A 'not so' Random Walk through Historical Aspects of Fractional Calculus: Anomalous Diffusion and Viscoelasticity

Vivek Sharma

Hatsopoulos Microfluids Laboratory
Department of Mechanical Engineering
Massachusetts Institute of Technology

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Brownian Motion according to Gamow, 1955, adapted from discussion in J. Philibert, *diffusion-fundamentals.org*, 4, 6.1 *(2006)*

massachusetts institute of technology

Fractional calculus: Why must we care?

Not all who wander are lost. JRR Tolkein

Perhaps to understand the following:

How far can a malaria causing mosquito get in a given time? How about a monkey that steals your glasses?

Mosquitoes do a random walk: Monkeys don't!

Why is root mean square distance covered by a drunken walk in N steps proportion to $N^{1/2}$ in most cases? Why some drunkards move greater or lesser distance?

Polymer chains show random walk statistics usually: but polyelectrolytes…

Diffusion in glasses and gels is different from diffusion in melts and solutions

Relaxation spectrum is typically described using a simple exponential: but some systems like to relax slowly, as in with stretched exponentials.

Thermorheological complexity, cooperatively and glass transition

Understanding diffusion was the biggest advance of twentieth century soft matter physics:

Anomalous diffusion is an experimental reality: need to grasp its implications.

H. Mehrer, *diffusion-fundamentals.org*, 11, 1 *(2009)*

Random Walk, Means, Diffusion, Levi flights

Random walk

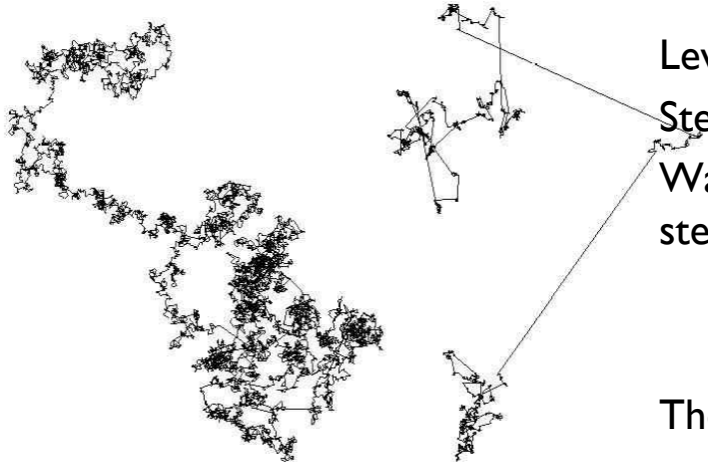
Why is root mean square distance covered by a drunken walk in N steps?

$$\left\langle \Delta x^2(\tau) \right\rangle = 2dD\tau$$

Dynamics in soft mater physics is primarily the study of Brownian Motion

Size of polymer coil is given by Gaussian distribution

Microrheology based on particle tracking!



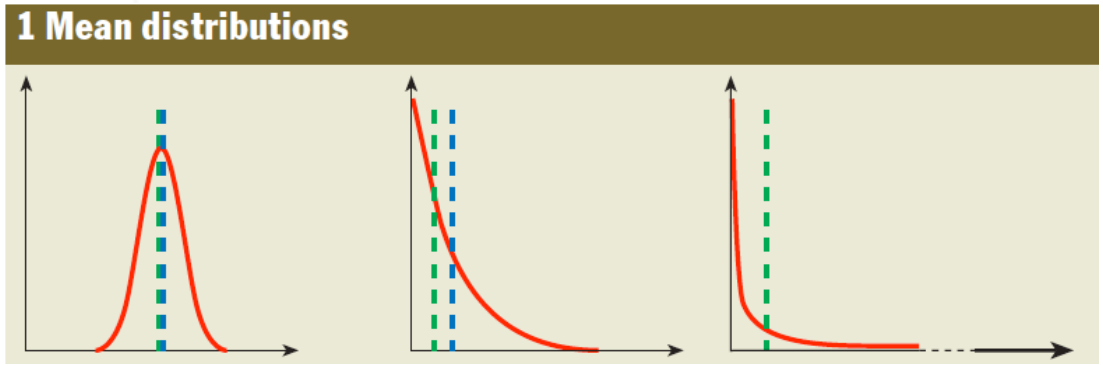
Levi flight

Steps are of irregular length

Walker ponders between steps

$$\left\langle \Delta x^2(\tau) \right\rangle \sim \tau^{\alpha}$$

The distribution has long tails!



