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Quantitative NMR monitoring of liquid ingress into repellent heterogeneous layered fabrics

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Abstract

Fabrics which are water repellent and repellent to other liquids are often constructed using multiple layers of material. Such a construction is preferable to a single layer of a liquid repellent textile because, under the action of an applied pressure, ingress of a liquid through the first layer can be halted by the second or subsequent layers. In the quantitative investigation of this problem, current techniques provide limited information on the progress and distribution of the liquid as it ingresses into a fabric. Moreover, many techniques require that the material is delaminated prior to analysis, and cannot be conducted in real time to measure the progress of a liquid through the textile substrate. In this work we demonstrate that unilateral NMR, which allows signal to be collected from a volume of interest in a material residing above the instrument, can be a powerful tool to quantitatively monitor the ingress of a liquid through a layered sample exhibiting pronounced heterogeneities in repellency. A known volume of oil was placed on the top of a model textile sample composed of three 80 μm thick layers. Spatially resolved one dimensional vertical NMR profiles of the system were acquired as a function of the pressure vertically applied to the top of the sample. These profiles show that the absolute liquid volume present in each layer of textile can routinely be measured within 4 minutes with a spatial resolution of 15 μm. If each individual layer exhibits different repellency to the test liquid, the complexity of the dynamics of the ingress can be investigated in great detail. An elegant application of the unilateral instrument was obtained in which the sensitive volume matched the region of interest of the individual layers of the textile under investigation.

Keywords: Repellency; Ingress; Unilateral NMR; Heterogeneous porous medium, CPMG.

1. Introduction.

The design of liquid repellent fabrics is extremely important to industrial and domestic applications that seek to minimise, or prevent liquid ingress from contaminating materials and personnel[1-5]. In order to render a textile liquid repellent a silicone or fluorocarbon coating is usually applied. A droplet of liquid will not wet a textile treated with a fluorocarbon coating if the contact angle formed between the liquid and the textile is sufficiently large[6-8]. However if the droplet is subjected to an applied pressure the droplet can be forced into or through the fabric. In designing protective clothing, knowledge of how liquids will interact with a textile material under various conditions of wear is crucial. Critical information includes the pressure at which the liquid is forced into the substrate and, at that breakthrough pressure, the location of the ingressing liquid within the textile. Simple experiments can be conducted whereby the applied pressure and the droplet size are varied and observation is used to assess whether liquid ingress has occurred. However, the determination of the location of the liquid inside the fabric is more complicated. If the textile can be de-laminated then the separate layers could be analysed gravimetrically or the individual layer could be extracted with a solvent and the amount of test liquid quantified by an appropriate spectroscopic technique (e.g. FTIR, mass spectroscopy or gas chromatography). All of these methods are however, either time-consuming, invasive/destructive or do not provide quantification of the amount of liquid that is able to penetrate into or through the fabric.

In an ideal experiment, the textile would be imaged so that the fate of the liquid droplet could be determined whilst an external pressure was applied. X-ray tomography[9] and neutron radiology[10] have been used as non-contact techniques to analyse water distribution in fabrics, but the use of these as bench-top instruments is difficult. In this work, we suggest that an alternative possibility for the non-invasive quantitative monitoring of liquid ingress within an opaque and complex fabric is to use Magnetic Resonance Imaging (MRI). In the literature, MRI has been reported for the determination of 1D profiles of moisture content and drying across the thickness of carpets[11-13]. A two-dimensional MRI investigation of water distribution in carpets has also been reported[13] but the substantial evaporation of water during the time duration (77 mins) of the experiment prevented the workers from being able to produce quantitative data. In our work we use the *profile* NMR MOUSE®[14], which is a simple bench-top instrument, to quantitatively monitor the ingress of oil into a model fabric consisting of three layers of meltblown polypropylene fibers with the outer layers possessing a fluoropolymer coating. The results show that it is possible to obtain spatially resolved one dimensional profiles of the absolute volume of liquid present at a given position across a selected slice of the fabric as liquid ingresses.

