On the cause and correction of the anomalously high contact angles measured on soils and granular materials

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ABSTRACT

Anomalously high water contact angles are often measured for soils or other granular materials when using a goniometer which is designed for use with flat surfaces. For many years such high contact angles have been rationalised in terms of Cassie and Baxter, and/or Wenzel models for contact angles on non-planar surfaces, but it is becoming increasingly apparent that the theories behind these models are fundamentally flawed. Here, we present an alternative interpretation of these anomalously high contact angles which takes into consideration how a water drop sits on the particulate surface, and propose a geometric correction factor to address this anomaly. Experimental data from studies with precisely arranged needles and spheres, and model and natural soils, were used to explore this approach and examine the validity of the method. Application of the correction factor to measurements of water drops on 1 mm diameter steel spheres hydrophobised with paraffin wax gave a reduction of the measured contact angle of $140.4(\pm0.6)°$ to a corrected contact angle of $108.2(\pm1.0)°$, which is within $3.5°$ of the flat-plane contact angle for water on the wax of $111.7(\pm0.6)°$. For paraffin wax coated soils, measured contact angles are shown to be $15–25°$ higher than comparable flat-plane contact angle. This correction factor may be useful in interpreting goniometer contact angle measurements of irregular surfaces since it is the flat-plane, rather than measured, contact angle which gives a measure of the polarity/hydrophobicity of the surface.

1. Introduction

Contact angles are widely used by soil scientists, geologists and material scientists, predominantly as an empirical measurement of the severity of the water repellency of surfaces such as natural and model soils or rock samples, as they are relatively straight forward to measure (Bachmann et al., 2000a; Bachmann and McHale, 2009; Chau et al., 2014; Leelamanie and Karube, 2009; Marmur et al., 2017; Shang et al., 2008; Yuan et al., 2013). The basis of the method is that water repellency can be assessed by considering the liquid surface contact angle (θ) which is determined by the balance of interfacial tensions at the three-phase (solid, liquid and vapour) contact line (Jaycock and Parfitt, 1981). At equilibrium, the liquid at the intersection between the three interfaces is stationary and the contact angle adopted is determined by the need for a resultant zero force acting at the three-phase contact line. The

balance of forces is given by Young's equation (Young, 1805), Eq. (1),

$$\cos\theta = \left(\gamma^{SV} - \gamma^{SL}\right)/\gamma^{LV} \tag{1}$$

where: θ is the solid–water contact angle, and γ is the surface tension between interfaces of solid-vapour (SV), solid-liquid (SL) and liquid-vapour (LV) respectively.

1.1. Theoretical models: contact angle measurements

In general, contact angles of irregular non-planar surfaces measured using a goniometer are higher than those of a flat surface of the same material (Bachmann et al., 2000b; McHale et al., 2005; Ahn, 2014). For many years this amplification of contact angle by surface structure has been interpreted in terms of the theoretical models of Wenzel (1936) for complete wetting of a jagged surface, and Cassie and Baxter (1944) for
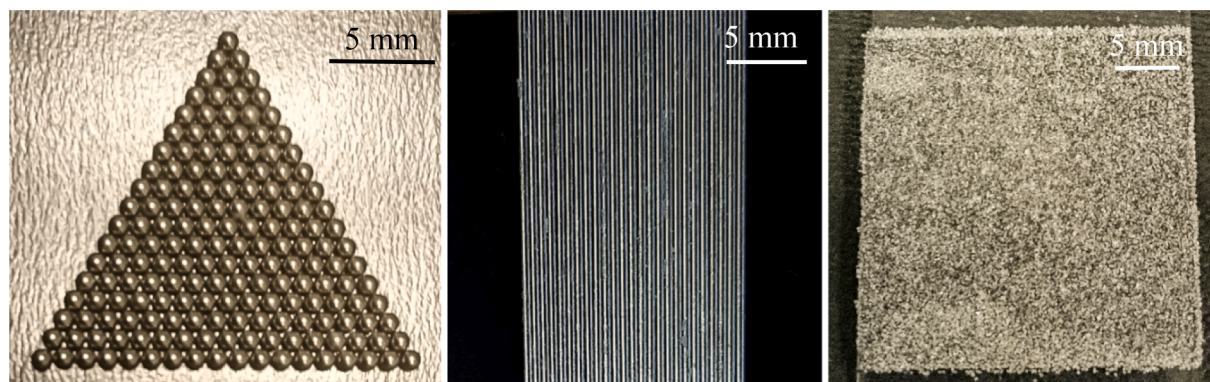
Fig. 1. Example samples set-ups of paraffin coated substrates for contact angle measurements: (left) steel spheres, (middle) ballpoint needles, (right) model soil.

