Critical Gels, Scott Blair and the Fractional Calculus of Soft Squishy Materials

Gareth H. McKinley
with Aditya Jaishankar

Hatsopoulos Microfluids Laboratory
Department of Mechanical Engineering, MIT

Partially from Bingham Lecture, 85th Annual Meeting of the Society of Rheology
Montréal, Québec (October 2013)

Power-Law Rheology, Fractional Calculus and the Yielding of Soft Squishy Materials

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January 2016

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Outline

- Scott Blair, Bingham and the dawn of Rheology
- Multi-scale materials and fractional diffusion
- Fractional Calculus and the "Spring-pot" (the *Scott-Blair element*)
  - The Fractional Maxwell Model & Fractional Kelvin-Voigt Models
  - Linear Viscoelastic properties
- Nonlinear Deformations and the Fractional K-BKZ Formulation
  - Xanthan gum as a model fractional material
  - Quantitative description of the Cox-Merz rule (and deviations from it)

- Don Plazek, (mis)quoting Novalis (1772-1801):
  Bingham Lecture, *J.Rheol.* **40**(6), 1996

"To become properly acquainted with a truth,
we must first have disbelieved it and disputed against it"

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G.W. Scott Blair (1902-1987)

GEORGE WILLIAM SCOTT BLAIR MA PhD DSc FRIC FInstP
(1902-1987) – 'THE MAN AND HIS WORK'

by

Prof. Howard A. Barnes, OBE, DSc, FREng,
Unilever Research, Port Sunlight, CH63 3JW.

A talk given on the occasion of the opening of the Scott Blair reading room at the University of Wales Aberystwyth, Dec. 15th 1999.

History

Younger rheologists might ask 'who was this man, Scott Blair, anyway?'. George William Scott Blair was for most of us the quintessential – *if eccentric* – Englishman,

After 30 years working on industrial rheology problems, I now feel a great deal of empathy with Scott Blair who was also struggling with industry's big problems, that is, with real materials that one **had** to look study, not just working on model systems of one's own making and to one's own liking. To many rheologists, George Scott Blair was given to flights of fancy into psycho-Rheology, fractional differentiation, etc. However, I think these were his honest attempts to try to explain real materials in real situations, which we still struggle with today.

Howard A. Barnes, *Biorheology* **37** (2000)

Obituary: P. Sherman, *Rheol. Acta*, **27**(1), 1988

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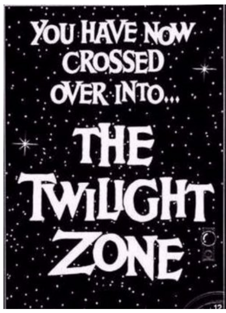
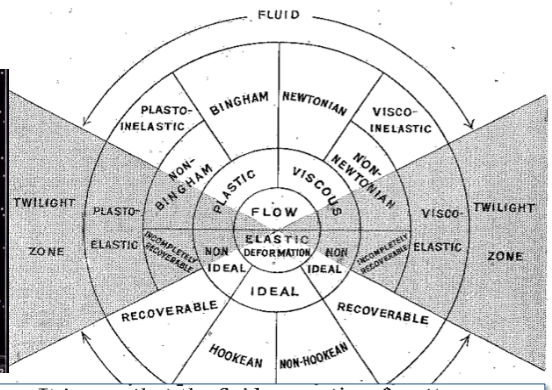
L. Bilmes
Nature **150**, p.432
October 1942

A Rheological Chart

FOLLOWING the classification of rheological properties discussed in NATURE of June 20, 1942, p. 702, the following chart is proposed. The chart, which is largely self-explanatory, is based on the scheme of classification proposed by Dr. Treloar and developed by Mr. D. C. Broome and the British Rheologists' Club.





It is seen that the fluid properties of matter occupy the upper regions of the chart and the solid properties of matter the lower, while between them on either side a twilight zone exists where solid and fluid properties subsist together. Ideal properties, therefore, lie north and south and real ones east and west.

The British Rheologists Club (1940s)
G.I.Taylor
R. Treloar
G.W. Scott Blair
V. Harrison

- Thanks to Sahm Nikoi & Simon Cox

(Scott Blair Collection, Aberystywth)

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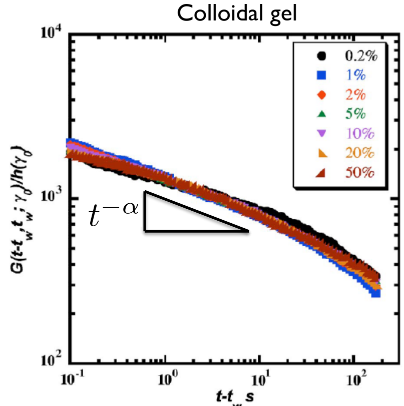
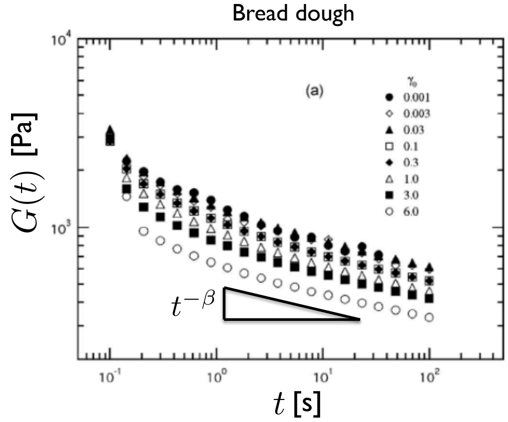
Stress Relaxation of Multiscale complex fluids

Colloidal gel



Yin, G., & Solomon, M. J. (2008). Journal of Rheology, **52**(3), 785.

Bread dough



Ng, T. S., & McKinley, G. H. (2008). Journal of Rheology, **52**(3), 417–449.

- Multi-scale complex fluids exhibit broad power law relaxation spectra with no easily discernible characteristic features.

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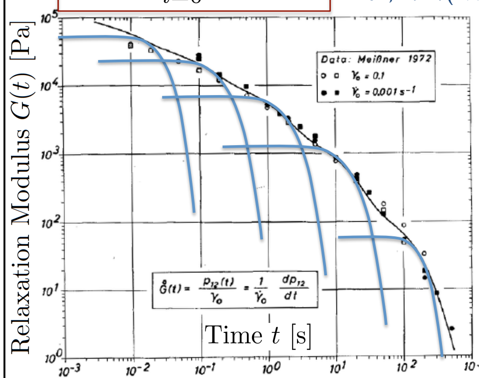
The Prony Series: Multimode Maxwell Model

$$\boxed{G(t) = \sum_{i=0}^{N} G_i e^{-t/\tau_i}}$$

High molecular weight LDPE (IUPAC A)

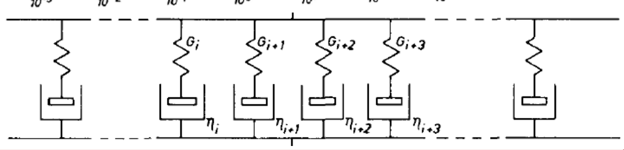
Laun, H. M. (1978). *Rheologica Acta*, 17, 1–15.



i	τ_i	G_i
1	10^3	1
2	10^2	1.8×10^2
3	10^1	1.89×10^3
4	10^0	9.8×10^3
5	10^{-1}	2.67×10^4
6	10^{-2}	5.86×10^4
7	10^{-3}	9.48×10^4
8	10^{-4}	1.20×10^5

"If the number of Maxwell or Voigt units is increased to the minimum number required for a series-parallel model to represent such a distribution at all adequately, the simplicity of the standard models is lost and, in addition, arbitrary decisions must be made in assigning suitable values to the model elements."

Tschoegl, N.W. (1989). The Phenomenological Theory of Linear Viscoelastic Behavior. Berlin: Springer-Verlag.