Stress relaxation is related to mean square displacement

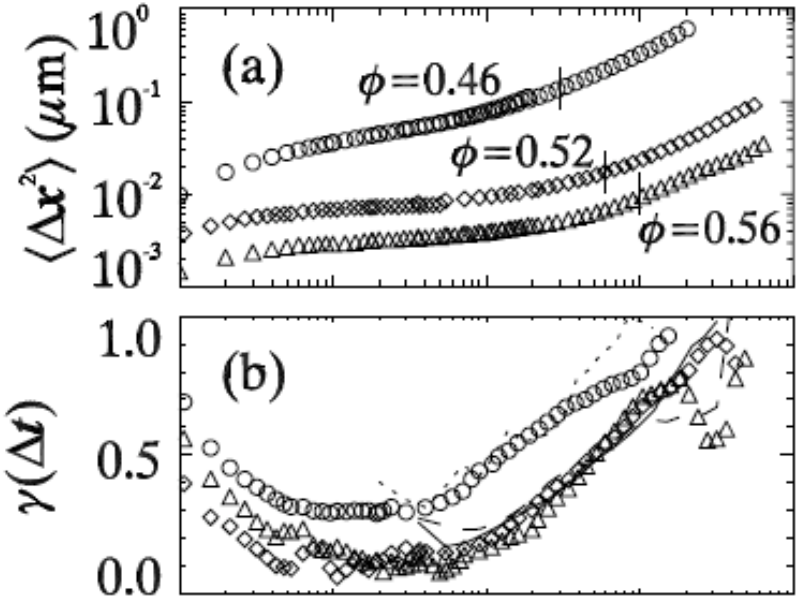
$$G^*(\omega) = \frac{k_B T}{\pi a i \omega \Im_u \left\langle \Delta x^2(t) \right\rangle}$$

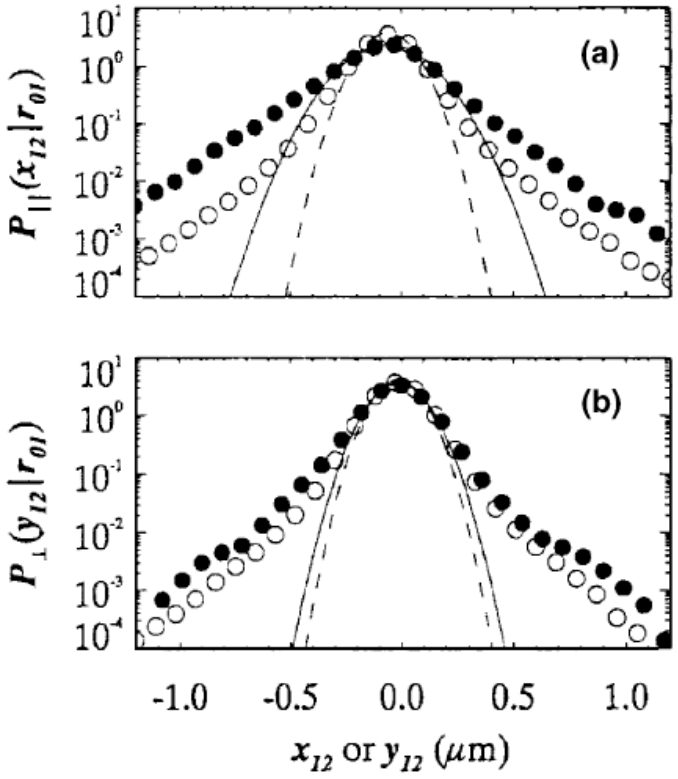
For a detailed description of diffusion, read Chandrasekhar, S., Reviews of Modern Physics, 1943. **15**(1): p. 1-89 (excellent review) and Doi, M. and S.F. Edwards, *The Theory of Polymer Dynamics.* 1986, Oxford: Oxford University Press.; J. Philibert, *diffusion-fundamentals.org*, 4, 6.1 *(2006)*
For discussion on Microrheology, see chapter by Gardel, Valentine and Weitz, at http://squishycell.uchicago.edu/papers/urheo_chapter.pdf

Random Walk, Means, Diffusion, Levi flights

Example of subdiffusion $\left\langle \Delta x^2(\tau) \right\rangle \sim \tau^{\alpha}$

Distribution with tails





Mean square displacement has a varying exponent

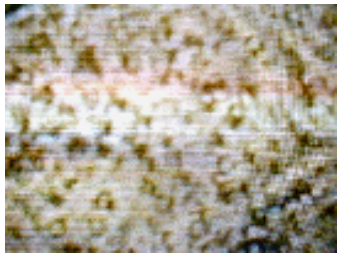
Colloidal PMMA particles, ϕ is volume fraction

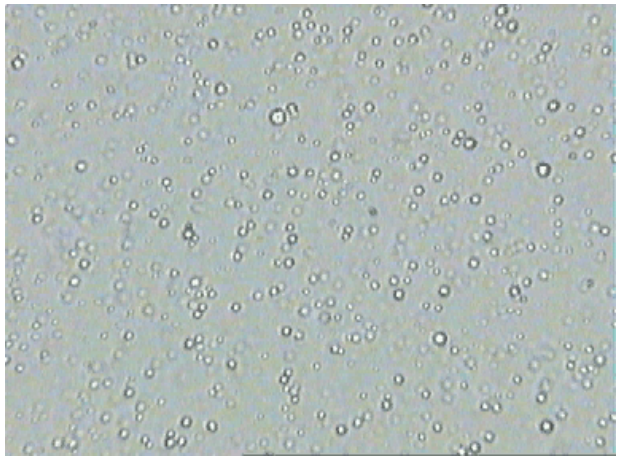
Images from DA Weitz and ER Weeks, Chemical Physics, 284, 2002. (See other papers by two researchers on similar effects)
Also recommended: The most famous example of anomalous diffusion in laminar fluid flow in rotating annulus: TH Solomon, ER Weeks and HL Swinney, *Phys. Rev. Lett*, 71, 24, 3965 (1993).