2. Experimental Method

2.1. NMR instrument

The NMR MOUSE® collects the NMR signal coming from a thin and flat volume of sensitivity (~200 μm x 20 mm x 20 mm) at 5 mm to 10 mm above the instrument. There are several designs[15-17] of relatively inexpensive NMR instrument that use permanent magnets to provide a strong polarising field and on which a sample may be placed for unilateral (one-sided) NMR imaging. In our *profile* NMR

MOUSE® a strong (11.4 T/m) magnetic field gradient resides across the selected slice. The presence of this strong gradient can successfully[18] be used in conjunction with the CPMG radio-frequency (rf) pulse sequence to collect spin echoes that can be processed so as to obtain spatially resolved one dimensional profiles of both the NMR relaxation rate and the absolute volume of liquid present at a given position across the slice. The *profile* NMR MOUSE® that we used, comprising the polarising magnets assembly and the rf coil, has the shape of a box (13 cm x 11 cm x 10 cm). By changing the height (referred to as the z-axis) of the rf coil horizontal plate on which the sample sits, relative to the magnet assembly, the height of the selected slice relative to the instrument can be changed from 10 mm to any smaller value. A remote slice allows the non-invasive exploration of thick objects, but the further the selected slice is from the instrument, the thinner it is, because the rf pulses need to be made longer, resulting in a narrower bandwidth. For studying the liquid ingress, the selected slice was 2 mm above the instrument, with optimal rf pulse time duration of 2.7 μs. The variation of the NMR signal detected across the slice thickness depends on the rf pulse shape, and needs to be measured. To do so, a homogeneous sample (a small vial with outside diameter 23 mm, inside diameter 19.8 mm and filled with oil) was placed on the instrument for calibration purposes. At any value of the z-axis, the density (100%) of oil and the transverse area (3.1 cm^2) of the sample under investigation are thus constants.

The NMR data was collected using a CPMG sequence with 40 spin echoes (echo time, TE = 510 μs, repetition time, TR = 170 ms, number of accumulated experiments = 1500). These were individually Fourier transformed and then averaged. This results in an approximately Gaussian profile, with a full width at half the maximum, FWHM, of 172 kHz. The thickness of the selected slice was established as follows. The linearity and the strength of the field gradient along the z axis were measured by using a thin (12 μm) layer of oil sandwiched between two microscope slides spaced apart with a 12 μm thick strip of mylar running all around the slide. The z coordinate of this thin sample was incrementally changed by interleaving a gradually increasing stack of 80 μm thick tracing paper sheets, the total thickness of which was measured for each trial. Each separate NMR experiment yielded spin echoes that were Fourier transformed, and the frequency of the peak of the data was plotted against the total thickness of the paper stack. Accurate measurement of the position of the selected slice is also thus obtained. Excellent linearity was observed, and a field gradient of 11.4 T/m was measured, resulting in the previously measured Gaussian FWHM of 355 μm. Since the signal frequency can be calibrated in the z- direction, spatially resolved measurements where liquid ingress occurs can be conducted without the need for moving the sample relative to the instrument.

2.2. Sample preparation

The model heterogeneous repellent textile sample was constructed from three layers of a non-woven material (17 gm^{-2}) supplied by Web Dynamics UK. These layers, each 80 μm thick, were approximately square (23 mm x 24 mm) and were composed of meltblown polypropylene fibers (approximately 10 μm in diameter) that had been consolidated into a non-woven textile. The middle layer of meltblown non-woven material was used as received but the outer layers were additionally rendered liquid repellent by a fluorocarbon coating prior to the construction of the three-layered non-woven material. Coating the materials with a fluorocarbon was achieved by the deposition (plasma-assisted polymerisation) of a thin (approximately 100 nm) fluoropolymer coating, as described

elsewhere[2]. This technique operates under vacuum so that the material's entire surface is coated with a fluoropolymer.

