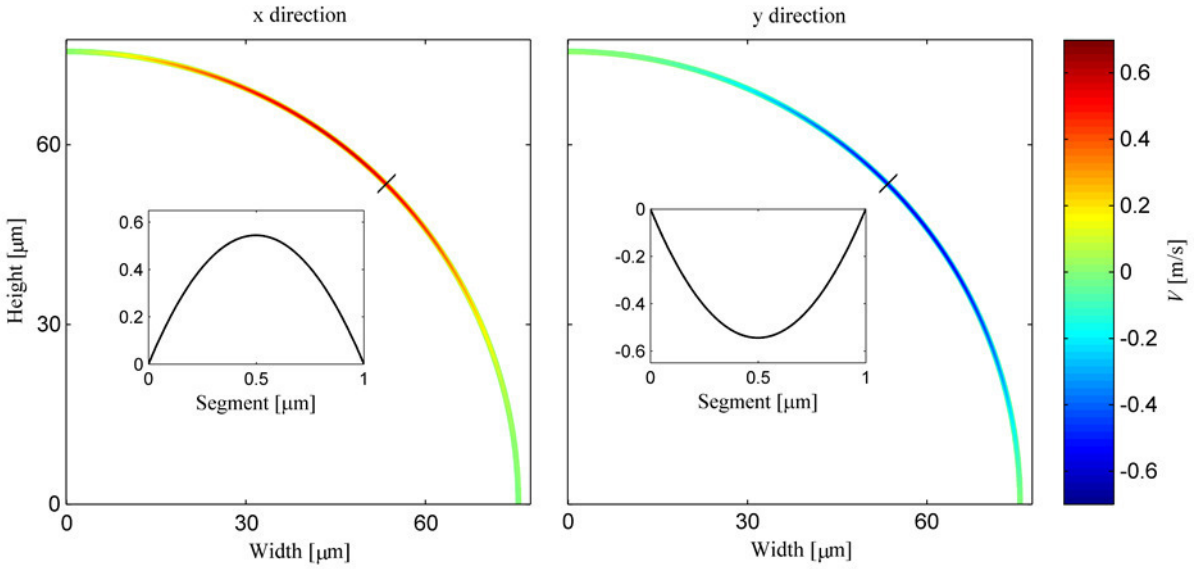


Figure ~~10~~ 11. Zoom-in to the top-right quadrant of the model shown in Figure 9 showing the fluid velocity components V_x and V_z, for a grain diameter d = 150 μm, a thickness of the interfacial water film a = 1 μm, and at the characteristic frequency. These fields correspond to the fluid pressure field shown in Figure 10~~9~~. The insets illustrate the profiles across the interfacial film where it is crossed by a black line.