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From Continuous Time Random Walks to Power-Law Rheology

Anomalous subdiffusion

Continuous Time Random Walk (CTRW) →

Fractional Diffusion Equation

$$\frac{\partial^\alpha}{\partial t^\alpha} P(x,t) = \frac{\partial^2}{\partial x^2} P(x,t)$$

Generalized Stokes Einstein Equation →

$$\tilde{G}(s) = \frac{k_B T}{\pi a s \langle \Delta \tilde{x}^2(s) \rangle}$$

Fractional Relaxation Modulus

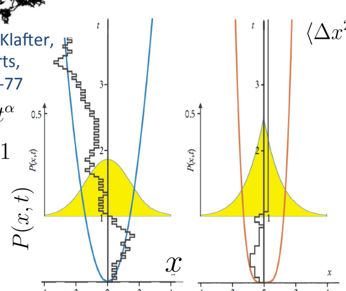
$$G(t) = S t^{-\alpha}$$

↓ $\langle \Delta x^2 \rangle \sim t^\alpha$

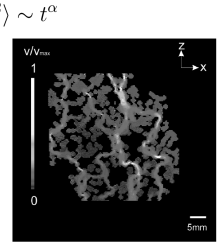
R. Metzler, J. Klafter, Physics Reports, (2000), **300**:1-77

$\langle \Delta x^2 \rangle \sim t^\alpha$

$0 < \alpha < 1$



I. M. Sokolov, J. Klafter, & A. Blumen, *Physics Today* (2002), **55**: 48-54.



A. Klemm , H.-P. Muller, R. Kimmich, Physica A, (1999), **266**:242-246

Percolation Network in Cheese

Diffusing particle in slow moving region (dark) is trapped until it reaches the fast-moving backbone (light)

- *What is a **fractional derivative** and how do we use it to model power-law rheology?*

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From Continuous Time Random Walks to Power-Law Rheology

Anomalous subdiffusion

Continuous Time Random Walk (CTRW) →

Fractional Diffusion Equation

$$\frac{\partial^\alpha}{\partial t^\alpha}P(x,t) = \frac{\partial^2}{\partial x^2}P(x,t)$$

$$\downarrow$$

$$\langle \Delta x^2 \rangle \sim t^\alpha$$

Generalized Stokes Einstein Equation →

$$\tilde{G}(s) = \frac{k_B T}{\pi a s \langle \Delta \tilde{x}^2(s) \rangle}$$

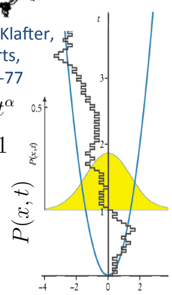
Fractional Relaxation

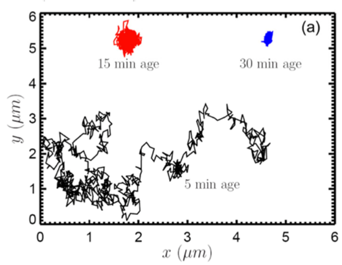
$$G(t) = St^{-\alpha}$$

R. Metzler, J. Klafter, Physics Reports, (2000), 300:1-77

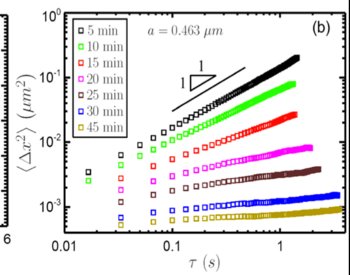
$$\langle \Delta x^2 \rangle \sim t^\alpha$$

$$0 < \alpha < 1$$





I. M. Sokolov, J. Klafter, & A. Blumen, *Physics Today* (2002), **55**: 48-54.



Rheological Aging in a Laponite Gel
Rich, McKinley, Doyle; *J. Rheology* **55**(2), 2011

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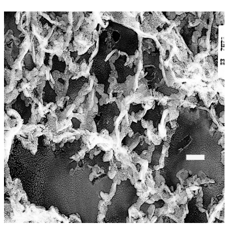
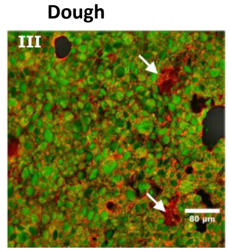
Ubiquity of Power-Law Rheology: Relationship to Microstructure

Laponite Dispersion



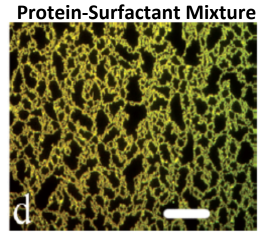
Courtesy J. W. Ruberti & Gavin Braithwaite (CPG)
Scale bar 30nm

Dough



S.H. Peighambardoust *et al.*, *J. Cereal Science*, (2006), 43.
Scale bar 80 μm

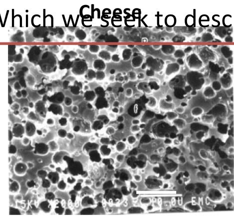
Air-solution interface of a Protein-Surfactant Mixture



Morris and Gunning, *Soft Matter*, 4, 2008. Scale bar: 10 μm.

Scale-free fractal microstructure leads to scale-free power-law relaxation behavior
Which we seek to describe using fractional calculus.

Cheese

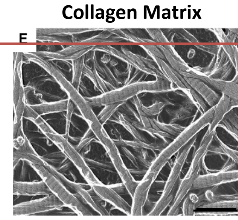


K. J. Aryana, Z. U. Haque, *Int. J. Food. Sci. Tech.*, 36, 2001. Scale bar 10 μm.

Actin Filaments

T. D. Pollard and J. A. Cooper, *Science*, 326, 2009.

Collagen Matrix



N Saeidi, E. A. Sander, J. W. Ruberti, *Biomaterials*, 30, 2009. Scale bar: 500 nm

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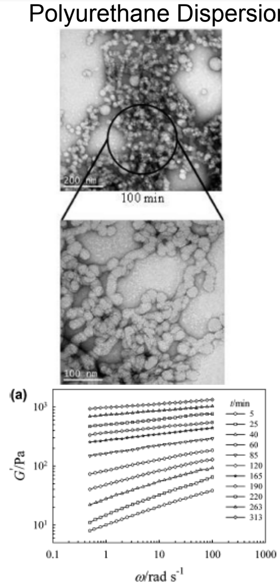
Some More Examples of Multi-scale Power Law Materials

Polyurethane Dispersions



Madbouly et al. Macromolecules, May 2013

Mucin Networks

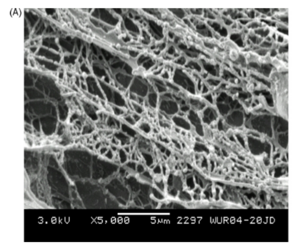
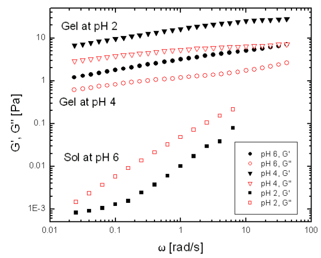


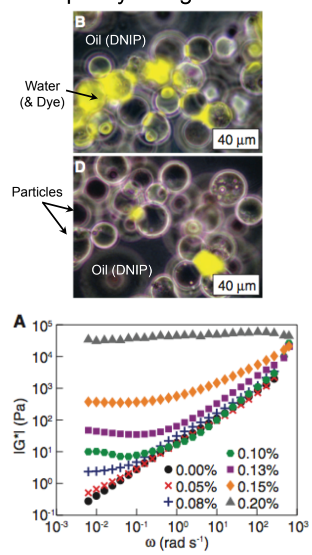
Fig. 1 – (A) Fresh saliva determined with Cryo SEM. A drop of cent

Schipper et al., Arch. Oral Biol. 52 (2007)



Celli, Ewoldt, GHM et al. PNAS ***106*** *(2009)*

Capillary-Bridged Pastes



Koos & Willenbacher, Science ***331*** *(2011)*

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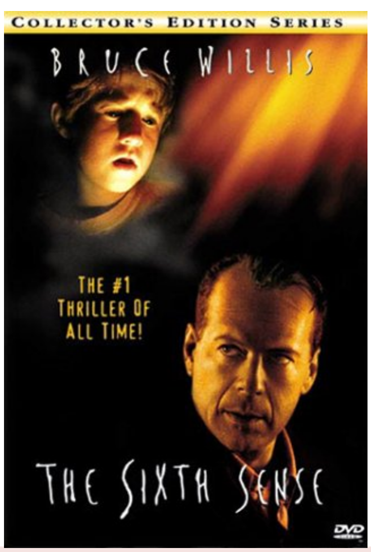
Power-Laws Everywhere!