When this textile sample was placed in the sensitive volume of the instrument, no signal was detected, thus confirming its transparency in the NMR experiment.

A combination of 1 mm and 166 μm thick microscopy slides were placed below the sample, so that the layered textile was centred with respect to the selected slice and a 7μL (±2%) droplet of oil (Duckhams 15W/40 Mineral formula) was deposited on the fabric, in the (x,y) centre of the sensitive area, using a Gilson pipette. The longitudinal relaxation time, T_1, of the oil was found to be lower than 100 ms and therefore allows the rapid collection of large signal-to-noise (SNR) by using a short T_R value. One 166 μm thick microscopy slide was placed above the system, followed by a 4 mm thick sample of rubber to provide a static reference for the z position of the system under investigation (Fig. 1a). This allows the z-position to be accurately determined despite slight variations in the strength of the permanent magnet assembly caused by slight changes in ambient temperature changes. In an NMR measurement continuously running over three days, we have observed apparent changes of up to 80 μm, in the position of the profile of a static sample placed on our instrument. These changes were periodic and synchronized with the on and off switching of the air conditioning system in our laboratory; the use of a microscope slide followed by a sample of rubber as a static reference allows compensation for this effect. The thickness of the glass between the rubber and the top of the sample is well above the spatial resolution of the instrument so that the signal from either the rubber or the sample can therefore be separated unambiguously during post-experiment signal processing.

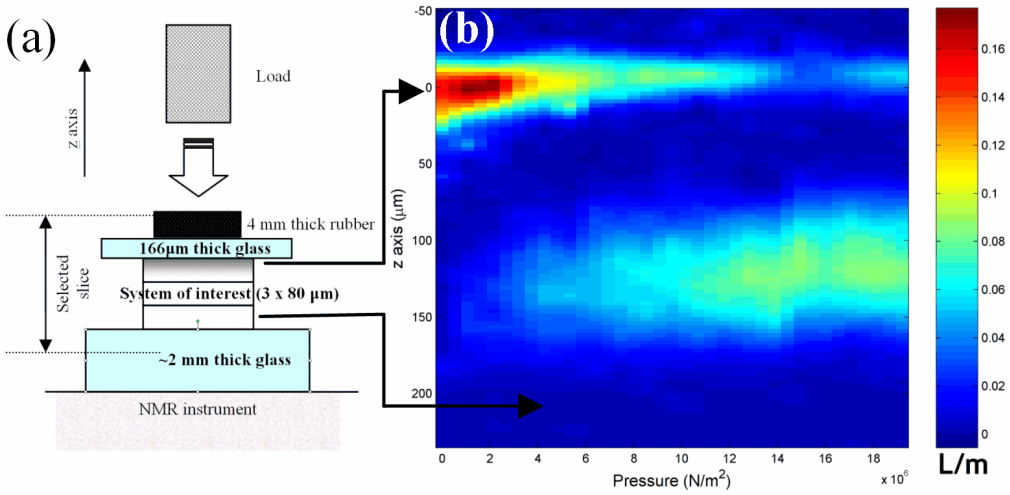

Fig. 1. (a) Sketch of experimental set up. (b) Color-coded contour plot of linear oil volume density as a function of z (vertical axis) and applied pressure (horizontal axis) revealing the dynamics of the ingress of the liquid into the system. Note the absence of signal within approximately 80 μm below zero, due to the repellent layer around this position. The origin of the z axis is aligned to coincide with the interface between the top of the system under investigation and the glass microscopy slide.

