

Response of quartz crystal resonators possessing a superhydrophobic surface

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Abstract—A quartz crystal resonator immersed in a water-glycerol solution has a systematically reducing resonant frequency and an increase in bandwidth of the resonance as the concentration of glycerol increases. This behavior is well-known and is accurately described by the Kanazawa and Gordon model, which provides a clear proportionality to the square root of the density-viscosity product of the mixture. It is also well-known that a hydrophobic surface having high aspect ratio protrusions can become superhydrophobic so that the liquid no longer retains contact with all points on the surface. In such a situation for a quartz crystal surface, it is expected that a decoupling of the acoustic wave will occur and the response may not then conform to the Kanazawa and Gordon model. In this work, we report on the behavior of quartz crystal resonators fabricated with 5-18 micron tall micro-post structures both before and after they have been treated with a fluorochemical to make them hydrophobic. We report contact angle data showing that the hydrophobic surfaces are super-repellent for the entire range of water-glycerol mixtures. We obtain and fit the impedance spectra to the Butterworth-van-Dyke model and show, in this extreme case, a complete change in acoustic response occurs. The impedance spectra show a rich mixture of behavior including resonances that become sharper as the concentration of glycerol increases and surfaces showing a decoupling of the acoustic wave response.

I. INTRODUCTION

Models describing how a quartz crystal microbalance (QCM) provides a sensor response as i) mass attaches to its surface from the vapor or the liquid phase, ii) a surface coating changes its viscoelasticity, or iii) the viscosity-density product of a liquid adjacent to the surface changes, are well-developed and experimentally verified [see e.g. 1,2]. In the first case, the Sauerbrey equation dictates that the frequency decreases in proportion to the deposited mass per unit area and the square of the frequency. In the second case, the frequency changes are accompanied by a broadening of the resonance as dissipation increases and the system can be described by a complex load impedance dependant on the viscoelastic parameters. In the third case, the broadening of the resonance again accompanies a frequency decrease as the viscosity-density product increases and this is described by the

Kanazawa and Gordon equation. For a Newtonian liquid, such as a water-glycerol mixture, the frequency decrease, Δf , and bandwidth increase, ΔB , occur in proportion to the square root of the viscosity-density product, and are related by $\Delta f = -\Delta B/2$. The frequency dependence of the response in the liquid is reduced to a 3/2 power-law because the QCM surface creates a damped shear mode oscillation in the liquid which decays within a characteristic penetration depth of the interface $\delta = (\eta/\pi f_s \rho)^{1/2}$ where ρ and η are the density and viscosity of the liquid and f_s is the resonant frequency.

Whilst the mass, viscoelastic and liquid models of response are well understood, the effect of roughness and microstructuring of a QCM surface is less well understood. At its most basic level, roughness may simply provide a change in the overall constant of proportionality in the Sauerbrey or Kanazawa and Gordon equations. For liquid phase operation, surface structuring has been proposed as a method of separating out the effect of viscosity from that of density [3]. Another effect which is less well-understood is that of changes in hydrophobicity of the sensor surface. It has been proposed that the no-slip boundary condition might be relaxed on a smooth, but hydrophobic QCM surface [4]. Models to describe such an interfacial slip situation on smooth and structured surfaces have been published [5,6], but debate continues on whether such slip explains otherwise anomalous QCM responses. An alternative to slip that has been suggested is that surface located gas pockets or trapped liquid acting as rigid mass might exist and behave effectively as a Sauerbrey-like mass [7,8]. Recently, significant advances have been made in understanding how high aspect ratio topography combines with hydrophobicity to determine the wetting of a solid surface [9]. It is now believed that steady flow of a Newtonian liquid across such a, so called superhydrophobic, surface can be described by a slip boundary condition [10].