bridge-like wetting over the top of protrusions (McHale et al., 2005). Both models are based on the *thermodynamics of surface energies*, i.e. the contact angle is calculated from the *energy* required to expand the surface via the destruction and creation of interfacial areas. This approach has been challenged by Gao and McCarthy (Gao and McCarthy, 2007, 2009), who noted that the contact angle measured from interactions between the liquid and solid interfaces is solely reliant on the three-phase contact line and not the interfacial areas within the contact perimeter of the wetted area. They give a compelling argument that Wenzel (1936) and Cassie and Baxter (1944) wrongly substituted Young's equation, which considers the *interfacial forces* along a contact line, with *interfacial surface energies*. Gao and McCarthy further suggest (Gao and McCarthy, 2007, 2009) that both Wenzel and Cassie and Baxter equations may inadvertently and coincidently produce results which are consistent with the theories, even though they are not scientifically sound. Both the Wenzel (1936) and Cassie and Baxter (1944) equations have adjustable parameters which can be used to fit data, and as a result these models can almost always give a fit for contact angle measurements. However, the required fitting parameter values are sometimes found to be physically unreasonable, for example, in the case of Cassie and Baxter, the inter-particle distance (i.e. the length of the air gap between particles) is an adjustable parameter which, for the best fit to the experimental data, is often required to be bigger than physically sensible (McHale et al., 2005; Ahn, 2014).

In agreeement with Gao and McCarthy (Gao and McCarthy, 2007, 2009), we suggest that Cassie and Baxter and Wenzel models are inappropriate to understand the anomalously high water contact angles for soil, and other particulate surfaces, when measured using a goniometer. This study aimed to: (i) examine the origin of the anomalous results in terms of the incorrect assumption that the surface plane of the sample used in measurement is the same as the surface plane at the point of contact; (ii) present the theoretical development of a geometric correction, which takes into consideration how a water drop sits on the soil surface, to demonstrate why contact angles measured using a goniometer designed for flat surfaces are always higher than expected when used for non-planar surfaces such as soils, without the need to invoke Cassie and Baxter or Wenzel effects; and (iii) present the experimental evaluation of this theory using contact angles for water drops on precisely controlled model substrates of hydrophobised steel balls and needles, and also hydrophobised acid-washed sand and soil particles.

2. Materials and methods

The experimental approach needed all of the different surfaces to be coated with the same well characterised hydrophobic material, which could be easily and reliably deposited from solution to give a homogeneous covering and which would give a moderately hydrophobic contact angle comparable to what might be expected for compounds naturally found on soils (Mainwaring et al., 2013); so a long chain alkane

(paraffin) wax was used. Steel needles and spheres were chosen as model substrates because they could be obtained of very precisely uniform size and arranged in precise regular arrays to allow clear goniometer imaging of the water drops on the surfaces. Acid-washed sand coated in the wax was chosen as a model soil as we have successfully used this approach in a number of previous studies (Balshaw et al., 2020; Mainwaring et al., 2004, 2013). In addition a wettable natural sandy soil, of the type we have worked with previously (Balshaw et al., 2020; Mainwaring et al., 2013; Doerr et al., 2005), was chosen so as to limit, as far as possible, additional hydrophobicity factors, so that the major factor under consideration was the hydrophobicity induced by coating with wax.

2.1. Materials

One millimetre diameter steel spheres and 0.53 mm diameter ballpoint steel needles were obtained from Simply Bearings Ltd and John James Needles (Redditch, United Kingdom) respectively. Acid-washed sand was obtained from Fisher Scientific (Loughborough, United Kingdom), and paraffin wax (m. pt 58-62 °C) was obtained from Sigma Aldrich (Dorset, United Kingdom). The 125-250 µm sieved fraction (used so as to keep particle size relatively homogeneous) of natural, wettable, sandy soil (0-5 cm depth) used, was obtained from Nicholaston, Gower, UK (51°35′N 04°06′W) and is referred to hereafter as UKC soil. Post collection, the soil was oven dried at 30 °C for 48 h and then initially sieved using a 2 mm sieve to remove any large pieces of organic debris.

2.2. Hydrophobisation of model and natural soil surfaces

To render the model materials hydrophobic they were coated with paraffin wax as follows. A small volume of a solution of paraffin wax in heptane (1.66 g paraffin wax in 100 ml heptane) was placed in a round bottom flask, along with an additional 20 ml of heptane to give a relatively large volume to ensure uniform deposition, followed by either, 4 g of 1 mm steel spheres, 200 steel ballpoint needles, or 4 g of acid-washed sand or natural soil. Wax was deposited from solution by rotary evaporation of solvent (40 °C, 120 rpm, increasing to 50 °C to dryness, then 15 min additional rotary evaporation), which allowed the wax solution to stay in liquid form during the coating process, until the substrate was dry and flowing freely within the flask.

