Colloidal Dispersions:

Controlling Interactions
and
Understanding the Consequences

William B. Russel
Department of Chemical Engineering
Princeton University

Colloid and Surface Chemistry Award Lecture

in memory of
Dudley A. Saville
1933-2006

March 2007

OUTLINE

Reflections on colloid science 1950-2000

model particles and experimental tools

forces and phase behavior

rheology and dynamics

Recent interests

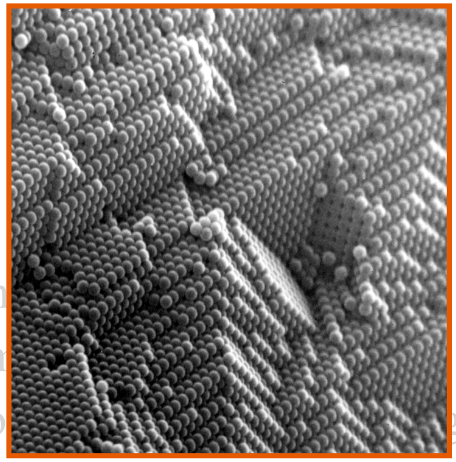
hard sphere crystals and glasses

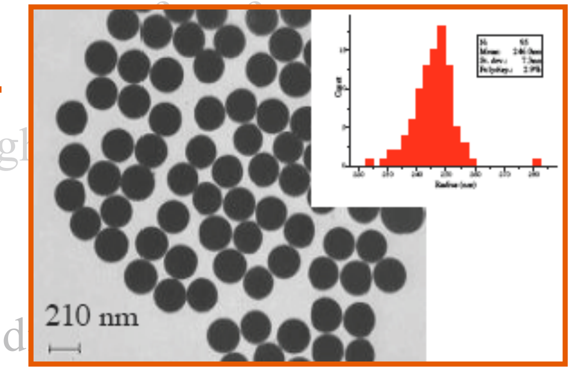
film formation and cracking

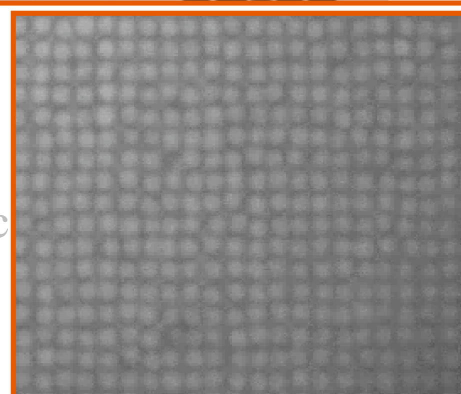
	model colloids	experimental techniques	principals
1956	polymer colloids		Vanderhoff
1968	silica		Stöber
1970	hydrous metal oxides		Matijevic
1974		dynamic light scattering	Schaefer, Pusey, Pecora
		modern rheometers	Rheometrics, Inc., Deer
		electrophoretic light scattering	Ware
1978		surface forces	Israelachvili
1979	octadecyl silica		de Kruif
1983		light scattering under shear	Ackerson and Clark
	quantum dots		Brus
1986	PMMA/PHSA		Ottewill
1988		dielectric spectroscopy	Saville
		rheo-optics	Fuller, Wagner
		SANS under shear	de Kruif
1990		TIRM	Prieve
1991		colloidal probe AFM	Ducker
	ellipsoidal latices		Carruthers, Keller, Ottewill
1992	plates and rods		Lekkerkerker, Philipse
1995		confocal microscopy	van Blaaderen, Wiltzius

model colloids — principals

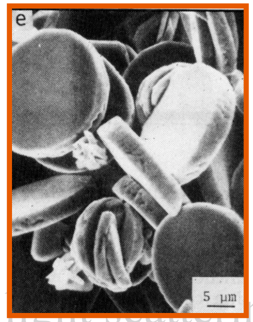
1956	polymer colloids		Vanderhoff
1968	silica		Stöber
1970	hydrous metal oxides		Matijevic
1974		dyn	Schaefer, Pusey, Pecora
		n	Rheometrics, Inc., Deer
		electro	Ware
1978			Israelachvili
1979	octadecyl silica		de Kruif
1983		ligl	Ackerson and Clark
	quantum dots		Brus
1986	PMMA/PHSA		Ottewill
1988		d	Saville
			Fuller, Wagner
			de Kruif
1990			Prieve
1991		c	Ducker
	ellipsoidal latices		Carruthers, Keller, Ottewill
1992	plates and rods		Lekkerkerker, Philipse
1995		confocal microscopy	van Blaaderen, Wiltzius



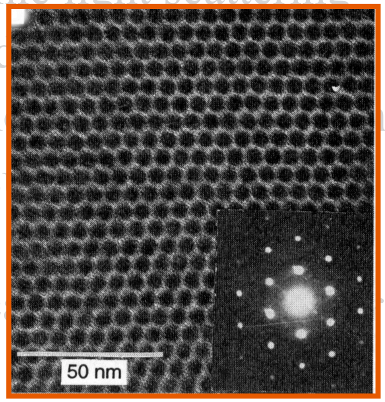




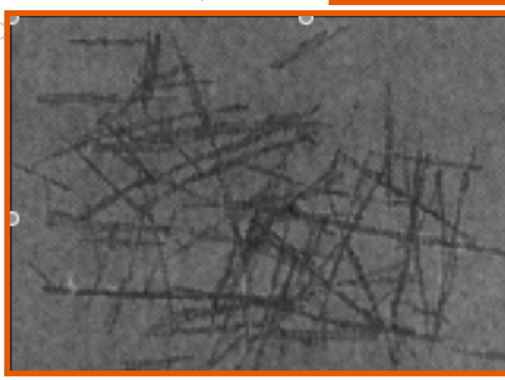
model colloids principals

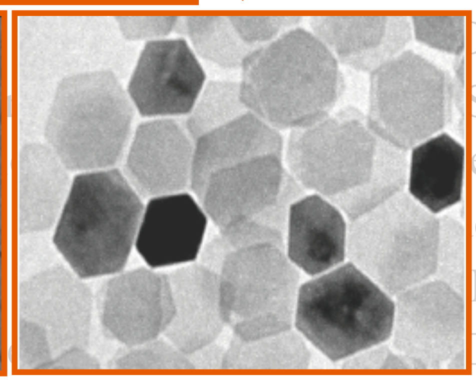


1956 polymer colloids Vanderhoff
1968 silica Stöber
1970 hydrous metal oxides → ← Matijevic
1974 dynamic light scattering Schaefer, Pusey, Pecora



mod Rheometrics, Inc., Deer
electroph g Ware
1978 s Israelachvili
1979 octadecyl silica de Kruif
1983 light sc Ackerson and Clark
quantum dots → ← Brus

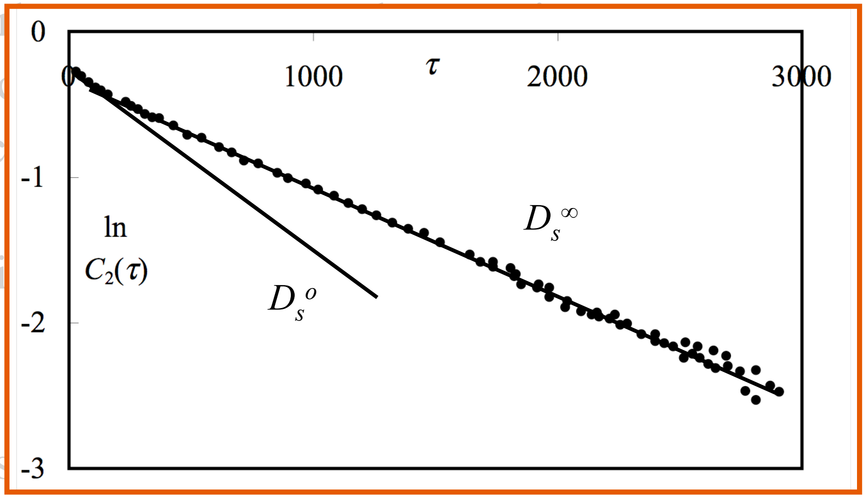


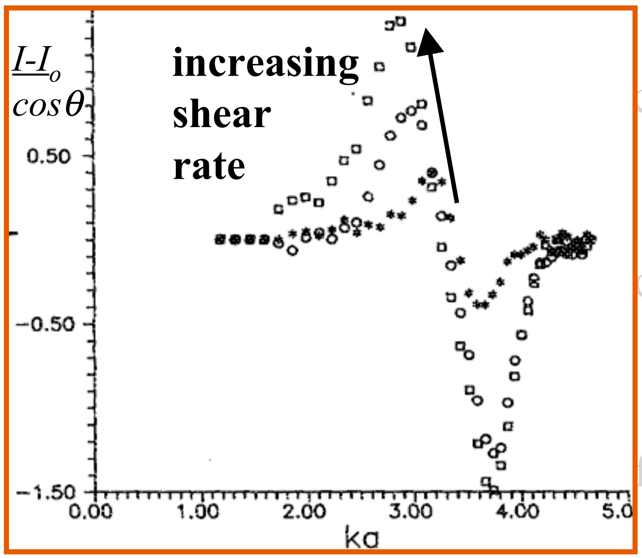


1986 PMMA/P Ottewill
1988 Saville
er, Wagner
e Kruif
1990 Prieve
1991 Ducker
ellipsoidal latices Carruthers, Ottewill, Keller
1992 plates, rods Lekkerkerker, Philipse
1995 confocal microscopy van Blaaderen, Wiltzius

