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

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with Aditya Jaishankar

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Department of Mechanical Engineering, MIT

Bingham Lecture
85th Annual Meeting of the Society of Rheology
Montréal, Québec October 2013

In Memoriam: Sean A. Collier

Gifts may be made to MIT for the Sean Collier Memorial Fund to establish the Collier Medal to be awarded to individuals who demonstrate the values of Officer Collier and other causes.

Outline

- Some History of G.W. Scott Blair and the Beginnings of the Society of Rheology
- Scott Blair, Soft Materials and Quasi-properties
  – The principle of intermediacy…
- Fractional Calculus and the "Spring-pot"
  – The Fractional Maxwell Model & Fractional Kelvin-Voigt Models
  – Nonlinear Deformations
- Applications to Real Materials and more complex flows

- 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"

Some History…

THE HISTORY

OF

THE SOCIETY OF RHEOLOGY

from

1924 - 1944

Compiled By

Eugene C. Bingham, A.B., Ph.D., Sc.D

Lafayette College

Easton, Pennsylvania

January, 1944

Scanned at the American Institute of Physics

Quoting W.H. Herschel (at the 3rd Plasticity Symposium, Lafayette College; 1928)

"I have always wondered what I am…

*…I know now, that I am a **Rheologist**"* (!)

"When the Society was organized in Washington in Dec. 1929 there was present as a Charter Member, Dr. George W. Scott Blair of England…"

e Lafayette

EASTON, PA., TUESDAY, NOVEMBER 26, 1935

'Panta Rhei' is Motto

Professor Bingham proposed the new word rheology formed from the Greek word "rheo" which is to "flow"—but "flow" in the larger sense of "deformation." Also at this meeting Professor Bingham brought forth the motto "panta rhei" or "everything flows." Although some naturally objected to the new word and its broadness, the majority of the men were satisfied and the new term held good.

The chemists and physicist found a certain satisfaction in having a name to call themselves by which really covered all that they were doing. That same year the Society of Rheology was formed with Professor Eugene C. Bingham as the first president. Immediately the new society became affiliated with the American Institute of Physics, which enabled it to publish rheological papers in the journal "Physics." At the present time there are about three hundred members in the society.

E.C.Bingham; ***History of the Society of Rheology 1924-1944***

AIP Niels Bohr Library for the History of Science

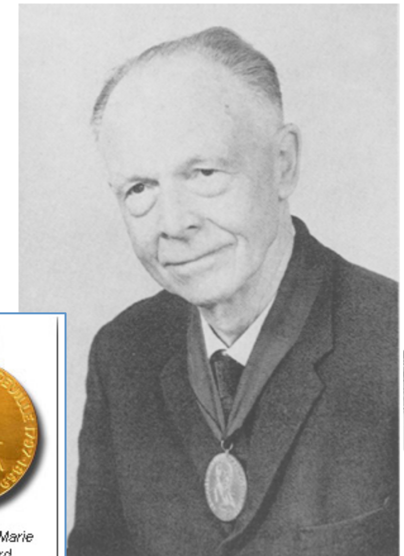
G.W. Scott Blair (1902-1987)

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.

Jean-Leonard-Marie Poiseuille Award



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

Psycho-rheology & Quasi-properties

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)

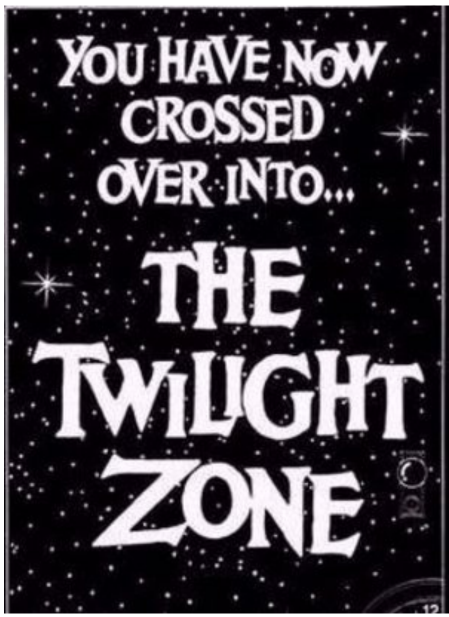
The behaviour of complex materials under stress is described in terms of entities which are not strictly 'physical properties'. These so-called 'quasi-properties' range from entities hardly distinguishable from dimensionally true physical properties to concepts which are much less clearly defined.

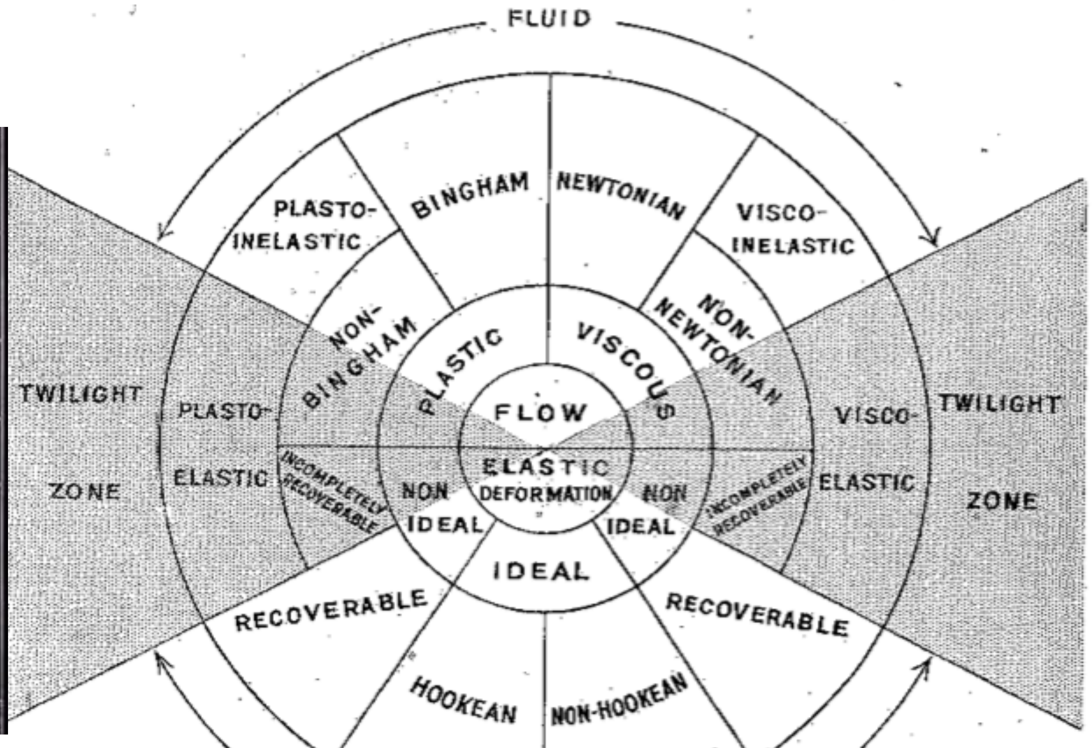
Firmness, Stickiness, Stringiness….the principle of intermediacy

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)

From Continuous Time Random Walks to Power-Law Rheology

Anomalous subdiffusion

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

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

$$0 < \alpha < 1$$

Continuous Time Random Walk (CTRW) →

Fractional Diffusion Equation

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

↓

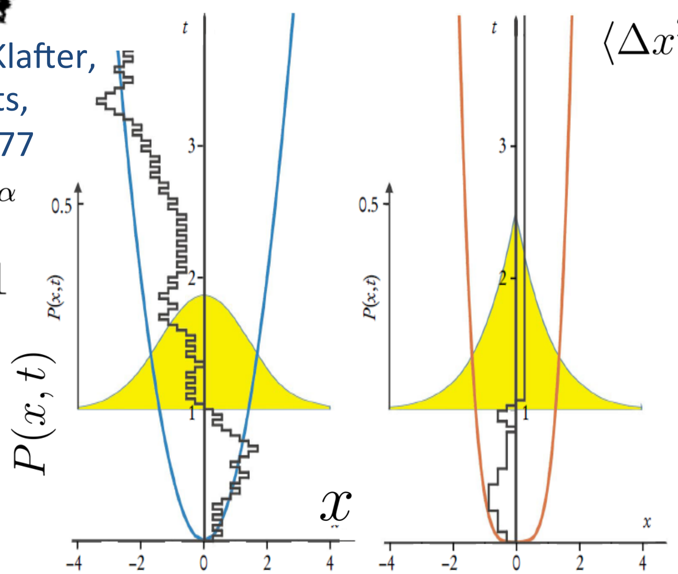
$$\langle \Delta x^2 \rangle \sim t^{\alpha}$$

Generalized Stokes Einstein Equation →

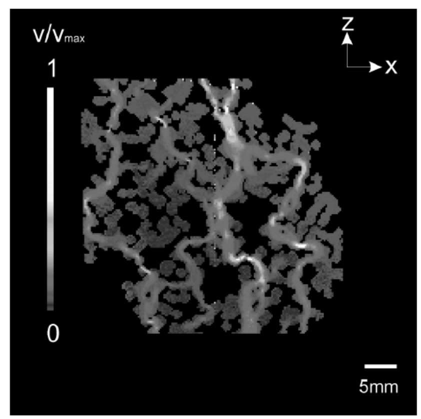
$$\tilde{G}(s) = \frac{k_B T}{\pi a s \langle \Delta \tilde{x}^2(s) \rangle}$$

Fractional Relaxation Modulus

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



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)

From Continuous Time Random Walks to Power-Law Rheology

Anomalous subdiffusion

Continuous Time Random Walk (CTRW)