The amount of wax laid down was calculated assuming complete deposition of wax added. For steel spheres and needles, wax laydowns were calculated using the geometric surface areas of the spheres and needles. By way of illustration, with these assumptions, the typical laydown used with steel spheres, of 7.21×10^{-4} g cm^{-2}, would give a wax layer of ~3.3 µm thickness; while that used for ballpoint needles, $(3.05 \times 10^{-4}$ g cm$^{-2})$ would give a wax layer of ~7.8 µm thickness. For acid-washed sand, laydowns were calculated from the surface area of the
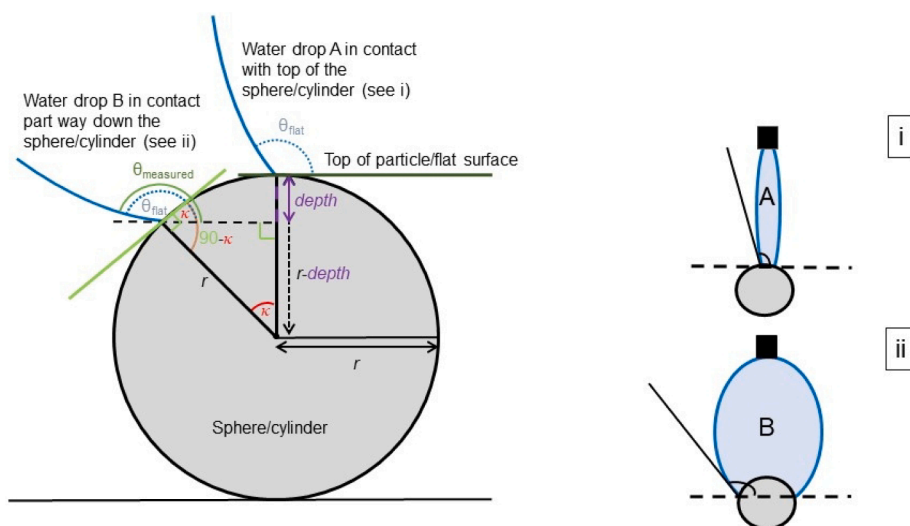
by, '*depth*', in the diagram. Geometrically, $\cos\kappa=(r-depth)/r$, so, if *r* is known and *depth* can be measured κ can be calculated. In our case, with the optical arrangement of the goniometer used, we could measure *depth* with adequate precision for particles of radius > ~0.5 mm.

acid-washed sand use, 292($\pm$3) $cm^2\,g^{-1}$ (Hallin et al., 2017). For soil, as a matter of convenience for comparisons, laydowns were calculated using the same surface area as acid-washed sand, (although we recognise this may be an overestimate of surface area because of the relatively large diameter, 125–250 µm, fraction used). Previous work has shown efficient laydowns of organics onto acid-washed sand and soils from solution using rotary evaporation to remove solvent (Mainwaring et al., 2013; Hallin et al., 2017).

2.3. Preparation of hydrophobised samples for goniometer measurements

Ballpoint needles were closely packed length-ways on a sheet of magnetic plastic. For steel spheres, a triangular stencil was used to create closed-packed arrays of spheres held in place on a sheet of magnetic plastic. These regular arrangements were essential to allow a clear view of the water-substrate contact. Acid-washed sand and UKC soil samples were prepared for goniometer measurement as described in Bachmann et al. (2000a, 2000b), where soil was sprinkled onto double-sided adhesive tape attached to a microscope slide, creating a single layer of soil grains. Example sample set-ups are shown in Fig. 1. At least three replicates of each sample were produced per measurement type. To assess the reproducibility of the measurements on the wax surface for the steel spheres, measurements were repeated over three consecutive days, with samples dried post-measurement in a desiccator overnight.

2.4. Contact angle measurement - goniometer and drop shape analysis software

A KRÜSS Easy Drop FM40 goniometer with Drop Shape Analysis (DSA) software was used to measure sessile drop dynamic advancing contact angles for water drops on the substrates. Dynamic drop measurements are measured whilst the drop volume is altered, either by being increased (advancing) or reduced (receding), and therefore the boundary surface is constantly changing, and this is very useful for this work since it permits analysis of the same drop as it increases in volume and advances over the substrate surface. (Static contact angle measurements use drops of fixed volume with the drop produced prior to measurement: we note that it is generally recognised that static contact angle measurements can be quite variable on non-homogeneous surfaces due to localised irregularities (KRÜSS Scientific, Technical note 312e, 2007), and where the surface is rough we believe the

factors discussed in this work contribute to this variability.) The Drop Shape Analysis (DSA) software provides a variety of different fitting methods for contact angle measurement all of which are described in more detail in Technical Note TN314e (KRÜSS, Scientific, 2008). The polynomial method (Tangent 2 method) was selected as the most appropriate for the measurements here, as it can adapt to a range of contour shapes.