"I see dead people…"



"I see power laws…"

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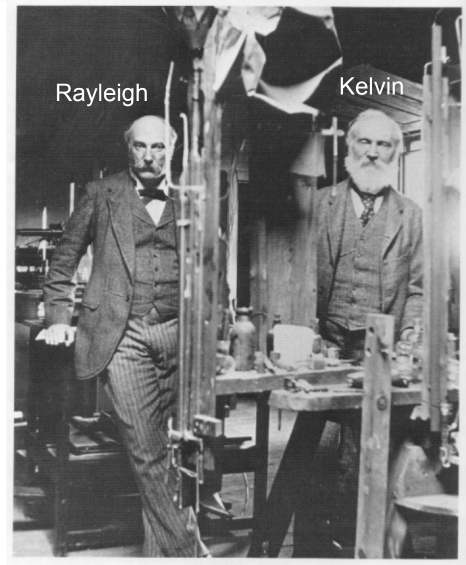
Modeling Power Law Rheological Materials (POLAR Materials)

"I am never content until I have constructed a mechanical model of the subject I am studying....
I often say that when you can measure what you are speaking about and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind",

1897 William Thomson (Baron Kelvin),
A Dictionary of Scientific Quotations (Oxford)



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A Brief History

- Discovered by one of the founding fathers of Calculus itself: Gottfried Leibniz
- Since captured the thoughts of such eminent mathematicians such as Bernoulli, Euler, Lagrange, Laplace, Fourier, Abel, Liouville, Riemann and Heaviside*
- Abel used it to elegantly solve the Tautochrone problem – What is the shape of the curve such that a bead placed at any point of the curve will fall to the bottom in the same time.
- Applications include electrical engineering, electro-analytical chemistry, biology, and most importantly viscoelasticity
- Fundamental idea – Fractional derivatives interpolate between integer order derivatives.

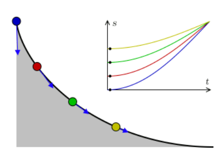
Gottfried Leibniz

$$\frac{\mathrm{d}^n}{\mathrm{d}t^n} \rightarrow \frac{\mathrm{d}^\alpha}{\mathrm{d}t^\alpha} \quad \alpha \in \mathbb{R}$$

$$\frac{d^{1/2}}{dt^{1/2}}\left(\frac{d^{1/2}x}{dt^{1/2}}\right) = \frac{dx}{dt}$$

$$\frac{d^\alpha}{dt^\alpha}[f_1(t) + cf_2(t)] = \frac{d^\alpha}{dt^\alpha}f_1(t) + c\frac{d^\alpha}{dt^\alpha}f_2(t)$$

The fractional derivative operator is a linear operator



A cycloid – Solution to the tautochrone problem

* B. Ross, *Historia Mathematica* (1977), **4**, 75-89.
Fractional differential equations, I. Podlubny, Academic Press, 1999
Fractional calculus and its applications, B. Ross (Ed.), Springer-Verlag, 1975

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Mathematical Definitions: Fractional Calculus

Leibniz in a letter To de l'Hôpital (1695): $\dfrac{\mathrm{d}^n}{\mathrm{d}t^n} \rightarrow \dfrac{\mathrm{d}^\alpha}{\mathrm{d}t^\alpha} \quad \alpha \in \mathbb{R}$

Example: $\dfrac{d^{1/2}}{dt^{1/2}}\left\{\dfrac{d^{1/2}x}{dt^{1/2}}\right\} = \dfrac{d^1x}{dt^1}$

Caputo Derivative: (*Integro-Differentiation*)

$$\frac{d^\alpha \gamma(t)}{dt^\alpha} = \frac{1}{\Gamma(m-\alpha)} \int_0^t (t-t')^{m-\alpha-1} \gamma^{(m)}(t')\, dt' \qquad m = \lceil \alpha \rceil \text{ (Ceiling)}$$

If $0 < \alpha < 1$

$$\boxed{\frac{d^\alpha \gamma(t)}{dt^\alpha} = \frac{1}{\Gamma(1-\alpha)} \int_0^t \underline{(t-t')^{-\alpha}} \dot{\gamma}(t')\, dt'} \qquad \boxed{G(t) = \frac{\sigma(t)}{\gamma_0} \sim t^{-\alpha}}$$

The fractional derivative is a linear operator: $\dfrac{d^\alpha}{dt^\alpha}[f_1(t) + c f_2(t)] = \dfrac{d^\alpha}{dt^\alpha} f_1(t) + c \dfrac{d^\alpha}{dt^\alpha} f_2(t)$

Laplace Transform: $\mathcal{L}\left\{\dfrac{d^\alpha}{dt^\alpha}\gamma(t); s\right\} = s^\alpha \tilde{\gamma}(s) - \cancel{\sum_{k=0}^{n-1} s^{\alpha-k-1}\gamma^{(k)}(0)}, \quad n-1 < \alpha \leq n$

Fourier Transform: $\mathcal{F}\left\{\dfrac{d^\alpha}{dt^\alpha}\gamma(t); \omega\right\} = (i\omega)^\alpha \tilde{\gamma}(\omega)$

- We incorporate these fractional derivatives into constitutive equations by generalizing the ideas of **springs and dashpots**

I. Podlubny, Fractional Differential Equations, *Academic Press*, 1999
T. Surguladze, *J. Math. Sci.*, (2002), 112: 4517-4557
T. Nonnenmacher, *Rheological Modelling: Thermodynamical and Statistical Approaches*, (1991), 7:309-320

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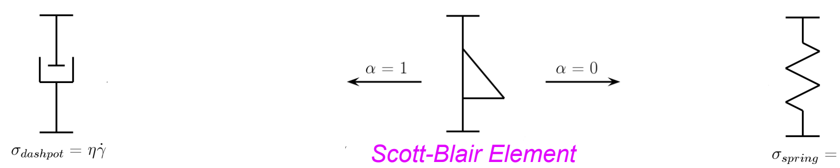
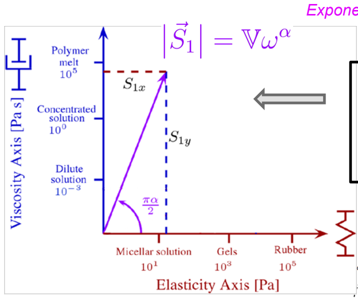
The Springpot as a Canonical Intermediate Element



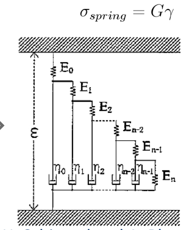
Scott-Blair Element

Exponent α and "Quasi-property" (scale factor) $\mathbb{V}$



$$\boxed{\sigma_{\text{spring-pot}} = \mathbb{V}\frac{d^\alpha \gamma}{dt^\alpha}}$$

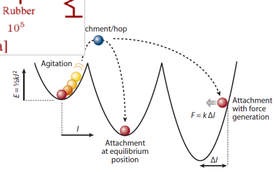
R. C. Koeller, *J. Appl. Mech.*, (1984), 51:299-307



H. Schiessel and A. Blumen, *J. Phys. Math, Gen.* (1993), **26**:5057-5069

$$G(t) = \mathbb{V}t^{-\alpha}$$

<u>SGR model:</u> Simplest case: Exponential distribution of energy states



$$G(t) = \left[\Gamma_{eq}\sqrt{\frac{\Gamma(\alpha+1)}{2\alpha^2}}\left(\frac{\alpha+1}{e}\right)^{\alpha+1}\right] t^{-\alpha}$$

A. Jaishankar, G.H. McKinley, *Proc. R. Soc. A*, 2012, **469**: 2012.0284

Kollmannsberger & Fabry, *Ann. Rev. Mater. Res.*, (2011), 41:75-97

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Psycho-rheology & Quasi-properties

(Texture Analysis & Scale Factors)

Royal Society **Publishing** *Informing the science of the future*

Author(s): G. W. S. Blair, B. C. Veinoglou, J. E. Caffyn
Source: *Proceedings of the Royal Society of London. Series A, Sciences*, Vol. 189, No. 1016 (Mar. 27, 1947), pp. 69-87

Limitations of the Newtonian time scale in relation to non-equilibrium rheological states and a theory of quasi-properties

By G. W. S. Blair, D.Sc. and B. C. Veinoglou, Ph.D.
In collaboration with J. E. Caffyn, B.Sc.