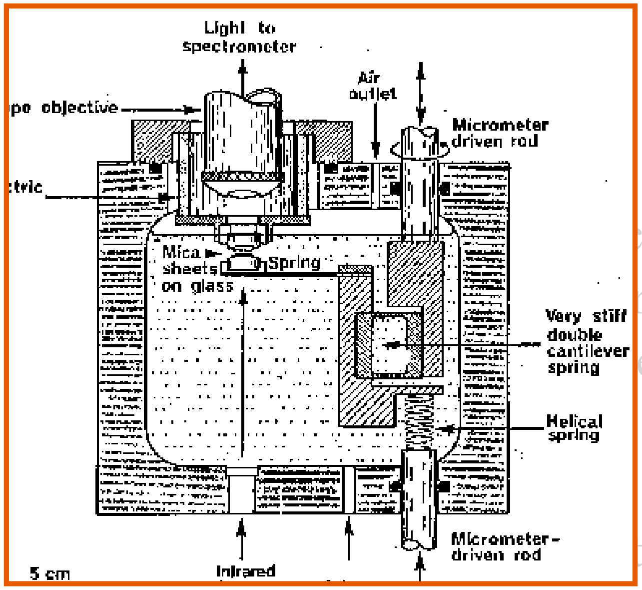
experimental techniques **principals**

1956	polymer colloids	Vanderhoff
1968	silica	Stöber
1970	hydrous metal oxides	Matijevic
1974	**dynamic light scattering**	**Schaefer, Pusey, Pecora**
	modern r	
	electrophoreti	
1978	surfac	
1979	octadecyl silica	
1983	light scatteri	
	quantum dots	
1986		
1988	ctric s **rheo-optics**	**Fuller, Wagner, de Kruif**
1990	TIRM	Prieve
1991	oidal probe AFM	Ducker
		Carruthers, Keller, Ottewill
1992		Lekkerkerker, Philipse
1995	focal microscopy	van Blaaderen, Wiltzius





experimental techniques **principals**



1956 Vanderhoff

1968 Stöber

1970 Matijevic

1974 light scattering Schaefer, Berne, Pusey, Pecora

n rheometers Rheometrics, Inc., Deer

etic light scattering Ware

1978 surface forces Israelachvili

1979

1983 te lark

quantum dots

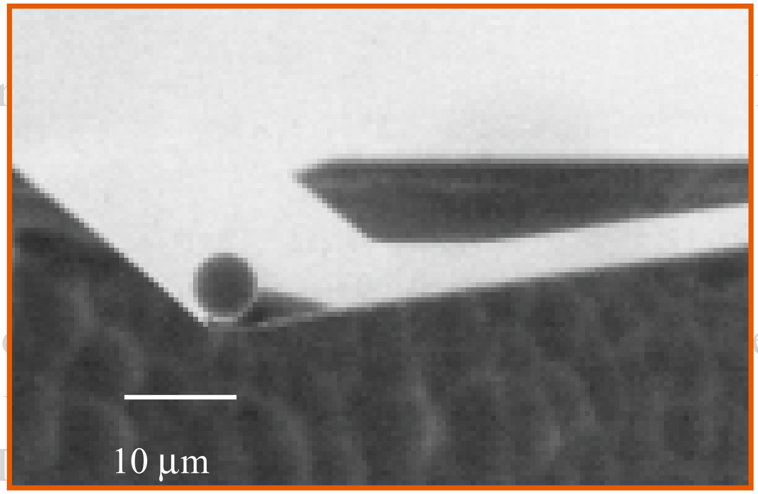
1986 PMMA/PHSA

1988 dielectric

rhe er

SANS

1990 T



1991 colloidal probe AFM Ducker

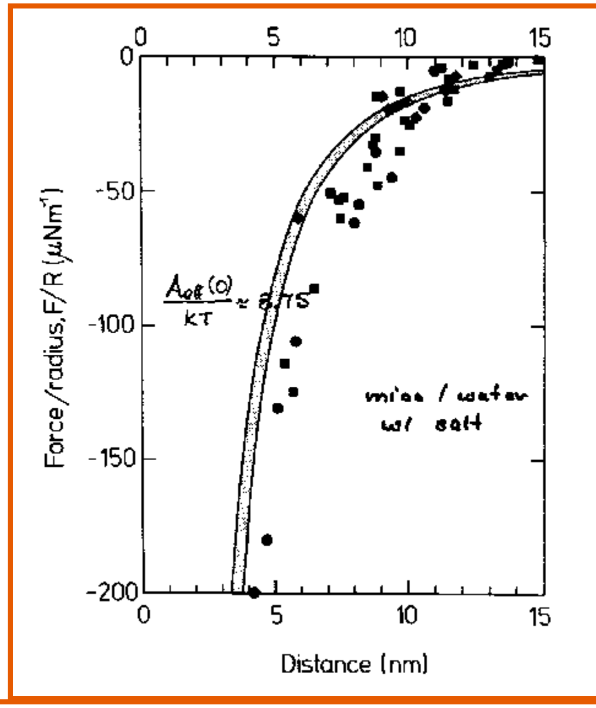
ellipsoidal latices Carruthers, Keller, Ottewill

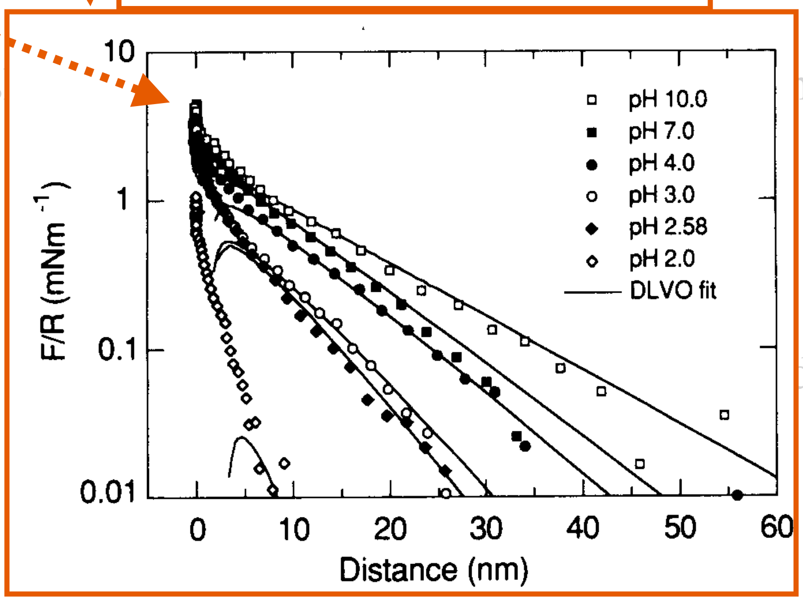
1992 plates and rods Lekkerkerker, Philipse

1995 confocal microscopy van Blaaderen, Wiltzius

	forces	phase transitions	principals
1966	electrostatic		Hogg, Healy, Fuerstenau
1968		polymeric stabilization	Napper
1969		colloidal crystals	Krieger, Hachisu
1970	dispersion		Ninham, Parsegian
1973	self-consistent field		Dolan, Edwards
1978	charge regulation		Healy, White
1979		Brownian/shear-induced flocculation	Higashitani, Schowalter
1980	scaling		de Gennes
1981		depletion gas/liquid/solid	Sperry, Vincent, Vrij, Gast
1983	hydration		Pashley, Israelachvili
1984		fractal growth	Witten, Weitz
1985	lattice theory, brushes		Scheutjens, Fleer, Tirrell
1986		hard sphere crystal	Pusey, van Megen
		gelation	Wiltzius, de Kruif
1987		hard sphere glass transition	van Megen, Pusey
1988	compressed brushes		Milner, Witten, Cates
1992		two-component depletion	Lekkerkerker, Pusey
	associative brushes		Milner, Witten
1994		adhesive sphere gels/spinodal/fluid-solid	Russel, Dhont, Zukoski
1996		liquid crystal transitions	Fraden, Lekkerkerker
1997		slow Brownian flocculation	Borkevec, Behrens
1999		non-ergodic transitions	Bergenholtz, Fuchs

	forces	principals
1966	**electrostatic**	**Hogg, Healy, Fuerstenau**
1968		Napper
1969		Krieger, Hachisu
1970	**dispersion**	**Ninham, Parsegian**
1973	self-consistent field	Dolan, Edwards
1978	**charge regulation**	**Healy, White**
1979		Higashitani
		Zeichner, Schowalter
1980	scaling	de Gennes
1981		Sperry, Vincent, Vrij, Gast
1983	**hydration**	**Pashley, Israelachvili**
1984		Witten, Weitz
1985	lattices & brus	heutjens, Fleer, Tirrell, Klein
		Pusey, van Megen
		Wiltzius, de Kruif
1987		van Megen, Pusey
1992		Lekkerkerker, Pusey
1994		Russel, Dhont, Zukoski
1996		Fraden, Lekkerkerker
1997		Borkevec, Behrens
1999		Bergenholtz, Fuchs