II. SLIP ON SUPERHYDROPHOBIC SURFACES

If a surface is slightly rough at a microscopic or nanoscopic level, water is able to follow the surface contours. If the surface is hydrophobic and the aspect ratio of its topography becomes high, the water no longer follows the

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contours of the surface, but bridges between topographic features. This type of surface suspends a droplet of water as if on a bed of nails and the reduced solid-water interfacial area allows far greater mobility for the droplet; the surface is often referred to as slippery [11]. Such a surface can be characterized by measuring the contact angle of the droplet and the hysteresis in the contact angle as liquid is added and withdrawn. Most recently, steady flow of water across a surface consisting of tall and hydrophobic micro-posts has been observed using micro particle image velocimetry. The velocity profiles observed in those experiments have been interpreted as consistent with a slip boundary condition [10]. Effectively, the liquid experiences no-slip at the solid-water interface above the posts and infinite slip at the air-water interface bridging between posts. Complementary experiments using cone-and-plate rheometers [12] and hydrofoils [13] also suggest a slip boundary condition, although there remains disagreement on the value of the slip lengths.

In parallel with the above work, we reported preliminary results for QCM frequency changes for a surface consisting of regularly spaced hydrophobic posts and water-polyethylene glycol (PEG) solutions [14]. Fujita *et al.* also reported that a superhydrophobic QCM surface consisting of a 1-2 μm thick polystyrene layer containing PTFE particles reduced energy loss [15]. Subsequently, Kwoun *et al.* reported a reduced frequency shift in water for multi-resonance devices coated with a hydrophobised 0.6 μm thick silica nanoparticle layer [16]. Whilst a reduced magnitude of energy loss and frequency shift for a QCM might be an indication of a slip boundary condition, the oscillating shear flow across a QCM surface differs from the steady flow used in the micro-PIV, cone-and-plate and hydrofoil experiments. It is therefore important to provide an extensive data set for QCM resonance responses for model hydrophobic micro-post surfaces in contact with a Newtonian liquid; that is the aim of this work.

III. EXPERIMENTAL METHODS

Square arrays of circular cross-section SU-8 photoresist micro-posts were prepared by photolithographic patterning on smooth 5 MHz quartz crystals of diameter 25 mm with gold electrodes. Posts were of diameter $d=5\text{ }\mu\text{m}$ and heights of $h=5, 10, 15$ and $18\text{ }\mu\text{m}$ in an array with a period of $L=10\text{ }\mu\text{m}$. Patterned crystals were hydrophobised by immersion in a dilute fluorocarbon containing solution (Grangers Wash-In), rinsing in deionised water and then heating for 20 minutes at 100°C ; patterns that have not been hydrophobised are referred to in this report as bare surfaces. Contact angles for water-glycerol mixtures were measured using a Krüss DSA 10 system using $5\text{ }\mu\text{l}$ droplets; this system analyzes droplet shape from a side profile view of the droplet. Quartz crystal frequency spectra were recorded in air and liquid at 25°C using an Agilent Technologies E5061A Network Analyser over the range 4.8-5.4 MHz. These spectra were fitted to a Butterworth van Dyke (BVD) model and bandwidth and series resonance frequency data extracted. To investigate Newtonian liquids, mixtures of distilled water and glycerol (99+% Fisher) were used and the concentration used to calculate the viscosity-density product. Experiments were conducted in an open lab with a typical relative humidity of between 45% and

50%. Since glycerol is hygroscopic, the viscosity-density product calculated using the nominal percentage weight concentration of glycerol is not accurate for concentrations above 80%.

IV. CONTACT ANGLE DATA

The droplet contact angle, θ , indicates whether a given mixture is in complete contact with a patterned substrate or whether the droplet skates between the tops of the micro-posts. For the glycerol concentration range 0% to 78.2% (by weight) the contact angle on bare (i.e. non-hydrophobised) flat SU-8 surfaces decreases steadily from 75° to 65° . For our design of pattern, the solid surface area fraction corresponding to the tops of the micro-posts is $\phi_s = \pi d^2 / 4L^2 = 0.196$. A Cassie-Baxter weighted average of the cosines therefore predicts that the contact angles for these mixtures on bare micro-post surfaces should be $\sim (138^\circ \pm 2^\circ)$. However, the measured contact angles on these surfaces varied from a maximum of 127° down to 86° depending on post height and glycerol concentration. If the mixtures fully penetrated between the micro-posts, contact angles lower than the flat surface values would be expected. This indicates that a partial penetration of the water-glycerol mixtures occurs between the surface features on our non-hydrophobised micro-post surfaces.