Distilled water was dispensed onto sample surfaces using a 1000 µl syringe with a 1.065 mm blunt tip needle. A small hanging drop of approximately 5 µl was expelled before being brought into contact with the substrate surface, and water was thereafter dispensed at a rate of 100 µl min^{-1} allowing the drop to advance across the surface until a final drop volume of 90 µl was obtained. Contact angles were measured using videos recorded at 6.25 fps. For needles, measurements were taken looking down the length of the needles; for steel balls, measurements were taken looking down the parallel rows of spheres. Where possible,
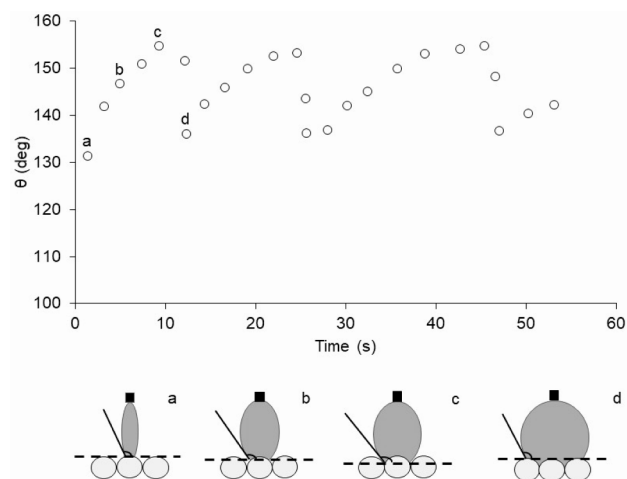
Fig. 3. Advancing angle measurements on a closely packed regular, undulating, surface (wax coated ballpoint needles) shows the sawtooth pattern of contact angles as $\theta_{measured}$ increases as a water drop advances over the surface, followed by a dip as it jumps to the next needle. (Measurements were made using horizontal baseline placement at the three-phase contact line point, rather than across the top of the particle surface.)

Table 1

Measured theta ($\theta_{measured}$) and corrected theta ($\theta_{corrected}$), in degrees, for three replicate samples (S1, S2, S3) of paraffin wax coated (laydown 3.05×10^{-4} g cm^{-2}) steel ballpoint needles (BN) (0.53 mm diameter). $\theta_{measured}$, $\theta_{corrected}$ and average $\theta_{corrected}$ were all measured/calculated from placing the baseline at the depth of the three-phase contact line (contact baseline), or across the top of the particle surface (top baseline).

Sample	$\theta_{measured\ (contact\ baseline)}$	$\theta_{corrected\ (contact\ baseline)}$	Average $\theta_{corrected\ (contact\ baseline)}$	$\theta_{measured\ (top\ baseline)}$	$\theta_{corrected\ (top\ baseline)}$	Average $\theta_{corrected\ (top\ baseline)}$
S1BN	148.2 ± 1.2	107.7 ± 1.5	108.0 ± 1.3	145.8 ± 0.8	105.4 ± 1.5	106.2 ± 1.3
S2BN	145.6 ± 1.4	104.1 ± 2.9		145.2 ± 1.2	103.7 ± 3.0	
S3BN	148.3 ± 1.1	112.5 ± 1.9		145.6 ± 1.0	109.8 ± 1.8	

and this was usually the case, the left and right contact angles for the drop were averaged for each point using the DSA software. If it was not possible to measure an angle for both sides the angle successfully extracted was taken as representative for that measurement. Advancing angles were measured at regular intervals through the video footage and an average contact angle calculated from these measurements to give an overall contact angle for each sample; errors are given as standard error on the mean. Measurements were carried out at 20-24 °C and 45-56% relative humidity.

3. Results and discussion

3.1. Planar and non-planar surfaces

For the paraffin wax deposited on a glass microscope slide a static contact angle of 111.7($\pm$0.6)° was obtained, which is in close agreement with the literature values of 110° and 111° for paraffin wax given by Pashley and Karamen (2004) and Jaycock and Parfitt (1981) respectively.