National Institute for Research in Dairying, University of Reading
(N.I.R.D)

(*Communicated by E. N. da C. Andrade, F.R.S.—Received* 30 *May* 1946)

The behaviour of complex materials under stress is described in terms of entities which are not strictly 'physical properties'. These so-called 'quasi-properties' range from entities hardly distinguishable from dimensionally true physical properties to concepts which are much less clearly defined.

Firmness, Stickiness, Stringiness….the principle of intermediacy

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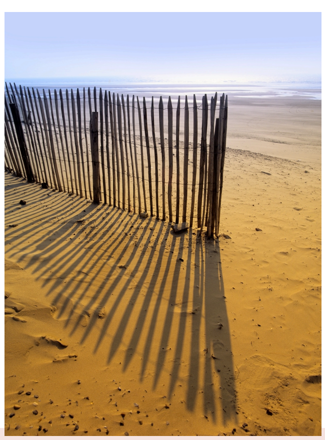
What Does the Fractional Derivative Represent?

- The idea that material time (or *rheological time)* inside the sample evolves in a different way than laboratory (Newtonian) time
  - Time derivatives become *non-local quantities* (Podlubny *et al*., *JCP* 2009)
  - Geometric & physical interpretation (Podlubny, *FCAA*, 2002)



GEOMETRIC AND PHYSICAL INTERPRETATION …
Fractional Calculus and Applied Analysis **5**(4), 2002

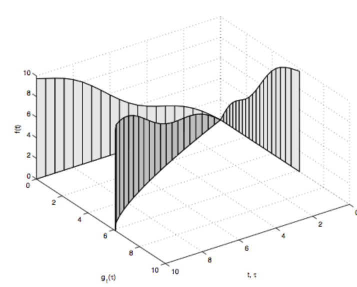


Figure 1: The "fence" and its shadows: ${}_0I_t^1 f(t)$ and ${}_0I_t^\alpha f(t)$, for $\alpha = 0.75$, $f(t) = t + 0.5\sin(t)$, $0 \le t \le 10$.

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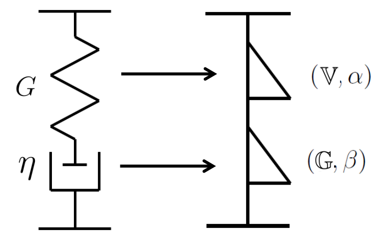
Building Rheological Constitutive Models

Fractional Maxwell Model

$$\sigma(t) + \frac{\mathbb{V}}{\mathbb{G}}\frac{d^{\alpha-\beta}\sigma(t)}{dt^{\alpha-\beta}} = \mathbb{V}\frac{d^{\alpha}\gamma(t)}{dt^{\alpha}}$$

$$0 \le \beta \le \alpha \le 1$$

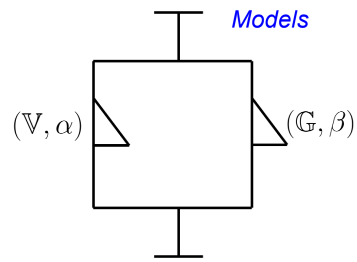
- Only models that have mechanical analogues are thermodynamically admissible .
- Order of the derivative on stress should be less than the derivative on the strain
- $\alpha, \beta > 0$



Four Parameter Models

Fractional Kelvin Voigt Model

$$\sigma(t) = \mathbb{V}\frac{d^{\alpha}\gamma(t)}{dt^{\alpha}} + \mathbb{G}\frac{d^{\beta}\gamma(t)}{dt^{\beta}}$$



Ch. Friedrich, *Rheol. Acta* **30**(1), 1991
Schiessel & Blumen, *J. Phys A. Math. Gen.* **26,** 1993

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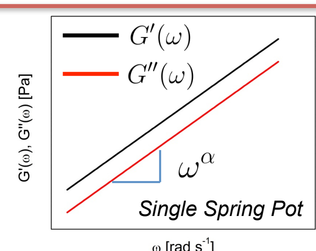
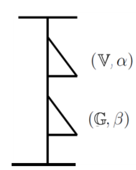
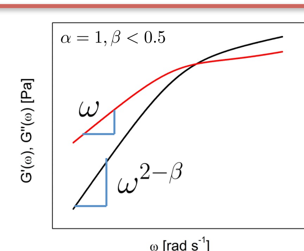
Versatility of Two Element Fractional Models

Fourier Transform to evaluate complex modulus



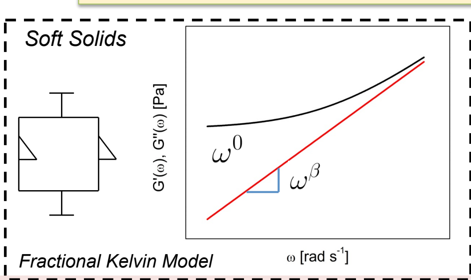




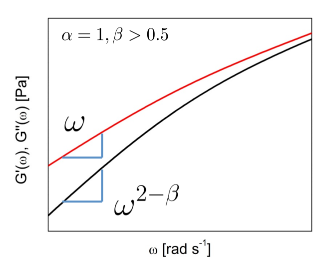
Cross-over Time

$$\lambda = \left(\frac{\mathbb{V}}{\mathbb{G}}\left[\frac{\cos(\pi\beta/2) - \sin(\pi\beta/2)}{\sin(\pi\alpha/2) - \cos(\pi\alpha/2)}\right]\right)^{\frac{1}{\alpha-\beta}}$$

Jaishankar, A., & McKinley, G. H. Proc. Roy. Soc. A, 469(2149), 2013



DEMO



http://demonstrations.wolfram.com/VisualizingFractionalRheologicalConstitutiveEquations/

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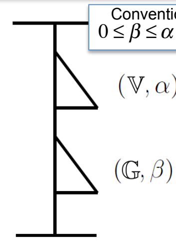
The Fractional Maxwell Model (FMM)

$$\boxed{\tau + \frac{\mathbb{V}}{\mathbb{G}}\frac{d^{\alpha-\beta}}{dt^{\alpha-\beta}}\tau = \mathbb{V}\frac{d^{\alpha}}{dt^{\alpha}}\gamma} \xrightarrow{\mathcal{F}} \frac{\mathcal{T}(i\omega)}{\mathcal{G}(i\omega)} = \frac{\mathbb{V}(i\omega)^{\alpha}\cdot\mathbb{G}(i\omega)^{\beta}}{\mathbb{V}(i\omega)^{\alpha}+\mathbb{G}(i\omega)^{\beta}}$$

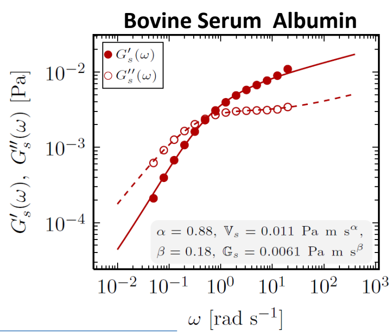
Convention: $0 \le \beta \le \alpha \le 1$

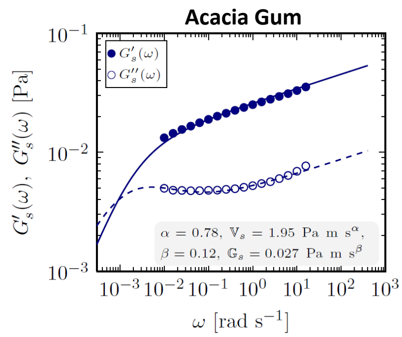


$\mathbb{V}$ and $\mathbb{G}$ are quasi-properties: $\mathbb{V} = E_1\lambda_1^{\alpha}$ $\quad \mathbb{G} = E_2\lambda_2^{\beta}$

$$G'(\omega) = \frac{\mathbb{V}\omega^{\alpha}\cdot\mathbb{G}\omega^{\beta}[\mathbb{V}\omega^{\alpha}\cos(\pi\beta/2) + \mathbb{G}\omega^{\beta}\cos(\pi\alpha/2)]}{(\mathbb{V}\omega^{\alpha})^2 + (\mathbb{G}\omega^{\beta})^2 + 2\mathbb{V}\omega^{\alpha}\cdot\mathbb{G}\omega^{\beta}\cos(\pi(\alpha-\beta)/2}$$

- Reduces correctly to Maxwell Model for $\alpha = 1$ and $\beta = 0$





Jaishankar, A. & McKinley, G. H. , *Proc. Roy. Soc. A*, **469**: 2012

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What about Step Strain?