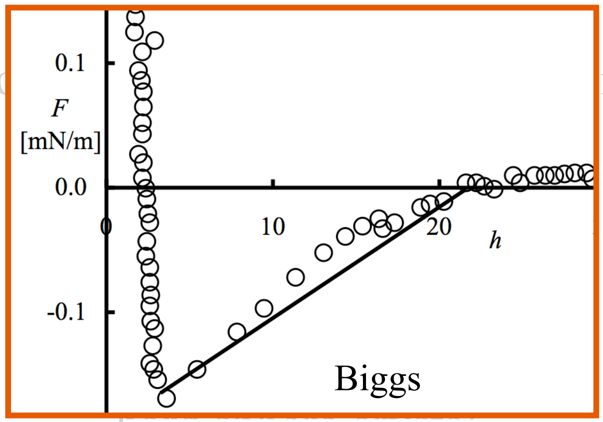




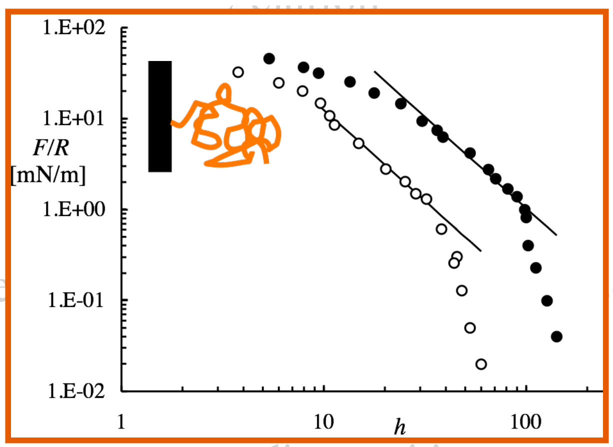
forces | **principals**

1966	electrostatic		Hogg, Healy, Fuerstenau
1968		polymeric stabilization	Napper
1969		colloidal crystals	Krieger, Hachisu
1970	dispersion		Ninham, Parsegian
1973	**self-consistent field**		**Dolan, Edwards**
1978	charge regulation		Healy, White
1979		Br … ion	Higashitani, Schowalter
1980	**scaling**		**de Gennes, Joanny**
1981			Sperry, Vincent, Vrij, Gast
1983	hydration		Pashley, Israelachvili
1984			Witten, Weitz
1985	**lattices & brushes**		**Scheutjens, Fleer, Tirrell, Klein**
1986			Pusey, van Megen
			Wiltzius, de Kruif
1987			van Megen, Pusey
1988	**compressed brushes**		**Milner, Witten, Cates**
1992			Lekkerkerker, Pusey
	associative brushes		**Milner, Witten**
1994		adhe … olid	Russel, Dhont, Zukoski
1996			Fraden, Lekkerkerker
1997			Borkevec, Behrens
1999		non-ergodic transitions	Bergenholtz, Fuchs

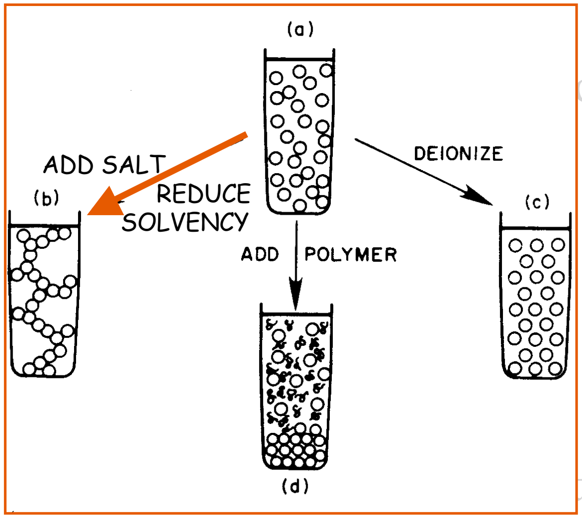
non-adsorbed polymer

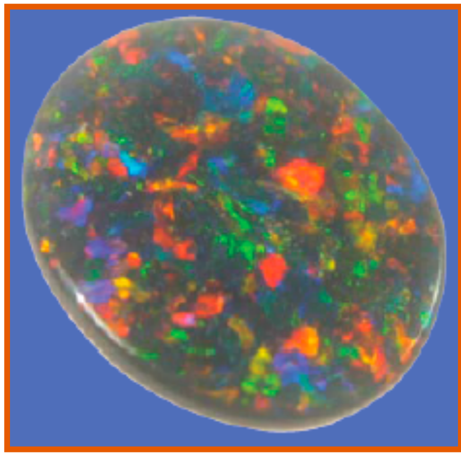


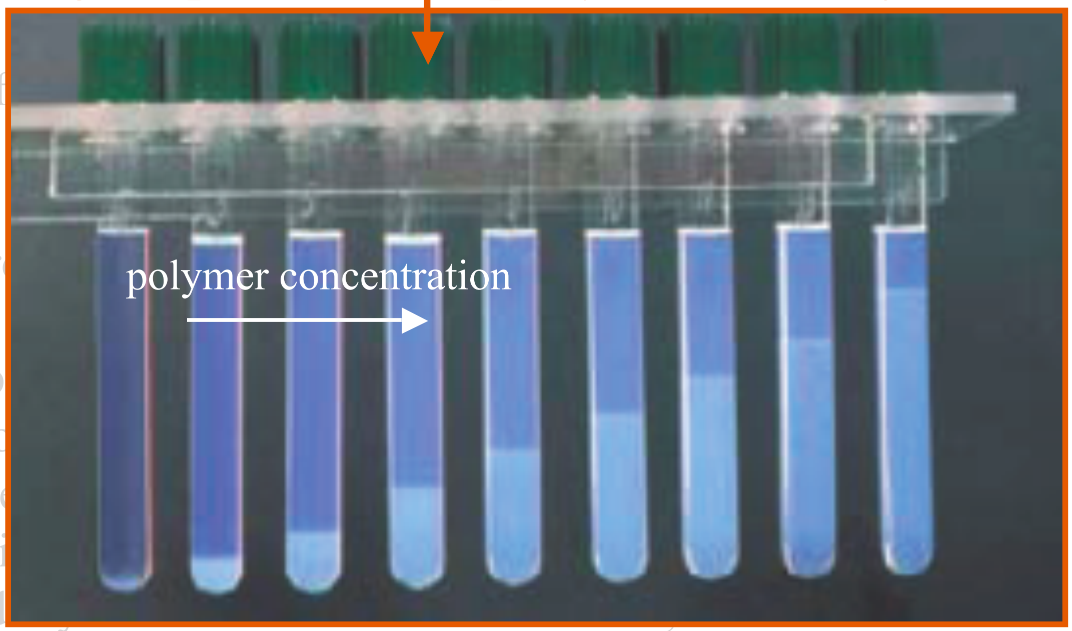
grafted brush



	phase transitions	**principals**
1966	electrostatic	Hogg, Healy, Fuerstenau
1968	**polymeric stabilization**	**Napper**
1969	olloidal crystals	Krieger, Hachisu
1970		Ninham, Parsegian
1973		Dolan, Edwards
1978		Healy, White
1979	**rapid Brownian flocculation**	**Higashitani**
	shear-induced flocculation	**Zeichner, Schowalter**
1980		de Gennes
1981	ion gas/liquid/solid	Sperry, Vincent, Vrij, Gast
1983	hydration	Pashley, Israelachvili
1984	**fractal growth**	**Witten, Weitz**
1985	lattices & brushes	Scheutjens, Fleer, Tirrell, Klein
1986	hard sphere crystal	Pusey, van Megen
	gelation	**Wiltzius**, de Kruif
1987	hard sphere glass transition	van Megen, Pusey
1992	two-component depletion	Lekkerkerker, Pusey
1994	adhesive sphere gel/spinodal/fluid-solid	Russel, Dhont, Zukoski
1996	liquid crystal transitions	Fraden, Lekkerkerker
1997	**slow Brownian flocculation**	**Borkevec, Behrens**
1999	non-ergodic transitions	Bergenholtz, Fuchs