Robert Brown's Confusion is our Brownian Diffusion

The Scottish botanist Robert Brown (1773 – 1858)

H. Mehrer, *diffusion-fundamentals.org*, 11, 1 *(2009)*





Brown's experiments reprise (Brown's Microscope: Linnean Society in London) :
B. J. Ford, *The Microscope,* **40** (4): 235-241, 1992. http://www.brianjford.com/wbbrowna.htm

A brief account of microscopical observations made in the months of June, July and August, 1827, on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies,

Film clip details: Fat droplets suspended in milk. Taken with a Russian 40X (N.A. 0.65) achromatic objective in bright field illumination. The image was projected into the video camera (Panasonic CL350 430 line resolution) without an eyepiece. The milk was very dilute, just a needle wetted with milk, dipped and mixed into a drop of distilled water on the slide and covered with coverslip. The droplets range in size from about 0.5 to 3 μm (1 μm is 1/1000th of a millimetre). http://www.microscopy-uk.org.uk/dww/home/hombrown.htm

Diffusion & Statistical Mechanics

The German-Jewish physicist Albert Einstein (1879 – 1955)

Ficks Law

$$\partial_t c(z,t) = \partial_z \left(D_m \partial_z c(z,t) \right)$$

Endless ways of solving diffusion equations are described in my favorite book:
J. Crank The Mathematics of Diffusion, Oxford Unversity Press, 2nd ed. (1975.)

Einstein's Insight: Mean squared displacement is the key & thermal forces and drag balance each other

$$\tau = \left\langle x^2 \right\rangle / D$$

$$D = k_B T / \zeta$$

von Smoluchowski's distribution: Number of particles at height *h* in atm or dispersion

$$\rho(h) \sim \exp(-mgh/kT)$$

$$\partial_t c(z,t) = \partial_z \left(D_m \partial_z c(z,t) + \kappa c(z,t) F^{ext} \right)$$

$$C(Z,T) = (4\pi T)^{-1/2} \left[\exp\left\{ -(Z-1)^2 / 4T \right\} + \exp\left\{ -(Z+1)^2 / 4T \right\} \right] \times$$

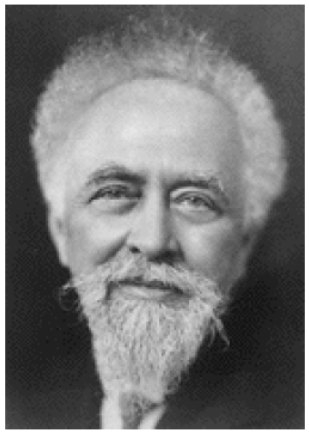
$$\exp\left\{ -(\varepsilon(Z-1) + \varepsilon^2 T)/2 \right\} + \frac{\varepsilon}{\pi^{1/2}} \exp\{-\varepsilon Z\} \int_{\frac{Z+1-\varepsilon T}{\sqrt{4T}}}^{\infty} dx \exp\left\{ -x^2 \right\}$$

The German physiologist Adolf Eugen Fick (1821 – 1901)

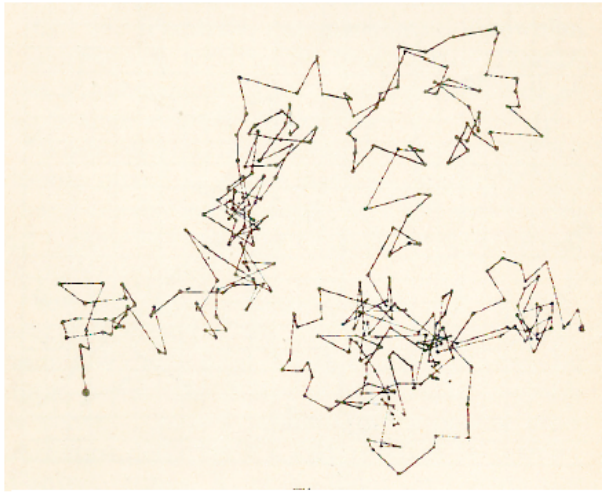
The Polish physicist Marian von Smoluchowski (1872 – 1917)

H. Mehrer, *diffusion-fundamentals.org*, 11, 1 *(2009)* Einstein, A., Annalen Der Physik, 1905. **17**(8): p. 549-560; Einstein, A., *Investigation on the theory of Brownian movement.* 1956, New York: Dover Publications; Einstein, A., Annalen Der Physik, 1906. **19**(2): p. 371-381.; von Smoluchowski, M., Annalen Der Physik, 1906. **21**(14): p. 756-780.; von Smoluchowski, M., Physikalische Zeitschrift, 1916. **17**: p. 557-571.; von Smoluchowski, M., Physikalische Zeitschrift, 1916. **17**: p. 585-599.; Langevin, P., Comptes Rendus Hebdomadaires Des Seances De L Academie Des Sciences, 1908. **146**: p. 530-533.; Chandrasekhar, S., Reviews of Modern Physics, 1943. **15**(1): p. 1-89; Haw, M.D., Journal of Physics-Condensed Matter, 2002. **14**(33): p. 7769-7779.