→

Fractional Diffusion Equation

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

↓

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

Generalized Stokes Einstein Equation

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

→

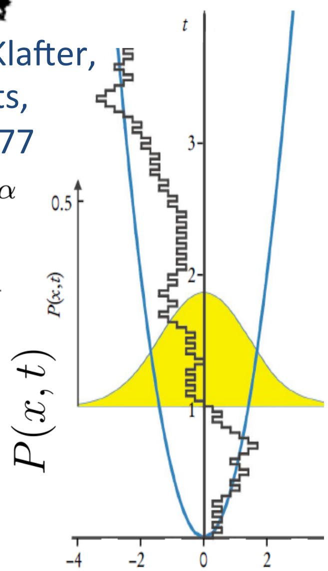
Fractional Relaxation

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

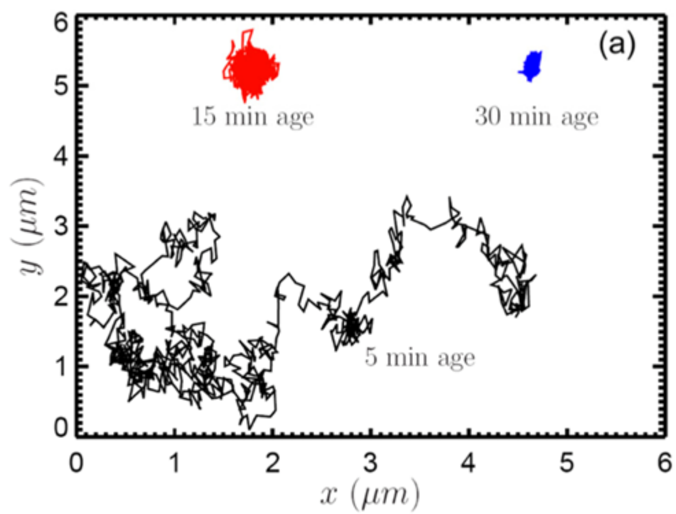
R. Metzler, J. Klafter, Physics Reports, (2000), 300:1-77

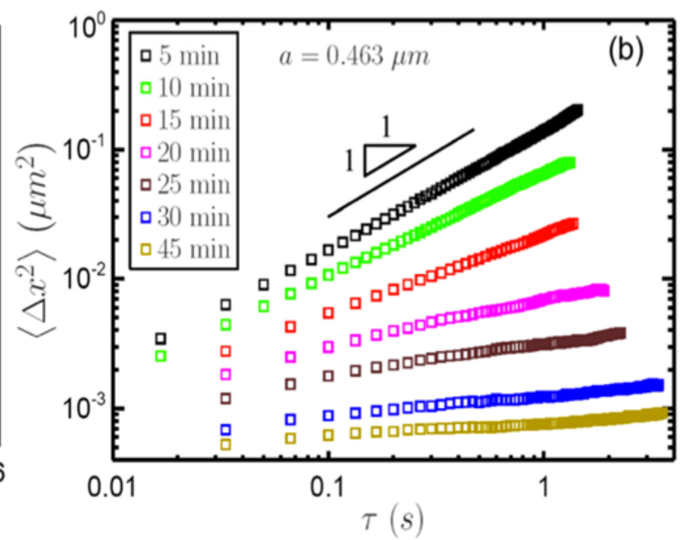
$$\langle \Delta x^2 \rangle \sim t^\alpha$$

$$0 < \alpha < 1$$



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



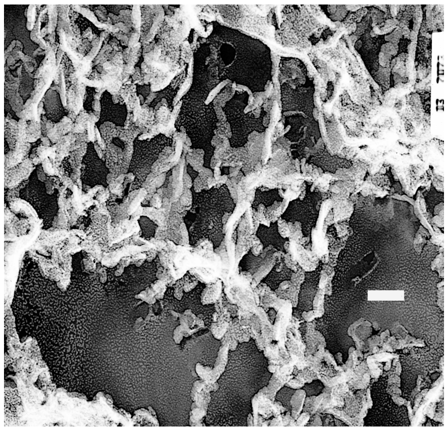


Rheological Aging in a Laponite Gel
Rich, McKinley, Doyle; *J. Rheology* **55**(2), 2011

HATSOPOULOS MICROFLUIDS LABORATORY

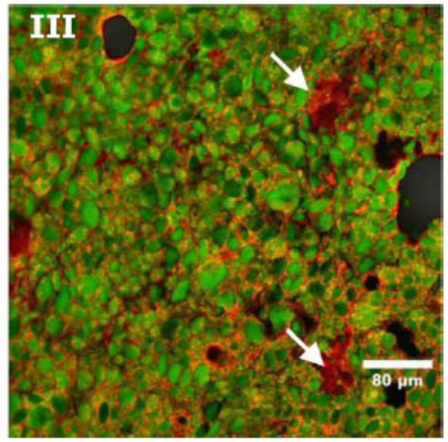
Ubiquity of Power-Law Rheology: Relationship to Microstructure

Laponite Dispersion



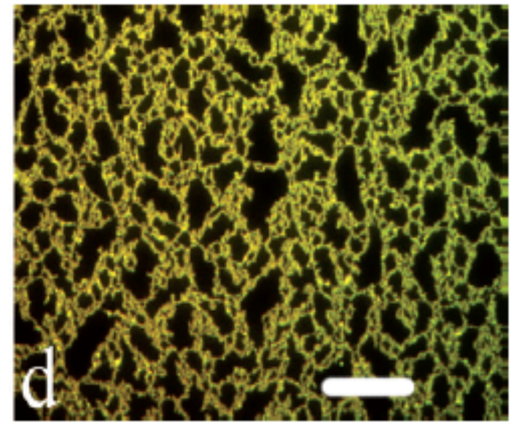
Courtesy J. W. Ruberti & Gavin Braithwaite (CPG)
Scale bar 30nm

Dough



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

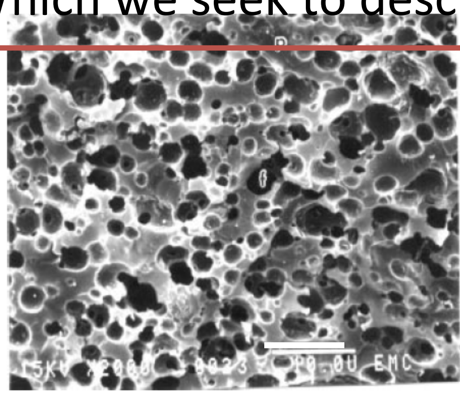
Air-solution interface of a Protein-Surfactant Mixture



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

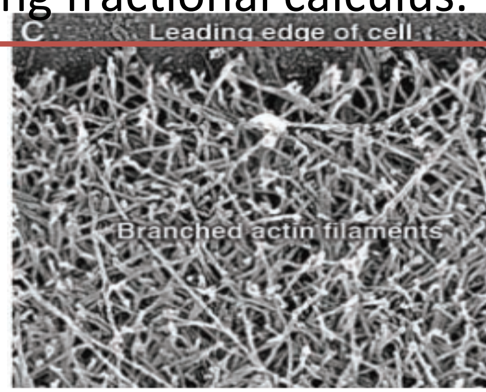
Scale-free fractal microstructure leads to scale-free power-law relaxation behavior
Which we seek to describe using fractional calculus.

Cheese



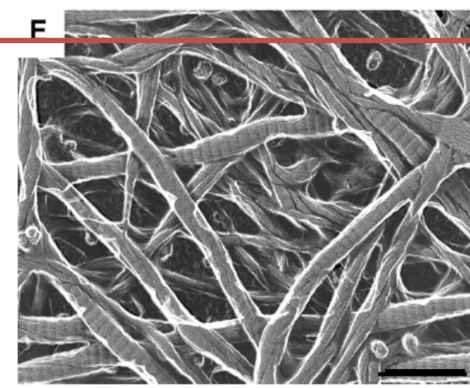
K. J. Aryana, Z. U. Haque, *Int. J. Food. Sci. Tech.*, 36, 2001. Scale bar 10 µm.

Actin Filaments



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

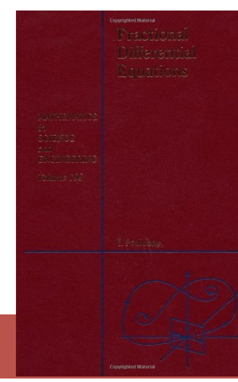
Collagen Matrix

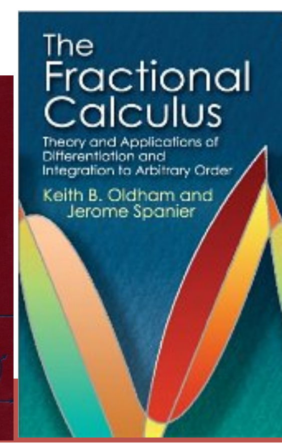


N Saeidi, E. A. Sander, J. W. Ruberti, *Biomaterials*, 30, 2009. Scale bar: 500 nm

A (Spring)-Potted History of Fractional Calculus in Rheology

- One of the earliest attempts at modeling power-law behavior was by P. G. Nutting: proposed the Nutting equation $\psi = \tau^{\beta}\gamma^{-1}t^{k}$ where β, k are constants.
- A. Gemant (1936) discussed the use of half differentials in rheology, but deemed it simply to be a useful mathematical symbol in later papers.
- G. W. Scott Blair (1939; 1947) greatly expanded Nutting's work, proposed the use of "intermediate" fractional differential equations through the principle of intermediacy and termed ψ a "quasi-property".
  - *Quasi-properties* are a class of quantities that differ from each other in dimensions of [M], [L] and [T]. For example the quantity $E\lambda^{\alpha}$ to be seen later. (*G* and *η* are special cases of a quasi-property for $\alpha = 0$ and $\alpha = 1$ respectively). Units of Quasi-properties: Pa s^{α}
- Bagley & Torvik, Koeller and Nonenmacher considered using *springpot elements* and constructing thermodynamically consistent constitutive models, and studied their response under various deformations.
- Schiessel & Blumen, and Heymans & Bauwens showed "tree" and "ladder" models can be reduced to fractional constitutive equations.
- **Podlubny** has contributed much to the physical meaning of fractional derivatives and numerical techniques to solve fractional differential equations (including MATLAB codes).





