Crack formation in colloidal films: the role of substrate constraint

M.I. Smith & J.S. Sharp

School of Physics and Astronomy & Nottingham Nanoscience and Nanotechnology Centre, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

e-mail: james.sharp@nottingham.ac.uk

1. Introduction

Crack formation in thin films of colloidal particles is a common technological problem encountered in the production of ceramic coatings, paints & glazes.

In a drying colloidal suspension, the reservoir of colloid (A) retreats due to evaporation, leaving a wet compact film of particles. Into this wet region (B) grow cracks. Later a dry front (C) develops which displays secondary cracking.
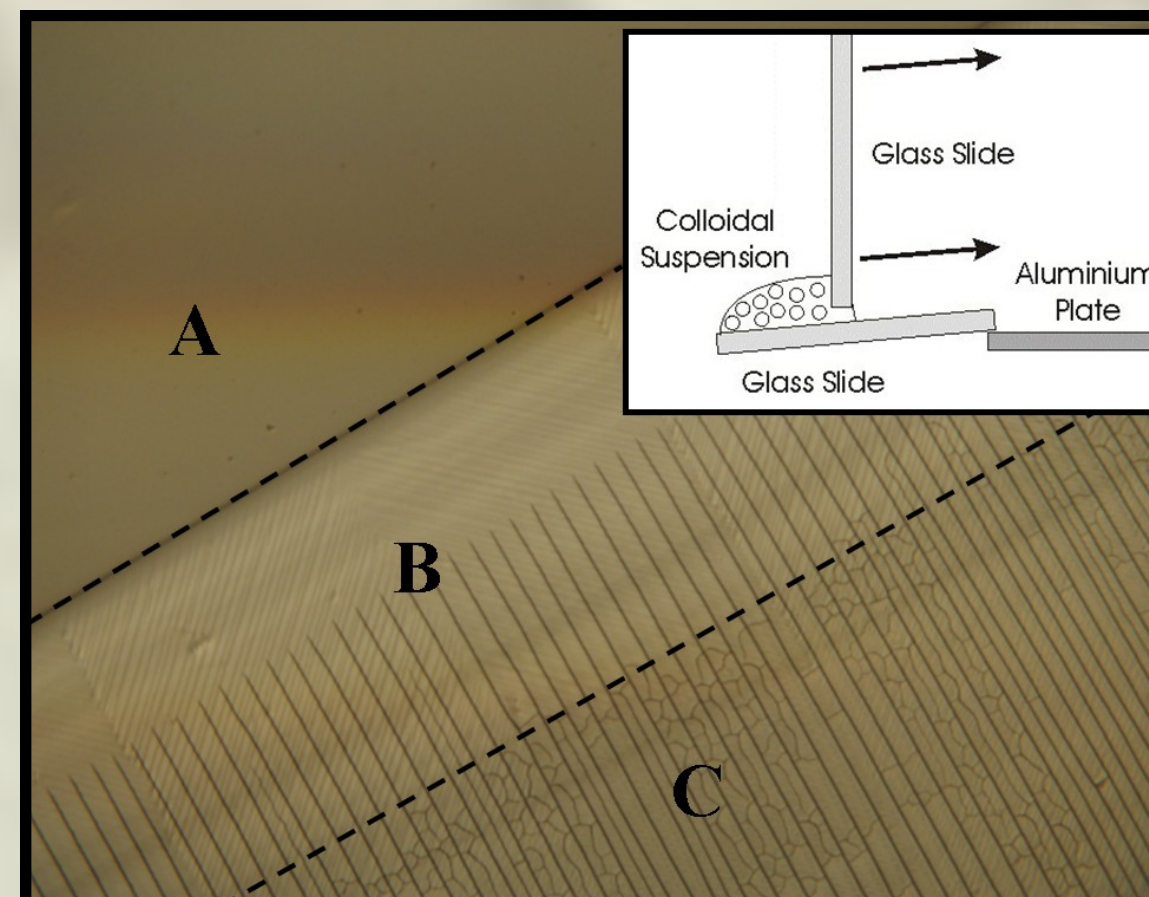