2.3. Experimental protocol for liquid ingress

Two types of experiments into liquid ingress were conducted. In the first, short applications of increasing pressure were used and in the second, ingress due to long duration steady state pressure combined with gravity and capillary flow was used. In the former case, prior to any NMR measurement, a light load (40 g) was systematically applied on the top of the system so as to keep the space between the individual layers a constant between successive experiments (each NMR measurement took approximately 4 minutes). In order to simulate various pressure loads acting on the droplet of oil, the 40 g load was replaced by increasing volumes of water in increments of 60 ml, added to a glass container placed on the top of the system. This mass can be converted into an effective applied pressure, because the weight is applied over the entire surface ($5.5\,cm^2$) of the sample. The heavy load was removed after a duration of 30 seconds and the 40 g load was re-placed onto the system prior to the NMR measurement. The experiment was repeated until a final water volume of 1080 ml was reached. The full protocol was repeated three times to assess the repeatability of the measurements. In the latter case of liquid ingress due to long steady state pressure combined with gravity and capillary action driven fluid flow, the full final load was not applied. Instead, the experiment was interrupted with a relatively light final load (180 g), just enough to ensure that some ingress through the first repellent layer had occurred. The light load was then replaced by the 40 g mass (as in all other measurements), and the ingress was then continuously monitored in an over-night NMR experiment for 18 hours, with profiles acquired every 25 minutes.

2.4. Data processing

A Matlab® code was developed in-house to first shift the raw NMR profiles along the z axis, by multiplying the complex spin echoes by a complex exponential with a linear phase gradient, until the rubber fronts were all matched to that of the first profile. This allowed correction for temperature drift effects. For each experiment, each digital point of the 40 profiles (except for the three first) was fitted to an exponential decay function in order to extract the profiles of the NMR amplitude and relaxation rate. The profiles of the local amplitude were then scaled according to that of the homogeneous sample, so as to obtain the local oil linear volume density at a position, z. The curvature of the selected slice dictates the spatial resolution (15 μm) of the profiles, rather than the digital spatial resolution (5 μm in this particular set-up). Each original pixel is therefore an integral of NMR signal collected over 5 μm. These processed NMR profiles were stacked from left to right, interpolated and plotted as greyscale countour plots (Fig. 1b). Further quantification of the same data was done as follows: the signal was integrated for z between -55 μm and 53 μm (the falling curve) and z between 53 μm and 214 μm (the increasing curve) and z between -55 μm and 214 μm (upper curve). These z boundaries for the integrals were chosen visually, based on the data in Fig. 1b. These integrals reveal the dynamics of the volume of oil found in each layer, and further validates the quantification of the data, as the total amount of oil measured in the system can be confirmed as remaining constant.

3. Discussion

The details of the ingress of oil are clearly displayed in Fig. 1b. The apparent increase in signal within the four first profiles at z = 0 is due to the thinner slice in which the oil is allowed to reside. The oil penetrates the second non-repellent layer even for the lightest load. Since no signal can be observed in the first 80 μm, the ingress process must be exploiting microchannels linking the first channel to the second. A steady state is reached for pressures higher than $14x10^6$ N/m^2, and by then, most of the oil has ingressed into the second layer. If further pressure was applied vertically, it would probably cause no further vertical ingress, since the sandwiched layer is non-repellent and encourages transverse flow. This three layered structure is therefore a very effective barrier to vertical flow. Indeed, when using a non-repellent layer on the top of the stack, vertical ingress has not been seen at all. Ingress across the third layer of the structure presented in Fig. 1 has never been observed either (both visually or by NMR), over the range of loads that has been explored. In Fig. 1, the greyscale value can also be interpreted as the product of the local porous medium saturation, by the transverse (x, y) saturated surface. Transverse field gradients could be used to spatially resolve the signal from a layer and so provide information on the dynamics of liquid saturation occurring within each layer.

In Fig. 2 the data has been processed so as to reveal the dynamics of the ingress in terms of the oil content in each layer. This plot also demonstrates that the signal coming from all of the oil in the fabric has been successfully monitored quantitatively. The same experiment was repeated four times and these repeats are shown in Fig. 3, together with the original experiment, for comparison purposes. Small variations are seen from one experiment to another, and these are most likely to be due to genuine experimental set up variations rather than from the NMR monitoring technique.