P. G. Nutting, *J. Franklin Inst.* (1921), **191**:679 and P. G. Nutting, *Proc. Amer. Soc. Test. Mater.* (1921), **21**:1162
G. W. S. Blair, B. C. Veinoglou and J. E. Caffyn, *Proc. Roy. Soc. Lond. A* (1947), **189**: 69-87
R. L. Bagley, *AIAA Journal,* (1988) **27**:1412-1417
R. L. Bagley and P. J Torvik, *J. Rheol.* (1986), **30**: Wharmby & Bagley, *J. Rheol.* (2013), **57**
H. Schiessel and A. Blumen, *J. Phys. Math, Gen.* (1993), **26**:5057-5069
N. Heymans and J. C. Bauwens, *Rheol. Acta.* (1994) **33**:210-219
** I. Podlubny, *Fractional Differential Equations*, 1999 (Academic Press)

A Rheometric Example

- Filler-matrix interactions (e.g. in filled elastomers), Hydrogen-bond interactions, hydrophobic "stickers",…

CONSTITUTIVE BEHAVIOR MODELING AND FRACTIONAL DERIVATIVES

Chr. Friedrich[a], H. Schiessel[b,c] and A. Blumen[b]

[a]Freiburg Materials' Research Center, Freiburg University, Stefan-Meier-Str. 21, 79104 Freiburg, Germany

[b]Theoretical Polymer Physics, Freiburg University, Rheinstr. 12, 79104 Freiburg, Germany

[c]Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA

Advances in the Flow & Rheology of Non-Newtonian Fluids (Parts A, B)
Eds: D.A.Siginer, D. DeKee, R.P. Chhabra (1999)

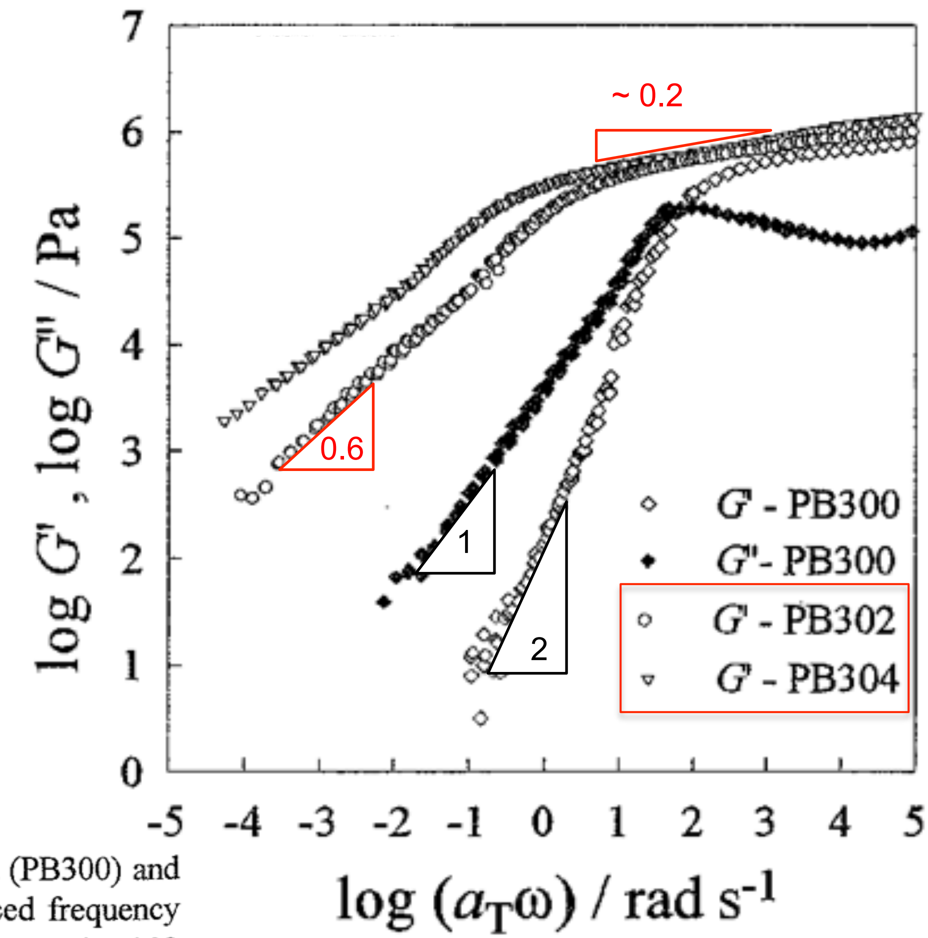
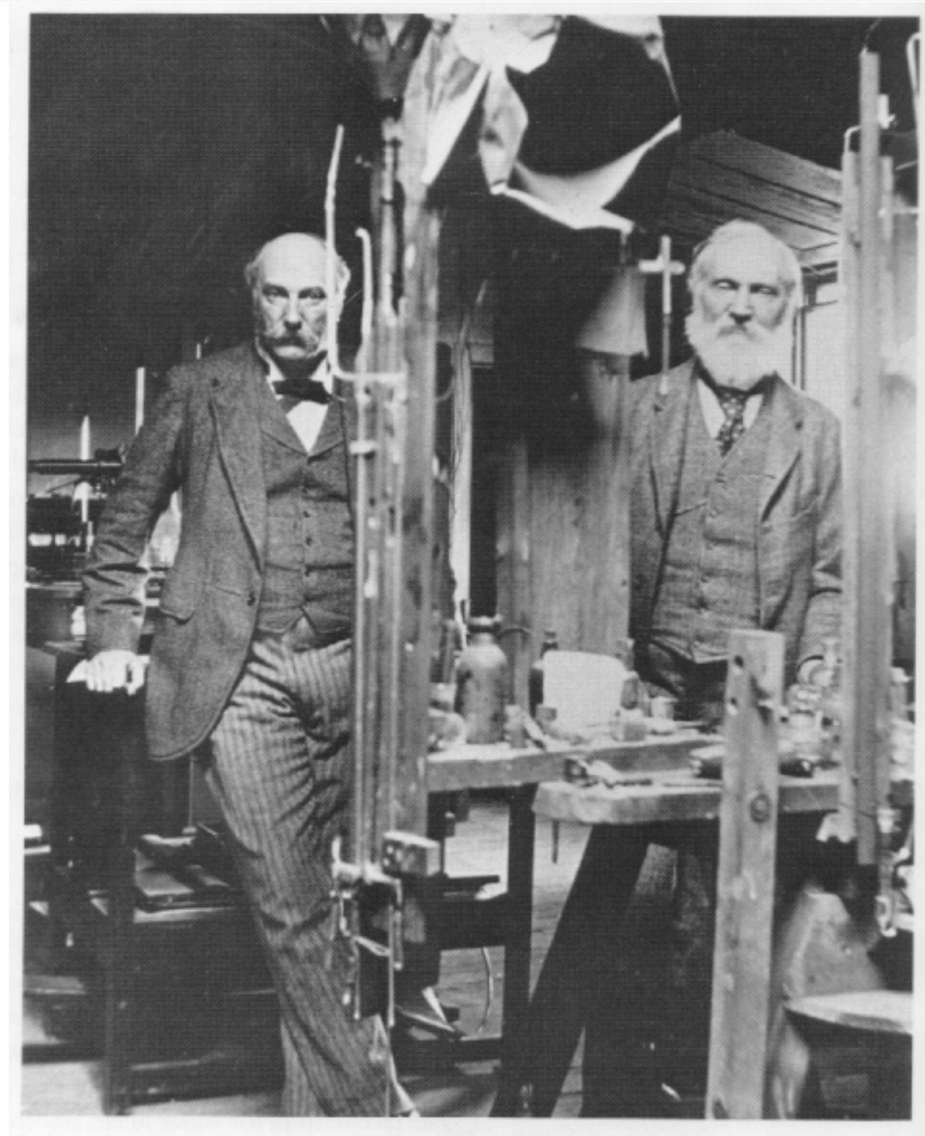


Figure 2. Storage modulus G' and loss modulus G'' of unmodified (PB300) and urazole modified polybutadiene (PB302 and PB304) vs. the reduced frequency $a_T\omega$. The molecular weight of all samples is M_W = 31 kg/mol; the samples 302 and 304 correspond to the 2 mol % and to the 4 mol % modification, respectively.

“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)



Mathematical Definitions: Fractional Calculus

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

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

Caputo Derivative:
(*Integro-Differentiation*)

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

(Ceiling)

If $0 < \alpha < 1$

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

$$G(t) = \frac{\sigma(t)}{\gamma_0} \sim t^{-\alpha}$$

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

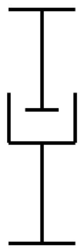
Laplace Transform: $\mathcal{L}\left\{\frac{d^\alpha}{dt^\alpha}\gamma(t); s\right\} = s^\alpha \tilde{\gamma}(s) - \sum_{k=0}^{n-1} s^{\alpha-k-1} \gamma^{(k)}(0), \;\; n-1 < \alpha \leq n$

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

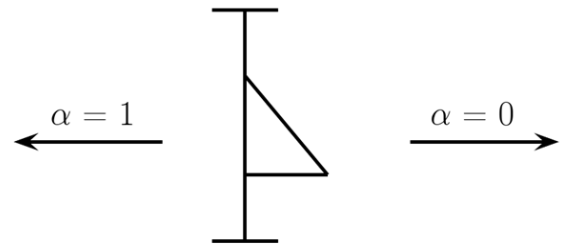
- We incorporate these fractional derivatives into constitutive equations by generalizing the ideas of **springs and dashpots**

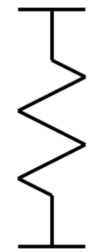
I. Podlubny, Fractional Differential Equations, *Academic Press*, 1999
T. Surguladze, *J. Math. Sci.*, (2002), 112: 4517-4557
T. Nonnenmacher, *Rheological Modelling: Thermodynamical and Statistical Approaches*, (1991), 7:309-320

