Using apps to bridge the gap between surfaces and coating formulations

RSC Formulation Science & Technology Group

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Prof Steven Abbott

Steven Abbott TCNF Ltd & Visiting Professor U Leeds

steven@stevenabbott.co.uk

www.stevenabbott.co.uk

Read all about it

- The free eBooks puts this talk into a wider context

- They use the apps I'll use in this talk
  - It's super easy
  - Just click on a link in the eBook to go straight to the app
  - More science books should be like that
    - But that's a different topic

- There are 350+ apps on my site
  - All free, open source, creative commons

  - The search button helps you find what you want
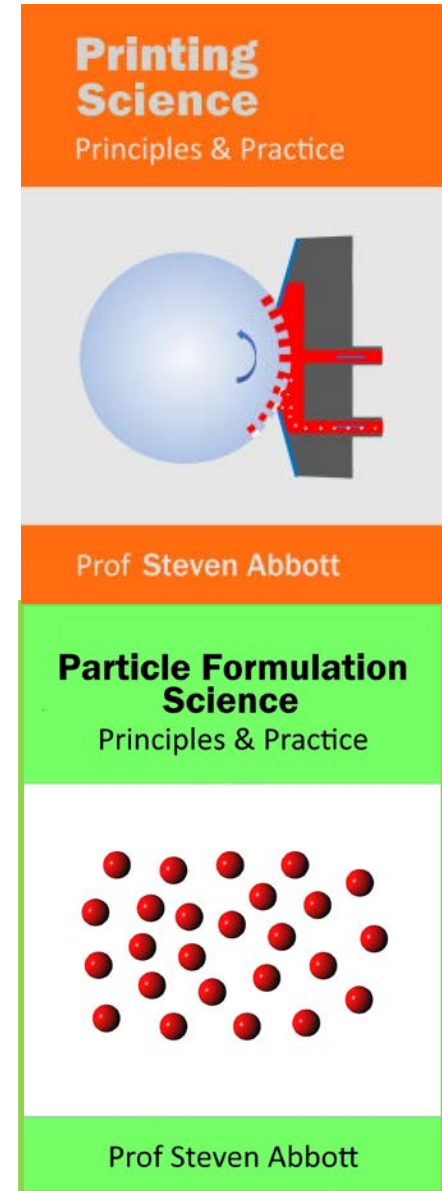
The poverty of standard approaches

- Surface energy, more surface energy (polar/disperse), contact angles
  - Maximum work for minimal useful information
  - The important values are almost never measured
- Some idealised polymer science at super-dilute concentrations
  - Academic excuse: It's too hard to show the science for relevant concentrations
- Some hand-waving about DLVO for particles
- More hand-waving about "depletion" or "bridging" flocculation
- Magical superdispersants
- "Functional coatings are industrially important so in this paper we present incomprehensible models that no one will ever use …"

Let's change things around

- Quick, hands on, scientifically sound, effective:
  - Sorting out pinholes, levelling, why things don't dewet
  - Getting the right solvent blend (greener, controlled)
  - Thinking through concentrated polymer solutions
  - Understanding diffusion into, out of and through coatings
  - Rational dispersion of particles

- I'm not trying to teach each of these in a high-speed talk
  - I'm showing that there are lots of (free) user-friendly resources to help you to better manage surface/coating issues
  - Download the talk and click on the links to get your own understanding

Pinholes and levelling

- Thickness & wavelength are more important than cosθ or surface tension

Pinholes

Thickness h μm	Diameter d μm	Contact angle θ °	Viscosity η cP	SurfTen σ mN/m
30.6	100	39	10	40

Hole will	Velocity v m/s
Open	1.26

Will grow if:
$$\frac{h}{d} < 2(1 - \cos\theta)$$

- Only linear in viscosity and low σ makes things worse!

Levelling

h μm	λ μm	η cP	σ mN/m	t
10	1860	10	40	5.76s

Levelling time:
$$t = \frac{3\eta\left(\frac{\lambda}{2\pi}\right)^4}{\sigma h^3}$$
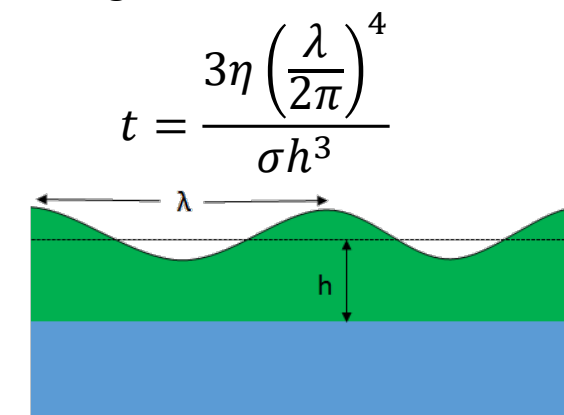
Everything *should* de-wet!