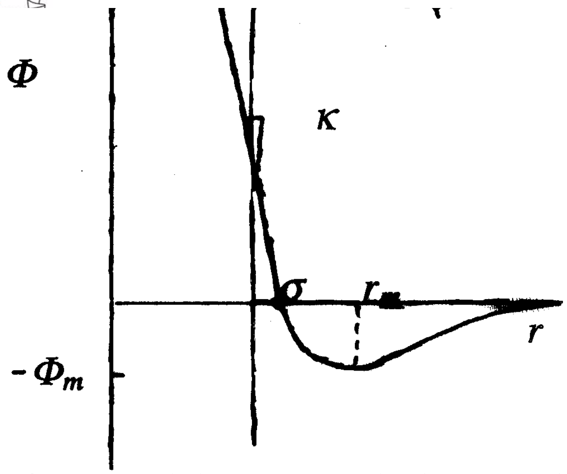


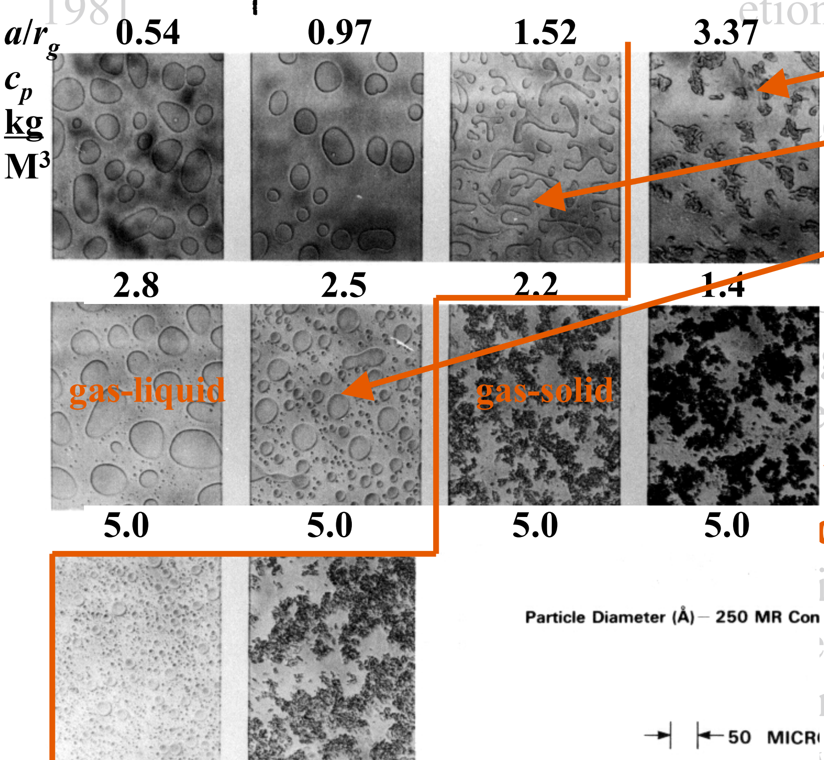




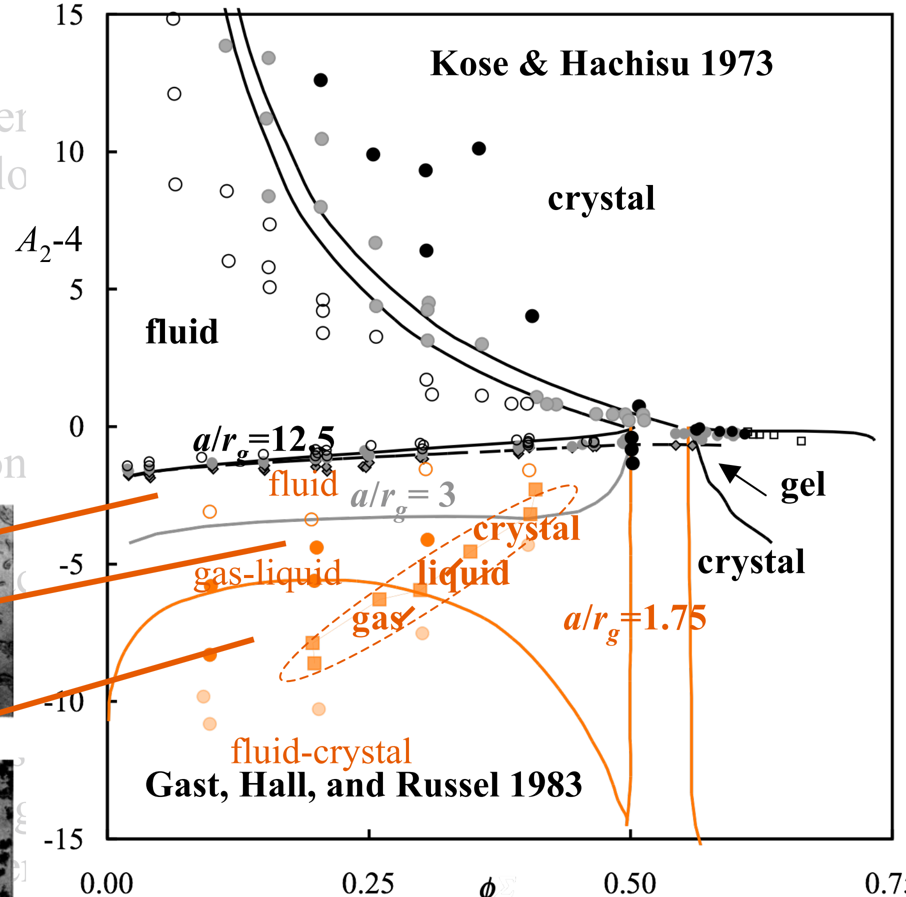
	phase transitions	principals
1966		Hogg, Healy, Fuerstenau
1968	polymeric stabilization	Napper
1969	**colloidal crystals**	**Krieger, Hachisu**
1970		Ninham, Parsegian
1973		Dolan, Edwards
1978		Healy, White
1980		de Gennes
1981	**depletion gas/liquid/solid**	**Sperry, Vincent, Vrij, Gast**
1983	hydration	
1984	f	
1985	lattice theory	
1986	polymer brushes	
	har	
1987	hard sp	
1992	two-co	
1993	adhe	
1995	adhesi	
1996	liquid	
	fluid-solid adhesive spheres	Zukoski
1999	non-ergodic transitions	Bergenholtz, Fuchs

1966
1968
1969
1970
1973
1978
1980
1981





Sperry 1984



two-component depletion

Lekkerkerker, Pusey. Poon

ymer

collo

ation

ive sphere gels — Grant, Russel

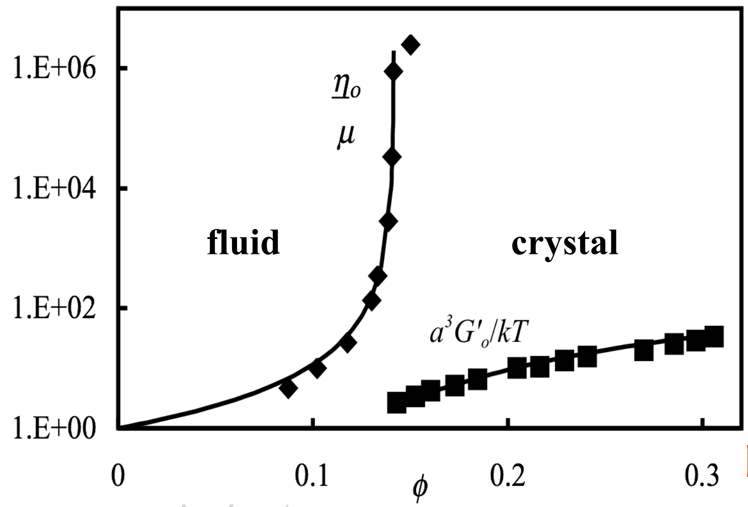
re spinodal/fluid-solid — Dhont, Zukoski

rystal transitions — Fraden, Lekkerkerker

nian flocculation — Borkevec, Behrens

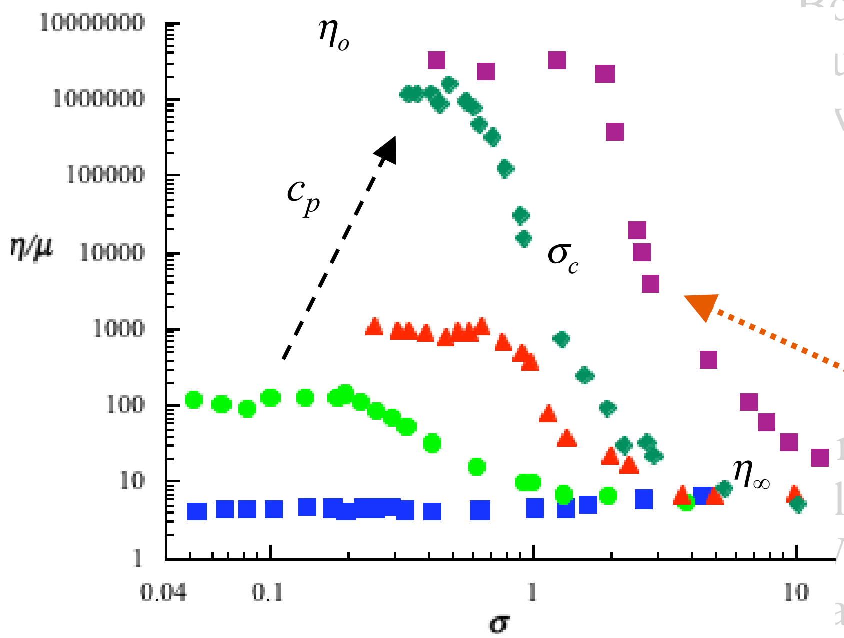
1999 non-ergodic transitions — Bergenholtz, Fuchs