The Springpot as an Intermediate Element

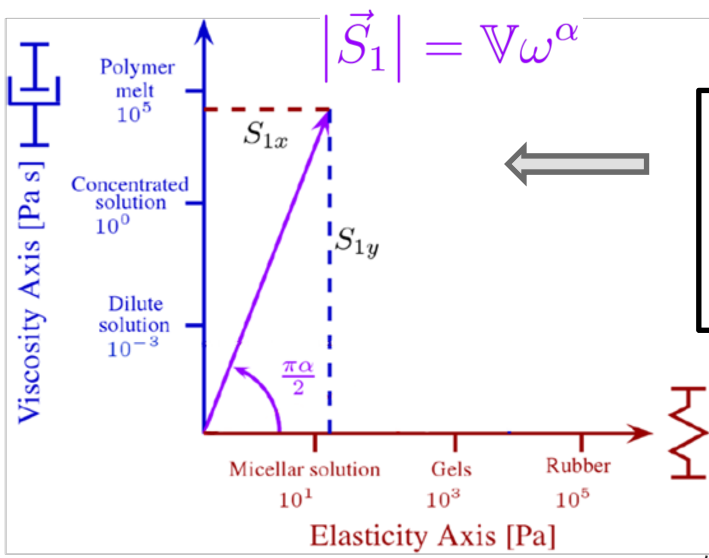


$\sigma_{dashpot} = \eta\dot{\gamma}$





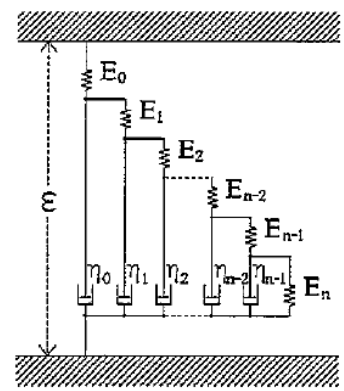
$\sigma_{spring} = G\gamma$



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

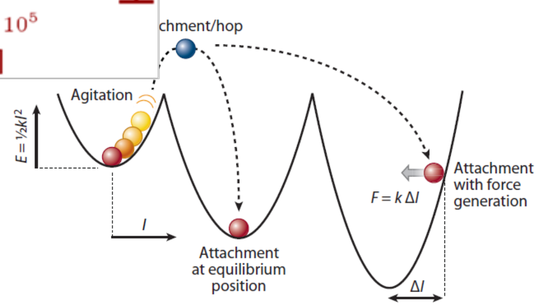
R. C. Koeller, *J. Appl. Mech.*, (1984), 51:299-307

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



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

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



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

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

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

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

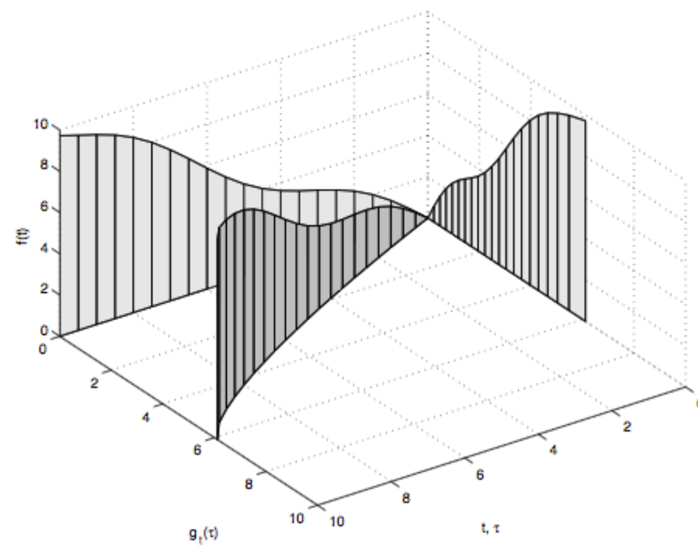
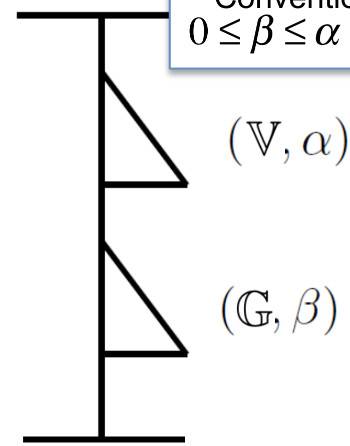


Figure 1: The "fence" and its shadows: ${}_0I_t^1 f(t)$ and ${}_0I_t^\alpha f(t)$, for $\alpha = 0.75$, $f(t) = t + 0.5\sin(t)$, $0 \le t \le 10$.

The Fractional Maxwell Model (FMM)

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

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

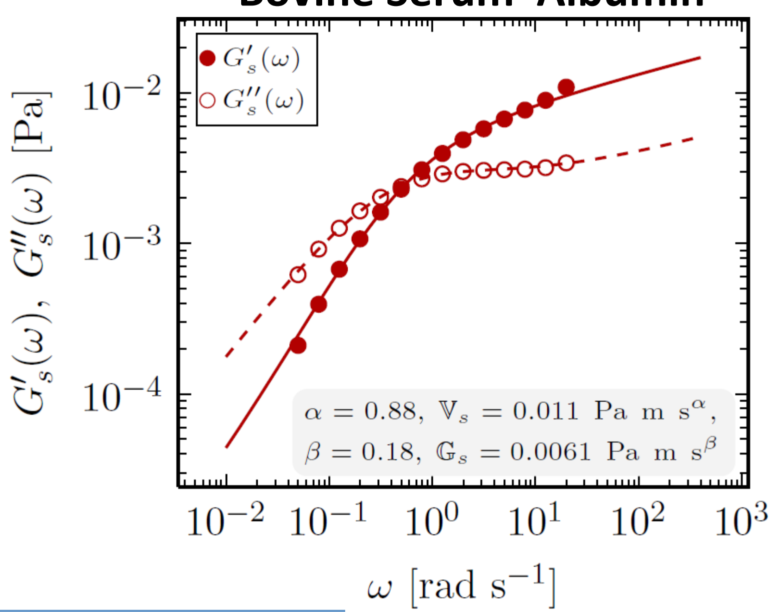


$\mathbb{V}$ and $\mathbb{G}$ are quasi-properties: $\mathbb{V} = E_1\lambda_1^{\alpha}$ $\mathbb{G} = E_2\lambda_2^{\beta}$

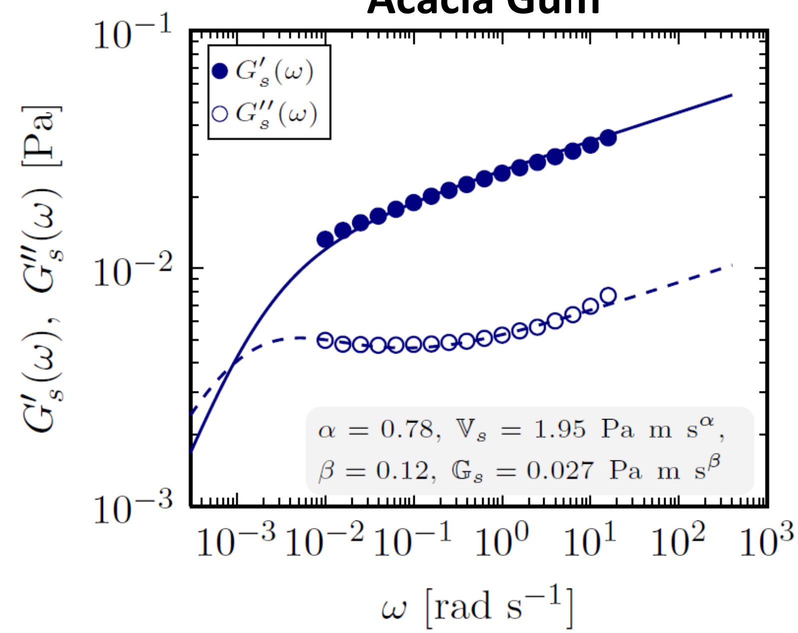
$$G'(\omega) = \frac{\mathbb{V}\omega^{\alpha}\cdot\mathbb{G}\omega^{\beta}[\mathbb{V}\omega^{\alpha}\cos(\pi\beta/2)+\mathbb{G}\omega^{\beta}\cos(\pi\alpha/2)]}{(\mathbb{V}\omega^{\alpha})^2+(\mathbb{G}\omega^{\beta})^2+2\mathbb{V}\omega^{\alpha}\cdot\mathbb{G}\omega^{\beta}\cos(\pi(\alpha-\beta)/2}$$

- Reduces correctly to Maxwell Model for α = 1 and β = 0

Bovine Serum Albumin



Acacia Gum



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

The Mittag-Leffler Function

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

Relaxation modulus for FMM

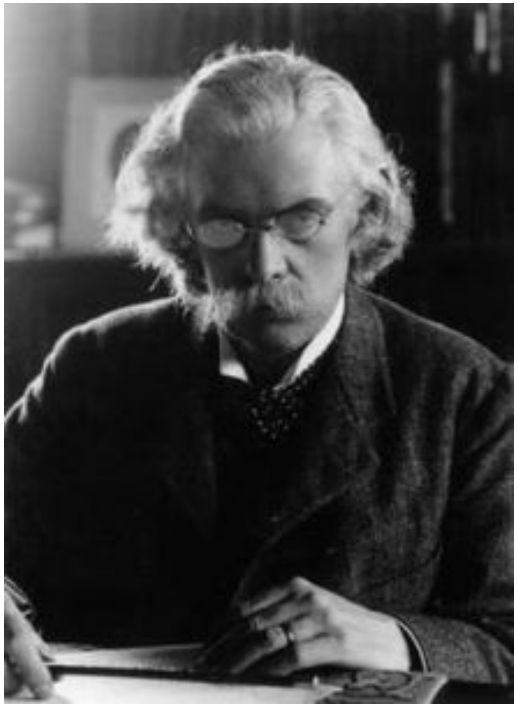
$$G(t) = \mathbb{G} t^{-\beta} E_{\alpha-\beta,1-\beta}\left(-\left(\frac{t}{\lambda}\right)^{\alpha-\beta}\right)$$

- 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 $\beta = 0$, but this result is general)

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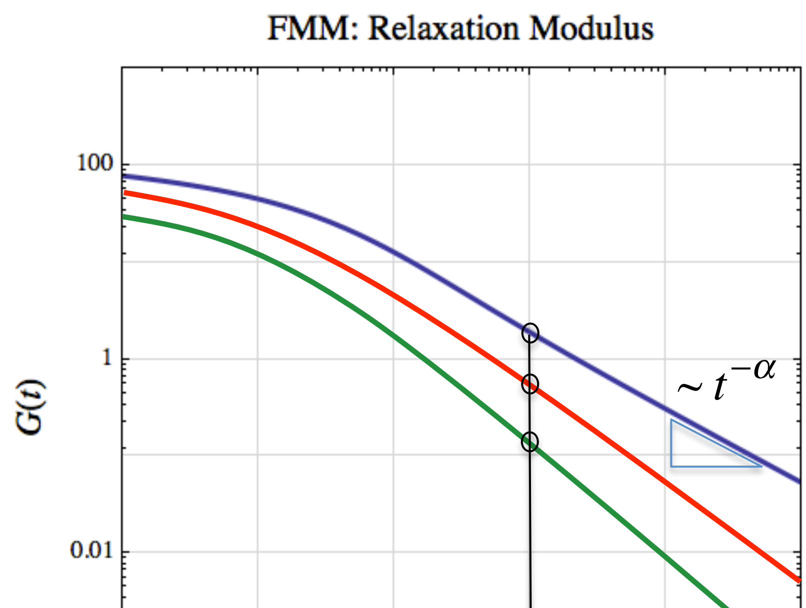
What are Quasi-properties?