From the above result, a non-planar surface covered in paraffin wax would be expected to show a contact angle of 111.7($\pm$0.6)° relative to the correct reference plane, i.e. tangent to the substrate surface, at the three-phase contact. However, because, during the measurement, the reference plane of the surface is taken as parallel to the top of the particle surface, $\theta_{measured}$, will usually be higher than the real contact angle because the tangent at the point of three-phase contact (and hence theoretically correct reference plane) is not parallel to the top of the particle surface because of the way the drop sits on the surface (see Fig. 2).

This gives rise to the typical sawtooth pattern of measured contact angles as the water drop runs down the side of one particle, a needle in this case, and then jumps to the top of the adjacent particle as the drop advances, as shown in Fig. 3.

3.2. Geometric correction of $\theta_{measured}$

Fig. 2 suggests a geometric correction may be made to $\theta_{measured}$ to obtain a corrected contact angle, $\theta_{corrected}$, which would be the same as that measured on a flat surface (θ_{flat}), as given in Eq. (2):

$$\theta_{corrected} = \theta_{measured} - \kappa \qquad (2)$$

And κ can be obtained from the radius of the particle, r, and the depth the drop sits from the top of the particle, (shown as *depth* in Fig. 2), via Eq. (3).

$$\kappa = \cos^{-1}((r\text{-}depth)/r) \qquad (3)$$

3.3. Ballpoint needles

Analysis using the geometric correction factor described in Fig. 2 and Eqs. (2) and (3) was applied to a series of advancing angle measurements on closely-packed ballpoint needles covered in paraffin wax; the results are presented in Table 1 and Fig. 4. Correction values were obtained for the left and right hand contact angles of the drop independently, and these were then averaged. Even using a flat baseline the experimentalist has a choice of placing the flat baseline at either the top of the surface (as