- This 5µm dot, 100µm radius at 290 cP *should* dewet in 70 ms to a 65µm dot
  - Even for a respectable contact angle of 40°
- But most prints/coats *don't* dewet
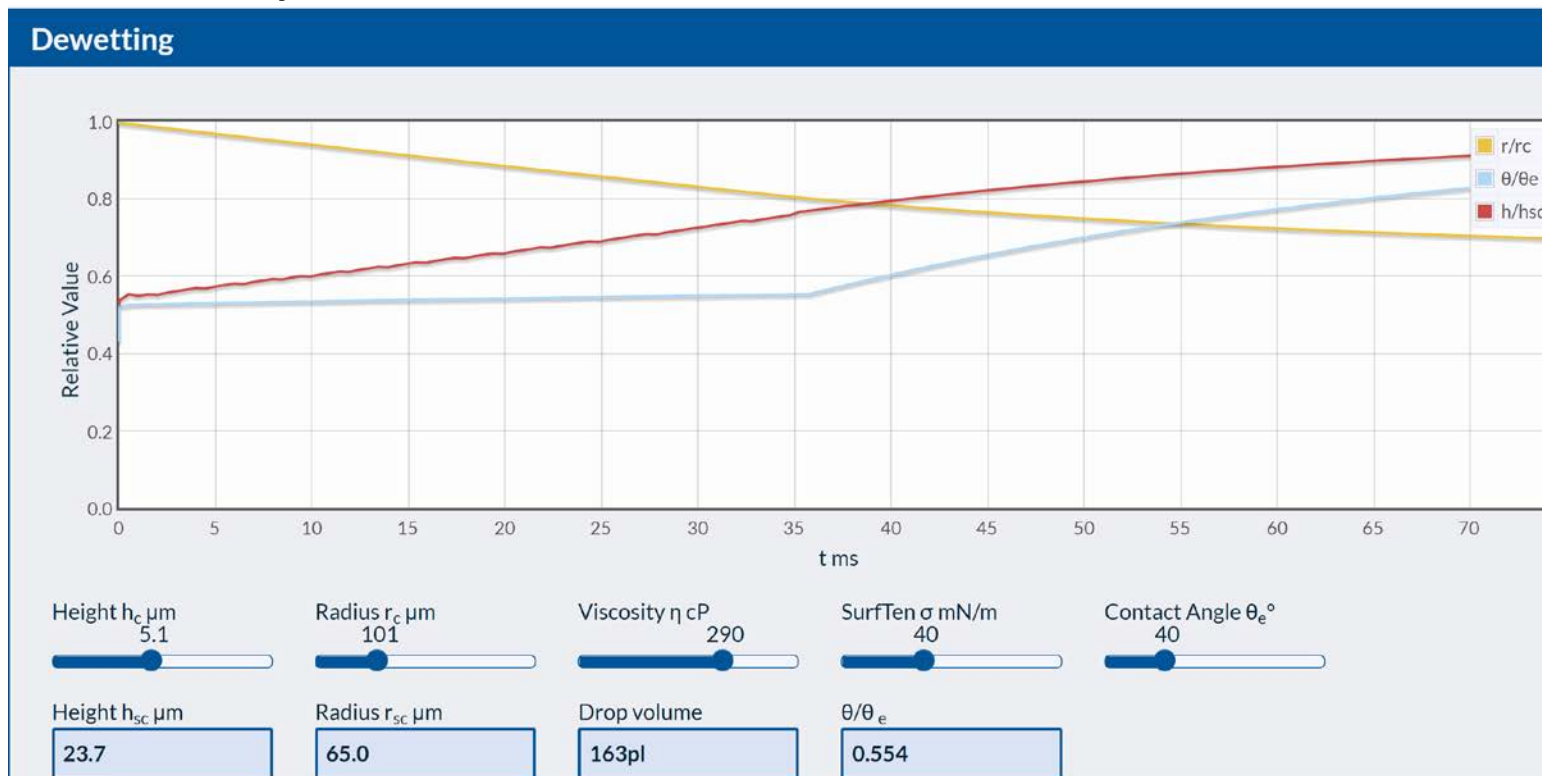
You measure contact angles on super-clean surfaces because contamination has a big effect