- 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!



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

Consistent with the common (pragmatic) practice of comparing:

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

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

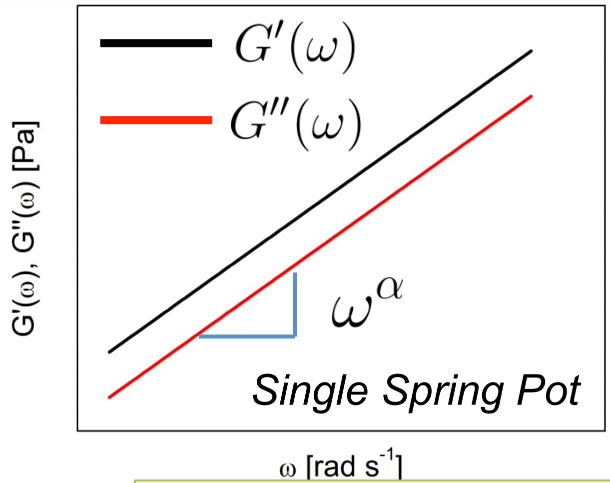
$$G(t_{ref}) = \left(\mathbb{V} t_{ref}^{-\alpha}\right)\left(t/t_{ref}\right)^{-\alpha}$$

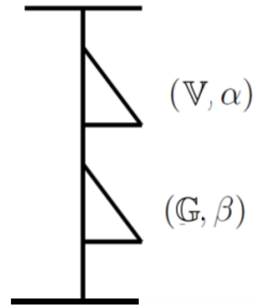
Reported value

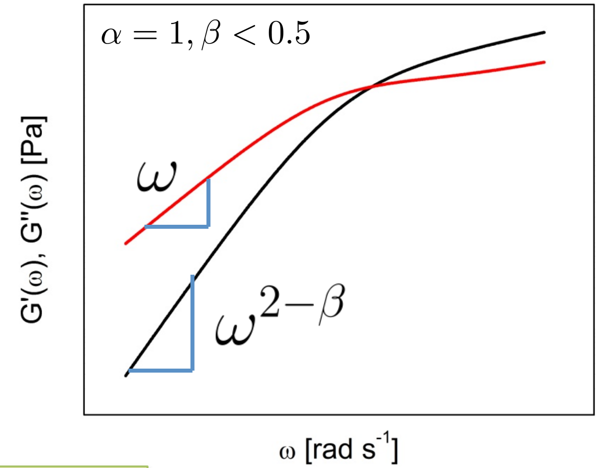
> In spite of the phenomenological nature of our approach, our results are far from being purely empirical or unrelated to fundamental concepts, but the fundamental concepts are not molecular but are concerned with the judgment of the rheological behaviour of materials by handling. Such judgments are 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*

Versatility of Two Element Fractional Models

Fourier Transform to evaluate complex modulus



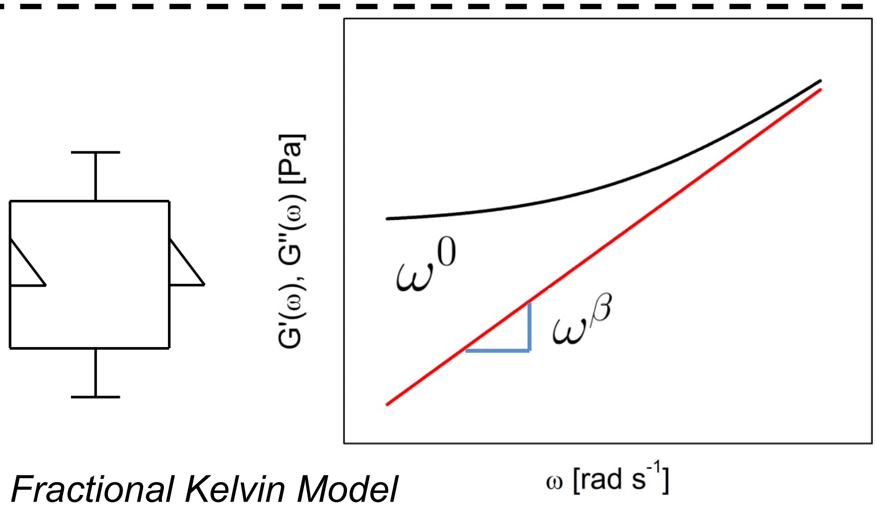




Cross-over Time

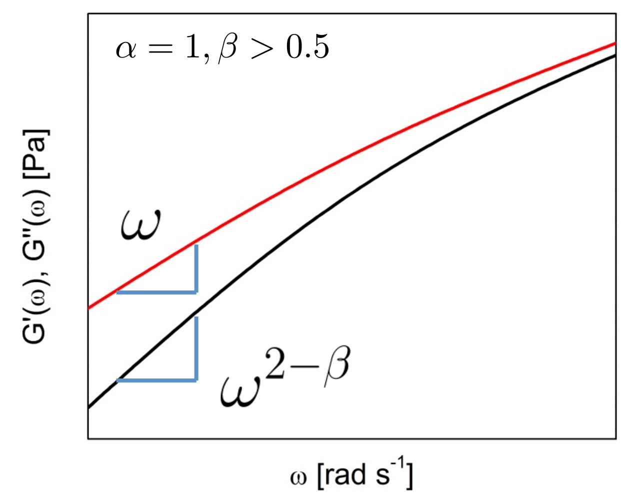
$$\lambda = \left(\frac{\mathbb{V}}{\mathbb{G}} \left[\frac{\cos(\pi\beta/2) - \sin(\pi\beta/2)}{\sin(\pi\alpha/2) - \cos(\pi\alpha/2)} \right] \right)^{\frac{1}{\alpha-\beta}}$$

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



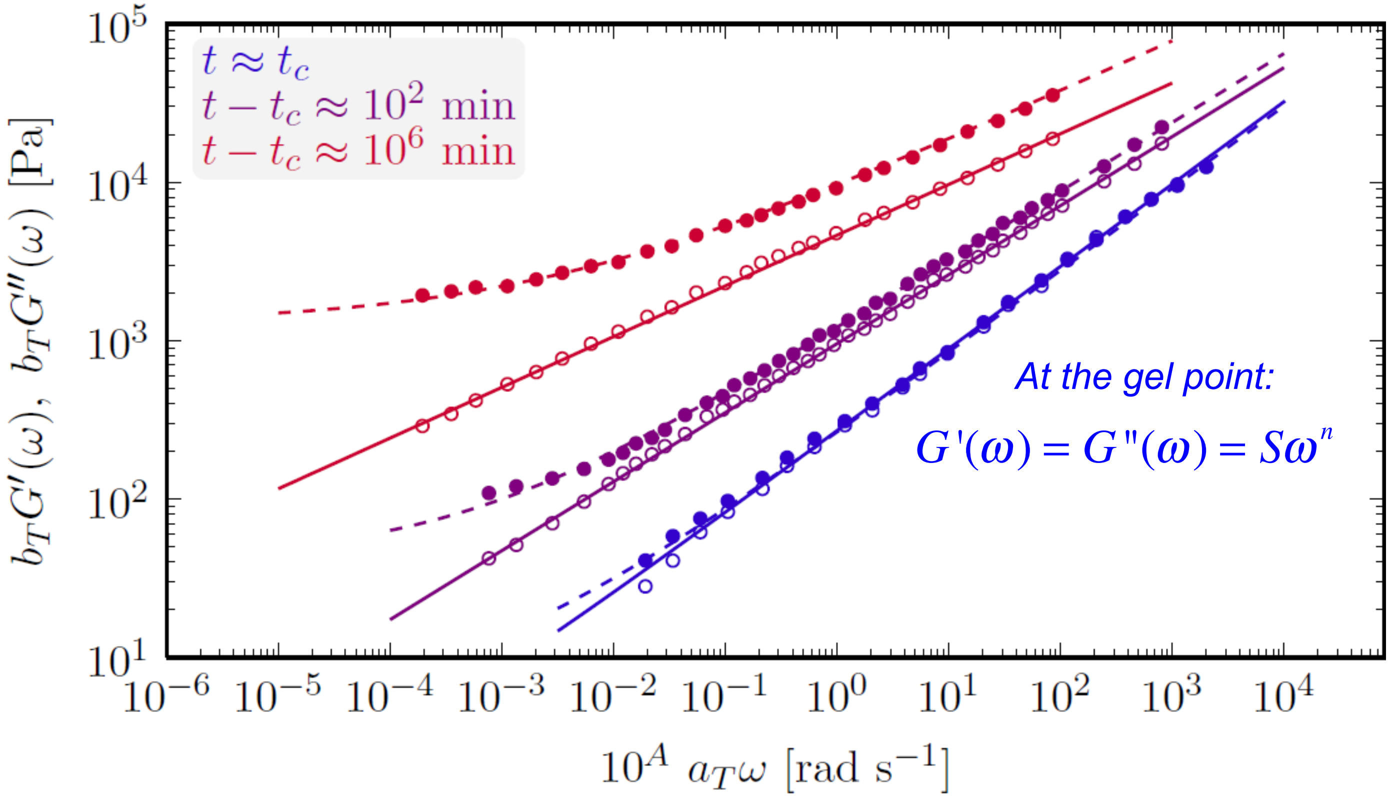
Fractional Kelvin Model

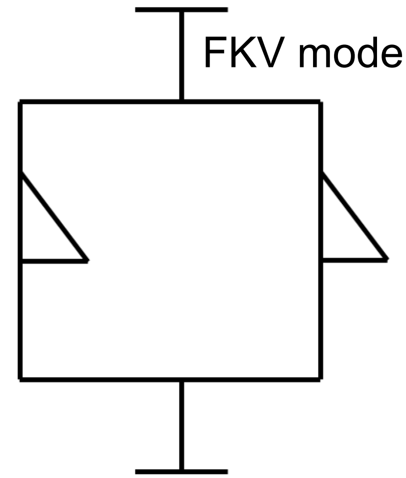
DEMO



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

Critical Gels (& beyond criticality)





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

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

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.