Figure 1— Optical microscope image of a drying suspension of 46nm PS colloid. Inset shows solution drawn across glass slide to produce 1D drying geometry.
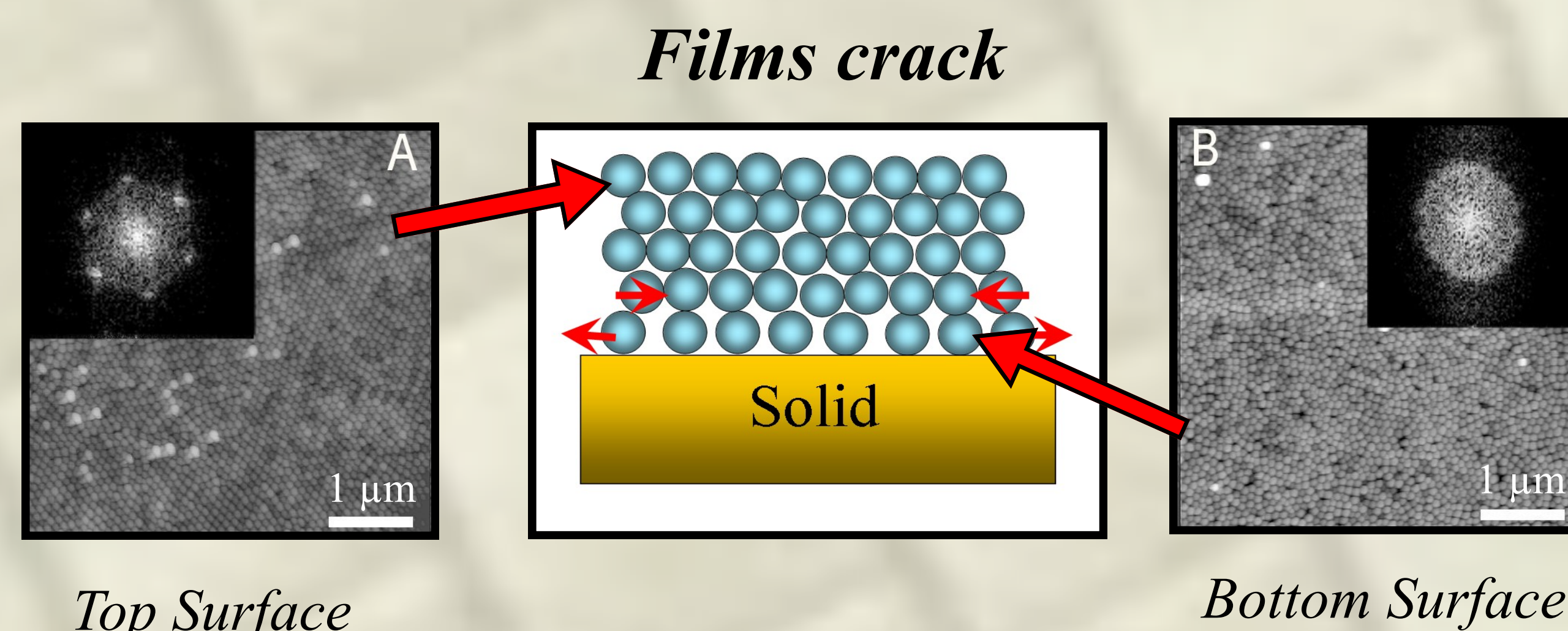
2. Substrate constraint

Glass Substrate

The film formed from drying a 100nm PS colloidal suspension on a rigid surface results in cracking. Atomic Force Microscopy of the particles reveals differences in the packing at the top and bottom surfaces of the film (see below).

A) Top surface of film composed of hexagonally close packed (HCP) particles. The inset shows the 2D FFT.

B) Bottom surface: the FFT shows no structure indicating the particles are randomly distributed.