On flat layers of SU-8 that have been hydrophobised, the contact angle increased to the range 115° - 100° , but with no systematic trend between these values as the glycerol concentration increases. The Cassie-Baxter equation therefore predicts that droplets fully suspended by our hydrophobised micro-posts should be increased to $\sim (150^\circ \pm 3^\circ)$. Experimentally, the contact angles were measured as $(152^\circ \pm 2^\circ)$, $(149^\circ \pm 2^\circ)$, $(146^\circ \pm 3^\circ)$ and $(143^\circ \pm 6^\circ)$, respectively, for the 5, 10, 15 and 18 μm tall posts. The agreement for the micro-post surfaces is good and indicates that all the glycerol mixtures with concentrations from 0% to 78.2% form suspended droplets on the hydrophobised micro-post surfaces. Examination of scanning electron micrographs shows that the fabrication process results in micro-posts that are narrower at the base and more rounded at their heads for the taller cases. This would explain the greater scatter in contact angle for the taller micro-posts.

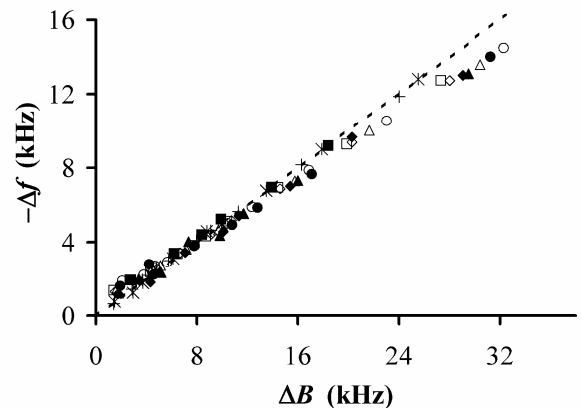


Figure 1. Frequency-bandwidth response of crystals spin coated with flat layers of SU-8 to immersion in water-glycerol mixtures.

V. QUARTZ CRYSTAL RESONANCE DATA

The contact angle data suggests that droplets of the glycerol-water mixtures deposit in a superhydrophobic state and so are suspended across the tops of the hydrophobised micro-posts. To confirm this remains the case when the liquid is introduced as a pool in the QCM cell, we applied pressure to force the liquid to penetrate into the gaps between micro-posts. As penetration occurred both a visual change in contrast of reflected light could be observed and the resonant spectra broadened and decreased in frequency. To confirm that the bare (non-hydrophobised) SU-8 and hydrophobic SU-8 provided a Newtonian liquid response to immersion in water-glycerol mixtures, spectra were taken for flat spin-coated films. Fig. 1 shows the frequency shift from the air value, Δf , and the change in bandwidth, ΔB , using open-symbols for bare surfaces and solid symbols for hydrophobised surfaces ($5\mu\text{m}=\square\square\square$, $10\mu\text{m}=\diamond\diamond\diamond$, $15\mu\text{m}=\triangle\triangle\triangle$ and $18\mu\text{m}=\circ\circ\circ$); the dotted line is the theoretical prediction with a slope of 0.5 and intercept of 0 from the Kanazawa and Gordon model for a Newtonian liquid. The nominal solution concentrations are 0%, 40%, 51.3%, 58.2%, 69.2%, 78.2%, 85.0%, 89.4%, 94.7% and 100%. Although the nominal concentrations above 80% will be inaccurate due to the hygroscopic nature of glycerol, the affect on the data in Fig. 1 for a Newtonian response should be to simply scale the positions of data points up and down the dotted line. The data for concentrations up to 78.2% lies in the lower left quarter of Fig. 1 and has a maximum frequency decrease of -9.2 kHz. The response for the bare polished crystal (+++) and hydrophobised polished crystal (***) are also shown.