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

$t - t_c$ [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

Power-Laws Everywhere!

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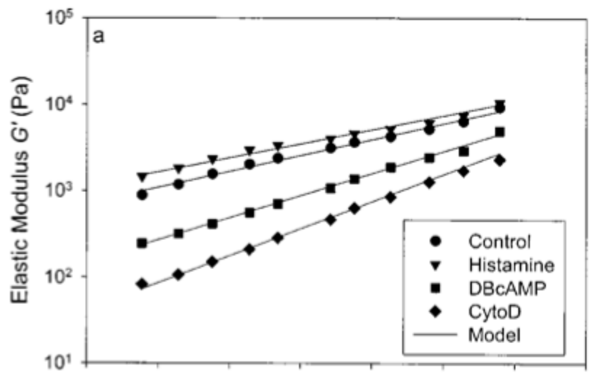
- The human body is a collection of soft solids, complex fluids and power-law rheology

Airway, Smooth Muscle

Fredberg & Coworkers

Ann. Biomed Eng. 2003



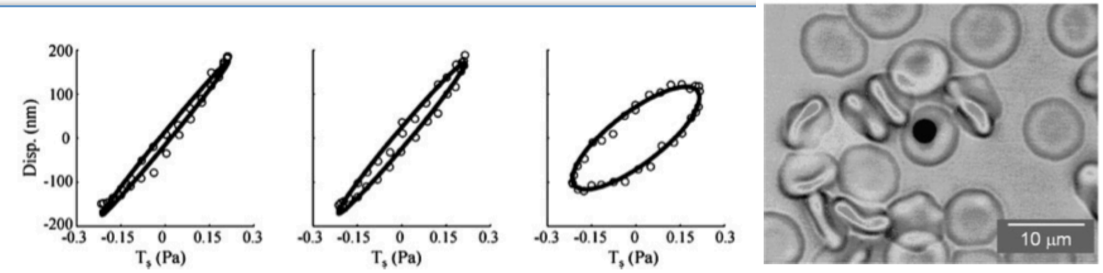


Fig. 4. RBC response to sinusoidal loading (0.75, 4, 30, and 100 Hz), applied specific torque T_s as a function of time *t* (*top* row); lateral displacement as a function of time *t* (*middle* row), where t_{max} is the duration of the 5 cycles; and displacement-torque loops for a representative bead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

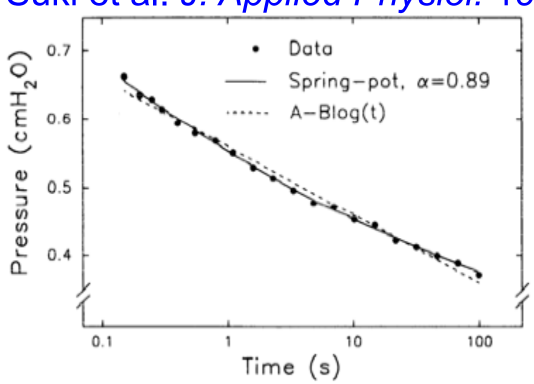
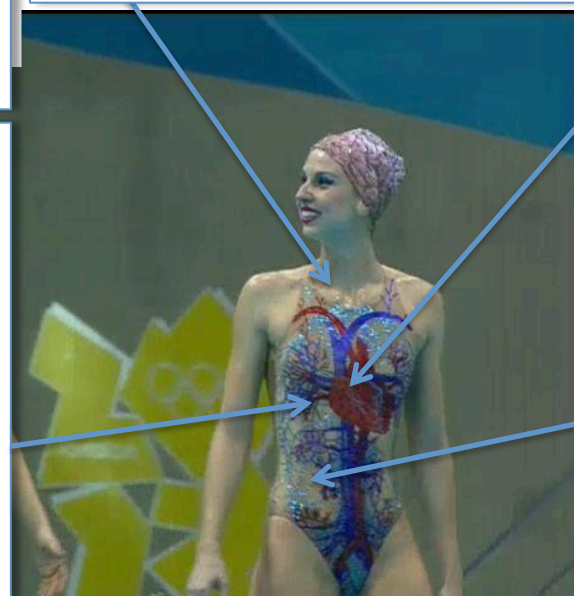


FIG. 3. Fits of power law relaxation (*Eq. 2*) and relaxation predicted by *Eq. 1* to stress relaxation in a rat lung taken from Peslin et al. (41). *A*, *B*, and α, parameters; *t*, time.