- Response of the FMM to a Step Strain? $\gamma(t) = \gamma_0 H(t)$

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HATSOPOULOS MICROFLUIDS LABORATORY

The Mittag-Leffler Function

- Response of the FMM to a Step Strain? $\gamma(t) = \gamma_0 H(t)$

Relaxation modulus for FMM

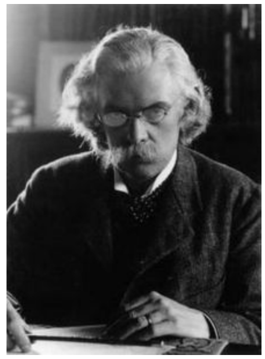
$$G(t) = \mathbb{G} t^{-\beta} E_{\alpha-\beta,1-\beta}\left(-\left(\tfrac{t}{\lambda}\right)^{\alpha-\beta}\right)$$

- Where $E_{a,b}(z)$ is the *Generalized Mittag-Leffler* function

$$E_{a,b}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(ak+b)}$$

Examples

$$E_{1,1}(-z) = e^{-z}$$
$$E_{1/2,1}(z) = e^{z^2}\operatorname{erfc}(-z)$$
$$E_{2,1}(z) = \cosh(\sqrt{z})$$



Gösta Mittag-Leffler
(1846 – 1927)

Royal Swedish Academy of Sciences

Fellow of Royal Soc. of London

Member of the Nobel Prize Committee (1903)
{Marie Curie}

- MLF asymptotes:
  - Stretched Exponential at short times
  - Power-law relaxation at long times

(Here I have set β = 0, but this result is general)

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The Mittag-Leffler Function

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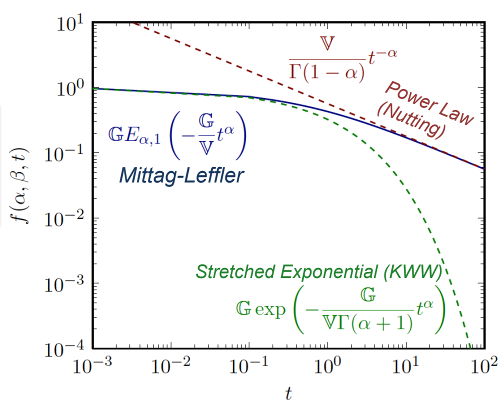

- MLF asymptotes:
  - Stretched Exponential at short times
  - Power-law relaxation at long times

(Here I have set β = 0, but this result is general)

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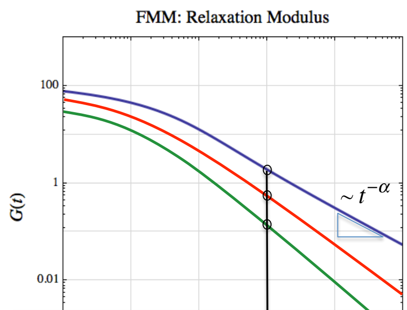
What are Quasi-properties?

- Quasi-properties provide a '**snapshot**' and quantitative measure of the spectrum of the dynamical relaxation processes taking place inside a real material
  - Different formulations may not only have different "values" of the quasi-property of interest but also different dimensional units!



$$\lambda_{characteristic} \sim (\mathbb{V}/\mathbb{G})^{1/(\alpha-\beta)}$$

Consistent with the common (pragmatic) practice of comparing:

- "the viscosity at $\dot{\gamma} = 1\text{s}^{-1}$"
- "residual stress after 10minutes relaxation"
- "The dynamic modulus at $\omega = 1\text{rad/s}$"

$G(t) \sim \mathbb{V} t^{-\alpha}$: $\mathbb{V}$ has units $[\text{Pa.s}^{\alpha}]$

$$G(t_{ref}) = \underbrace{\left(\mathbb{V} t_{ref}^{-\alpha}\right)}_{\text{Reported value}} \left(t/t_{ref}\right)^{-\alpha}$$

In spite of the phenomenological nature of our approach, our results are far from being purely empirical or unrelated to fundamental concepts, but the fundamental concepts are not molecular but are concerned with the judgment of the rheological behaviour of materials by handling. Such judgments are said to be subjective in the sense that they relate to states of feeling but the particular class with which we are concerned are reproducible as statistical distributions and may thus be defined and assessed quantitatively. *Scott Blair & Caffyn, Phil Mag 1949*

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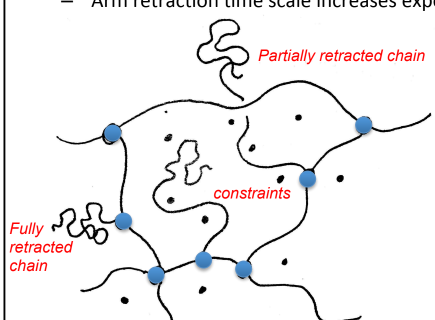
The Curro & Pincus Model

- Very slow stress relaxation of randomly crosslinked elastomeric networks (τ = time scale)
  - "Dangling Arms" retract out of their own tube through network of entanglements
  - Arm retraction time scale increases exponentially with length



Monomer density ϱ

Crosslink density $\nu << \varrho$

Probability of a given monomer being a crosslink $q = \nu/\varrho << 1$

Experiment Chasset & Thirion (1965)

$$(E - E_\infty)/E_\infty = (t/\tau)^{-\alpha}$$

Probability of finding a link for an *n*–mer: $P(n) = q(1-q)^{n-1}$

Residual stress from dangling chain of length *n* $\sigma_{dangling} \sim n - l_{retract}(t)$

Arm retraction time scale dangling chain of length *n* $\tau(n) \sim \tau_{seg} \exp(kn)$

$$\frac{E_{dangling}}{\nu k_B T} = \left(\frac{t}{\tau_{av}}\right)^{-(\nu/\rho k)}$$

Curro & Pincus, *Macromol.* 1983

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HATSOPOULOS MICROFLUIDS LABORATORY

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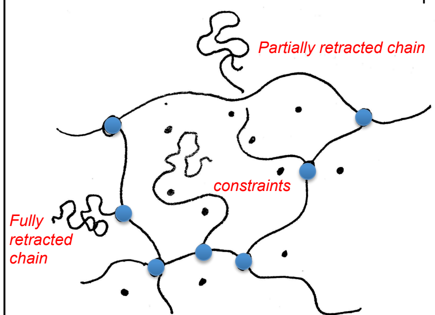

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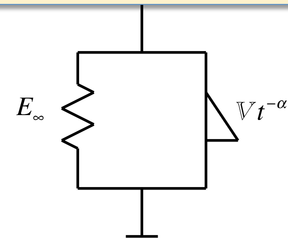

Fractional Kelvin-Voigt Model

$$G(t) = \nu k_B T + \left(\nu k_B T \tau_{av}{}^{\alpha}\right) t^{-\alpha} \equiv E_\infty + \mathbb{V} t^{-\alpha}$$

where $\alpha \equiv \nu/\rho k$ $\quad E_\infty \equiv \nu k_B T$ $\quad \mathbb{V} \equiv (\nu k_B T \tau_{av}{}^{\alpha})$ $\quad \tau_{av} = \tau_{seg}\left(k_B T \nu^2/\rho\zeta\right)^{-\alpha\rho/\nu}$