1964 Bingham stress Michaels, Bolger
1972 hard spheres Krieger
pair interactions Batchelor
shear thickening Hoffman
1974 Schaefer, Pusey, Pecora
1978 Ermak, McCammon
O'Brien, White

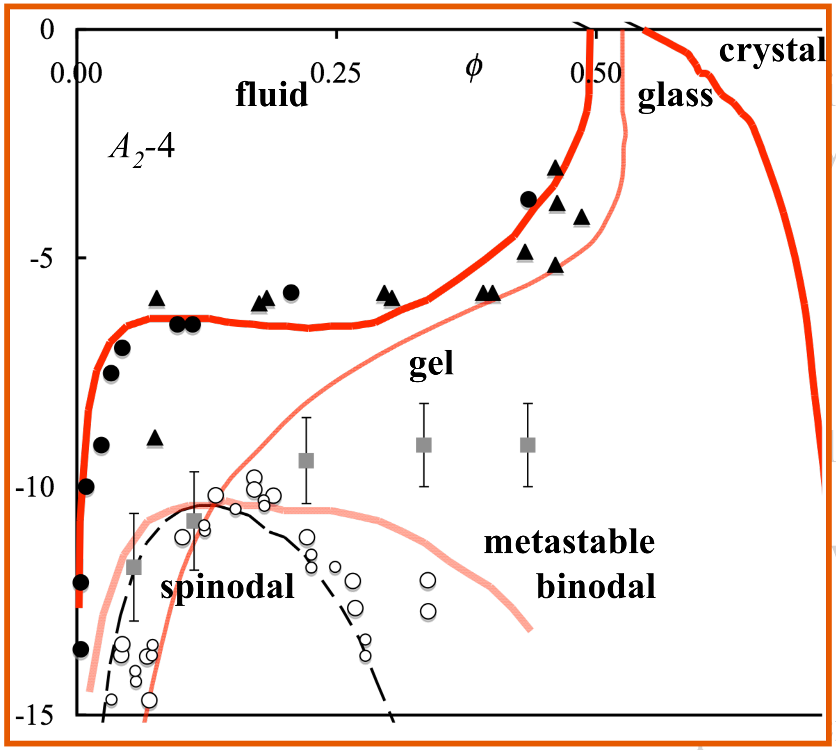


charged spheres **Krieger, Russel, Buscall**

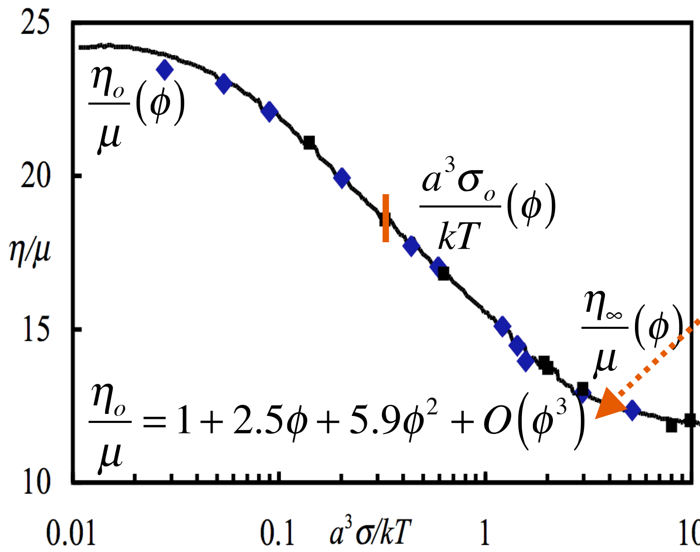
1981 dielectric response White
1984 associative polymers Rohm & Haas
Stokesian dynamics Rossis, Brady
1986 consolidation of gels uscall, White
ville, Zukoski
1989 electrorheology Zukoski
1991 **adhesive hard sphere** **de Kruif**
Megen, Pusey
1992 thickening mechanism Brady
1993 **depletion / fluid** **Buscall**
1995 shear thickening nder, Wagner
1997 elasticity of gels l, Russel, Zukoski
2000 eitz, Kegel,
an Blaaderen

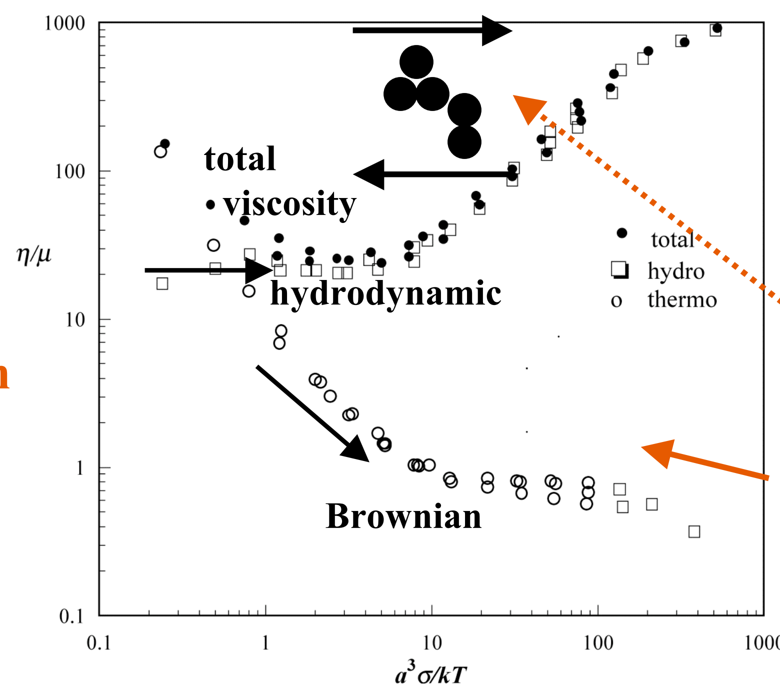


	phase transitions	**principals**
1966		
1968		
1969		
1970		
1973		
1978		Healy, White
1980		de Gennes
1981	uid/solid	Sperry, Vincent, Vrij, Gast
1983		Pashley, Israelachvili
1984	wth	Witten, Weitz
1985		Scheutjens, Fleer
1986		Tirrell
	rystal	Pusey, van Megen
	gelation	Wiltzius, **de Kruif**
1987	**hard sphere glass transition**	**van Megen, Pusey**
1992	two-component depletion	Lekkerkerker, Pusey
1993	**adhesive sphere gels**	**Grant, Russel**
1995	**adhesive sphere spinodal/fluid-solid**	**Dhont, Zukoski**
1996	liquid crystal transitions	Fraden, Lekkerkerker
1997	slow Brownian flocculation	Borkevec, Behrens
1999	**non-ergodic transitions**	**Bergenholtz, Fuchs**



1964	Bingham stress	Michaels, Bolger
1972	**hard spheres**	**Krieger**
	pair interactions	**Batchelor**
	shear thickening	**Hoffman**
1974		Schaefer, Pusey, Pecora
1978		Ermak, McCammon
		O'Brien, White
	charged spheres	Krieger, Russel, Buscall
1981		White
1984	associative polymers	Rohm & Haas
	Stokesian dynamics	**Bossis, Brady**
1986	consolidation of gels	Buscall, White
		Saville, Zukoski
1989	electrorheology	Zukoski
1991	adhesive sphere fluid	de Kruif
		van Megen, Pusey
1992	**thickening mechanism**	**Brady**
1993	depletion / fluid	Buscall
1995	**shear thickening**	**Bender, Wagner**
1997	elasticity of gels	call, Russel, Zukoski
2000		Weitz, Kegel,
		van Blaaderen





FLUIDS, GLASSES, AND CRYSTALS

Adventures encountered while tagging along with Paul Chaikin

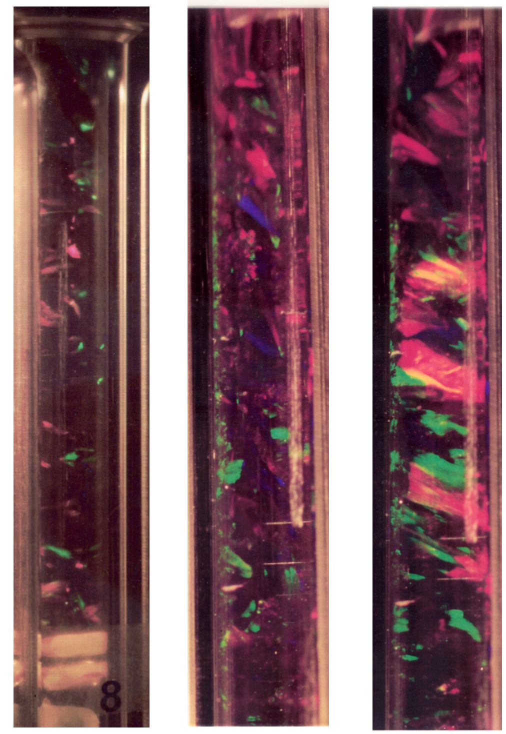
Princeton University Jixiang Zhu Martin Rutgers See-Eng Phan Zhengdong Cheng
NASA Glenn W.V. Meyer R.B. Rogers
Bristol University R.H. Ottewill
Crews of Space Shuttle Columbia, STS-73, 83

Is the disorder-order transition affected by (μ−)gravity?