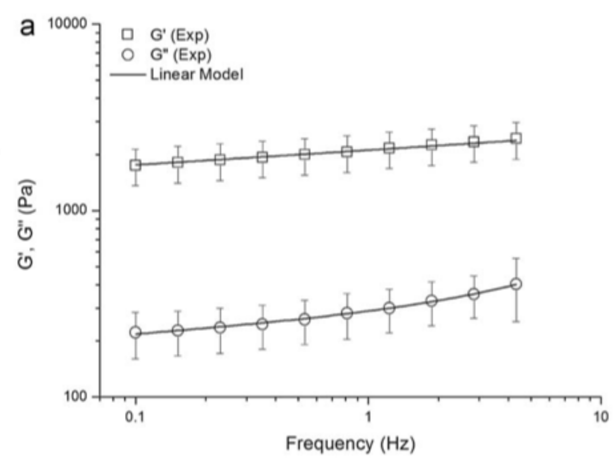


London Olympics 2012

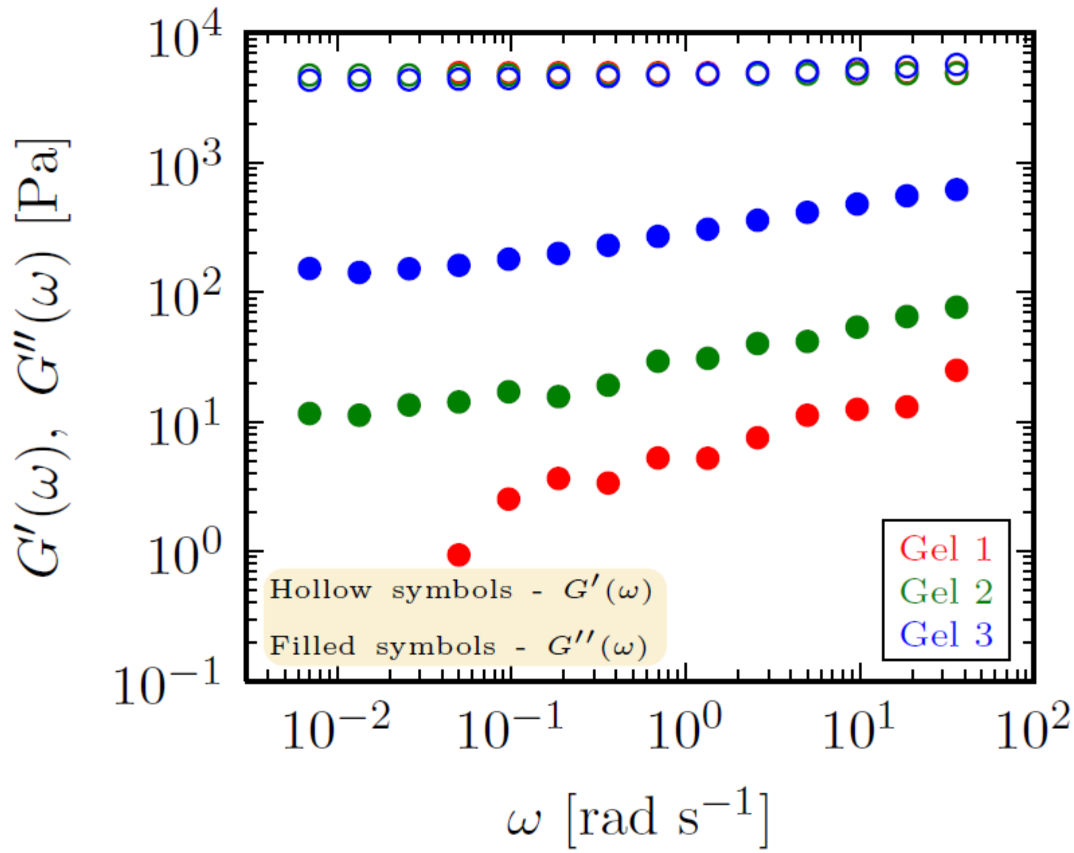
Liver & Kidneys

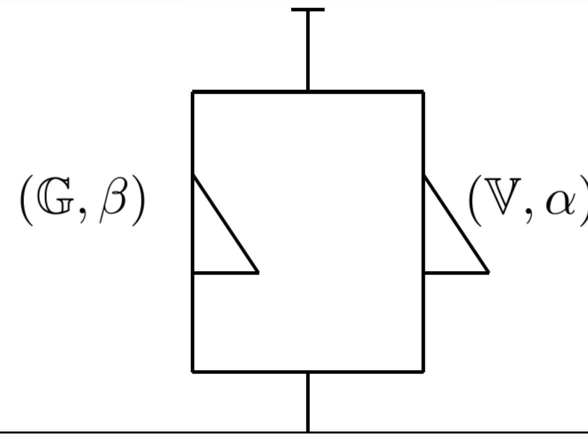
Nicolle, Vezin & Palierne

J. Biomech. 2010



'Creepy Gels' & The Fractional Kelvin Voigt Model





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

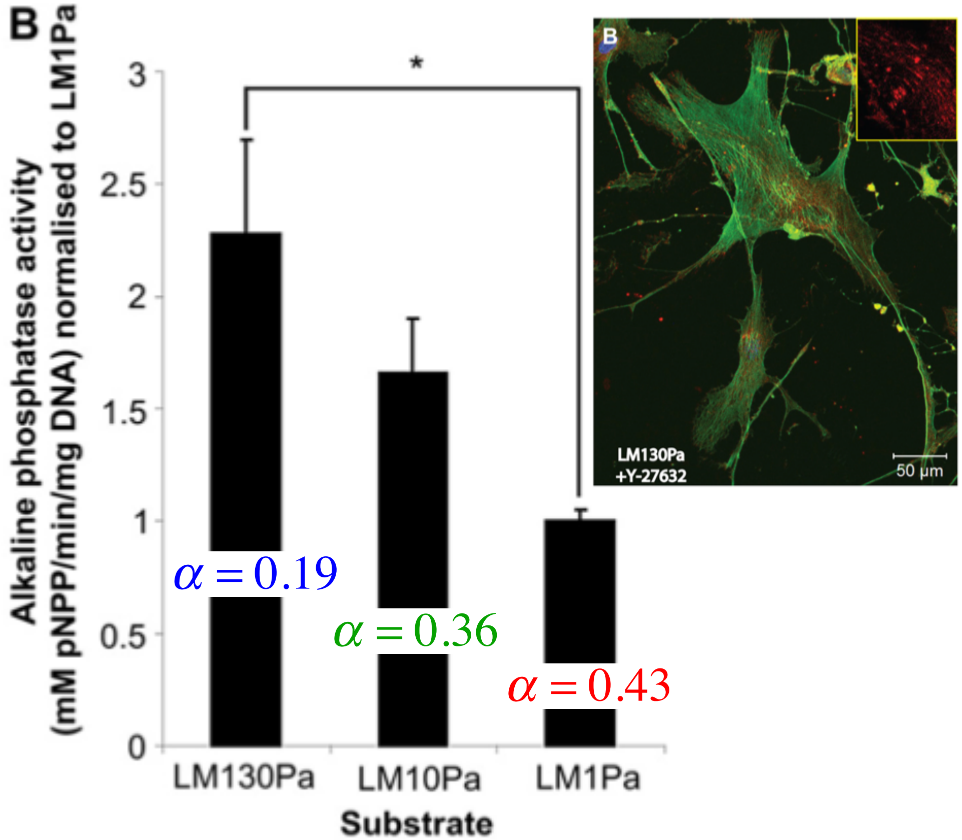
$$G'(\omega) = \mathbb{V}\omega^\alpha \cos\left(\frac{\pi}{2}\alpha\right) + \mathbb{G}\omega^\beta \cos\left(\frac{\pi}{2}\beta\right)$$
$$G''(\omega) = \mathbb{V}\omega^\alpha \sin\left(\frac{\pi}{2}\alpha\right) + \mathbb{G}\omega^\beta \sin\left(\frac{\pi}{2}\beta\right)$$

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

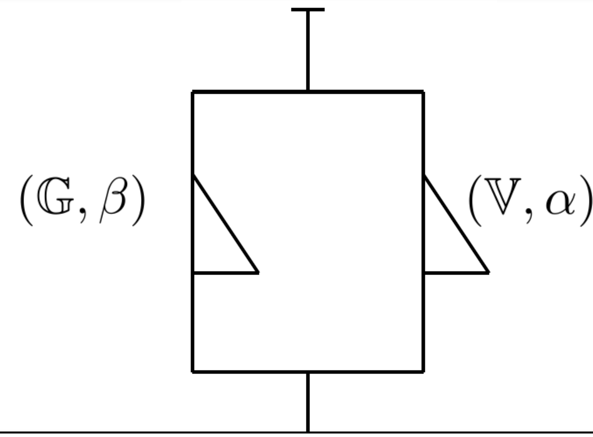
Only *three* parameters required (β = 0) to capture the rheological behavior of these protein gels across the whole experimental range of data.

'Creepy Gels' & The Fractional Kelvin Voigt Model



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.

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



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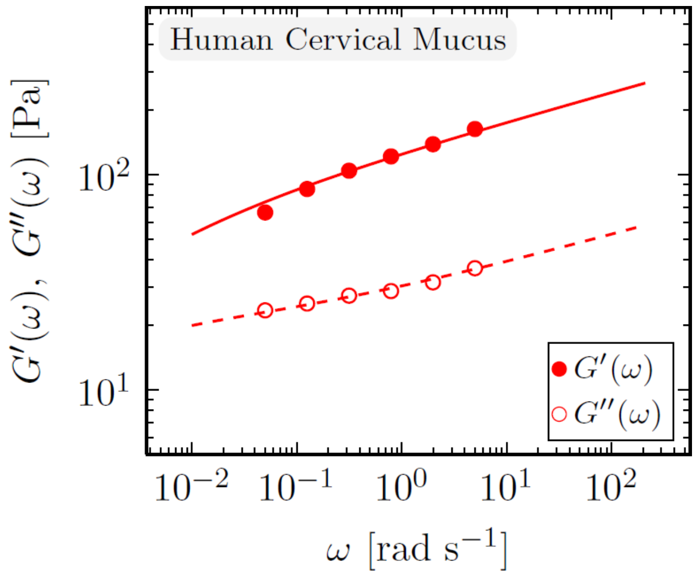
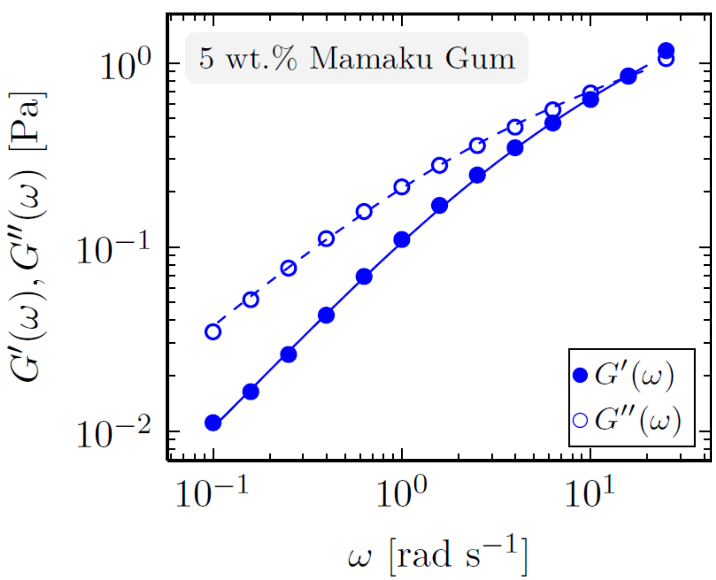
Versatility of Two-Element Fractional Models: Data

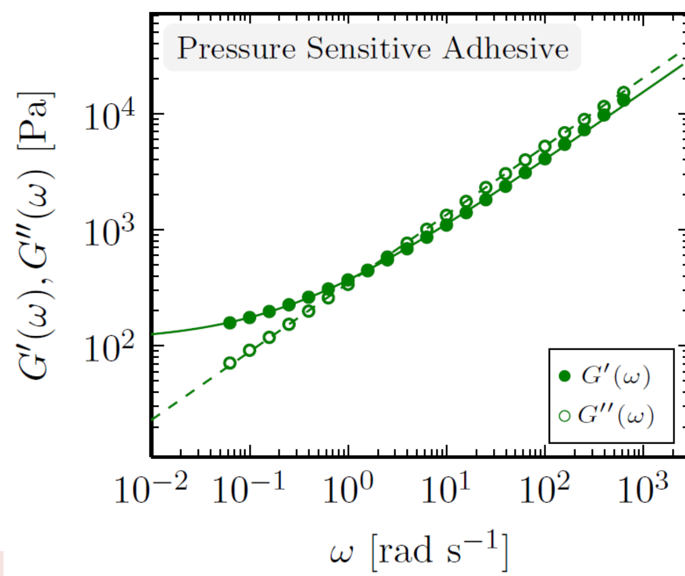


Cervical Mucus
Quasiproperty strongly correlated with preterm birth risk
Grace Yao, AJ, GHM et al., PLoS ONE, 2013

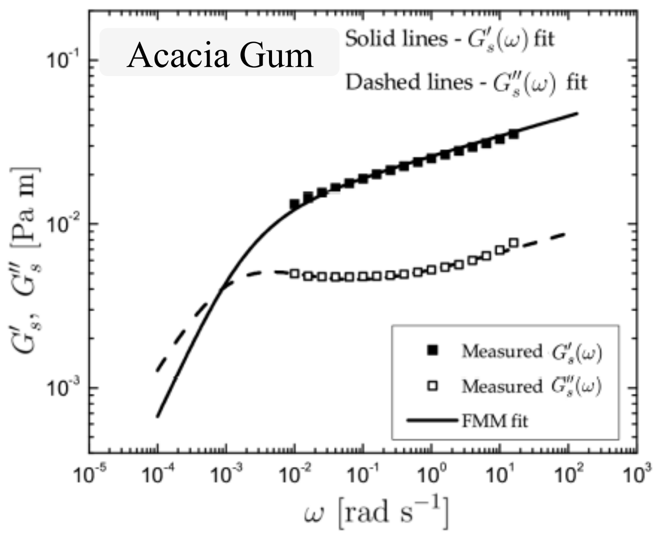


Mamaku Gum (Black Fern)
Jaishankar A., Wee M., McKinley G.H., *et al.,* SOR Pasadena, 2013

Silicone Pressure Sensitive Adhesive
Data from Wyatt N.B. , Grillet A.M., Hughes L.G. , SOR 2013



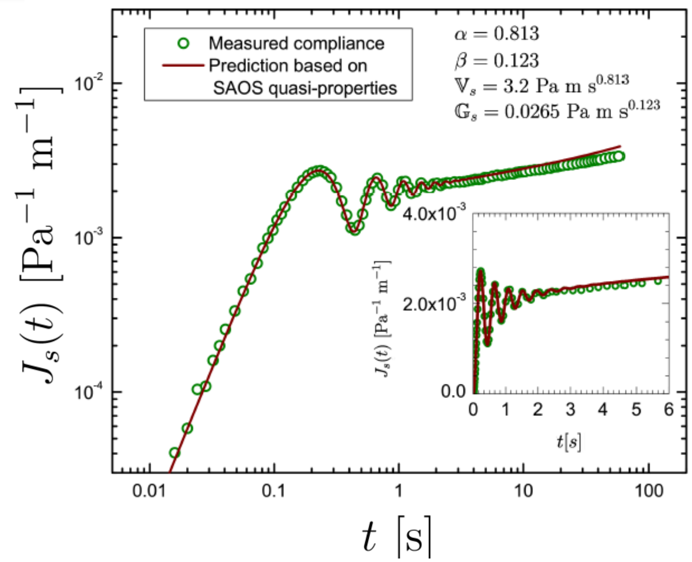
Predictions Using Fractional Material Response