Brownian Motion: Molecular Reality & Three Nobel Prizes



The French physicist Jean Baptiste Perrin (1870 – 1942)



Molecular reality, Avogadro's hypothesis were accepted after Perrin's experiments, where he not only tracked particles as shown here, but used a microscope to count the number present at each height!

(Svedberg did a similar experiment & designed ultracentrifuge, whereas Zsigmondy designed ultramicsroscope: these and related historical aspects discussed in my paper: V. Sharma, K. Park and M. Srinivasarao, MSER, 65, 1 (2009)

THE Svedberg
30 August 1884 – 25 February 1971

Sedimentation

Svedberg designed ultracentrifuge to determine size of nanoparticles

$$F_{total} = F_d + F_b + F_c + F_f = 0$$

$$S = v / \omega^2 r = (m - m_o) / \zeta$$

Zsigmondy
1 April 1865 – 23 September 1929

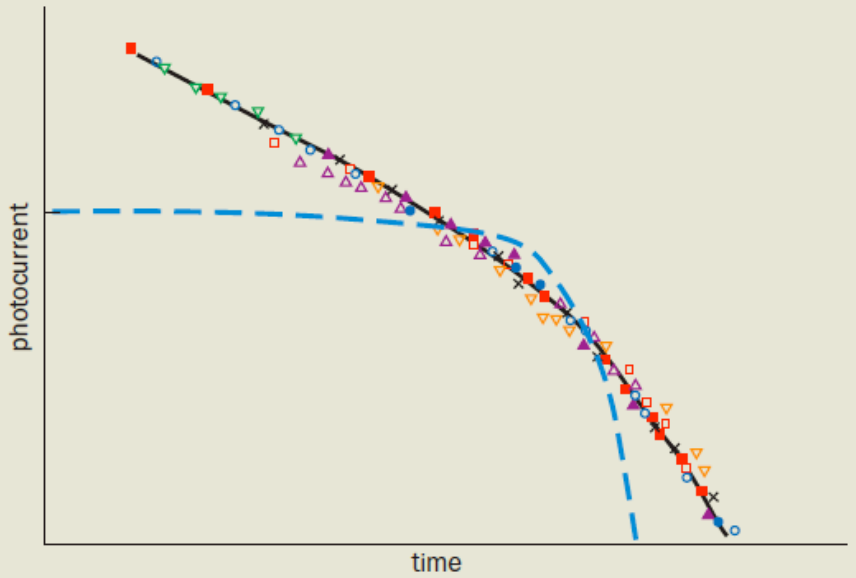
H. Mehrer, *diffusion-fundamentals.org*, 11, 1 *(2009)* Svedberg, T. and K.O. Pedersen, *The Ultracentrifuge*. 1940, Oxford: Oxford University Press. Svedberg, T. and A. Tiselius, *Colloid Chemistry*. Second ed. 1928, New York: The Chemical Catalog Company, Inc.; Zsigmondy, R., *Colloids and the ultramicroscope*. 1909, New York: John Wiley & Sons, Inc.; Zsigmondy, R., *The Chemistry of Colloids*. 1917, New York: John Wiley & Sons, Inc.; Perrin, J., *Brownian motion and molecular reality*. Annales De Chimie Et De Physique, 1909. **18**: p. 5-114.Perrin, J., *Atoms*. 2nd ed. 1923, London: Constable & Company Ltd.

Anomalous diffusion: Albratross around the neck!

TONY PALLISER/ BIRDLIFE

Strange behaviour – albatrosses fly by the rules of anomalous diffusion.

2 Anomalous diffusion in photocopiers



In the 1970s researchers measured the transient photocurrent in amorphous thin films that form the core of photocopier machines (data points). The blue dashed line indicates the expected behaviour if this diffusion process followed Fick's equation, which led Scher and Montroll to describe the process using broad distributions of waiting times. Both axes are logarithmic. This became the best known example of anomalous subdiffusion in nature. From H Scher and E Montroll 1975 *Phys. Rev.* B **12** 2455–2477

Highly readable introduction

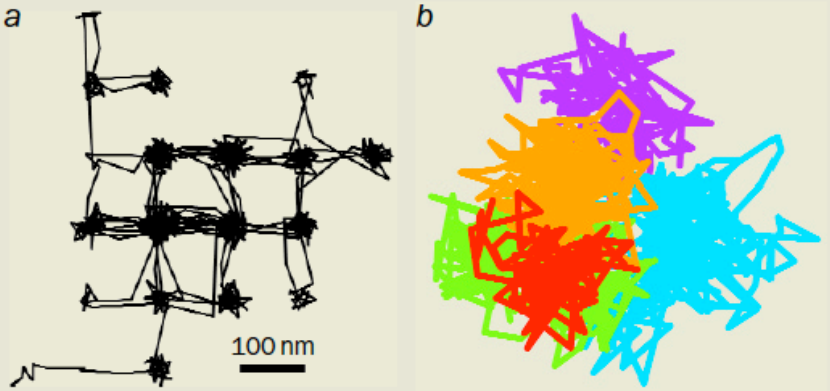
J. Klafter & I. M. Sokolov, *Physics World*, 29 *(August 2005)*