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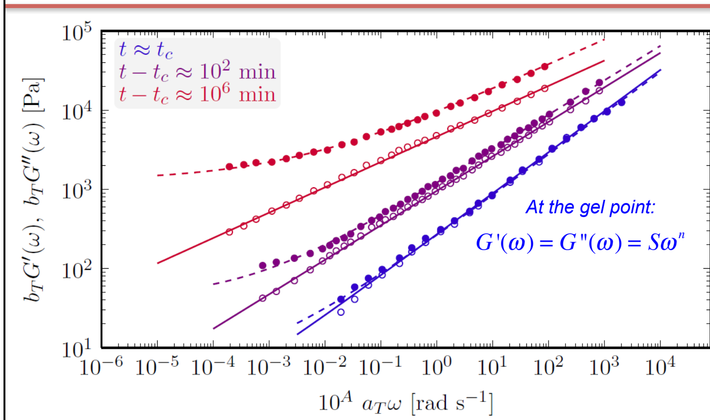
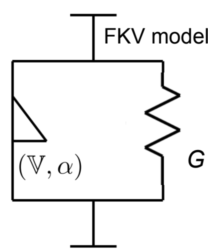
Critical Gels (& beyond criticality)





$$G'(\omega) = G + \mathbb{V}\omega^\alpha \cos(\tfrac{\pi}{2}\alpha)$$

$$G''(\omega) = G + \mathbb{V}\omega^\alpha \sin(\tfrac{\pi}{2}\alpha)$$

Data from Winter, H. H. & Chambon, F. 1986, Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. *Journal of Rheology* **30**, 367–382.

$t - t_c$ [min]	α	$\mathbb{V}$ [Pa s$^\alpha$]	$\mathbb{G}$ [Pa]
0	0.52	367.3	13.97
10^2	0.44	1512	42.07
10^6	0.32	9596	1283

- Only **three** parameters required to capture the behavior of the time-evolving cross-linking reaction beyond the gel point.

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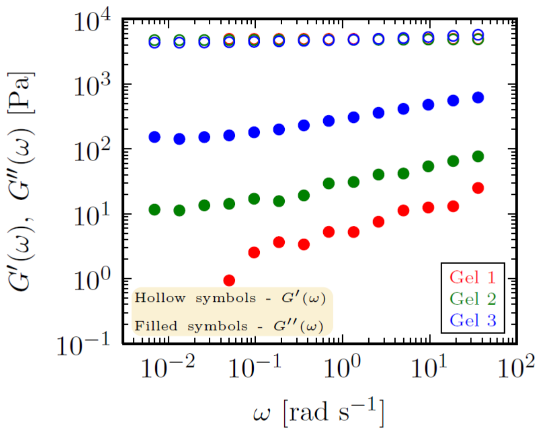
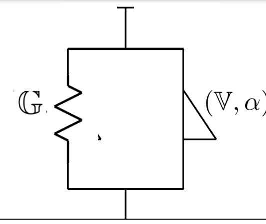
'Creepy Gels' & The Fractional Kelvin Voigt Model





$$\sigma(t) = \mathbb{V}\frac{d^\alpha \gamma(t)}{dt^\alpha} + \mathbb{G}\frac{d^\beta \gamma(t)}{dt^\beta}$$

$$G'(\omega) = \mathbb{V}\omega^\alpha \cos\left(\frac{\pi}{2}\alpha\right) + \mathbb{G}\omega^\beta \cos\left(\frac{\pi}{2}\beta\right)$$
$$G''(\omega) = \mathbb{V}\omega^\alpha \sin\left(\frac{\pi}{2}\alpha\right) + \mathbb{G}\omega^\beta \sin\left(\frac{\pi}{2}\beta\right)$$

Mesenchymal Stem Cells growing on weakly crosslinked gels
Data from Cameron, A. R., Frith, J. E. & Cooper-White, J. J. 2011, *Biomaterials* **32**, 5979–5993.

Gel	α	$\mathbb{V}$ [Pa s$^\alpha$]	$\mathbb{G}$ [Pa]
LM1Pa	0.426	5.216	6434.30
LM10Pa	0.362	78.61	6444.09
LM130Pa	0.190	1038.74	4835.88

Only *three* parameters required (β = 0) to capture the rheological behavior of these protein gels across the whole experimental range of data.

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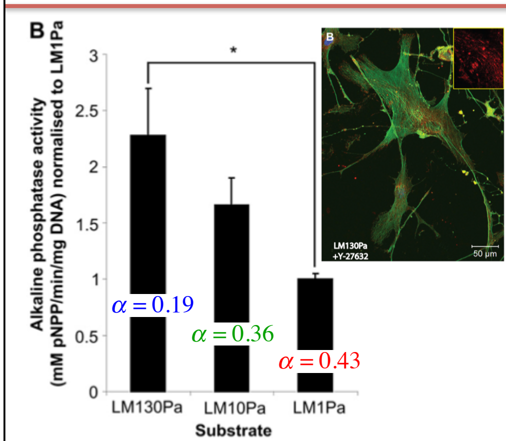
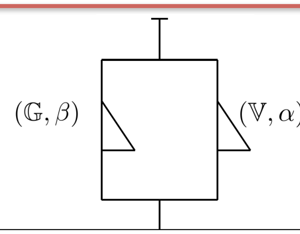
'Creepy Gels' & The Fractional Kelvin Voigt Model





$$\sigma(t) = \mathbb{V}\frac{d^\alpha \gamma(t)}{dt^\alpha} + \mathbb{G}\frac{d^\beta \gamma(t)}{dt^\beta}$$

$$G'(\omega) = \mathbb{V}\omega^\alpha \cos\left(\frac{\pi}{2}\alpha\right) + \mathbb{G}\omega^\beta \cos\left(\frac{\pi}{2}\beta\right)$$
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LM130Pa	0.190	1038.74	4835.88

220% increase in phosphate expression activity
On gels with higher viscoelastic loss modulus
=> controlled "creepiness"

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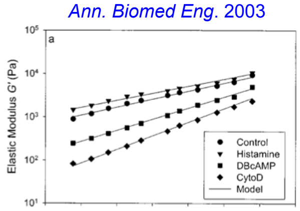
Power-Laws Everywhere!

- The human body is a collection of soft solids, complex fluids and power-law rheology

Airway, Smooth Muscle
Fredberg & Coworkers
Ann. Biomed Eng. 2003



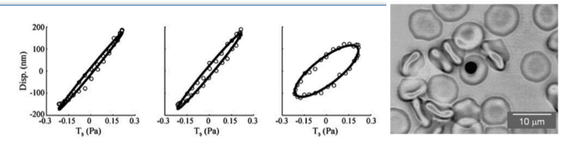


Fig. 4. RBC response to sinusoidal loading (0.75, 4, 30, and 100 Hz), applied specific torque T_s as a function of time t (*top row*); lateral displacement as a function of time t (*middle row*), where t_{max} is the duration of the 5 cycles; and displacement-torque loops for a representative bead at different frequencies (*bottom row*). Solid lines are fits to sinusoidal function to the displacement response. *f*, Frequency.

Red Blood Cell Membranes
S.Suresh & Coworkers, *AJP Cell Physiol.* 2007; Craiem & Magin, Phys. Biol (2010)

Lung Tissue
B. Suki et al. *J. Applied Physiol.* 1994

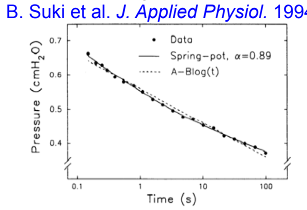
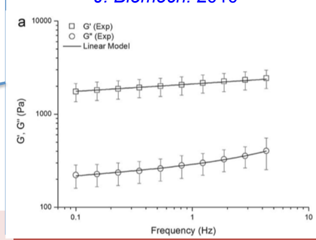


FIG. 3. Fits of power law relaxation (*Eq. 2*) and relaxation predicted by *Eq. 1* to stress relaxation in a rat lung taken from Peslin et al. (41). *A*, *B*, and *α*, parameters; *t*, time.