This indicates a mismatch strain between the top and bottom surfaces of the colloidal film due to packing differences.
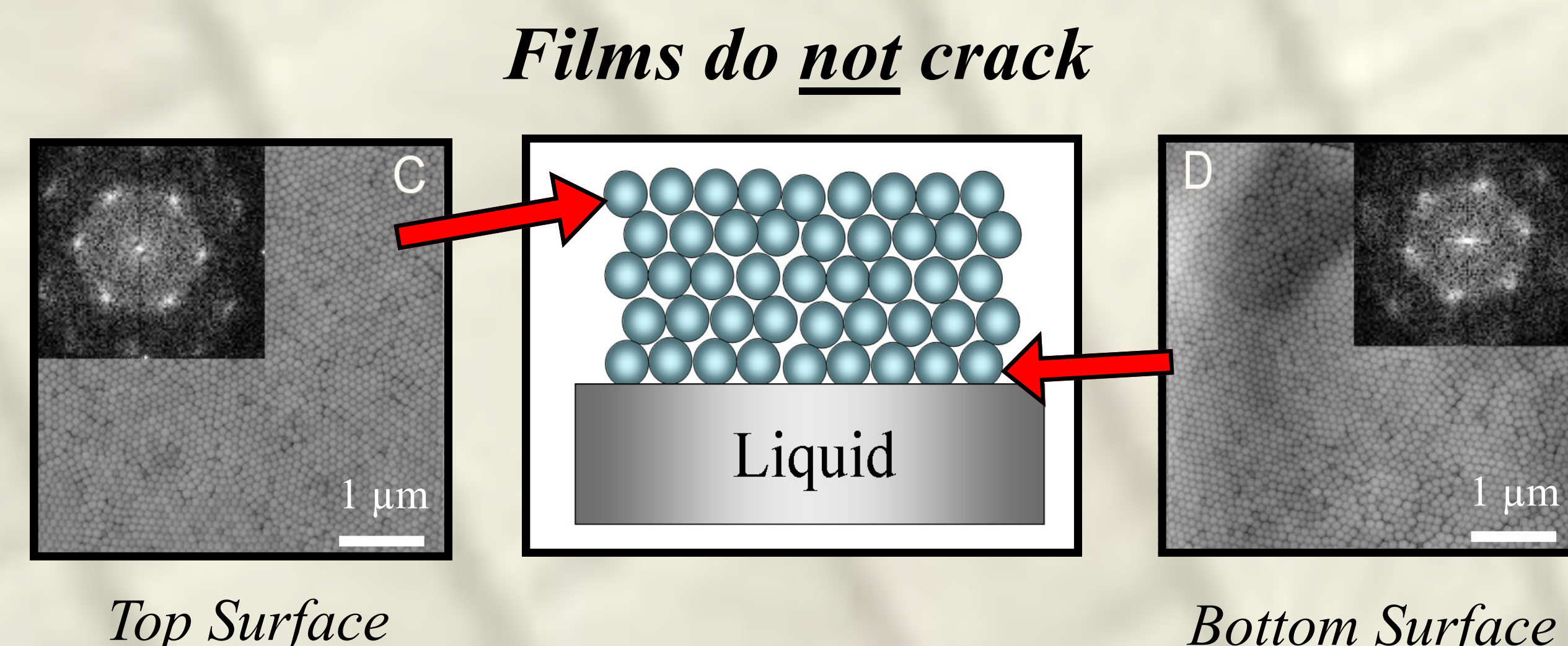
Films crack

Top Surface   Bottom Surface

3. No constraint

Mercury Substrate

To test the importance of substrate constraint on the cracking mechanism we remove it by drying films on a liquid.

C) Top surface shows HCP ordering

D) With the constraint removed particles at the bottom surface also form HCP structures.

Films do <u>not</u> crack

Top Surface   Bottom Surface

Cracking is linked to a mismatch strain between the film and substrate

4. Compliant substrates

Varying mechanical properties of substrate alters strength of constraint imposed on film.

Polyisoprene was crosslinked to produce different moduli substrates

47nm colloidal suspension was dried on the different elastomeric substrates.