But (apart from inkjet) any printing/coating instantly "contaminates" the surface

So your θ measurements are worthless

So, measure receding contact angles if you can – but most people don't "because it's difficult"

https://www.stevenabbott.co.uk/practical-coatings/Dewetting.php

For good coatings, use a bad surfactant

- Everyone uses the Surfynol acetylenic surfactants
  - They are uniquely good at producing good coatings
  - Lots of bad explanations why

- The real explanation? They have a high CMC
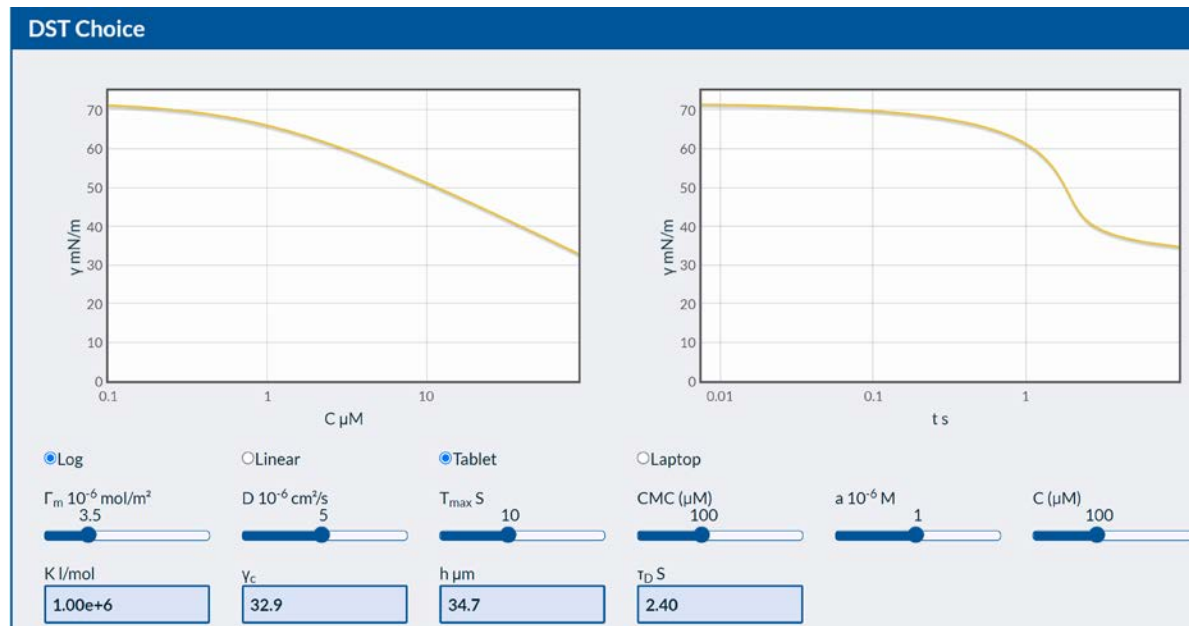
This is all about DST – Dynamic Surface Tension

It turns out that the fastest way to reach equilibrium surface tension in high-speed coatings …
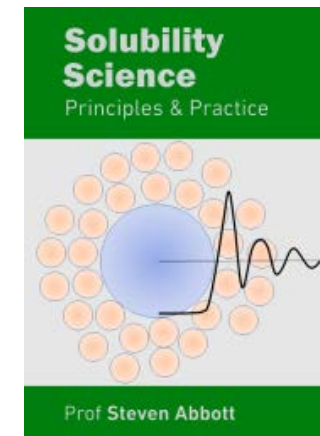… is to have a high CMC
Read the app (and the quoted paper) to learn more

https://www.stevenabbott.co.uk/practical-surfactants/dst-choice.php

A greener solvent (blend)

- Usually no single green solvent is a great replacement for your current one
  - Cost, solubility, evaporation rate …
- So you need a smart blend, usually with a high and low boiler
  - Starting blend is an OK solvent, the low boiler is cheap and easily lost for fast processing
  - The remaining high boiler is a good solvent to allow the coating to relax

This assumes that you know about
Hansen Solubility Parameters
Easy to learn about in:

Solubility Science
Principles & Practice

Prof Steven Abbott

https://www.stevenabbott.co.uk/practical-solubility/solvent-blends.php

Polymer solubility

- Good old Flory-Huggins theory based on the χ parameter
  - Happily we can get χ parameters from Hansen Solubility Parameters
  - Here we have spinodal decomposition into dilute polymer in solvent and concentrated solvent in polymer
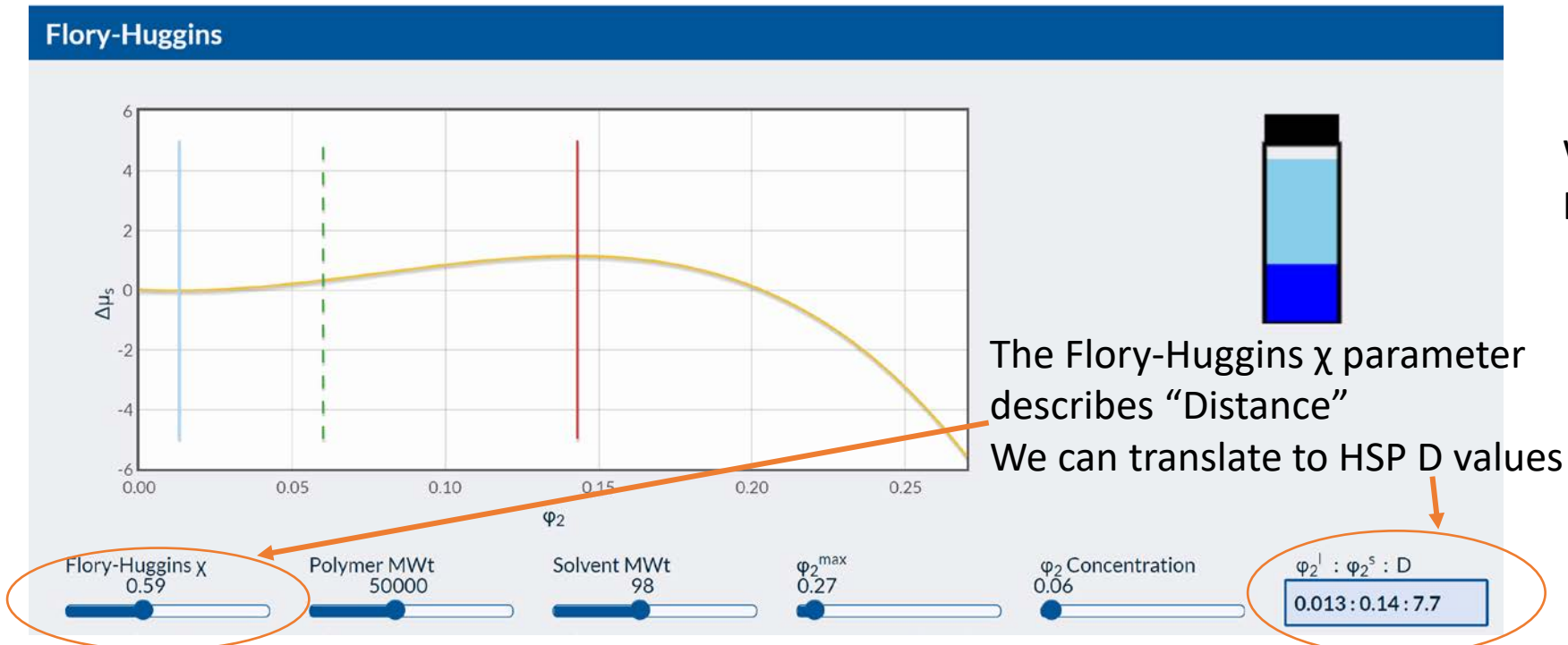
What's "spinodal decomposition"? It's explained on the app page

