Forces between zinc sulphide surfaces; Amplification of hydrophobic interaction by surface charge.

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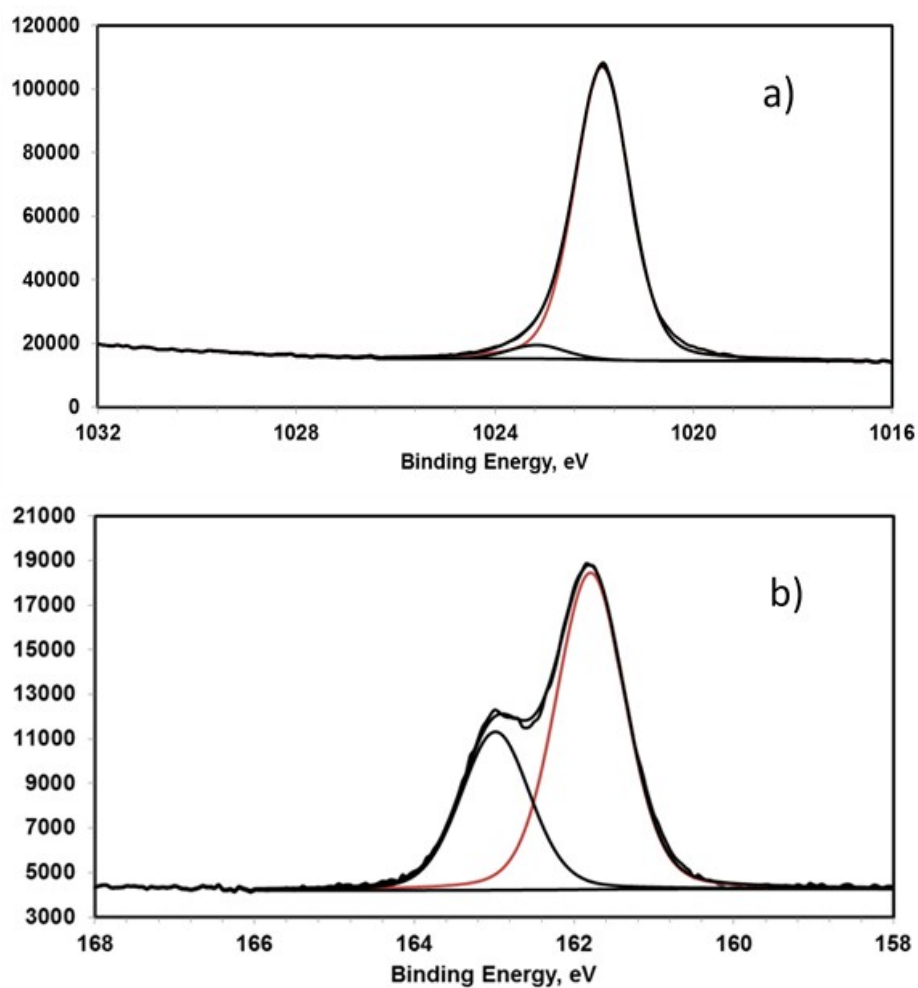**S1 XPS spectra of the Zinc Sulphide surfaces used in this study**

Figure S1 The high resolution spectra for (a) Zn 2p 3/2 binding energy at 1021.9 eV and (b) S 2p 3/2 binding energy at 162.8 eV. This is consistent with ZnS in either zincblende or wurtzite structures.

Table S1 XPS elemental analysis of magnetron sputter coated ZnS surfaces

Element	%
O	16.5
C	35.4
S	21.5
Zn	26.6

S2 Calculated distance dependent Hamaker Coefficients for ZnS coated surfaces

Distance-dependent Hamaker coefficients were calculated for the multilayer system silica-silicon-ZnS - water – ZnS-silica as shown in Figure S2. The thickness of the single silicon layer was 2 nm. The thickness of the two ZnS layers was taken to be 15 nm and 30 nm, respectively. The distance-dependent Hamaker coefficient here refers to the coefficient A(L) determining the van der Waals interaction energy, $U_{vdW}(L) = -A(L)/(12\pi L^2)$. Here L is the distance between the ZnS - water interfaces, i.e. the thickness of the intermediate water layer. Hamaker coefficients are shown with and without retardation due to the finite speed of light (we note that the finite thickness of the layers induces distance-dependence even in the nonretarded case). The horizontal line marks the conventional Hamaker constant for silica-water-silica at 0.596×10^{-20} J. The conventional Hamaker constant for silicon-water-silicon is 9.52×10^{-20} J.
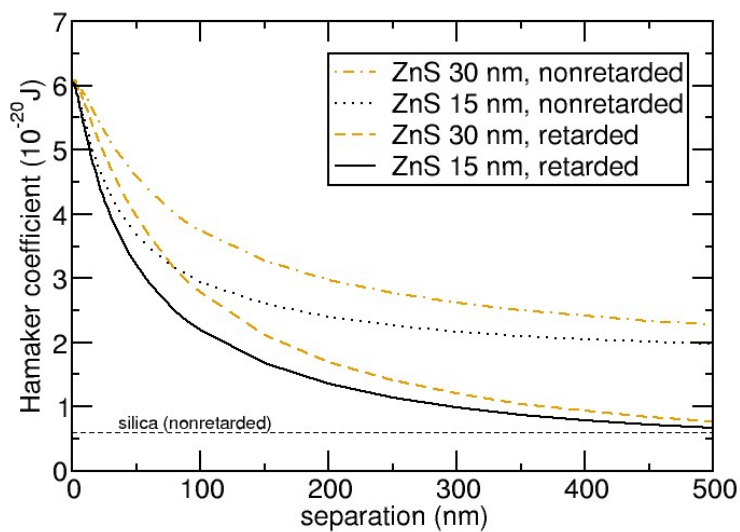