London Olympics 2012

Liver & Kidneys
Nicolle, Vezin & Palierne
J. Biomech. 2010



Most Foods and Consumer Products are Multiscale Materials that are well-described by Fractional Constitutive Models

Unilever

Nestlé Research

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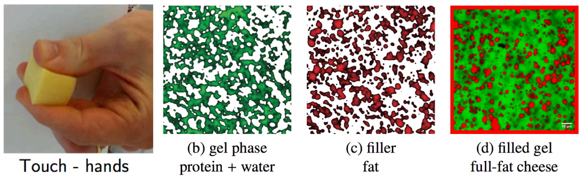
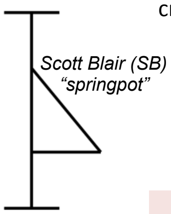
The Fractional Firmness of Fromage

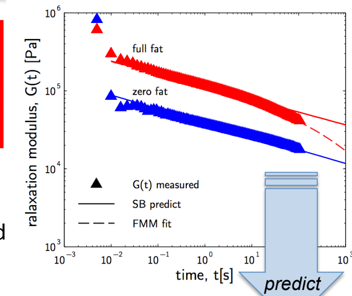
With Dr. Timo Faber (Friesland-Campina, TU/Eindhoven)

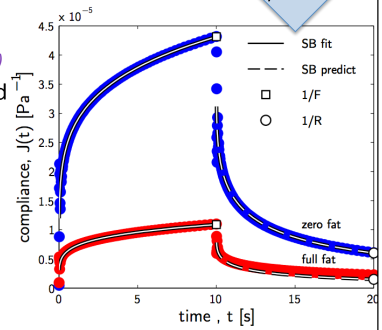


- "Semi-hard cheeses" are emulsion-filled gels (**droplet modulus** > **matrix modulus**)
- Characterized by very broad relaxation dynamics and heuristic measures of
  – *"Firmness" (F), "Springiness" (S), "Rubberiness" (R)*
- No yield stress; expect slow unbounded creep over long time scales



auto-rheomorphic!





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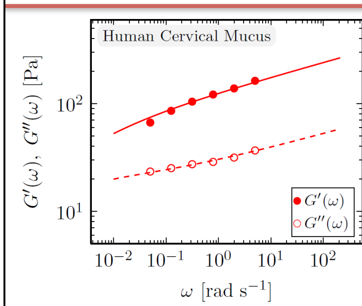
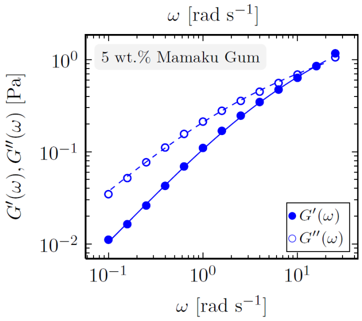
Versatility of Two-Element Fractional Models: Data

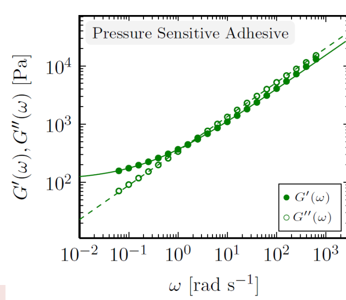


Cervical Mucus
Quasiproperty strongly correlated with preterm birth risk
Grace Yao, AJ, GHM et al., PLoS ONE, 2013

Mamaku Gum (Black Fern extract)
Jaishankar A., Wee M., McKinley G.H., *et al., Carbohyrate Polymers,* **123** 2014

Silicone Pressure Sensitive Adhesive
Data from Wyatt N.B. , Grillet A.M., Hughes L.G. , SOR 2013; *in preparation*
"tackiness" is a fractional property





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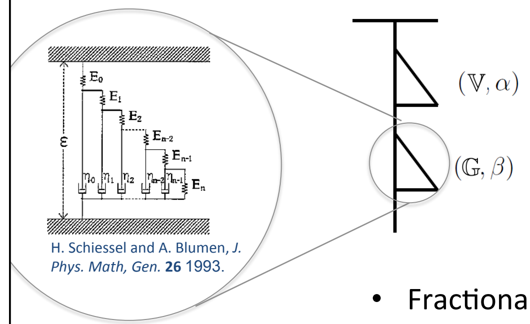
Recap of Fractional Linear Viscoelasticity

Fractional Maxwell Model
(2 Scott Blair elements in series)



Characteristic time scale
(moment of the Mittag=Leffler spectrum)

$$\tau_{characteristic} \sim (\mathbb{V}/\mathbb{G})^{1/(\alpha-\beta)}$$

$$0 \le \beta < \alpha \le 1$$

Collapses to Maxwell-Debye relaxation in limit: $\alpha \to 1; \beta \to 0$

- Fractional Derivative is *non-local* in time
- *Very* broad relaxation spectrum
  - *Cox-Merz rule?*

R. Larson, *Rheol. Acta* **24** *1995*
M. Renardy, *JNNFM* **68**, 1997

• But what about nonlinear rheology of fractional materials?

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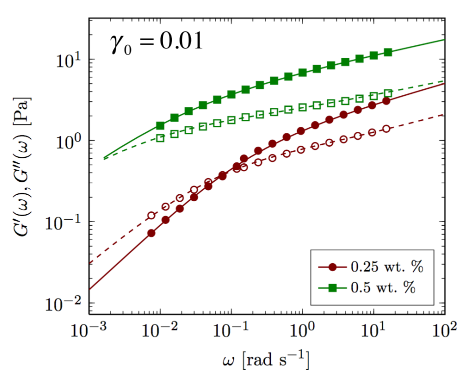
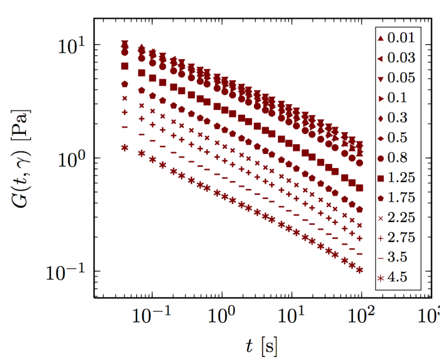
Nonlinear Fractional Rheology

- Fractional models (FMM, FKVM) provide a compact description of broad range of time scales characterizing foods, gels, and other multiscale structured materials
  - What about the nonlinear rheology (dependence on rate of deformation)?
- Canonical system for study: Xanthan gum solutions
  - Widely used food hydrocolloid, rheological "model" thickener…
  - Strain-sensitive, pH-sensitive 'pre-gel'

Song, Kuk, Chang, *KARJ* **18**(2), 2006

$$G(t,\gamma_0) = G(t)h(\gamma_0)$$





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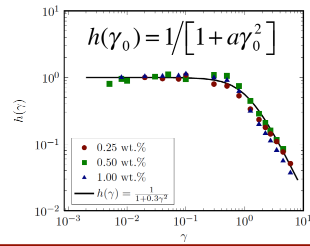
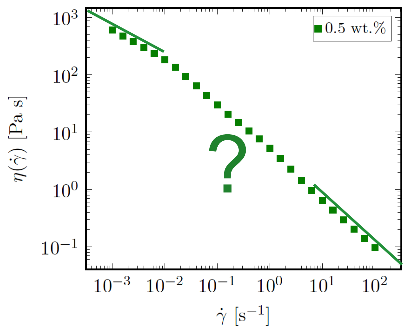
Fractional K-BKZ Formulation

- Determine the linear relaxation dynamics (Fractional Maxwell Model)
- Determine the damping function *h(γ)* (universal for all concentrations, strains)
- *Can we predict the nonlinear material response?*





$$\boldsymbol{\sigma} = \int_{-\infty}^{t} m(t-t')\left[2\frac{\partial U}{\partial I_1}\boldsymbol{C}^{-1} - \cancel{2\frac{\partial U}{\partial I_2}\boldsymbol{C}}\right] dt'$$