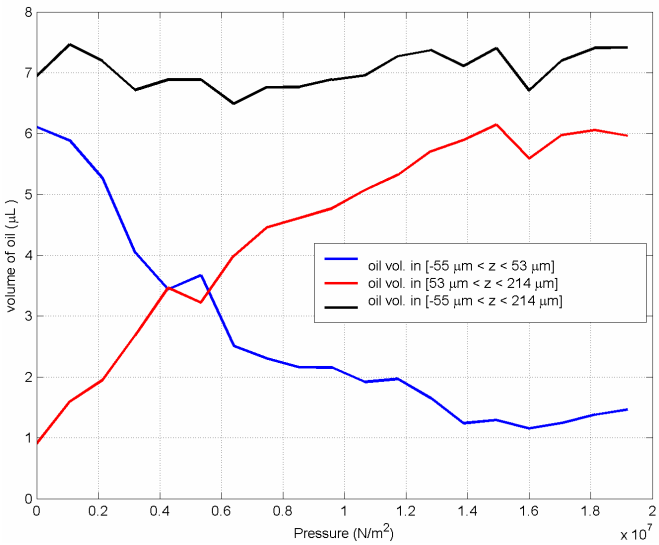

Fig. 2. The same data as in Fig. 1, but with each NMR profile integrated over a specific range of z-values, to show the fluid dynamics in each individual layer.

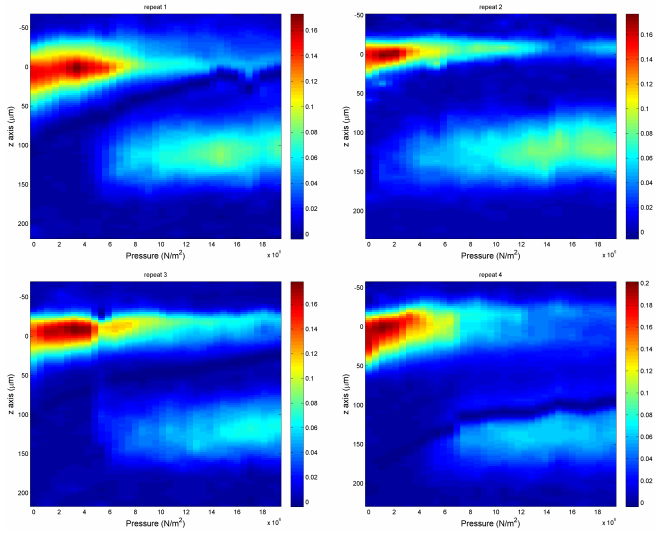

Fig. 3. Color-coded linear oil volume density as a function of *z* (vertical axis) and applied pressure (horizontal axis) for the four repeats that were done in similar conditions to that of Fig. 1.

The time-course of the results from the overnight experiment are shown in Fig. 4, in the same way as in Fig. 1, but with a horizontal axis that shows the time at which the profile was acquired. The first profile demonstrates that some oil has passed the barrier of the repellent layer. Slow ingress from the top layer to the middle one, due to both gravity and capillary action, is clearly seen in the profiles following the first one. This suggests that the continuity of the fluid between the two layers has been retained, at least at a few transverse locations, when only 40g of vertical load is present in the system. The usual lack of signal is also seen between the two layers, suggesting again that this continuity is fulfilled with a very small, not measurable, volume of oil. The post-acquisition quantification method used and demonstrated in Fig. 2 did not yield a constant signal for the overnight experiment. Instead, a total signal loss of approximately 15% is seen, suggesting that in these lengthy experiments the oil eventually spreads transversally to locations where the drop in B_1 field homogeneity is too poor for quantitative assessment of oil density.