Fig. 2 shows the equivalent data to Fig. 1 for bare (non-hydrophobised) surfaces with micro-posts of heights 5, 10, 15 and 18 μm ; the straight dotted line is the Kanazawa and Gordon model. The 15 μm ($\triangle\triangle\triangle$) and 18 μm ($\circ\circ\circ$) tall micro-post surfaces have a linear response with the Kanazawa and Gordon model slope of 0.5, but also have offsets of ~ 5.7 kHz and 4 kHz (shown by the solid lines), respectively. The data for the 5 μm ($\square\square\square$) tall micro-post surfaces also appears linear with a slope of 0.5 and offset of 3.4 kHz (shown by the solid line) until the glycerol concentration exceeds 78.2%. The 10 μm ($\diamond\diamond\diamond$) tall micro-post surfaces do not obviously show any linear regime and at the highest concentrations ($>89.4\%$) the frequency shift changes sign. Fig. 3 shows the equivalent data obtained after the micro-post surfaces had been hydrophobised; the symbols are the same as in fig. 3, but are filled symbols to indicate the surfaces have been hydrophobised. To enable comparison to Fig. 2, the dotted and solid lines are the same. The 15 μm and 18 μm tall micro-post surfaces have changed from linear curves to arcs. The bandwidth for the 15 μm case also becomes negative indicating a sharpening of the resonance. The surface with the 15 μm micro-posts (the lowest height case) now shows a linear behavior across the full range of glycerol concentrations. The surface with the 10 μm micro-posts has a much reduced frequency decrease. In this case there are data points below the axis for glycerol concentrations above 78.2% and these indicate an overall positive frequency shift compared to air.

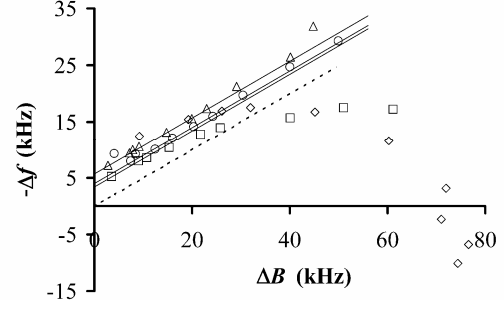


Figure 2. Frequency-bandwidth changes for bare post surfaces.

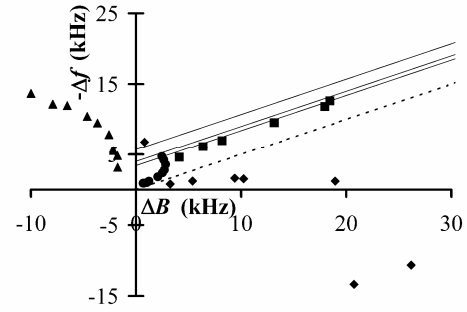


Figure 3. Frequency-bandwidth changes for hydrophobised post surfaces.

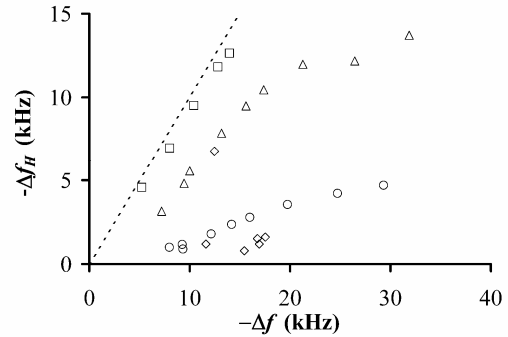


Figure 4. Influence of hydrophobisation on crystal frequency shift.