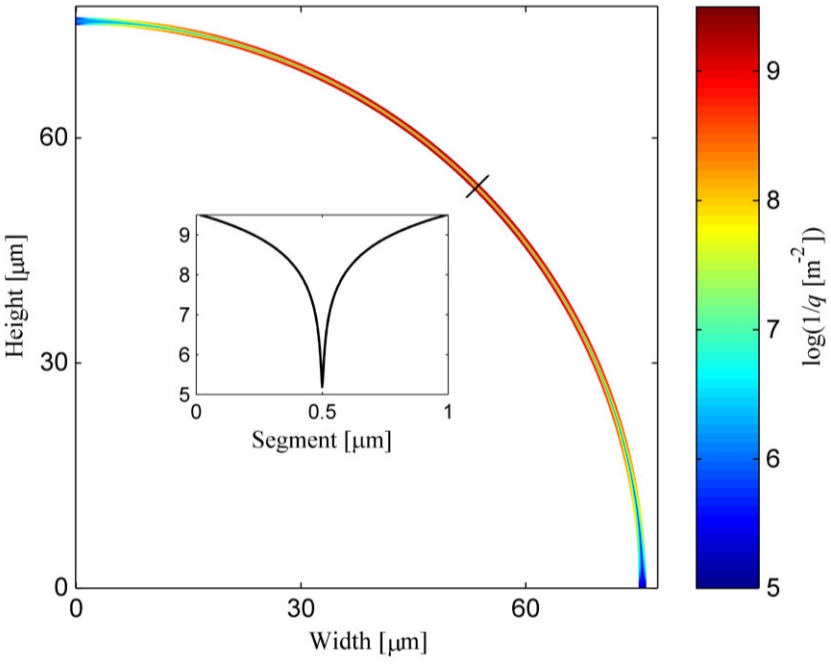


Figure ~~11~~ 12. Zoom-in to the top-right quadrant of the model shown in Figure 7 showing the local attenuation $1/q$, for a grain diameter d = 150 μm, with a water film thickness a = 1 μm, and at the characteristic frequency. This field corresponds to those shown in Figures 10~~9~~ and 1~~0~~1. The inset illustrates the profile across the interfacial film where it is crossed by a black line.

4.2 Effects of water pockets and water bridges

In this subsection, a few alterations are added to the basic ~~three phase~~ model illustrated in Figure 7. These alterations ~~are based~~base on more detailed observations obtained from SRXCT, such as water pockets ~~that have been detected~~ in non-porous GH or a water bridge that might occur connecting two neighboring interfacial water films (Figure 1~~2~~3). For this, the effect of these features on the P-wave modulus dispersion and attenuation (Figure 1~~3~~4) is studied and compared to results obtained from corresponding models where these features have not been considered.

The inclusion of water pockets has a modest effect on the attenuation and dispersion, while it reduces the overall value of the P-wave modulus, as a certain volume of GH is replaced by a much less stiff material (water). ~~Concurrently,~~The modest increase in attenuation is associated with a more compressible effective background; no attenuation occurs within the water pockets.

The connecting water bridge introduces an additional length scale for the dissipation process, as fluid flow and dissipation will also occur through this relatively short and wide path. This explains the additional attenuation peak observed at higher frequencies, while the previous peak at 2×10^3 Hz suffers a slight reduction in magnitude. A reduction in magnitude occurs because the pressure equilibration process involving the water bridge causes a reduction in pressure in the region connected to the bridge and thus a reduction of the previously discussed (Figure 9~~8~~) pressure gradient between this region and the sides of the circular interfacial water film. The dispersion agrees with the attenuation curve, with two inflections~~,~~ corresponding to the two attenuation peaks~~,~~ between the high- and low-frequency limits.

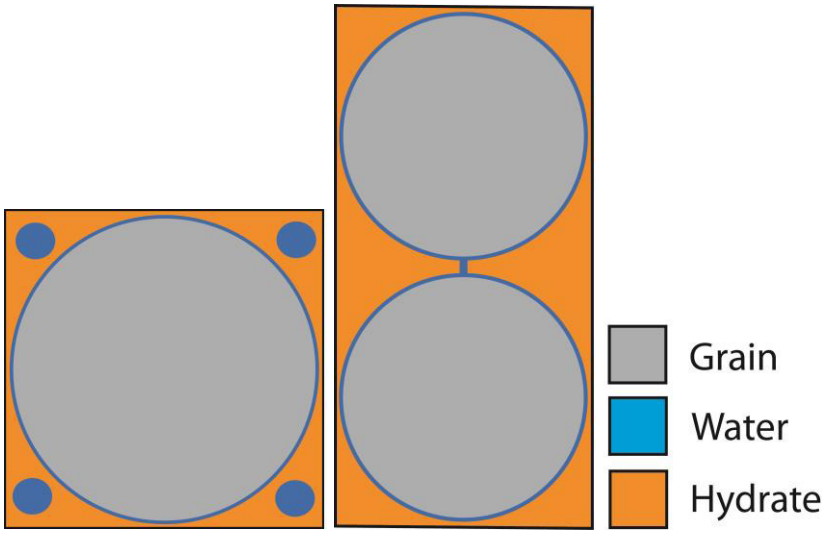


Figure 1~~3~~2. Fundamental blocks of two periodic media representing loose sandstone grains which are separated from the embedding GH background by a thin interfacial water film. On the left water pockets are located in the GH background and on the right the interfacial water films are connected to another through a water bridge**.**