For mathematical details:

R. Metzler and J. Klafter, *Physics Reports* 339, 1-77, (2000)

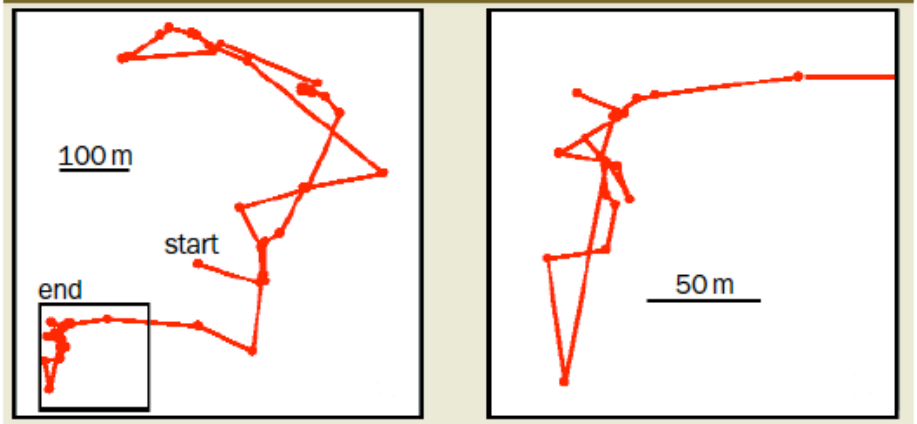
Anomalous diffusion: Is it monkey business?

3 Subdiffusion in cells



Researchers have found that the way proteins diffuse across cell membranes can be described by anomalous diffusion that is slower than the normal case. (*a*) This is a simulation of such a random walk, which shows a 2 ms timeframe over which a protein "hops" between 120 nm^2 compartments thought to be formed by the cell's cytoskeleton. (*b*) The experimental trajectories of proteins in the plasma membrane of a live cell (shown in a 0.025 ms timeframe) provide evidence for this trapping nature, as shown by the different colours. The long residence times in these compartments is thought to be the origin of the anomalous behaviour.

4 Superdiffusion in monkey behaviour



The typical trajectories of spider monkeys in the forest of the Mexican Yucatan peninsula display steps with variable lengths, which correspond to a diffusive process that is faster than that of normal diffusion. An example of such a trajectory is shown on the left. A magnified part of it is shown on the right; this image looks qualitatively similar to the larger-scale trajectory, which is an important property of Lévy walks. Similar behaviour is found in the foraging habits of other animals, and could mean that anomalous diffusion offers a better search strategy than that of normal diffusion.

J. Klafter & I. M. Sokolov, *Physics World*, 29 *(August 2005)*

Examples of anomalous diffusion occur in fluid flow (TH Solomon, Weeks & Swinney, PRL (1993), Bartumeus, F. et al, Animal foraging, Ecology (2005), studies of earthquakes (Corral, PRL (2006)), transmission of light (Barthelemy, et al, Nature, 453 (2008), Glasses, Gels, Protien dynamics (W Min et al, PRL (2005)), and so on

The Original GrandPa of Rheology: Scott-Blair

Scott-Blair studied an amazing array of fluids varying from cheese, dough, mucous, soils, butter to human milk!

Biography

Born in 1902 in Weybridge, Surrey. Passed away in 1987 at Grist Cottege, Oxfordshire.
1920: Studied Chemistry at Trinity College, Oxford (project on colloidal chemistry for honors degree). Employment as Colloid Chemist in firm of Henry Simon;
1927: Published his first rheology paper, on viscometry of flour suspensions.
1927-1937: Employed at Rothamsted Experimental Station to study rheology of soils and clays; studied rheology of dough and honey as well,
1929: Got Rockerfeller Fellowship to come to Cornell; Chaired first Society of Rheology meeting and became friends with Bingham and Reiner!
1936: Awarded a DSc in 1936 at University of London, where his dissertation was forwarded by Prof. Fruedlich (worked on thixotropy): possibly the first PhD awarded for rheology as we know it.
1937-1967: Joined Dept. of Chemistry first, then as chair of Physics at NIRD (National Institute on Research in Dairying): Worked on rheology of milk, butter and cheese, effect of temperature on viscosity of bull serum, rheometry for determining if mucous from cows, rheology of human milk, pioneered biorheology and hemorheology (organized first conference on blood flow), used fractional calculus to describe certain experimental results, wrote papers on psychorheology. Published 250 papers; 7 books.
Received numerous awards, was on editorial board of many journals (as Editor-in-Chief of Biorheology, which he cofounded with A Copley.