is standard practice), or a little lower into the bulk at the depth of the three-phase contact line (dashed horizontal line in Fig. 2). Due to the curvature of the drop surface, using the top of the particle surface as a flat baseline gives a slightly lower contact angle, $\theta_{measured(top\ baseline)}$, than does using a flat baseline at the depth of the three-phase contact line, $\theta_{measured(contact\ baseline)}$ (Table 1). The average of the three replicate
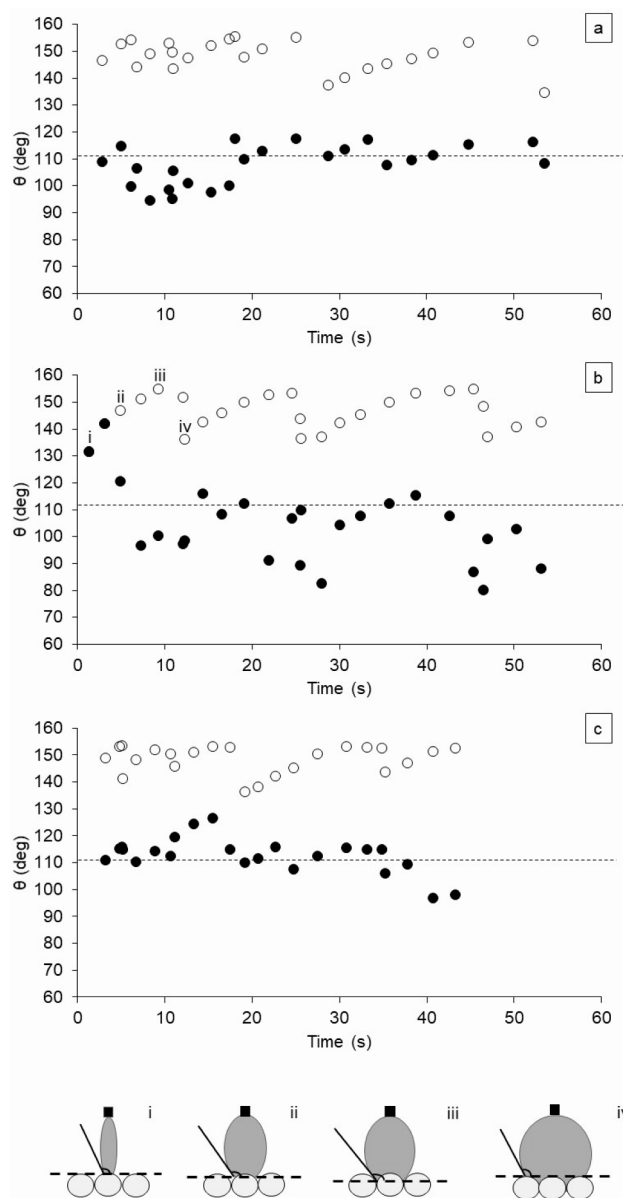
Fig. 4. Contact angle measurements on three replicate samples of 0.53 mm diameter metal ballpoint needles (BN) coated with paraffin wax (laydown 3.05×10^{-4} g cm^{-2}): (a) S1BN, (b) S2BN and (c) S3BN. Open circles, measured contact angle ($\theta_{measured(contact\ baseline)}$); filled circles, corrected contact angle ($\theta_{corrected(contact\ baseline)}$); the dashed line gives the contact angle for paraffin wax on a flat surface.
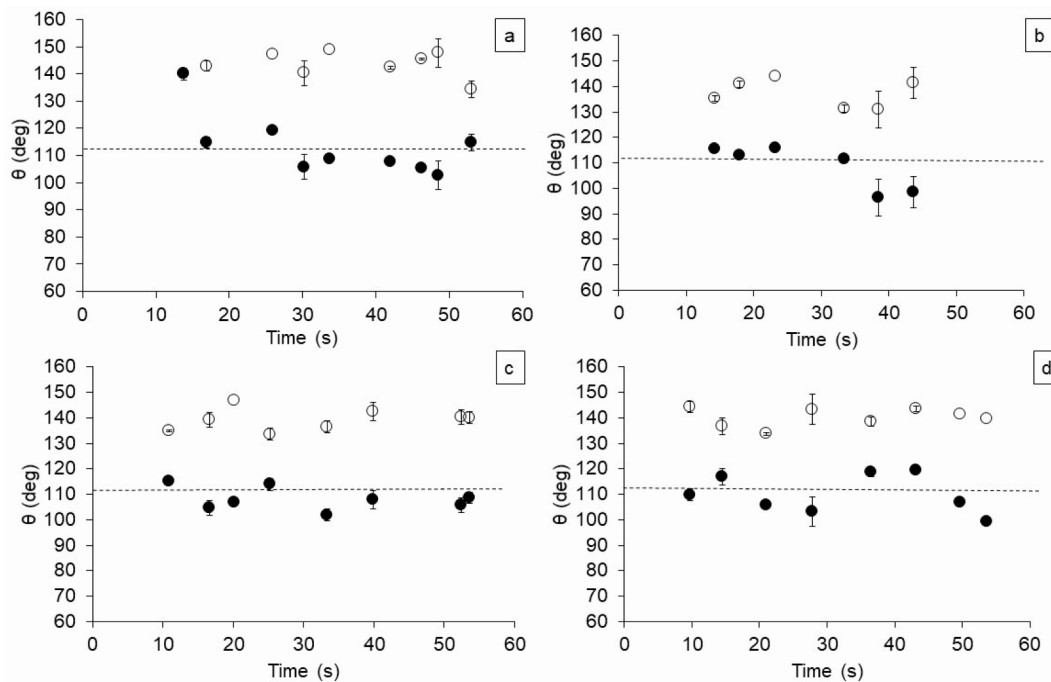
Fig. 5. Contact angle measurements on 1 mm diameter steel spheres coated with paraffin wax (laydown 7.21×10^{-4} g cm^{-2}): (a) S1SST2, (b) S2SST1, (c) S3SST3 and (d) S4SST3. Open circles are $\theta_{measured(contact\ baseline)}$ contact angle, filled circles are $\theta_{corrected(contact\ baseline)}$; the dashed line gives the contact angle for paraffin wax on a flat surface. Where S indicates sample number, SS identifies steel sphere substrate and T gives the test number.

Table 2

Measured theta ($\theta_{measured}$), corrected theta ($\theta_{corrected}$) and averaged corrected theta ($\theta_{corrected}$), in degrees, for four replicate samples (S1, S2, S3, S4) of paraffin wax coated (laydown 7.21×10^{-4} g cm^{-2}) steel spheres (SS) (1 mm diameter). $\theta_{measured}$, $\theta_{corrected}$ and average $\theta_{corrected}$ were all measured/calculated from placing the baseline at the depth of the three-phase contact line (contact baseline), or across the top of the particle surface (top baseline). Samples were retested over three consecutive days (Test 1-3), water drops were removed and samples were placed in a desiccator between measurements.