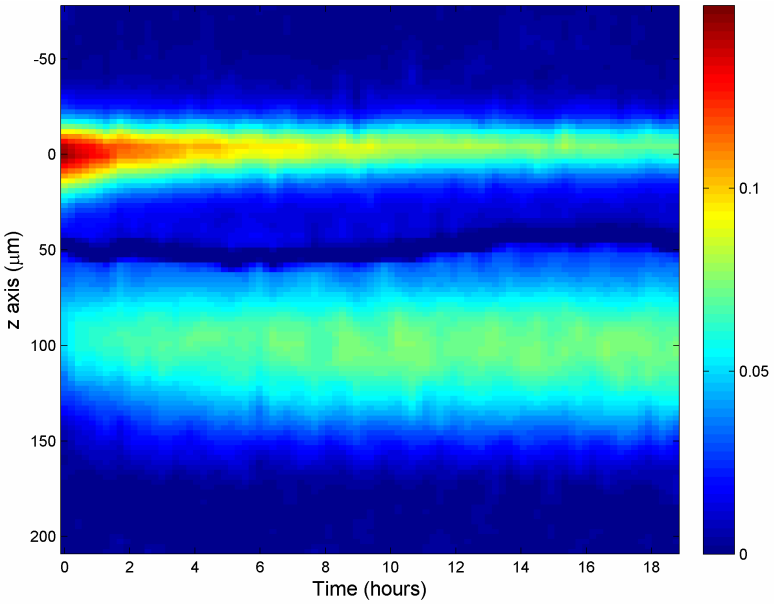

Fig. 4. Color-coded linear oil volume density as a function of z (vertical axis) and time (horizontal axis) for the over-night experiment.

4. Conclusion

This work demonstrates a promising method to quantitatively and non-invasively explore the dynamics of liquid ingress into a complex layered liquid-repellent fabric. We have shown that a low-field unilateral NMR instrument can provide an excellent match between the geometry of the system of interest and the features of the measuring device, thus allowing a suitable choice of spatial and temporal resolution and overcoming the usual limitation of MRI. This match of geometries also allows exploitation of the Fourier Transformed NMR signal, rather than physically moving the instrument relative to the sample as is usually done. The approach can be extended to more complex fabrics and liquids with different wetting properties.

Acknowledgments

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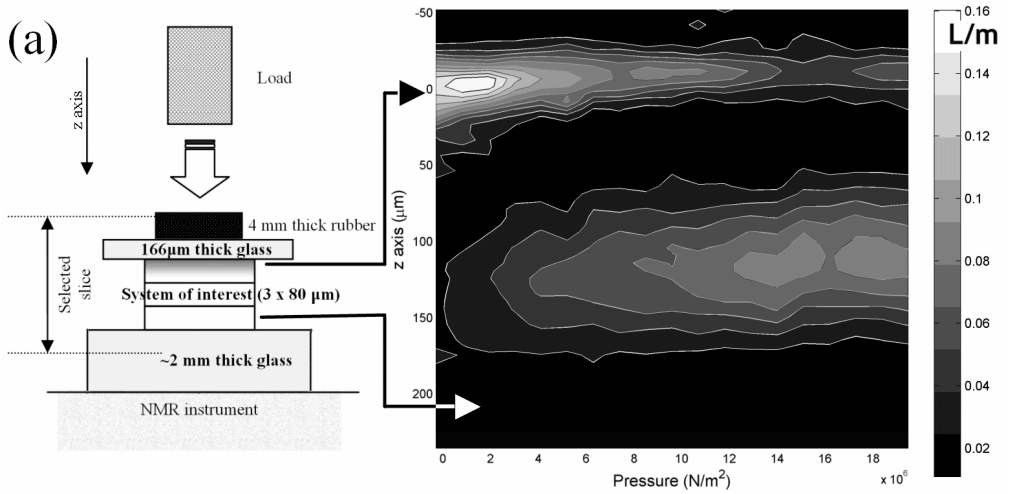