The Original Rheologist who pioneered
BOOKS

An Introduction to Industrial Rheology, P. Blakiston, Philadelphia, 1938 (German edition, trans.H. Kauffmann, Dresden & Leipzig, Steinkopff, 1940).
A Survey of General and Applied Rheology, Pitman & Sons, London, 1944, 2nd edn., 1949.
Foodstuffs: Their Plasticity, Fluidity and Consistency (Monographs on Rheology), Elsevier, Amsterdam,1953.
Measurements of Mind and Matter, Philosophical Library, New York, 1956.
Agricultural Rheology, joint author with Markus Reiner, Routledge & Kegan Paul, London, 1957.
Elementary Rheology, Academic Press, London & New York, 1969.
An Introduction to Biorheology, Elsevier Scientific Publishing Company, Amsterdam; New York,1974.

*HA Barnes, Biorheology, 37, 259 (2000)

Fractional derivatives: Who, what, why, when?

$$d^{\alpha} y / dx^{\alpha}$$

L'Hospital: What if α be 1/2? Leibnitz (1695) replies: "It will lead to a paradox." Then he added prophetically, "From this apparent paradox, one day useful conclusions will be drawn."

Wallis (1655) proposed infinite product for $\pi/2$; in 1697 Leibnitz suggested the same result follows from differential calculus using $\alpha = 1/2$ and $y = x$

S. F. Lacroix (1819) devoted less than two pages (out of 700 page text on calculus) to generalize

$$\frac{d^m y}{dx^m} = \frac{n!}{(n-m)!} x^{n-m} \qquad \frac{d^{1/2} y}{dx^{1/2}} = \frac{\Gamma(a+1)}{\Gamma(a+1/2)} x^{a-1/2}$$

Euler & Fourier mentioned derivatives of arbitrary order: provided no applications/examples {Perhaps left it as an exercise for future mathematicians}

Niels Henrick Abel (1823) finds first application: Tautochrone problem, i.e. finding shape of wire in a vertical plane, such that bead slides to lowest point in same time, irrespective of initial condition!

Liouville gets interested and published papers (in 1832 & 1855); Riemann in 1847

Mini-controversy… then Heaviside (1890s) pokes fun at mathematicians. People ignore him & FC!

Commonly used notation comes from Harold T. Davis*

HIGHLY RECOMMENDED *B. Ross, *Fractional Calculus and its Applications (1974)*

The Why and When of Fractional Calculus: Contexts from Stretched Relaxation and Polymer Physics/ Viscoelasticity

Vivek Sharma

Hatsopoulos Microfluids Laboratory
Department of Mechanical Engineering
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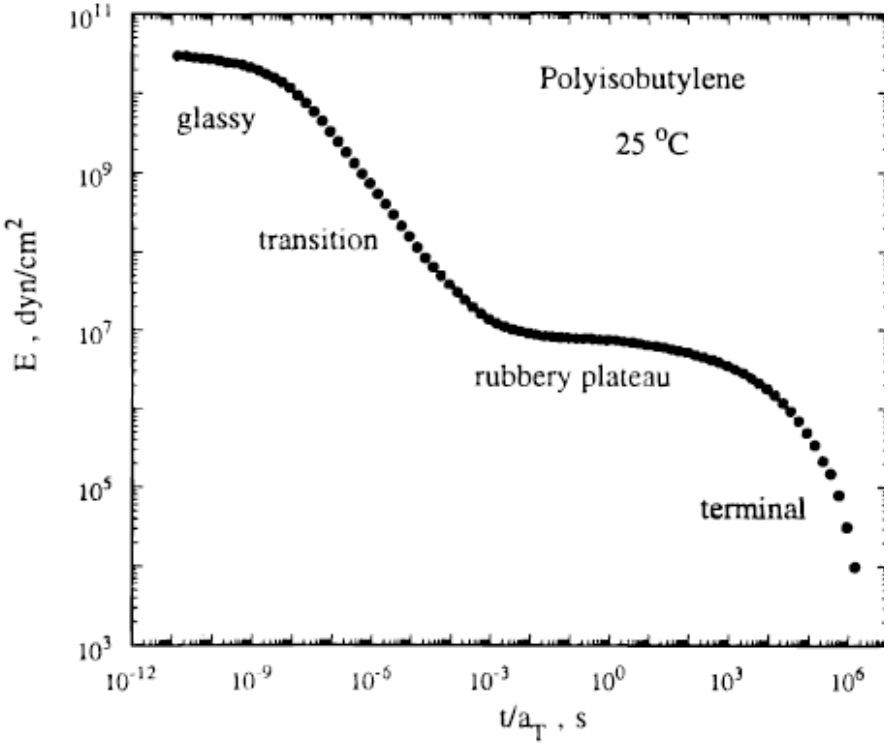
June, 2010