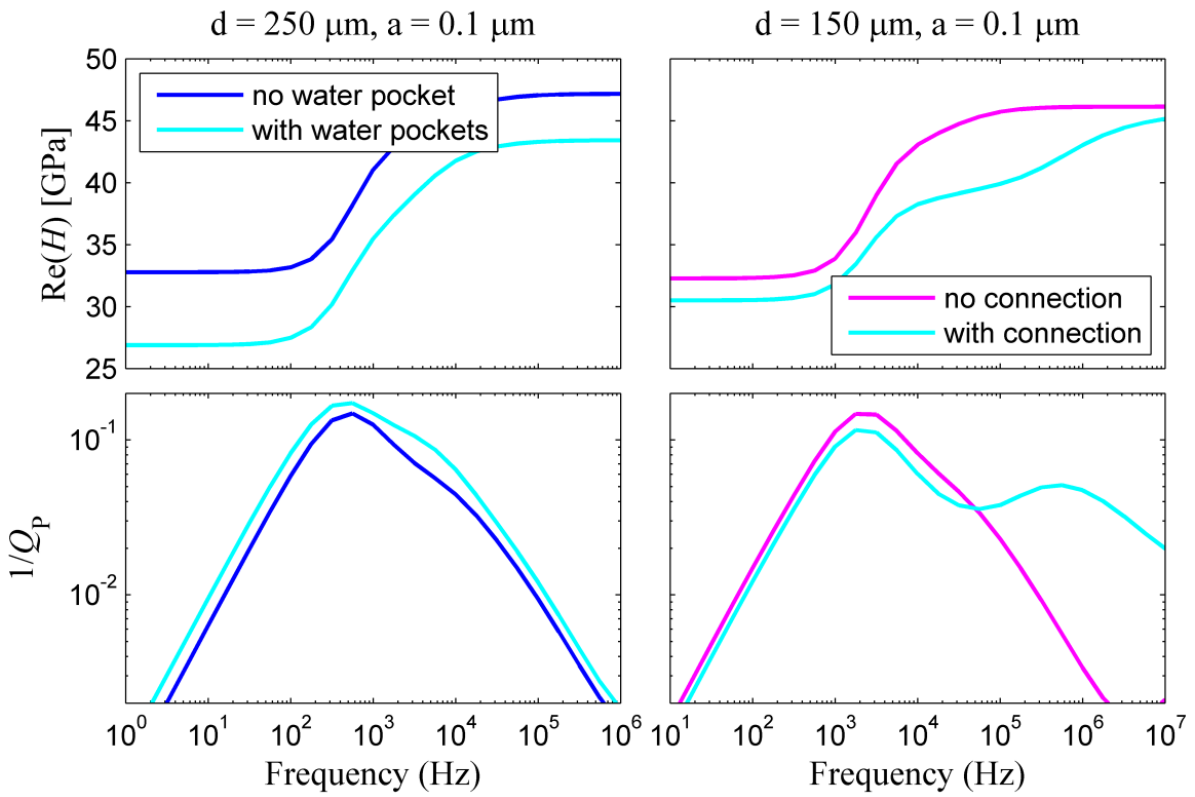


Figure 1~~4~~3. Real part of P-wave modulus, H, and corresponding P-wave attenuation, $1/Q_P$, as functions of frequency, for the models shown in Figure 1~~2~~3 in comparison with the corresponding results from the model shown in Figure 7 and given in Figure ~~9~~8. The grain diameter d and thickness a of the interfacial water film are indicated in the plot titles.

4.3 Evaluation of 3D effects

The ~~following~~is subsection considers a comparison between the results of the simulation illustrated in Figures 10~~9~~-12~~1~~, for the 2D model shown in Figure 7, and those of a simulation performed on its 3D counterpart. Our 3D model consists of a sphere in the middle of a cube (Figure 15~~4~~), ~~consequently~~ for which a centered cross section matches the 2D model shown in Figure 7. The ~~aperture~~ thickness of the water film is 1 μm and the grain diameter is 150 μm (as for Figures ~~9~~10-12~~1~~). The numerical results are shown in Figure 15~~6~~ with an excellent agreement between the results from the 2D and 3D models in terms of magnitude and characteristic frequency of attenuation. Indeed this was expected due to the radial symmetry of the spherical interfacial water film. This outcome indicates that 3D effects are small for the adopted geometry. ~~Furthermore,, t~~The results based on simple 2D models approximate well ~~according to~~ the dissipation magnitude and frequency dependence of their corresponding 3D scenarios. The difference in the overall value of the real-valued ~~Young's~~ P-wave modulus is associated with a larger relative quantity of soft GH and a lower relative quantity of stiff quartz in the 3D model.