The Flory-Huggins χ parameter describes "Distance"
We can translate to HSP D values

https://www.stevenabbott.co.uk/practical-solubility/polymer-solubility.php
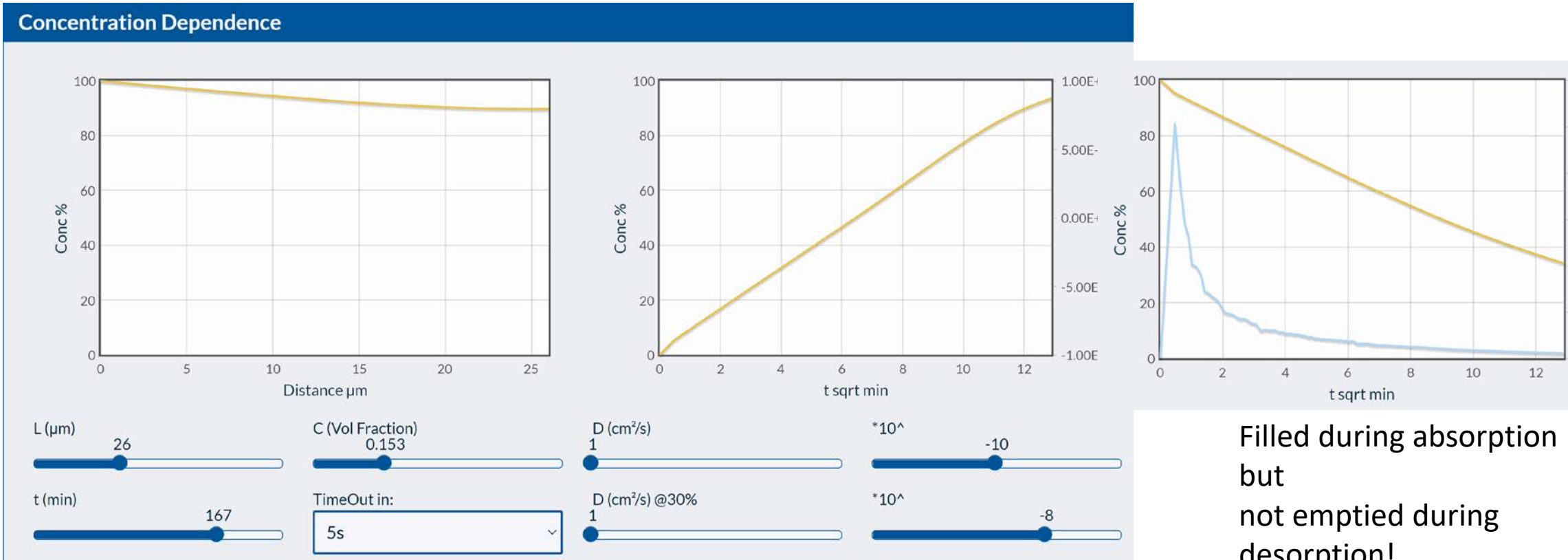
Concentrated polymer solutions

- They're complicated, we don't have perfect tools
  - Code for "The academic community focusses on irrelevant low concentrations"
- But at least get to know about polymer entanglement, M_c etc.

https://www.stevenabbott.co.uk/practical-solubility/polymer-viscosity.php

Diffusion shouldn't be mysterious

But it involves differential equations so can be a bit tricky ... unless you have an app

- It's just concentration gradient * diffusion coefficient, D
  - But D is concentration dependent, which gives a worrying asymmetry
    - This can ruin your day

Concentration Dependence

L (µm)	C (Vol Fraction)	D (cm²/s)	*10^
26	0.153	1	-10

t (min)	TimeOut in:	D (cm²/s) @30%	*10^
167	5s	1	-8

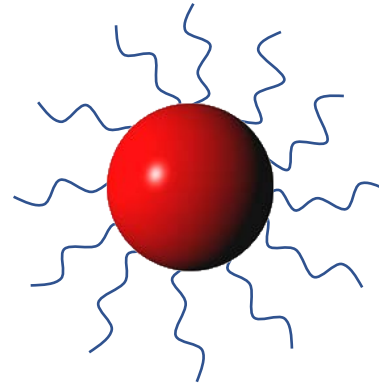https://www.stevenabbott.co.uk/practical-solubility/diff-cdepend.php

Filled during absorption but
not emptied during desorption!