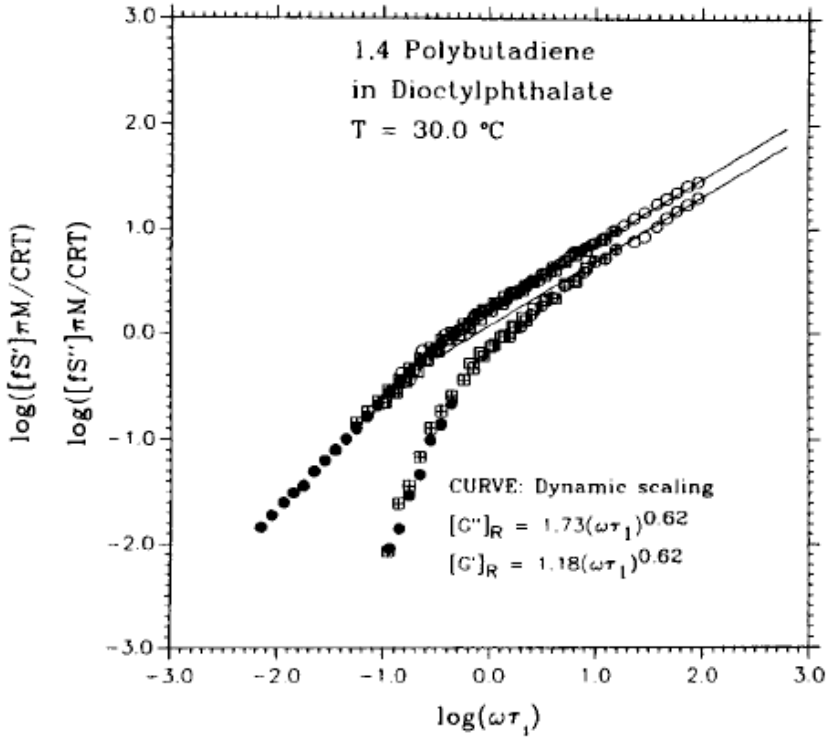
massachusetts institute of technology

Relaxation and Polymer physics: Reprise

Relaxation Modulus: Time-temperature superposition used to get data in different regimes

Described at length in Ferry's Viscoelastic properties of polymers, 3rd ed., John Wiley & Sons (1980)





Bead-spring models: generalized form: Rouse for unentangled melt, Zimm for dilute solutions.

More generalized approach necessary to describe frequency dependence in glassy materials & gels.

$$G^*(\omega) = \frac{cRT}{M}\sum_p \frac{\omega\tau_p}{1+\omega\tau_p}$$

Details about bead spring models in Doi, M. and S.F. Edwards, *The Theory of Polymer Dynamics.* 1986, Oxford: Oxford University Press.;
Plots from Lodge and Muthukumar, J. Phys. Chem,, 100, 13275, 1996: a highly readable summary of physical chemistry of polymers.

Nutting, Scott-Blair and psychology of rheologists

Nutting's equations (1921) $s = at^n F^m$

Nutting was studying hard stearine pitch: with force, F & displacement, s

This was long time ago. 1920 Staudinger proposed that rubber and solutions of cellulose, startch, etc were composed of long chain molecules. Received Nobel Prize for this work!

(Highly recommended, another personal favorite: Polymers: The Origins and Growth of a Science by H. Morawitz)

This is before rheology term was known/accepted. Remember Scott-Blair was there at 1929 meeting of SOR as chair.

Maxwell's model (1867/68) was known. He wrote down his famous equation.

Meyer (1874) wrote down the expression for Kelvin-Voigt model.

Kelvin (1865, 1878) did the experiments on damping of metals, but wrote no formulae.
Voigt (1865, 1892) generalized Meyer's idea to anisotropic media.

Interesting trivia: Bolzmann's superposition principle criticized Meyer. Meyer disliked Boltzmann's paper; Boltzmann's was more general. We have forgotten Meyer, while Boltzmann killed himself!

Tanner and Walters, Rheology: A Historical Perspective,Elsevier 1998

Scott-Blair noted that firmness judged by hand and functions similar to Nutting's equation are correlated

$$S \Big/ \frac{d^\alpha \sigma}{dt^\alpha} = \chi$$

Interesting papers (some with co-authors): GW Scott-Blair, J. Colloid Sci (1947), Phil Mag, 7, 40, 300 (1949); J. Sci. Instrum. 19, 88, 1942; Amr. J. Psychology, 56, 2, 234 (1943), etc Scott-Blair not only used fractional calculus, but also wrote about philosophy & psychology of rheology as a science. He hwasn't a fan of tensorial models and complex mathematics that came to dominate rheology after 1950s though!

History of Stretched Exponentials: Who is the daddy now?

Rudolf (Hermann Arndt) Kohlrausch (b 1809) (the father) introduced stretched exponential to interpret charge relaxation in a Leiden jar (RK in figure)

R. Kohlrausch, *Progg. Ann Phys. Chem.* 91, 179 (1854)

$$Q_t = Q_0\left[\exp(-Bt^{\alpha})\right]$$

Friedrich (Wilhelm Georg) Kohlrausch (b 1840) (the son) introduced stretched exponential to interpret mechanical relaxation in a galvanometer threads (studied by papa in 1847 and Weber in 1830s) (FWK in figure)