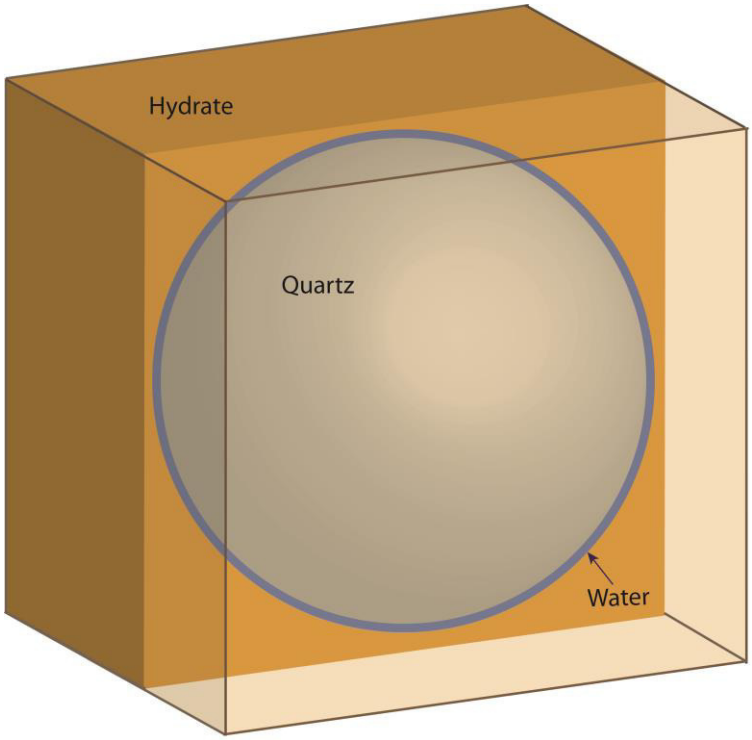


Figure 154: The 3D counterpart of the model shown in Figure 7: Fundamental block of a periodic medium representing unconsolidated quartz grains which are separated from the embedding GH background by a thin interfacial water film.

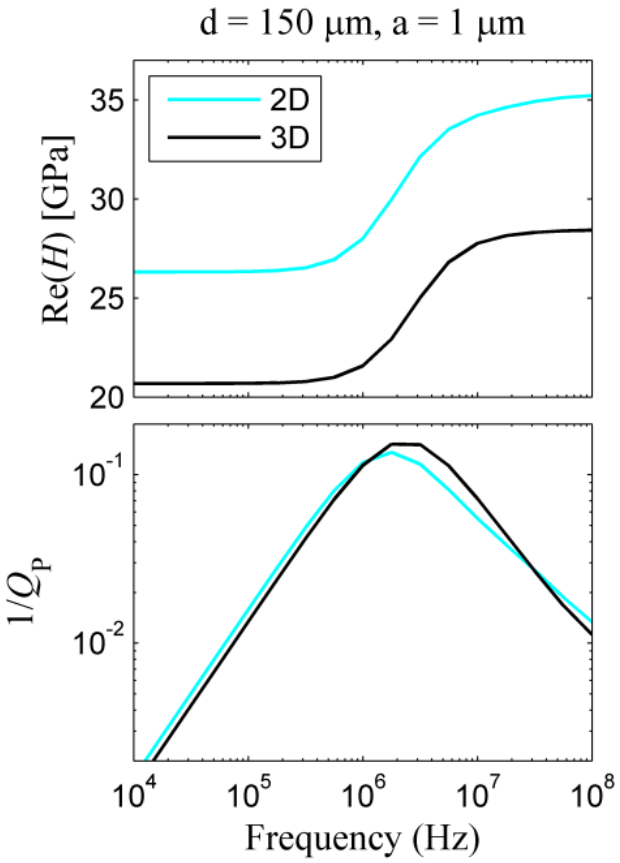


Figure 1~~5~~6. Real part of P-wave modulus, H, and corresponding P-wave attenuation, $1/Q_P$, as functions of frequency, for the 2D model shown in Figure 7 and for its 3D counterpart shown in Figure 1~~5~~4. The grain diameter d and thickness a of the interfacial water film are indicated in the plot title. The fields shown in Figures 1~~0~~9-12~~1~~ correspond to this 2D simulation**.**