As the substrate modulus decreases the crack spacing (λ) increases for a given film thickness (H).
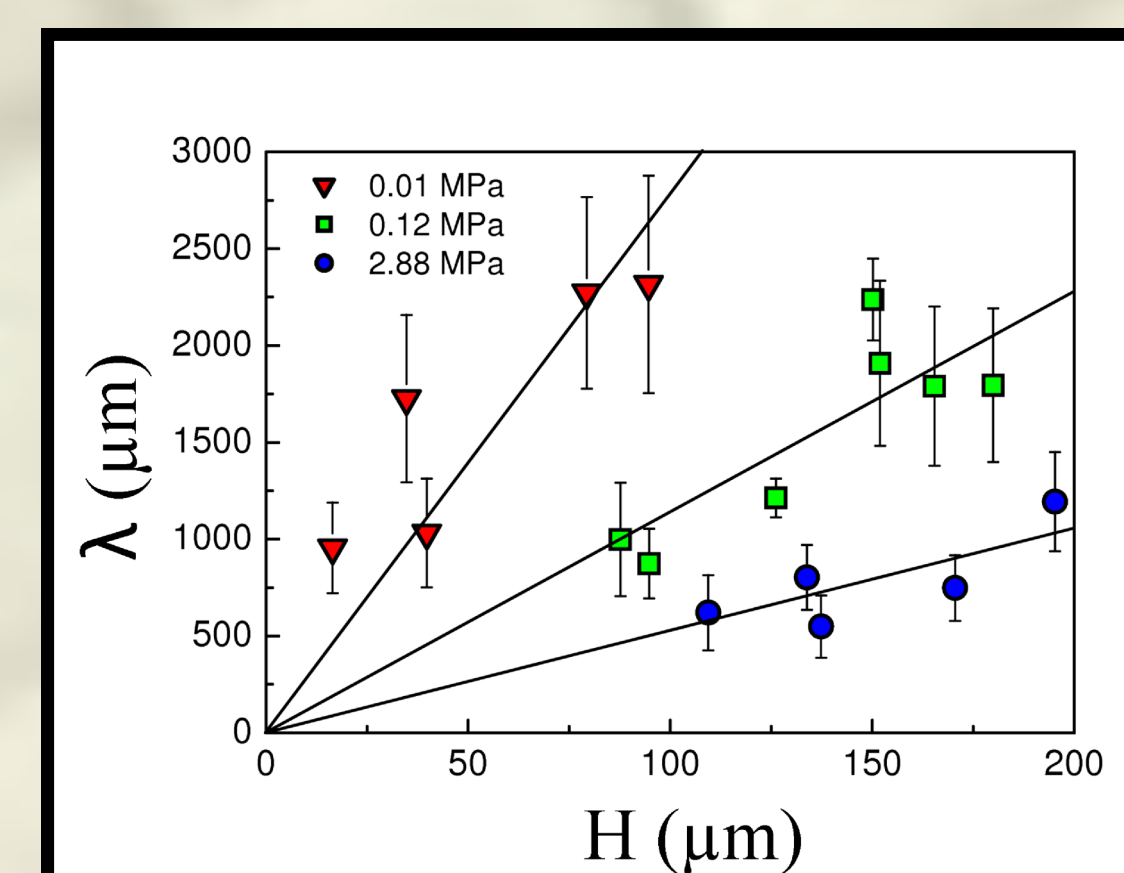

Figure 4 - Crack length scale (λ) vs Film Thickness (H) for different substrate moduli

5. Compliant substrates

As the substrate modulus decreases the crack length scale for a given film thickness increases.

Creating crack interfaces requires energy. The more energy stored in the film, the more cracks.

Strain energy is stored in both film and substrate. The ratio depends on their relative mechanical properties.