Sample	Test	$\theta_{measured\ (contact\ baseline)}$	$\theta_{corrected\ (contact\ baseline)}$	Average $\theta_{corrected\ (contact\ baseline)}$	$\theta_{measured\ (top\ baseline)}$	$\theta_{corrected\ (top\ baseline)}$	Average $\theta_{corrected\ (top\ baseline)}$
S1SS	1	142.1 ± 1.8	101.2 ± 2.0	108.6 ± 2.2	136.8 ± 0.9	96.0 ± 2.7	103.9 ± 2.6
	2	143.2 ± 1.5	113.2 ± 3.8		137.7 ± 0.7	107.6 ± 4.7	
	3	143.1 ± 1.4	111.3 ± 4.3		139.0 ± 1.0	107.2 ± 4.9	
S2SS	1	137.3 ± 2.3	108.5 ± 3.6	105.0 ± 1.6	137.4 ± 1.4	108.6 ± 3.1	102.0 ± 2.1
	2	140.2 ± 2.1	104.0 ± 2.6		137.1 ± 1.2	100.9 ± 3.6	
	3	141.7 ± 0.8	102.4 ± 2.1		136.8 ± 0.8	97.5 ± 3.1	
S3SS	1	137.7 ± 1.4	111.6 ± 5.5	110.1 ± 2.0	136.6 ± 1.4	110.5 ± 5.8	107.9 ± 2.1
	2	139.9 ± 3.3	110.6 ± 3.9		137.5 ± 1.2	108.2 ± 2.8	
	3	139.2 ± 1.5	108.0 ± 1.6		136.2 ± 0.6	105.1 ± 2.3	
S4SS	1	137.9 ± 1.6	108.1 ± 3.4	109.2 ± 1.8	136.0 ± 0.7	106.2 ± 4.1	105.9 ± 1.9
	2	140.5 ± 3.7	109.4 ± 3.4		136.5 ± 2.4	105.4 ± 3.1	
	3	140.2 ± 1.3	110.0 ± 2.7		136.1 ± 0.8	106.0 ± 3.0	

samples (Fig. 4a-c) for $\theta_{measured(contact\ baseline)}$ was 147.3($\pm$0.7)°, and after the correction factor was applied this gave $\theta_{corrected(contact\ baseline)}$=108.0($\pm$1.3)°, which is within ~3.7° of that measured for paraffin wax on a flat surface. When using top of the surface baseline measurements ($\theta_{measured(top\ baseline)}$), correction gave a slightly lower value but still within ~5° of that measured for paraffin wax on a flat surface.

3.4. Steel spheres

Fig. 5 and Table 2 presents results for measurements using wax-coated steel spheres.

Measurements using a baseline at the depth of the three-phase contact line gave an average $\theta_{measured\ (contact\ baseline)}$=140.4($\pm$0.6)°, which after the correction factor was applied reduced to $\theta_{corrected\ (contact\ baseline)}$=108.2($\pm$1.0)° (see Fig. 5a-d). This is within 3.5° of the flat surface contact angle for water on paraffin wax measured here. Again, contact angles measured using a flat top of particle baseline are a few degrees lower than those using the depth of the three-phase contact line, with

$\theta_{corrected(top\ baseline)}$=104.9($\pm$1.0)°. For these non-planar surfaces, this geometric approach thus successfully provides a sensible correction term, and gives a sound theoretical basis, for the high contact angles measured on these non-planar surfaces.

The larger θ_{flat} of the surface the smaller the correction factor expected, because the larger θ_{flat} the lower the depth at which the drop will contact adjacent particles. For example, consider the two cases where θ_{flat}=90° and θ_{flat}=180°, and simplifying the discussion by assuming the drop is large enough that the curvature of the water surface is small compared to the size of the particles. When the surface has θ_{flat}=90° the water drop surface makes a right angle to the tangent at the particle surface; it projects vertically up when contacting the top of the particle, and then, as the drop moves down the side of the particle $\theta_{measured}$ increases until, from the geometry, at 90°+60°=150° it makes contact with the adjacent particle; so the correction factors required as the drop advances over the spheres range from 0–60°. But for a surface giving θ_{flat}=180° the water drop surface follows the tangent at the particle surface, and so extends horizontally from the top of the particle and so
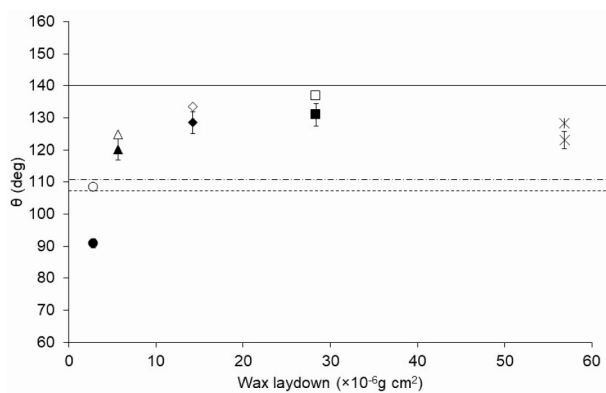
Fig. 6. Average $\theta_{measured(top\ baseline)}$ against wax laydown for the 125–250 μm sieved fraction of natural UKC soil (filled shapes and cross; with error bars shown) and acid-washed sand coated in paraffin wax (open shapes and star). Solid line shows average $\theta_{measured\ (contact\ baseline)}$ (140.4±0.6°) on steel spheres and dashed line shows $\theta_{corrected\ (contact\ baseline)}$ (108.2±1.0°). The contact angle measurement for wax on a flat surface at 111° is represented by the dot and dash line. Laydowns are as follows: 2.84×10^{-6} g cm^{-2} (circle), 5.86×10^{-6} g cm^{-2} (triangle), 14.2×10^{-6} g cm^{-2} (diamond), 28.4×10^{-6} g cm^{-2} (square) and 56.8×10^{-6} g cm^{-2} (cross and star).