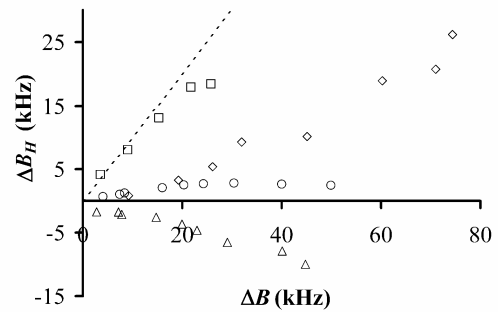


Figure 5. Influence of hydrophobisation on crystal bandwidth.

Fig. 4 and Fig. 5 show the frequency, Δf_H , and bandwidth, ΔB_H , shifts on the hydrophobised micro-post surfaces compared to the shifts on the bare micro-post surfaces for the full range of water-glycerol mixtures; the dotted lines are to guide the eye and have a slope of unity. In all cases, the effect of hydrophobisation is to reduce the magnitude of the changes compared to the bare surfaces. The least influenced by the hydrophobisation is the surface with the 5 μm ($\square\square\square$) tall micro-posts. For the 10 μm ($\diamond\diamond\diamond$) and 15 μm ($\triangle\triangle\triangle$) tall micro-posts there are significant reductions in both the frequency and bandwidth shifts when the surfaces are hydrophobised. The surfaces with 15 μm ($\triangle\triangle\triangle$) tall micro-posts are unusual in that resonant curves become sharper than in air; we confirmed that this behavior was reproducible using several surfaces. This appears to be related to a broader initial resonance in air. The frequency shift-bandwidth shift data indicates that the quartz crystal response of bare (non-hydrophobised) micro-post surfaces to water-glycerol solutions of up to around 80% glycerol is similar in type to that of flat surfaces, i.e. the response of these surfaces obeys the equation $\Delta f = -0.5\Delta B + k$, where k is a non-zero constant dependent on the height of the micro-posts. While the same may be argued for the surfaces with hydrophobised 5 μm tall micro-posts, it is not the case for the surfaces possessing 10 μm , 15 μm and 18 μm tall micro-posts, which have been hydrophobised. In these cases, involving the higher aspect ratios, the effect of the change in surface chemistry is to modify the type of acoustic response from the quartz crystal rather than simply its magnitude. The data for the 18 μm ($\circ\circ\circ$) shows a distinctive decoupling effect.

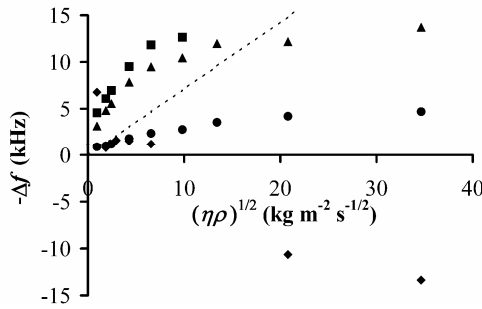


Figure 6. Dependence of the bandwidth on the viscosity-density product for hydrophobised micro-posts.

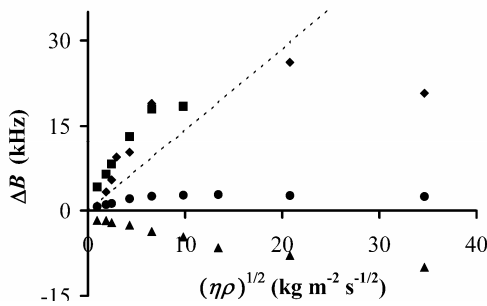


Figure 7. Dependence of frequency shift on the viscosity-density product for hydrophobised micro-posts.