J. Zhu, et al., Nature **387** 883-885 (1997)

YES!

- **dendritic growth of crystallites**
- **crystallization of glasses**

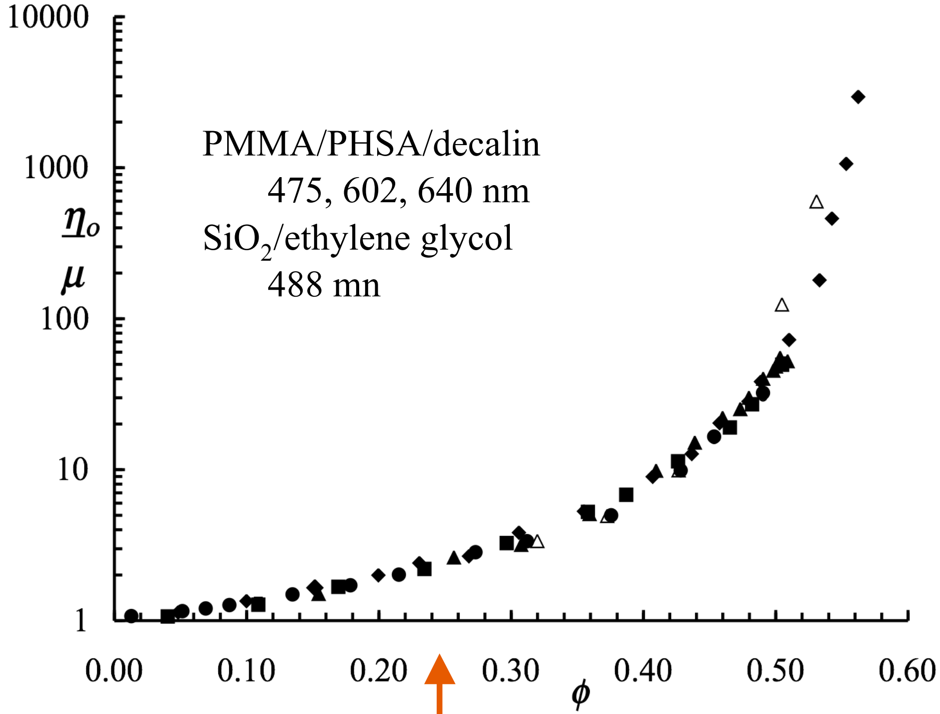


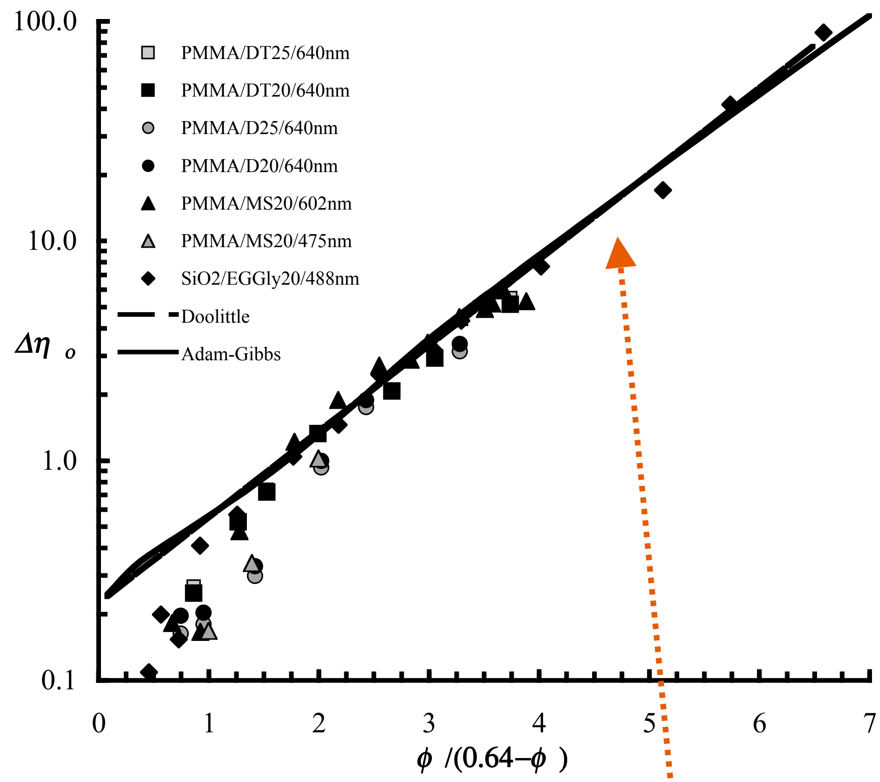
ϕ= 0.58 0.59 0.63

HARD SPHERE GLASS OR METASTABLE FLUID?

- simulations by Torquato - osmotic pressure diverges as $\Pi \sim 1/(0.64-\phi)$

  $\rightarrow$ no thermodynamic transition
- glasses crystallize in microgravity but not on earth



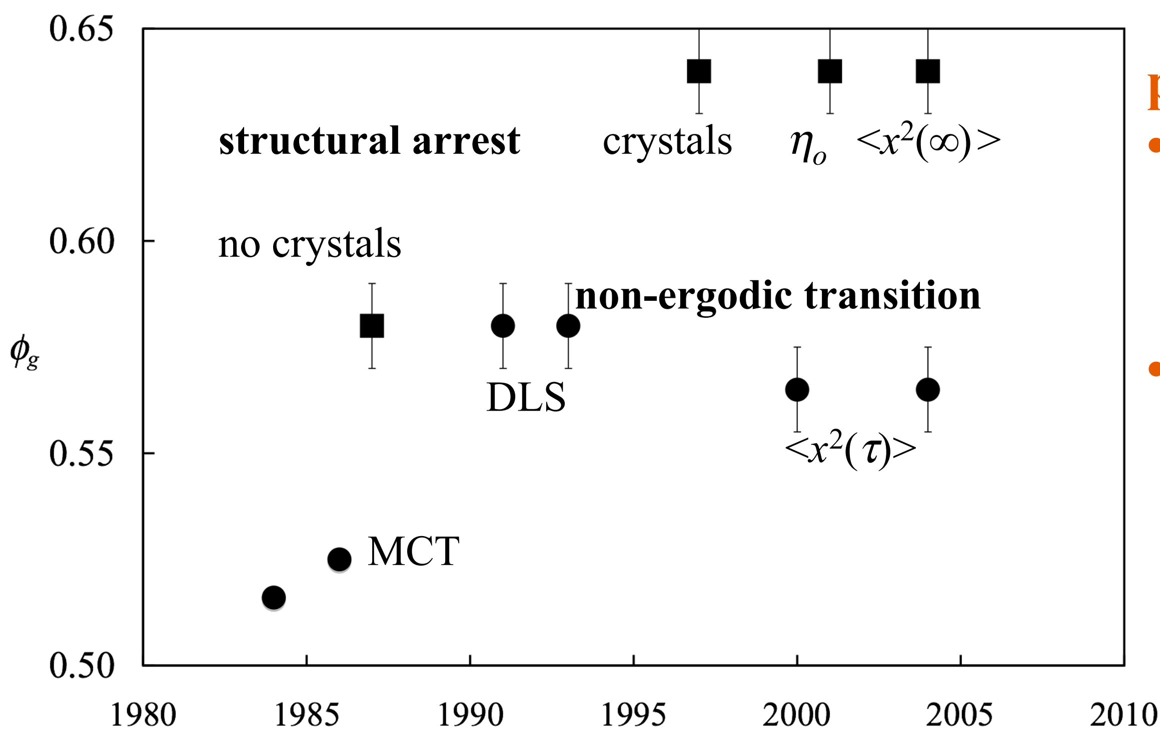


- measurements of (very) low shear viscosities by Phan and Cheng

  $\rightarrow$ consistent with **exponential divergence at ϕ= 0.64** *a la* Adam-Gibbs ■