Figure S2 Calculated Hamaker coefficients for the van der Waals interaction between ZnS coated surfaces

S3 Effect of pH on the measured force in the range 3.8 < pH < 4.8

Figure S3 shows the interaction forces between ZnS surfaces over the pH range of 3.8 < pH < 4.8. Throughout this range there is a substantial attraction that is attributed to the long range hydrophobic attraction.
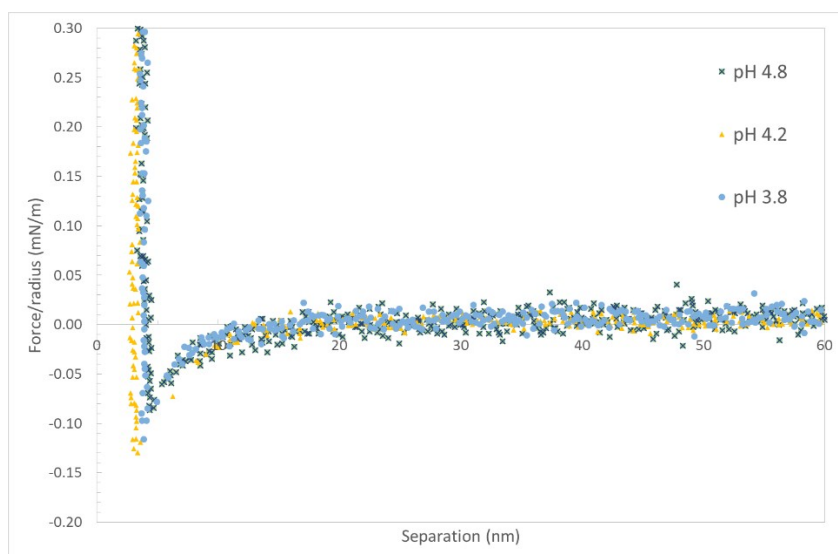

Figure S3 Normalised approach forces for sputter-coated ZnS in 10^{-3}M NaCl in the range 3.8 < pH < 4.8. The attraction is evident throughout this pH range with a maximum around pH 4.2

S4 Effect of pH on the measured adhesion between ZnS surfaces

Some sample measurements of the adhesion between ZnS surfaces at a range of pH are shown in Figure S4 below. Adhesion measurements show variation from one measurement to the next. So statistical measures of the adhesion values obtained are provided in table S2
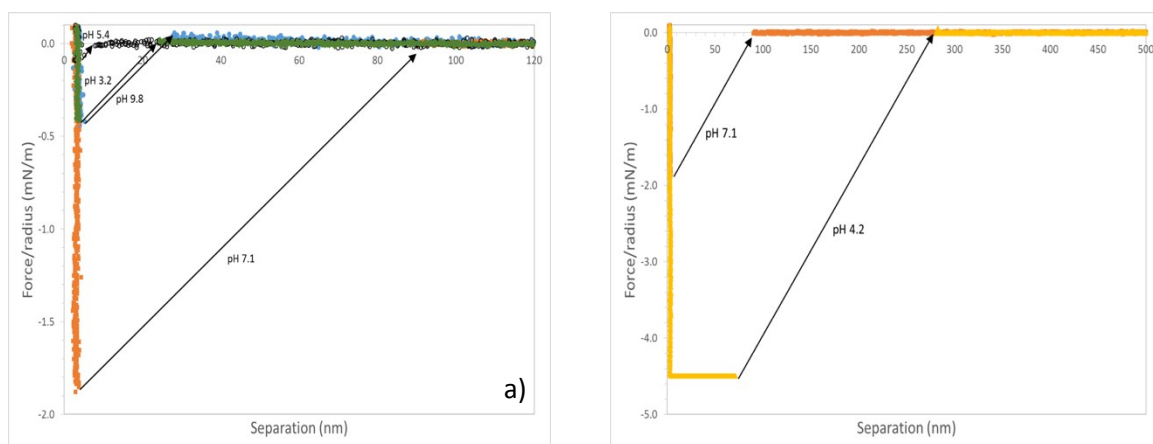

