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

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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”
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…”
GEORGE WILLIAM SCOTT BLAIR MA PhD DSc FRIC FInstP (1902-1987) — ‘THE MAN AND HIS WORK’

by

Prof. Howard A. Barnes, OBE, DSc, FEng,
Unilever Research, Port Sunlight, CH63 3fW.

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)
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
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.
From Continuous Time Random Walks to Power-Law Rheology

Anomalous subdiffusion

Continuous Time Random Walk (CTRW)

Fractional Diffusion Equation

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

Generalized Stokes Einstein Equation

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

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

0 < \alpha < 1


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


Fractional Relaxation Modulus

\[ G(t) = S t^{-\alpha} \]
From Continuous Time Random Walks to Power-Law Rheology

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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

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

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


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

$$0 < \alpha < 1$$


Rheological Aging in a Laponite Gel

Rich, McKinley, Doyle; J. Rheology 55(2), 2011
Ubiquity of Power-Law Rheology: Relationship to Microstructure

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

Laponite Dispersion
Courtesy J. W. Ruberti & Gavin Braithwaite (CPG)

Dough

Dough Air-solution interface of a Protein-Surfactant Mixture

Cheese

Collagen Matrix
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 $\beta$, $k$ 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 $\psi$ 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 $\eta$ are special cases of a quasi-property for $\alpha = 0$ and $\alpha = 1$ respectively). **Units of Quasi-properties:** Pa s$^\alpha$
- 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).

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**References**

A Rheometric Example

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

CONSTITUTIVE BEHAVIOR MODELING AND FRACTIONAL DERIVATIVES

Chr. Friedrich\textsuperscript{a}, H. Schiessel\textsuperscript{b,c} and A. Blumen\textsuperscript{b}

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Figure 2. Storage modulus $G'$ and loss modulus $G''$ of unmodified (PB300) and urazole modified polybutadiene (PB302 and PB304) vs. the reduced frequency $\alpha_T \omega$. 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)
The fractional derivative is a linear operator:

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

Laplace Transform:

\[
\mathcal{L} \left\{ \frac{d^{\alpha}}{dt^{\alpha}} \gamma(t); s \right\} = s^{\alpha} \bar{\gamma}(s) - \sum_{k=0}^{n-1} s^{\alpha-k-1} \gamma^{(k)}(0), \quad n - 1 < \alpha \leq n
\]

Fourier Transform:

\[
\mathcal{F} \left\{ \frac{d^{\alpha}}{dt^{\alpha}} \gamma(t); \omega \right\} = (i\omega)^{\alpha} \tilde{\gamma}(\omega)
\]

\[\text{Example:} \quad \frac{d^{1/2}}{dt^{1/2}} \left\{ \frac{d^{1/2} x}{dt^{1/2}} \right\} = \frac{d^1 x}{dt^1}\]

If \(0 < \alpha < 1\):

\[
\frac{d^{\alpha}}{dt^{\alpha}} \gamma(t) = \frac{1}{\Gamma(1-\alpha)} \int_0^t (t-t')^{-\alpha} \bar{\gamma}(t') \, dt'
\]

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

\[\text{We incorporate these fractional derivatives into constitutive equations by generalizing the ideas of springs and dashpots}\]

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I. Podlubny, Fractional Differential Equations, Academic Press, 1999
The Springpot as an Intermediate Element

\[ \sigma_{\text{dashpot}} = \eta \dot{\gamma} \]

\[ \sigma_{\text{spring}} = G \gamma \]

\[ |\bar{S}_1| = \nabla \omega^\alpha \]

SGR model: Simplest case: Exponential distribution of energy states


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](image.png)

Figure 1: The “fence” and its shadows: $0I_t^1 f(t)$ and $0I_t^\alpha f(t)$, for $\alpha = 0.75$, $f(t) = t + 0.5 \sin(t)$, $0 \leq t \leq 10$. 