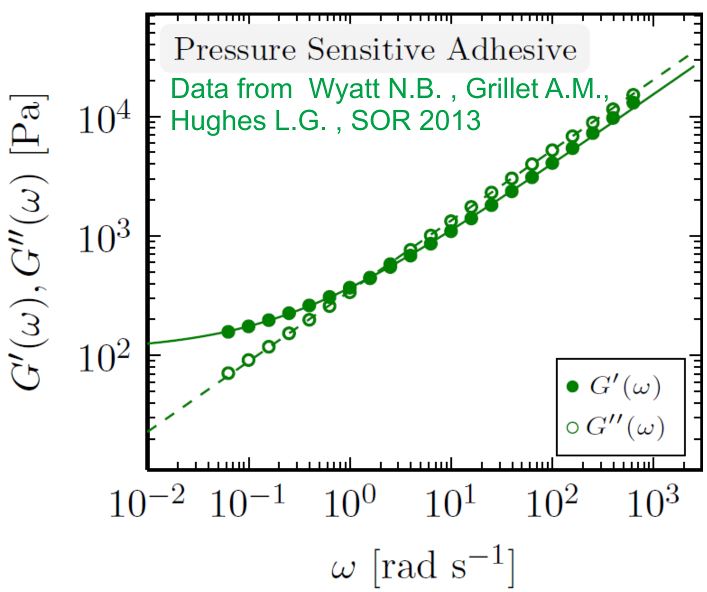


a priori prediction of creep ringing from SAOS

Interfacial rheometry

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

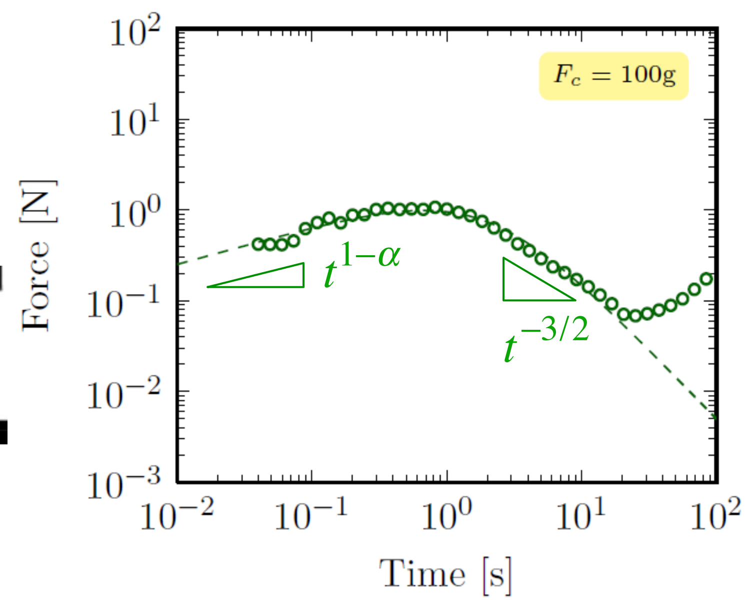




Prediction of tack force from SAOS

Extensional rheometry

Jaishankar, A. GHM, et al., SOR2013 Paper GS21 *Thursday Morning, 9:30am*



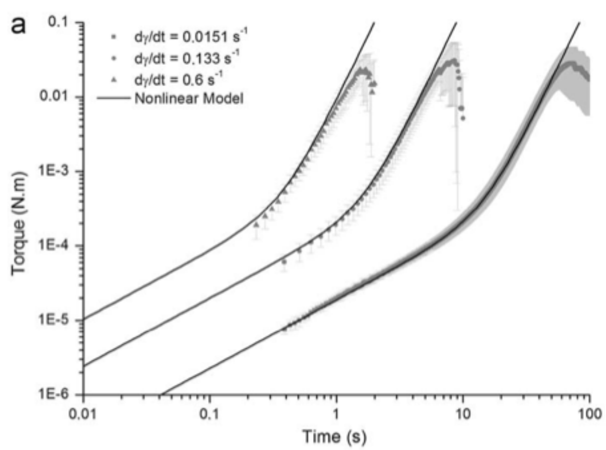
Where Next? Nonlinear Fractional Models

- Limited to description of *linear viscoelastic properties*; need to incorporate finite strain deformations
- Formulation of the Fractional Upper Convected Maxwell Model (FUCM)
  - Correctly done by Yang, Lam & Zhou JNNFM 2010

$$\tau_{ij} = \tau_{[0]ij}(\mathbf{r}, t, t) = \int_0^t G(t - t'')\gamma_{[1]ij}(\mathbf{r}, t, t'')\mathrm{d}t'',$$

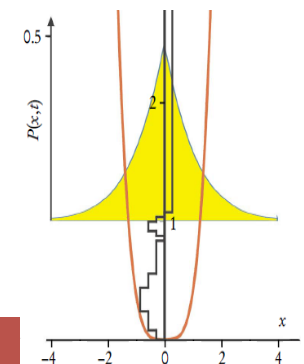
where $G(t)$ is the relaxation modulus:

$$G(t) = E\left(\frac{t}{\lambda}\right)^{\alpha-\beta} E_{\alpha,1-\beta+\alpha}\left[-\left(\frac{t}{\lambda}\right)^{\alpha}\right].$$



- Measurements show that the Cox-Merz Rule is alive and well for these kinds of materials
  - V. Sharma, B. Keshavarz, GHM *In Prep* (2013)
- Time-Strain Separability appears to hold
  - Bread Dough; Roger Tanner & coworkers (2002-2012)
  - Gluten Gels; Trevor S.-K. Ng & GHM, *J. Rheol* (2008, 2010)
  - Kidney Tissue; Palierne & coworkers, *J. Biomech* (2010)

- (Non)Brownian Dynamics of Dumbbells/Network Segments
  - Modify underlying dynamics from usual Weiner process
  - Instead sample from a **Mittag-Leffler Distribution**
  - Yun Zhang, Lin Zhou & Pam Cook, Paper GS13, Wed. 2:20pm



Summary

- The language of *fractional calculus*, *spring-pots* and *quasi-properties* provide an **ontology** for describing the properties of real-world soft materials
  - Quantitatively capture the linear viscoelastic properties of real materials in a compact format
  - Analytic expressions are available for creep, LVE, step strain (*Mittag-Leffler function*)…
- The familiar Maxwell and Kelvin-Voigt models are thus **special cases** of a more general (and more generally applicable) class of fractional LVE models
- Quasi-properties differ from material to material in the dimensions of mass *M*, length *L* and time *T*, depending on the power α. It may thus be argued (G.W. Scott Blair *et al*.) that they are not true material properties because they contain non-integer powers of the fundamental dimensions of space and time.
- Such quasi-properties appear to compactly describe textural parameters such as the 'firmness' and 'tackiness' of real-world material.

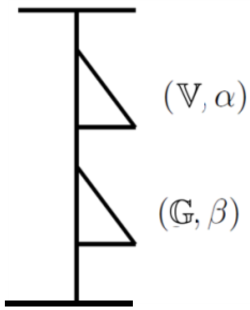
They are numerical measures of a dynamical process (such as creep or relaxation) in a material rather than of an equilibrium state.

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)

"The Language of –Ness"

Firmness, Springiness
Stickiness, Tackiness
Sliminess, Stringiness
Cohesiveness
Chewiness
:



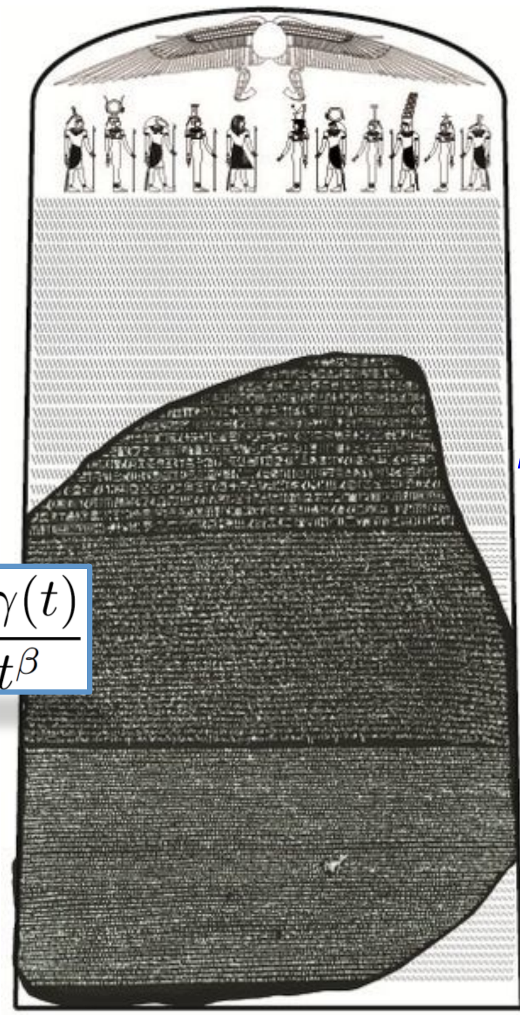
$$\sigma(t) = \mathbb{V}\frac{d^\alpha \gamma(t)}{dt^\alpha} + \mathbb{G}\frac{d^\beta \gamma(t)}{dt^\beta}$$

:

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

Quasiproperty

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

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

With Thanks to

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  Paula Vasquez
  Nahn-Ju Kim
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  Laura Casanellas
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  Aditya Jaishankar
  Bavand Keshavarz
  Justin Kleingartner
  Divya Panchanathan
  Setareh Shahsavari
  Michela Geri
  Caroline Wagner

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  Peyman Pakdel
  Alp Öztekin
  Aaron Avagliano
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  Gavin Braithwaite
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  Christian Clasen
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  Hojun Lee
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  Osman Basaran
  Gary Leal
  Ron Larson
  Tom McLeish
  David James
  Susan Muller
  Tam Sridhar
  David Boger
  Adam Burbidge
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