R.G. Larson, *Constitutive equations for polymer melts and solutions*, Butterworths, 1988

$$m(t-t') = \frac{\partial G(t-t')}{\partial t} \qquad \boldsymbol{C}^{-1} = (\boldsymbol{F}^{-1})^T \cdot \boldsymbol{F}^{-1} \qquad 2\frac{\partial U}{\partial I_1} = h(\gamma)$$

$$\boxed{\boldsymbol{\sigma} = \int_{-\infty}^{t} \frac{\partial G(t-t')}{\partial t'} h(\gamma)\boldsymbol{C}^{-1}\, dt'}$$

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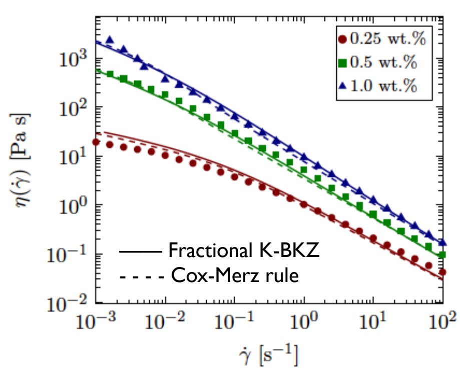
Nonlinear Model Predictions

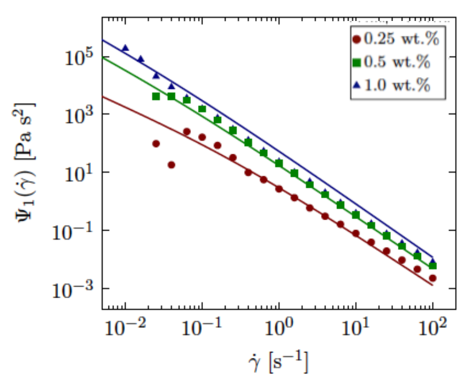
Steady Shear Viscosity

$$\eta(\dot\gamma) = -\mathbb{G}\int_0^\infty u^{-\beta}E_{\alpha-\beta,-\beta}\left(-\frac{\mathbb{G}}{\mathbb{V}}u^{\alpha-\beta}\right)\cdot\frac{1}{1+0.3(\dot\gamma u)^2}\,du$$



First Normal Stress Coefficient

$$\Psi_1(\dot\gamma) \equiv \frac{N_1}{\dot\gamma^2} = -\mathbb{G}\int_0^\infty u^{1-\beta}E_{\alpha-\beta,-\beta}\left(-\frac{\mathbb{G}}{\mathbb{V}}u^{\alpha-\beta}\right)\frac{1}{1+0.3(\dot\gamma u)^2}\,du$$



There are no fitting parameters: LVE response + damping function completely determines steady shear response.

There is no zero shear viscosity ! $\lim_{\dot\gamma\to 0}\eta(\dot\gamma) \sim \dot\gamma^{\alpha-1}$

Jaishankar and McKinley, *Journal of Rheology* **58**(6) 2014,

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One model to rule them all

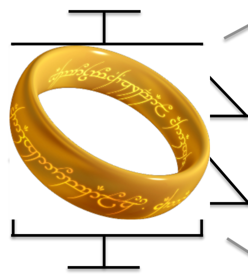
- Unify linear viscoelastic rheology {G', G"} and Generalized Newtonian Fluid Models $\eta(\dot{\gamma})$

Power law fluid

$$\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1}$$

- Polymer melts and solutions

Fractional Zener Model



Cross and Carreau Models

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{[1 + (\dot{\gamma}/\dot{\gamma}^*)^2]^{(1-n)/2}}$$

- Polymer melts and solutions
- Worm-like micelles

Herschel-Bulkley Model

$$\eta(\dot{\gamma}) = \frac{\tau_y}{\dot{\gamma}} + m\dot{\gamma}^{n-1}$$

- Yielding materials like pastes, slurries and concentrated suspensions

- Stretched exponential-type relaxation.
- Multimode Maxwell behavior with only a few parameters.
- Quantifies offsets observed in Empirical rules such as the Cox-Merz rule, Gleissle mirror relations
- Agrees exactly with the Rutgers-Delaware rule.

Jaishankar and McKinley, *Journal of Rheology* ***58****(6)*, 2014.

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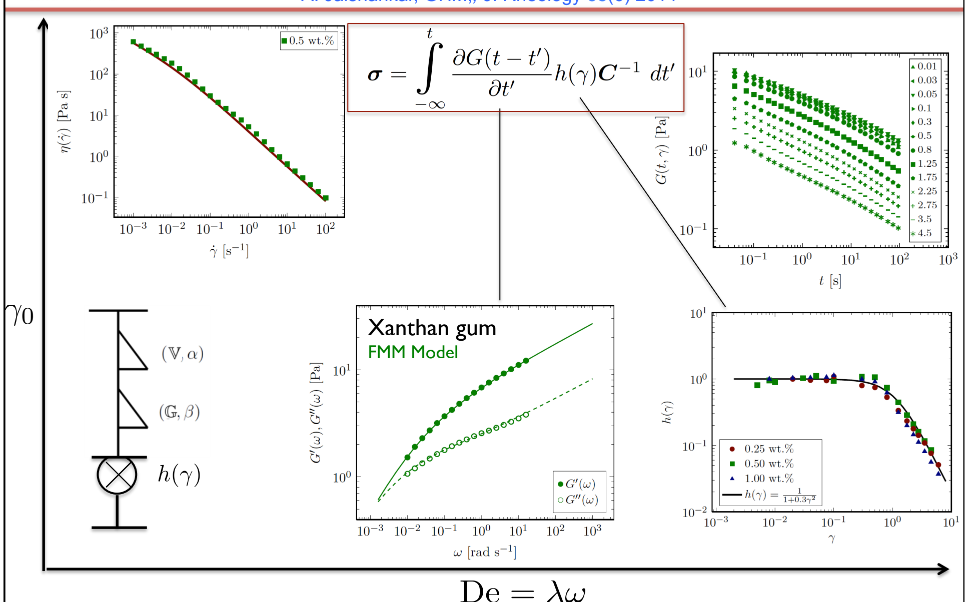
Nonlinear Rheology: The Fractional K-BKZ approach

A. Jaishankar, GHM,, J. Rheology **58**(6) 2014



A.C. Pipkin (1972); *Lectures in Viscoelasticity*

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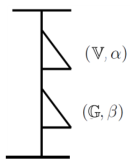
The Rhosetta Stone of Rheology

- Spring-pots and quasi-properties form the common language for transliteration between fractional calculus and important *"technological properties"* (Reiner, 1964)

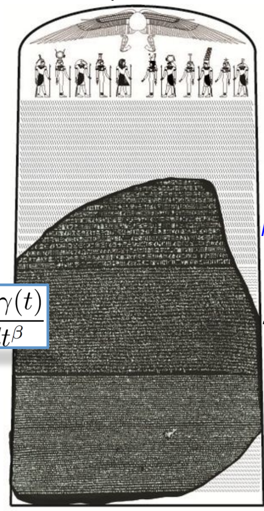


$$\sigma(t) = \mathbb{V}\frac{d^{\alpha}\gamma(t)}{dt^{\alpha}} + \mathbb{G}\frac{d^{\beta}\gamma(t)}{dt^{\beta}}$$

:

Fractional Calculus
The Mittag Leffler Function
The Caputo Derivative

$$\frac{d^{\alpha}\gamma(t)}{dt^{\alpha}} = \frac{1}{\Gamma(1-\alpha)}\int_0^t (t-t')^{-\alpha}\dot{\gamma}(t')\,dt'$$



hieroglyphics

"demotic"

Ancient Greek

"The Language of –Ness"
Firmness, Springiness
Stickiness, Tackiness
Sliminess, Stringiness
Cohesiveness
Chewiness
:

Quasiproperty

$$\mathbb{V} \doteq \left[\mathrm{Pa.s}^{\alpha}\right]$$

$$\sigma_{\mathrm{spring-pot}} = \mathbb{V}\frac{d^{\alpha}\gamma}{dt^{\alpha}}$$

http://en.wikipedia.org/wiki/Rosetta_Stone 41

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Acknowledgments

- **Aditya Jaishankar, Bavand Kesharvarz**

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