HARD SPHERE GLASSES

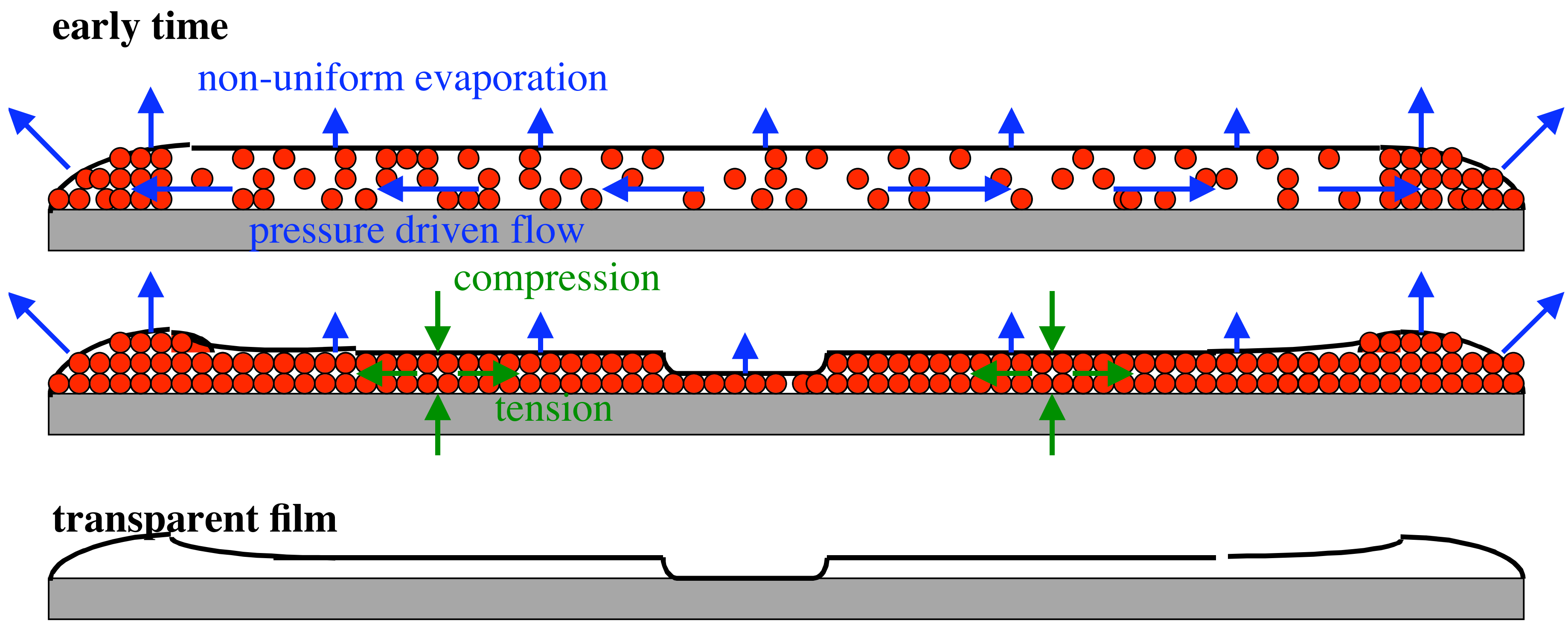
- **non-ergodic transition**
  - mode coupling theory
  - dynamic light scattering - van Megen, Pusey, Underwood
  - real space dynamics via confocal microscopy - Weeks & Weitz, Kegel
- **dynamic arrest**
  - crystallization or not - Pusey & van Megen, Zhu et al.
  - (very) low shear viscosities - Phan and Cheng
  - real space dynamics via confocal microscopy - Kegel



perhaps…

- **structural arrest at random close packing $\phi = 0.64$**
- **non-ergodic transition at $\phi = 0.56$-0.58**

Film Formation, Non-Uniformities, and Cracking Driven by Capillary Pressure



water flows

stresses

Collaborators

P.R. Sperry Rohm & Haas

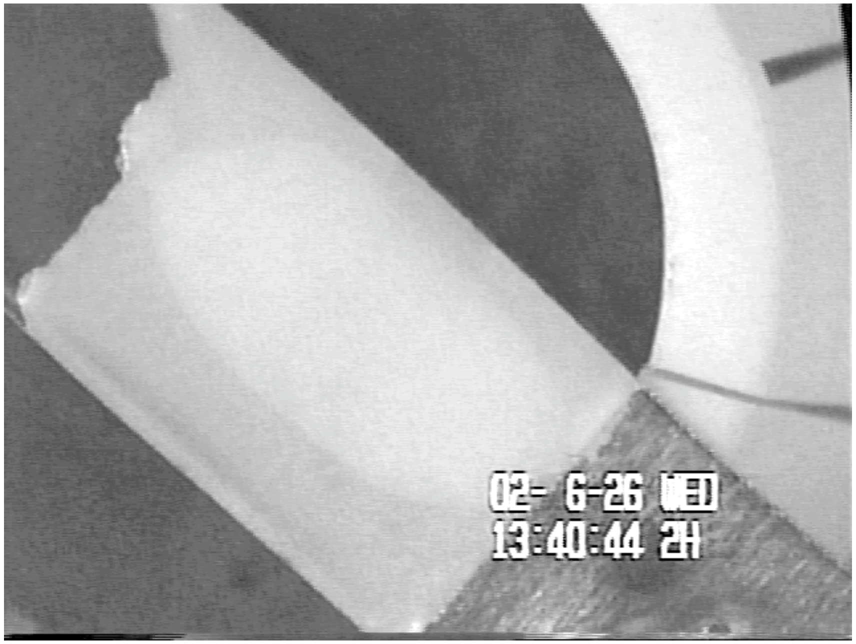
A.F. Routh *97 Cambridge Univ.

M. Tirumkudulu IIT Bombay

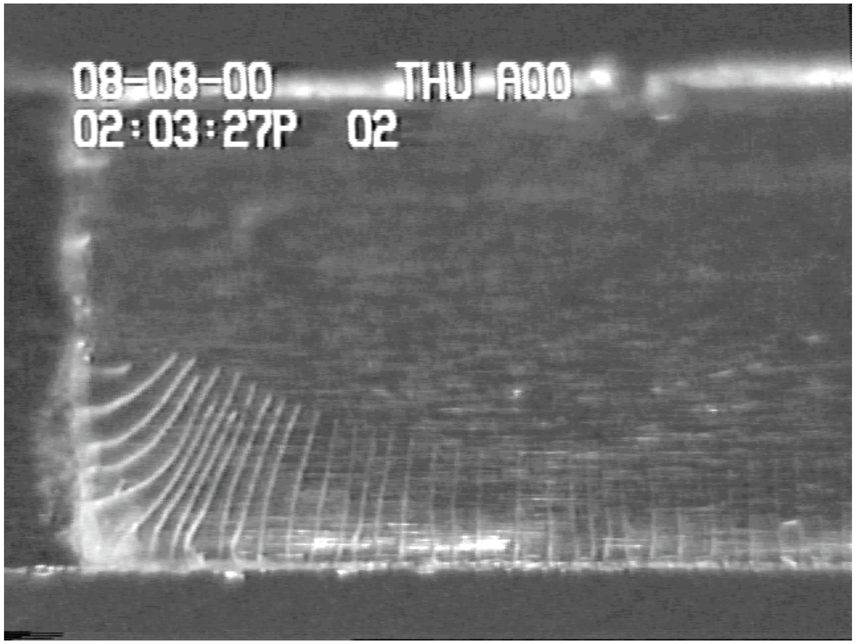
Weining Man *05

Film Cracking: High T_g Particles

$2a$=342 nm h_{dry}=79.5 μm
E=2.5 μm/min, RH=66%, T=23.5 °C

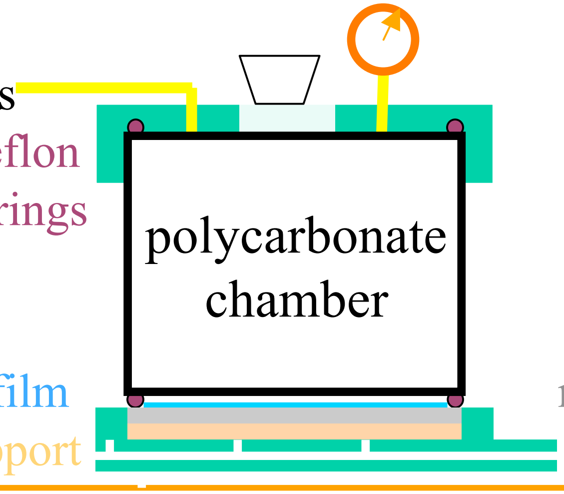


$2a$=95 nm h_{dry}=101 μm
E=6.7 μm/min, RH=35%, T=24.4 °C



Simple and reproducible, but how to understand the mechanism?