the maximum $\theta_{measured}$ will not be much greater than 180° before contact with the next particle is made.

3.5. Model and natural soils

The key to evaluating this method experimentally was the use of regular arrays of particles of a suitable size for measurements of the required precision. Soils are not homogeneous and preparing a regular array is not easy, furthermore the particle size is rather small for measurements of the precision required. However, the principle remains the same, and we would expect the measured contact angle on soil coated in paraffin wax to be around the same as that on steel spheres. To explore this, wax-coated acid-washed sand and the 125–250 μm fraction of the natural soil were both coated with variable laydowns of paraffin wax to see if $\theta_{measured\ (top\ baseline)}$ advancing angles were in a similar range to those obtained on wax coated needles and spheres. (We used $\theta_{measured(top\ baseline)}$ because depth correction could not be made on these samples of smaller particles with sufficient accuracy to obtain meaningful results).

The average $\theta_{measured(top\ baseline)}$ contact angle is presented in Fig. 6 against wax application for acid-washed sand and natural soil. The data shows that above *ca.* 3×10^{-6} g cm^{-2} laydown contact angles are independent of laydown, but at laydowns lower than this the contact angle is reduced presumably because these do not give a fully consistent wax coverage over all particles.

Average advancing angles ($\theta_{measured(top\ baseline)}$) on model and natural sandy soil coated with paraffin wax are *ca.* 15-25° higher than θ_{flat} for paraffin wax (111°), somewhat lower than those for paraffin wax on spheres or needles (see Figs. 5a-d and 6). We suggest, as a reasonable explanation for this, that the maximum depth the water drop can reach on close packed spheres is higher than that for the loose packed, small diameter, irregular, soil particles. If, in a soil, as a consequence of the loose packing and heterogeneous particle size and shape, the water drop transfers the drop front from particle to particle at a lower relative depth than would be possible for homogeneous spheres then the maximum, and therefore averaged, advancing contact angle will be smaller on the soil than on close packed heterogeneous spheres. Further experimental work, or modelling, of natural soils would be necessary to evaluate this idea, and such work would require the use of equipment with higher resolution than was available for this study. However, the explanation for the observation that $\theta_{measured}$ is *ca.* 15–25° higher than θ_{flat} remains the same, i.e. it is a feature of the mode of measurement rather than any

fundamental change in surface contact angle or surface hydrophobicity. Thus, for soils and particles coated with typical hydrophobic organics such as waxes with θ_{flat} ~110°, overestimates of contact angle of the order of 15–25° are to be expected, and such values have, indeed, been found by other workers in the field (McHale et al., 2005; Ahn, 2014). Consideration of this correction factor when evaluating goniometer contact angle measurements will help in a better estimation of the flat surface contact angle of the compounds inducing soil water repellency. Thus, contact angle measurements may be able to offer more information about the polarity/hydrophobicity of the compounds adsorbed to the soil surface rather than just giving an indication of the severity of the repellency present.

The findings presented here also have wider implications for application of the geometric correction factor to other fields of research that use contact angle measurements on a variety of granular, heterogenous surfaces. For example, for the measurement of the wettability of tablets, powders (Buckton, 1993; Alghunaim et al., 2016), and for assessing fabrication methods for the production of superhydrophobic surfaces (Liu et al., 2011).

4. Conclusions

The geometric correction factor introduced here gives a theoretical basis for understanding the anomalously high contact angles measured for granular surfaces when using a goniometer designed for flat surfaces. These experiments support the notion that the Cassie and Baxter (1944) and Wenzel (1936) models are inappropriate for the interpretation of measured contact angles on irregular surfaces such as soils. Even for samples where correction cannot be precisely made because measurements of the required precision cannot be obtained, the theoretical basis for the increased measured contact angle over that expected for a plane surface remains sound. Overestimates of flat-plane contact angles of the order of 15–25° for granular surfaces are to be expected when measurements are made using goniometers designed for flat surfaces.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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