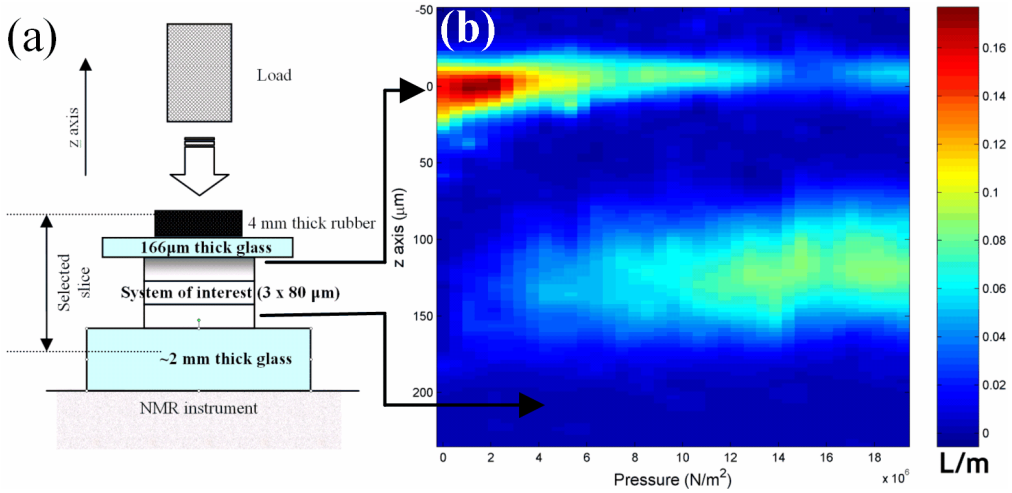

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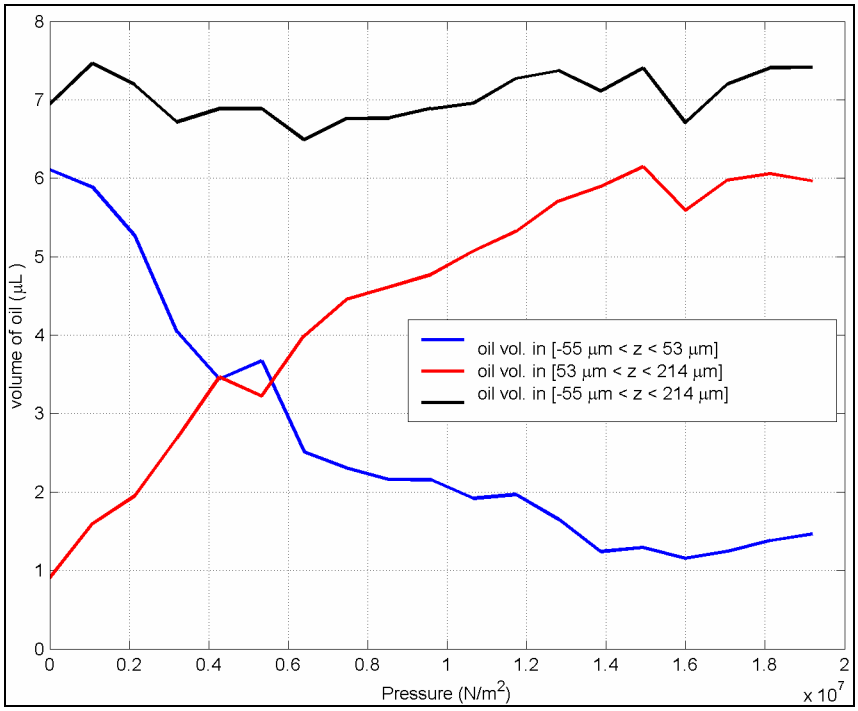