Create uniform and controllable capillary pressure field by suppressing evaporation in a pressure filtration cell



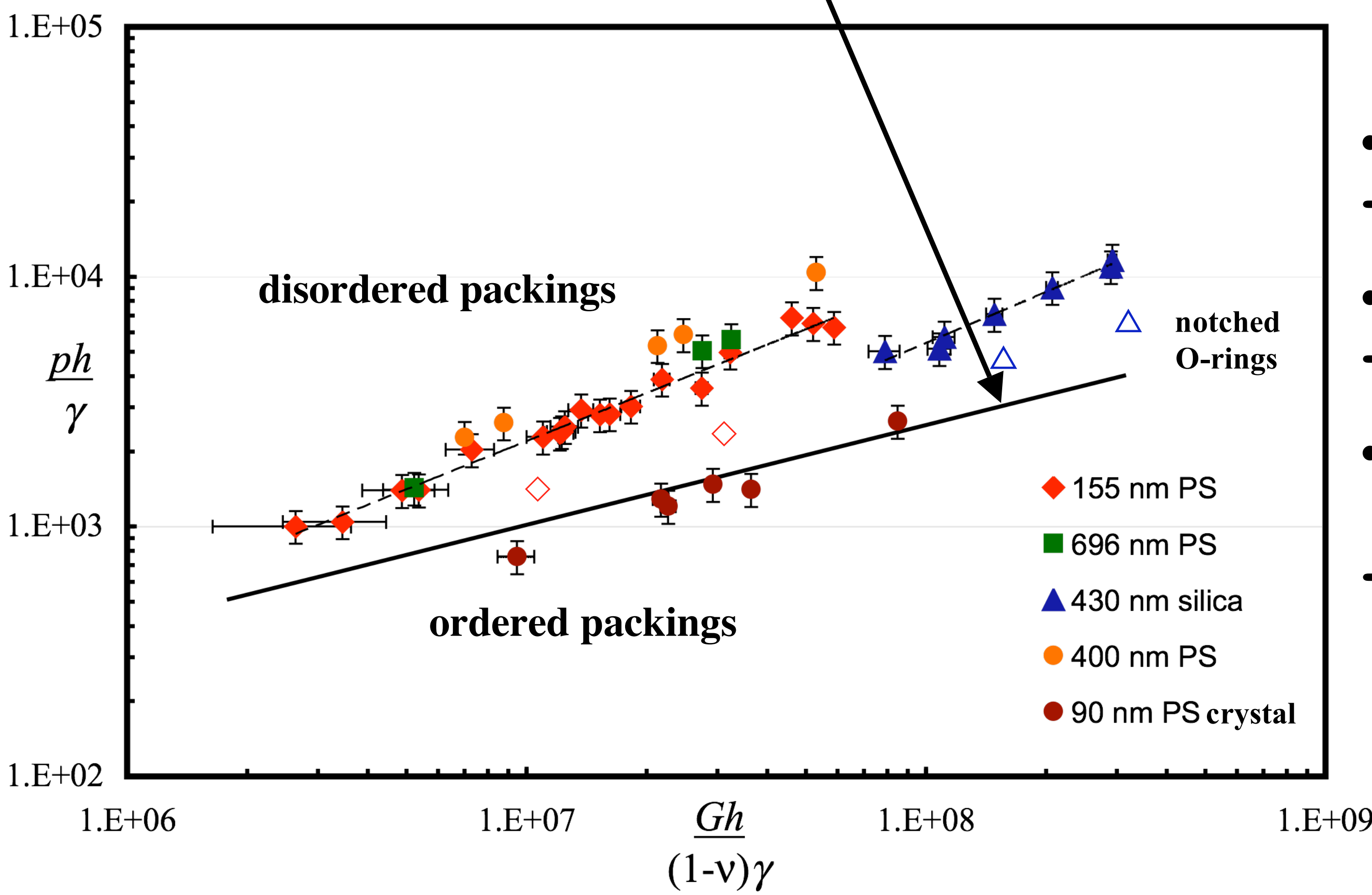
Capillary Pressure Required for Cracking

- pressure at first crack independent of particle radius
  ➜ two dimensionless variables ph/γ $Gh/(1\text{-}\nu)\gamma$
  one must be function of the other
- energy criterion

$$-\frac{hp_{cap}^{crack}}{\gamma} \cong 2.0\left(\frac{Gh}{(1-\nu)\gamma}\right)^{2/5}$$

variables

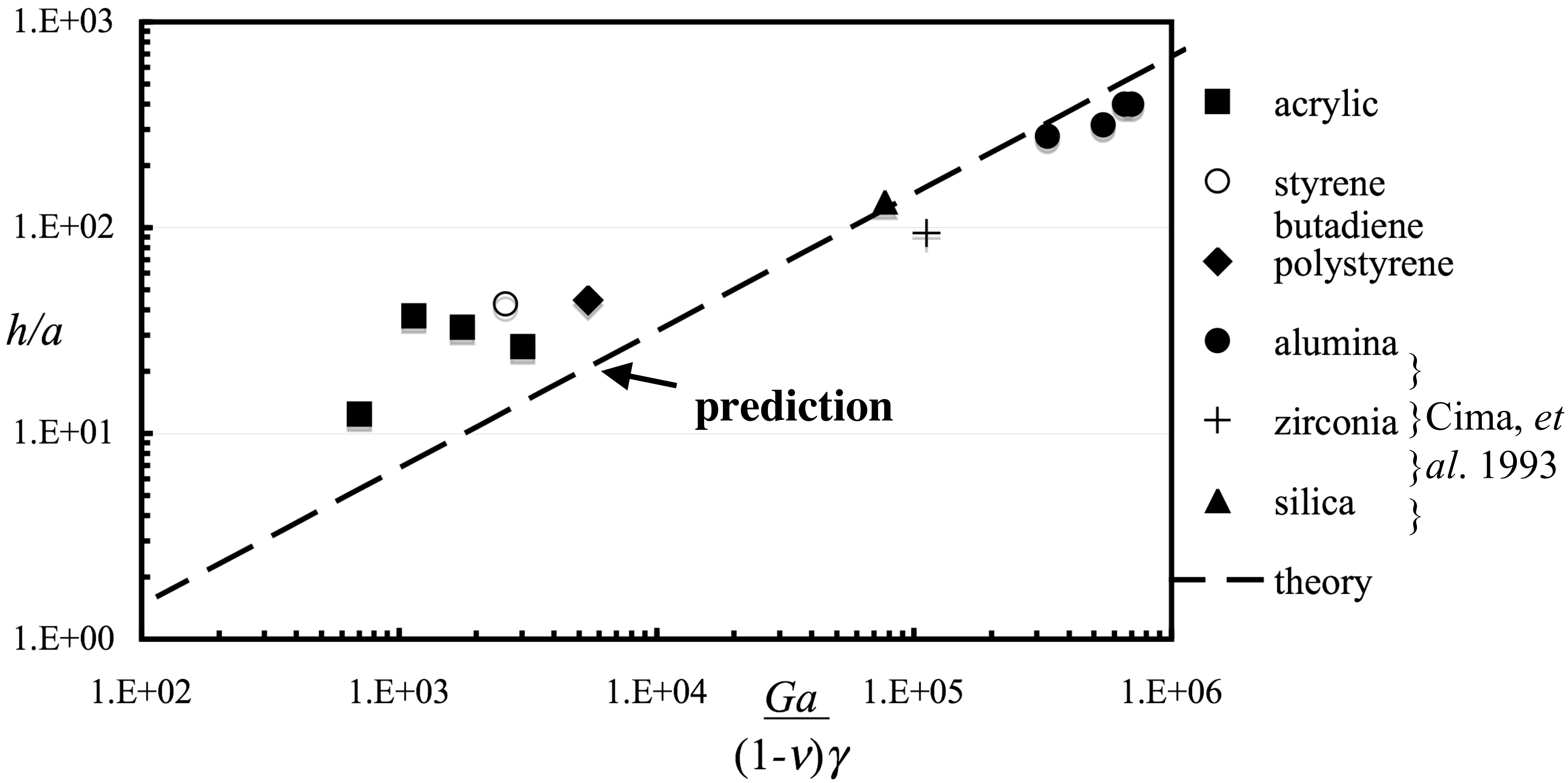
p	kg/m-s
h	m
γ	kg/s
$G/(1-\nu)$	kg/m-s



- energy criterion
  ➜ **lower bound**
- packing flaws
  ➜**initiate cracks**
- grain boundaries and notches
  ➜ **nucleation sites**

Critical Thickness via Spin Coating

K.B. Singh & M.S. Tirumkudulu (in preparation)



- **hypothesis**: When capillary pressure exceeds 12.5γ/a without causing cracking, the water front simply recedes into film.

$$-\frac{p_{cap}^{max} h}{\gamma} = 2.0\left(\frac{Gh}{(1-\nu)\gamma}\right)^{2/5} \Rightarrow \frac{h_{crit}}{a} = 0.047\left(\frac{Ga}{(1-\nu)\gamma}\right)^{2/3}$$

With thanks to

Priscilla on our 35th anniversary

my advisers, colleagues,
students, and postdocs

the scientists and engineers who comprise
the international and interdisciplinary
colloids community