VI. CONCLUSION

The transition from a hydrophobic surface to a superhydrophobic surface with fully suspended liquid has a strong effect on the acoustic response. The data obtained for hydrophobic micro-post surfaces is rich in its behavior. According to height of micro-post the surfaces can i) behave in a similar manner to the bare surfaces, ii) show anomalous behavior at the highest concentrations of glycerol, iii) have a narrower bandwidth as concentration increases, or iv) show a decoupling of the acoustic response. An implication of this work is that current models of acoustic wave sensor response will have limited applicability when high aspect ratio topography, either from surface structuring or from surface roughness, couples to hydrophobic surface chemistry. In particular, any liquid phase acoustic wave sensor possessing a rough surface and involving a mass attachment that can change the hydrophobicity may show an unusual response.

REFERENCES

- [1] D. S. Ballantine, *et al.*, Acoustic Wave Sensors, London: Academic Press, 1996.
- [2] M. J. Thompson and D. C. Stone, Surface-launched Acoustic Wave Sensors, John Wiley (1997).
- [3] S. J. Martin, G. C. Frye and K. O. Wessendorf, "Sensing liquid properties with thickness-shear mode resonators," *Sens. Act.*, vol A44, pp. 209-218, 1994.
- [4] W. C. Duncan-Hewitt and M. Thompson, "4-layer theory for the acoustic shear-wave sensor in liquids incorporating interfacial slip and liquid structure," *Anal. Chem.*, vol 64, pp. 94-105, 1992.
- [5] J. S. Ellis, G. McHale, G. L. Hayward and M. Thompson, "Contact angle-based predictive model for slip at the solid-liquid interface of a transverse-shear mode acoustic wave device," *J. Appl. Phys.*, vol 94, pp. 6201-6207, 2003.
- [6] G. McHale and M. I. Newton, "Surface roughness and interfacial slip boundary condition for quartz crystal microbalances," *J. Appl. Phys.*, vol 95, pp. 373-380, 2004.
- [7] S. J. Martin, G. C. Frye, A. J. Ricco and S. D. Senturia, "Effect of surface-roughness on the response of thickness-shear mode resonators in liquids," *Anal. Chem.*, vol 65, pp. 2910-2922, 1993.
- [8] S. J. Martin, "Interactions of acoustic waves with thin films and interfaces - Closing remarks," *Farad. Discuss.*, vol 107, pp. 463-476, 1997.
- [9] R. Blossey, "Self-cleaning surfaces - virtual realities," *Nature Materials*, vol 2, pp. 301-306, 2003.
- [10] P. Joseph, *et al.*, "Slippage of water past superhydrophobic carbon nanotube forests in microchannels," *Phys. Rev. Lett.*, vol 97, art. 156104, 2006.
- [11] D. Quéré, A. Lafuma and J. Bico, "Slippy and sticky microtextured solids," *Nanotechnology*, vol 14, pp. 1109-1112, 2003.
- [12] C. H. Choi and C. J. Kim, "Large slip of aqueous liquid flow over a nanoengineered superhydrophobic surface," *Phys. Rev. Lett.*, vol 96, art. 066001, 2006.
- [13] S. Gogte, *et al.*, "Effective slip on textured superhydrophobic surfaces," *Phys. Fluids*, vol 17, art. 051701, 2005.
- [14] C. R. Evans, G. McHale, N. J. Shirtcliffe and M. I. Newton, "The effect of SU-8 patterned surfaces on the response of the quartz crystal microbalance," *Sens. Act.*, vol A123-24, pp. 73-76, 2005.
- [15] M. Fujita, H. Muramatsu and M. Fujihira, "Energy dissipation at ultrasonically oscillating superhydrophobic surface in various liquids," *Jap. J. Appl. Phys.*, vol 44, pp. 6726-6730, 2005.
- [16] S. J. Kwoun, R. M. Lee, R. A. Cairncross, P. Shah and C. J. Brinker, "Characterization of superhydrophobic materials using multiresonance acoustic shear wave sensors," *IEEE Trans. Ultrason. Ferroel. Freq. Control.*, vol 53, pp. 1400-1403, 2006.