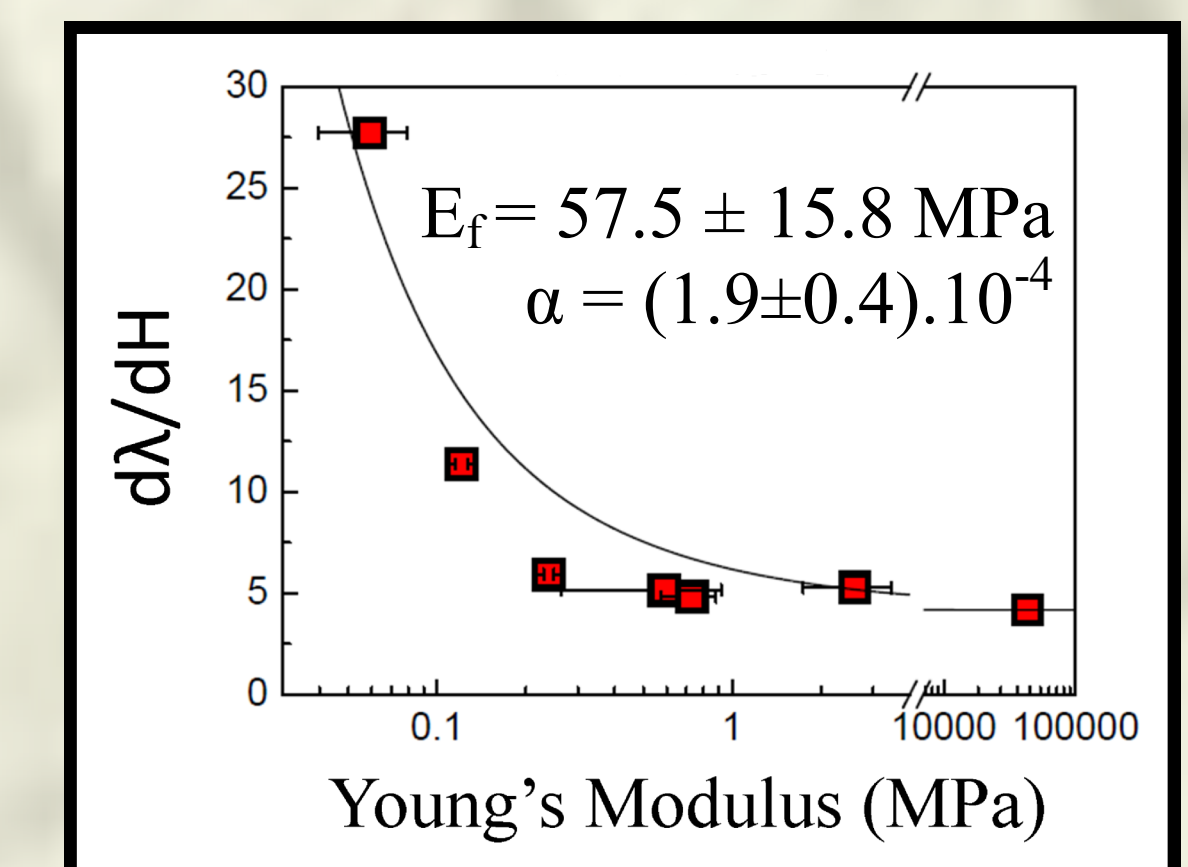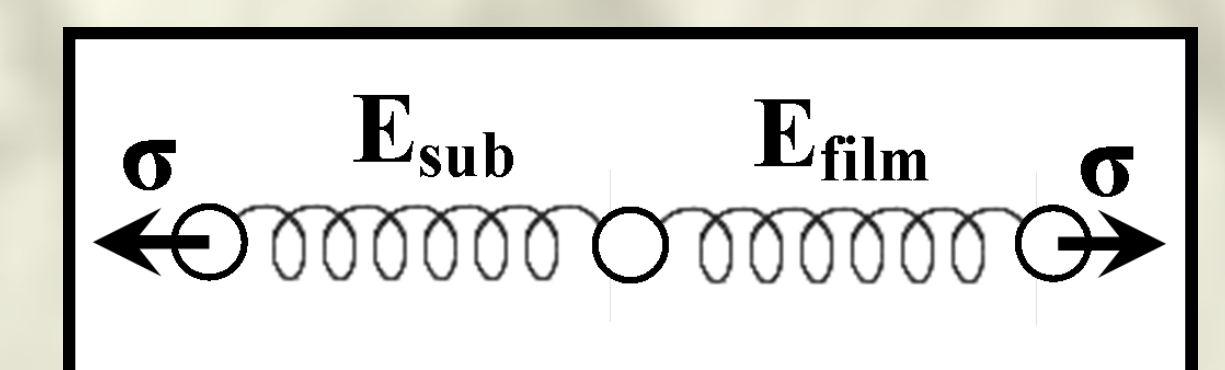In softer substrates, less energy stored in film with which to create cracks.