5. CONCLUSIONS

~~Thin i~~Interfacial water films between sediment grains and the embedding GH matrix ~~have~~ were recently ~~been~~ observed in GH-bearing sediments through synchrotron-based micro-tomography at a spatial resolution down to 0.38 μm. Based on these data, we have determined the appearance and thicknesses of such ~~thin interfacial water~~ films ~~have been (geometrically) determined~~. With this knowledge, a new conceptual squirt flow model, which refers to a spherical ~~thin fluid~~water film coating the solid grains, was introduced for GH-bearing sediments. This geometry differs ~~e novelty of this model is constituted with respect to its geometry, as compared to~~from the classical squirt flow models ~~that~~ involv~~ed~~ing ~~interconnected~~ microcracks, interconnected or ~~microcracks~~ connected to spherical pores ~~instead of interfacial fluid films~~. Numerical simulations were performed to calculate the energy dissipation in the proposed model, considering a range of scenarios. Our results show that squirt flow in ~~thin~~ spherical interfacial water films can cause large and frequency-dependent P-wave attenuation in a broad frequency range including seismic frequencies. ~~Additionally, this effect does depend upon the interfacial water films being connected to any other type of pore.~~

TheA numerical solution scheme is based on a set of coupled equations that reduce to Hooke's law in the subdomains of the model corresponding to the elastic solid materials (grains and GH) and to the quasi-static, linearized Navier-Stokes equations in the subdomains corresponding to the fluid (water) has been used. The results for our conceptual model show that the P-wave attenuation peak is shifted to lower frequencies with decreasing thickness of the interfacial water film and with increasing grain size (or the length of the film), as analogously known for the microcrack aperture and length in classical squirt flow models. Furthermore, we tested the effect of inserting water pockets in an embedding GH matrix and the effect of connecting two neighboring thin interfacial water films through a water bridge. In general, the water bridges have a stronger effect on energy dissipation than the water pockets. Introducing such connections between neighboring interfacial water films causes a broadening of the P-wave attenuation spectrum towards higher frequencies. On the other hand, the presence of water pockets in the GH background only causes a slight overall increase in P-wave attenuation. Although the majority of our simulations were performed for 2D models, additional results of a 3D simulation showed that 3D effects are small for the basic 2D models that we have considered.

Our results represent a strong base to explain fundamental processes in GH-bearing sediments and support previous speculations (Guerin and Goldberg, 2002; Dvorkin and Uden, 2004, Priest et al., 2006) that squirt flow is an important attenuation mechanism in GH-bearing sedimentssuch media, even at frequencies as low as those in the seismic range. This strengthens the perception that P-wave attenuation may be used as an indirect geophysical attribute to estimate GH saturation. Nevertheless, further studies considering more realistic geometries for the microstructure of GH bearing sediments are necessary for a successful strategy to estimate GH saturations where hydrate is distributed in a dispersed manner instead of massive layers. This study simply represents the first attempt to understand P-wave attenuation in unconsolidated sediments having large simple structures investigating on grains embedded in GH and occurs in reservoirs of GH saturations around 90%. For such a following study, our aim is to implement the segmented 3D images obtained from synchrotron-based micro-tomography as a direct model input for numerical investigations whereby realistic , considering also grain-to-grain contacts will be taken into account. Depending on the number and sizes of the grain-to-grain contacts Q, as a ratio of the imaginary part and the real part of the complex modulus, will change. TAt the moment this approachhe step towards more realistic structures as a model input is challenging due to the corresponding large computational demand. Furthermore, such model input d and it and requires additional segmentation steps for the 3D images that, such as to allow for a smoothing of the stairs-like resolution artifacts at the boundaries of the interfacial water films. Furthermore, the image segmentation bears significant errors concerning the accuracy of the film thickness. With these future steps, our model will involve effects of a varying grain skeleton and different GH appearances as observed in laboratory samples and in nature.

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