Figure S4 Normalised forces between ZnS surfaces measured upon separation at different pH in 10^{-3}M NaCl. The arrows indicate the spring instability that accompanies the separation of the surfaces that occurs when the restoring force of the cantilever spring exceeds the adhesion. The value of the restoring force immediately prior to the separation of the surfaces is taken as the normalised adhesive force. The force at pH 4.2 was plotted in (b) and compared with that at pH 7.1 to illustrate the magnitude and range of the adhesion compared to the other pHs. Note the horizonal data measured at F/R= -4.5 mN/m for pH 4.2 is a result of the deflection of the cantilever exceeding the range of the sensor. In this case the adhesion value can be estimated from the jump-out distance and the spring constant.

Table S2 Effect of pH on the measured adhesion forces between ZnS surfaces

pH	Adhesion (mN/m)		
	Max	Mean	Median
9.8	0.77	0.35	0.36
7.1	2.80	2.26	2.23
5.4	1.04	0.55	0.68
4.2	7.60	3.50	2.88
3.2	3.14	0.83	0.52

S5 Fitting of Force measurement data using DLVO-R

The model employed to treat the roughness takes the surface position to be the average position of surface heights. Asperity contact is added as an explicit repulsive contribution to the total force. Therefore the surface separation is defined as the distance between the average height of two interacting surfaces. The DLVO theory with roughness (DLVO-R)[1] requires two adjustments.

Firstly, using the probability distribution of surface heights, the noncontact (DLVO type) surface force is averaged over all the surface elements between all the statistically possible surface separations. Roughness was included in the model by assuming a Gaussian roughness distribution with the magnitude described by the rms roughness. The roughened noncontact interaction energy $G_{nc}(L)$ at surface separation L, used to calculate surface forces, is derived from the interaction between smooth surfaces, G_{smooth}, by averaging over the roughness distribution,

$$G_{nc}(L) = \int dh \frac{e^{-h^2/2\sigma_m^2}}{\sigma_m\sqrt{2\pi}} G_{smooth}(L+h) \tag{S5.1}$$

where σ_m is the mean rms roughness $\sigma_m = \sqrt{\sigma_1^2 + \sigma_2^2}$ averaged over the rms roughnesses σ_1 and σ_2 of each surface. The roughness average of eq.(S5.1) is applied to the conventional smooth noncontact (DLVO) interaction.

Secondly, the surface asperities start to compress each other before the separation between the average heights of the surfaces becomes zero. The asperity contact force is also averaged over all the possible surface heights considering a hemispherical asperity with low aspect ratio (height/base diameter). The contact interaction energy is determined by the reduced radius $1/R_r = 1/R_1 + 1/R_2$ of asperity tips and the reduced Young's modulus of the two surfaces, $1/E_r = 1/E_1 + 1/E_2$ (taking Poisson ratios of the materials to be 1). The asperity contact radius is estimated from images of the surface. The precise value has a very minor effect on the compliance and the assignment of zero surface separation. When the surface height distribution is taken to be Gaussian with mean rms σ_m then the contact force (normalised to the radius r of the colloidal probe) may be approximated by

$$f_{contact}(L)/r \approx \left(\frac{E_r 2\sqrt{2}}{5}\right) \frac{\sigma_m^4 \, e^{-L^2/2\sigma_m^2}}{\sqrt{R_r} \, L^2 \sqrt{L}}$$

(S5.2)

This expression is an approximation. We use the exact analytical expression which involves Bessel functions. The total force sums both components, the roughened noncontact force derived from eq.(S5.1) and the contact force of eq.(S5.2). In practice when fitting force curves the compliance is matched to the asperity contact force and in this manner the separation of the surfaces at contact is set relative to the average position of the interface and the zero of separation in the experimental data is determined. Other than this modification to the method for assigning the compliance and the zero of separation the conversion of the raw force data from deflection versus piezo translation to force versus separation follows the standard method developed by Ducker, Senden and Pashley[2].

The DLVO interaction for smooth surfaces is then calculated using the Hamaker coefficient described above in S2 to describe the Van der Waals interaction and the algorithm of Chan Pashley and White[3] to calculate the electrostatic interaction with constant charge and constant potential boundary conditions. This calculation generates the interaction energy between smooth surfaces, G_{smooth}, required in equation S5.1 to calculate the DLVO-R interaction. The surface potential and fitted Debye length are obtained by iterating the DLVO-R calculation whilst adjusting the values of these parameters to obtain a fit to the data. The method has been shown to substantially improve the fitting of force data even on surfaces with low levels of roughness[4].

References

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