Figure 5 - The crack length scale dependence upon the substrate modulus. Fit to data is from the model.

$$ \sigma \quad E_{sub} \quad\quad E_{film} \quad \sigma $$

A Simple Model:

We assume a thick compliant substrate, a layer of particles in contact and constrained by the substrate and the rest of the film of thickness H .

Considering the particle packing, top and bottom enables us to calculate the strain in the film (ε_f), relative to the value measured on glass using AFM (ε_0) and the youngs moduli of the film (E_f) and substrate (E_s).
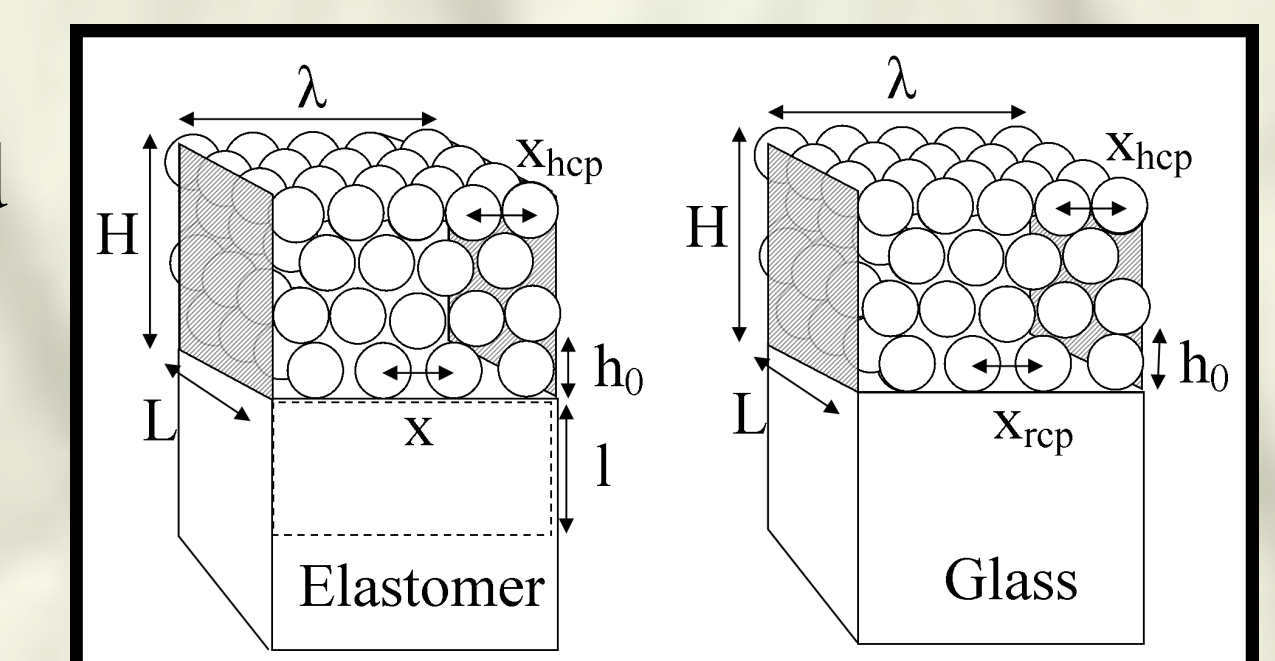
We balance the strain energy in the film with the energy required to create a crack.

$$ \frac{d\lambda}{dH} = \frac{4\gamma}{E_f h_0 \varepsilon_0^2}\left(1 + \alpha\frac{E_f h_0}{(3E_s^2 kT)^{1/3}}\right)^2 $$

5. Conclusions

- Substrate constraint is important in driving cracking
- Crack length scale is modified at low substrate modulus

M.I. Smith, J.S. Sharp, Langmuir **27**, 8009 (2011).
"Effects of substrate constraint on crack pattern formation in thin films of colloidal polystyrene particles"