Rational dispersion of particles

- We don't have this:

- We have this:

- So we use solubility science
  - Yes, particles are "soluble" with χ
  - Stat therm proof from Shimizu
  - "Dispersed" is an unhelpful term

- Don't take my word for it!
  - We use χ parameters in SF theory
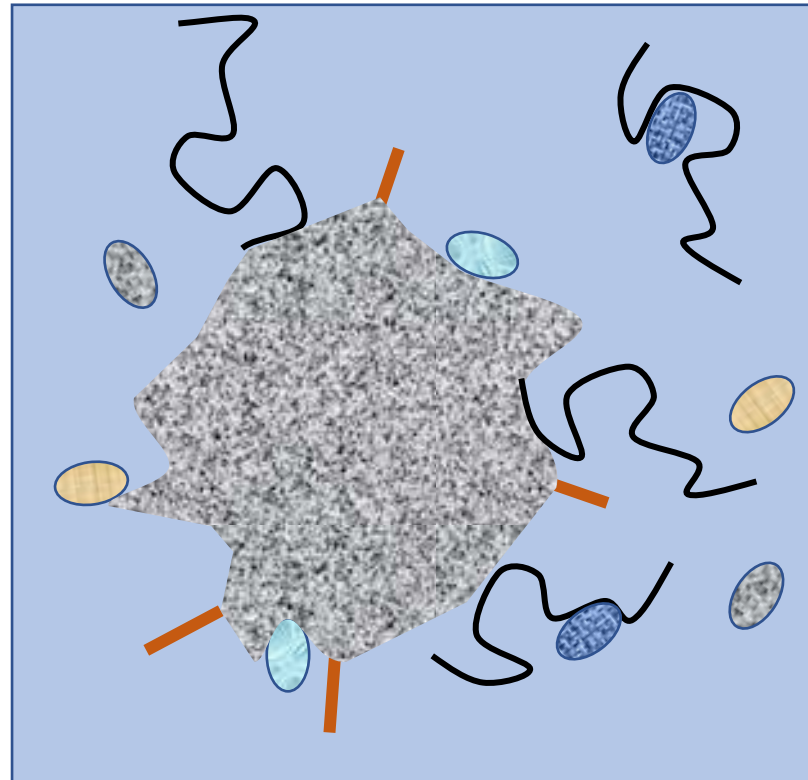
Classic "dispersion science" is surprisingly unhelpful

DLVO isn't much good (I have an app if you want to try)

Not much to show for decades of blah

The solubility approach unlocks a large range of helpful tools. See last year's RSC talk!

Scheutjens-Fleer theory

- A particle can interact with the solvent and polymer
- The polymer can be an A-B di-block or comb and A & B can interact with the particle, the solvent and each other
- Interactions are calculated via χ and χ$_S$ parameters
  - Which can be calculated from HSP Distance
- The Self-Consistent Field calculations give you how much polymer is:
  - Free
  - In "trains" on the particle surface
  - In "loops" (most of the polymer)
  - In "tails"
  - And where the A and B polymers are
- It's worked since the 1970s and is based on classic solubility science
  - Unfortunately it was too hard for anyone other than an academic expert to use
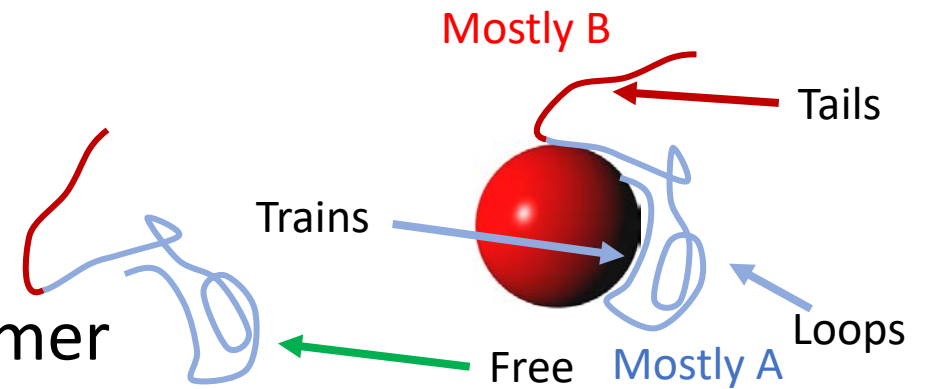
Now we can use SF theory in an app!