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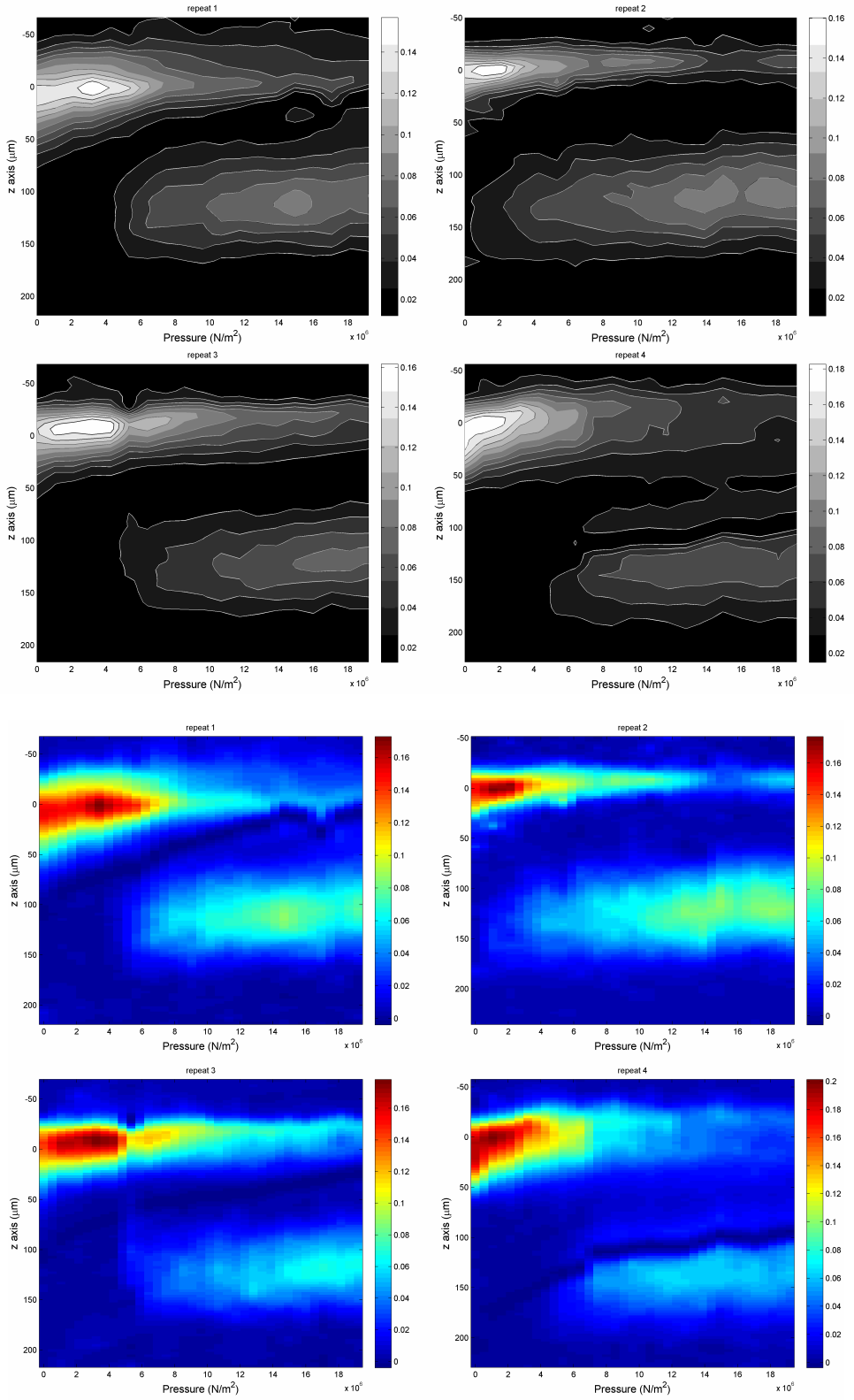

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