Fractional Calculus and Applied Analysis 5(4), 2002
The Fractional Maxwell Model (FMM)

\[ \tau + \frac{V}{G} \frac{d^{\alpha-\beta}}{dt^{\alpha-\beta}} = \frac{V}{dt^\gamma} \]

\[ \mathcal{F} \left( \frac{\tau(i\omega)}{G(i\omega)} \right) = \frac{V(i\omega)^\alpha \cdot G(i\omega)^\beta}{V(i\omega)^\alpha + G(i\omega)^\beta} \]

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

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

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

---

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

Relaxation modulus for FMM

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

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

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

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

(Here I have set $\beta = 0$, but this result is general)

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}
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!

\[
\lambda_{\text{characteristic}} \sim \left(\frac{V}{G}\right)^{1/(\alpha-\beta)}
\]

Consistent with the common (pragmatic) practice of comparing:

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

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

\[
G(t_{\text{ref}}) = \left(\frac{V t_{\text{ref}}^{-\alpha}}{t/t_{\text{ref}}}\right)^{-\alpha}
\]

*Reported value*

*Scott Blair & Caffyn, Phil Mag 1949*
Versatility of Two Element Fractional Models
Fourier Transform to evaluate complex modulus

Cross-over Time

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

Fractional Kelvin Model

Single Spring Pot

DEM0

http://demonstrations.wolfram.com/VisualizingFractionalRheologicalConstitutiveEquations/
Critical Gels (& beyond criticality)


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

\[
G'(\omega) = G''(\omega) = S\omega^n
\]

At the gel point:

\[
G'(\omega) = G + \nu\omega^\alpha \cos\left(\frac{\pi}{2}\alpha\right) \\
G''(\omega) = G + \nu\omega^\alpha \sin\left(\frac{\pi}{2}\alpha\right)
\]

<table>
<thead>
<tr>
<th>(t - t_c) [min]</th>
<th>(\alpha)</th>
<th>(\nu) [Pa s(^\alpha)]</th>
<th>(G) [Pa]</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>0.52</td>
<td>367.3</td>
<td>13.97</td>
</tr>
<tr>
<td>(10^2)</td>
<td>0.44</td>
<td>1512</td>
<td>42.07</td>
</tr>
<tr>
<td>(10^6)</td>
<td>0.32</td>
<td>9596</td>
<td>1283</td>
</tr>
</tbody>
</table>
Power-Laws Everywhere!

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

- Airway, Smooth Muscle
  Fredberg & Coworkers

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

- Red Blood Cell Membranes

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

- London Olympics 2012

Fig. 3. Fits of power law relaxation ($E(t)$) and relaxation predicted by Eq. 1 to stress relaxation in a rat lung taken from Peslin et al. (41). $A$, $B$, and $\alpha$, parameters; $t$, time.
Only three parameters required (β = 0) to capture the rheological behavior of these protein gels across the whole experimental range of data.

Mesenchymal Stem Cells growing on weakly crosslinked gels

220% increase in phosphate expression activity
On gels with higher viscoelastic loss modulus
=> reduced “creepiness”
Versatility of Two-Element Fractional Models: Data

**Cervical Mucus**
Quasiproperty strongly correlated with preterm birth risk

**Mamaku Gum** (Black Fern)

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


Predictions Using Fractional Material Response

\[ a \text{ priori} \text{ prediction of creep ringing from SAOS} \]

\[ \text{Interfacial rheometry} \]

Jaishankar, A. & McKinley, G. H.,


\[ \text{Prediction of tack force from SAOS} \]

\[ \text{Extensional rheometry} \]

Jaishankar, A. GHM, et al.,

SOR2013 Paper GS21

Thursday Morning, 9:30am

\[ F_c = 100\text{g} \]

\[ t^{1-\alpha} \]

\[ t^{-3/2} \]
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

\[ \tau_{ij} = \tau_{[0]}(r, t, t') = \int_0^t G(t - t'')\nu_1 \eta(r, t, t'')dt'', \]

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

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

• 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)

• (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 $\alpha$. 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

Fractional Calculus
The Mittag Leffler Function
The Caputo Derivative

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

Quasiproperty

\[
\mathbb{V} \dot{\sigma}_{spring-pot} = \mathbb{V} \frac{d^\alpha \gamma}{dt^\alpha}
\]

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