- This is an A-B di-block with the A mostly as trains & loops, and B as a long tail sticking out into the solution
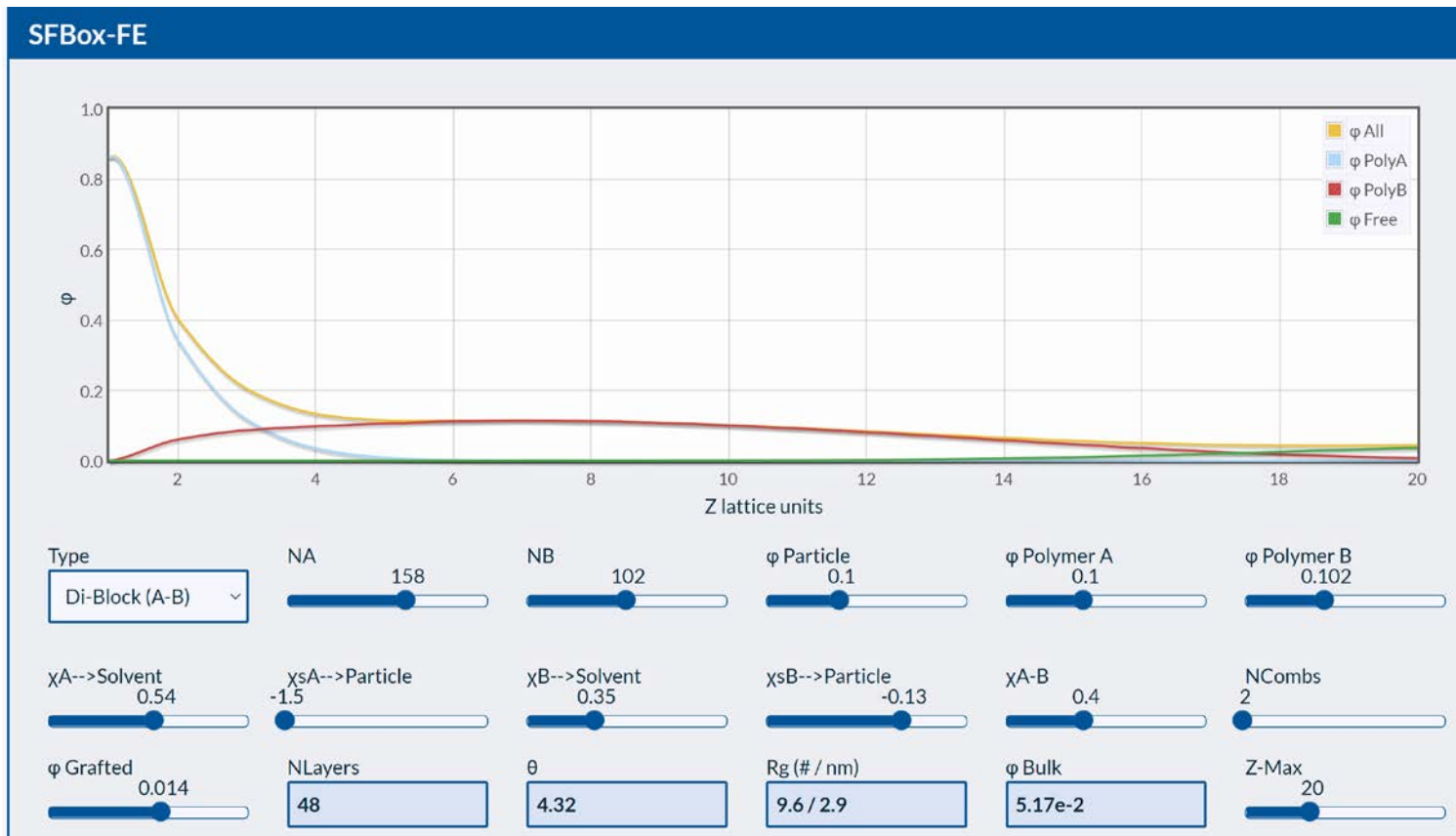
All apps shown so far have used my code and run on your machine.

SF Theory is far too complex for that and so I am using, with gracious permission, the awesome **SF Box** from **Prof Frans Leermakers** of Wageningen U.

It runs on my server, with the front end sending the input parameters and graphing the data returned by SF Box.

So you can run SF simulations on a phone!

https://www.stevenabbott.co.uk/practical-solubility/SF-Theory.php

Functional Films & Coatings unchained

- I've rushed through the apps to show you the possibilities
- Try them for yourself, learn what you can from them …
  - www.stevenabbott.co.uk/Practical-Coatings
  - www.stevenabbott.co.uk/Practical-Solubility
  - www.stevenabbott.co.uk/Practical-Particles
  - www.stevenabbott.co.uk/Practical-Rheology
- … and if there's an error, or something missing or you want a new app, let me know at steven@stevenabbott.co.uk

- Now to your questions and comments