F. Kohlrausch, *Progg. Ann Phys. Chem.* 119, 337 (1863)

R. Kohlrausch, *Progg. Ann Phys. Chem.* 72, 353/393 (1847): wrong paper cited by Palmer et al, PRL, 53, 958 (1984)

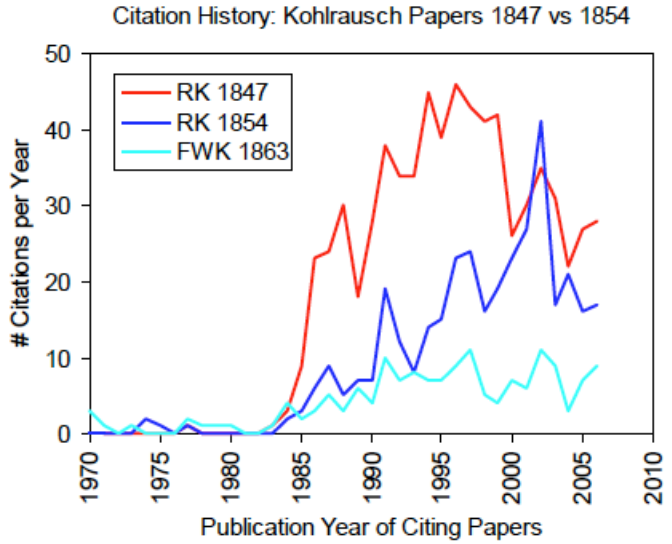
The term "stretched exponential" coined in RV Chamberlain et al in PRL, 52, 867(1984)

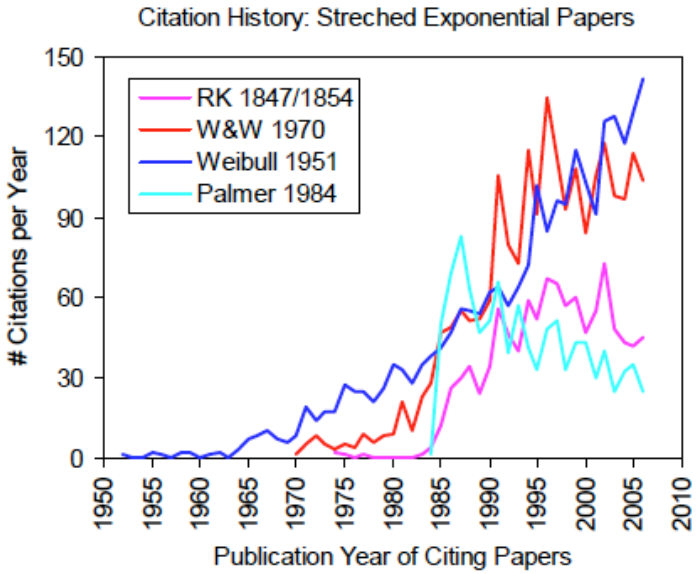
Williams and Watts in 1970 rediscover the stretched exponential and use it for studying polymers

But how and why?

"Non-symmetrical dielectric relaxation behavior arising from a simple empirical decay function"

G Williams and DC Watts, Trans. Farad. Soc. 66, 80 (1970)





Response functions, symmetry and lack of it!

Dielectric relaxation

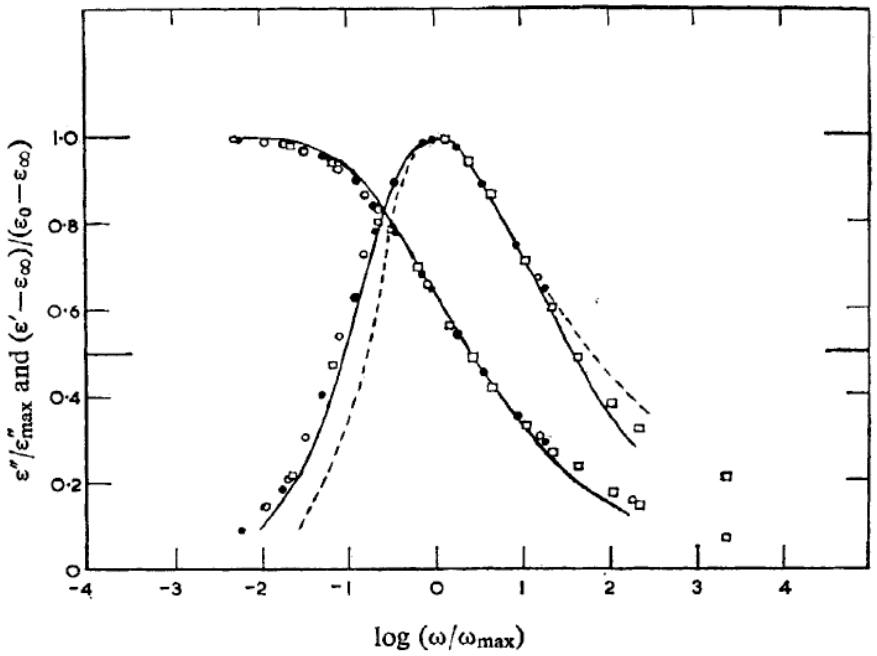
$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty dt \exp(-i\omega t)\left[\frac{-d\gamma}{dt}\right]$$

Again for single relaxation

$$\gamma(t) = \exp[-(t/\tau)] \qquad \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau}$$

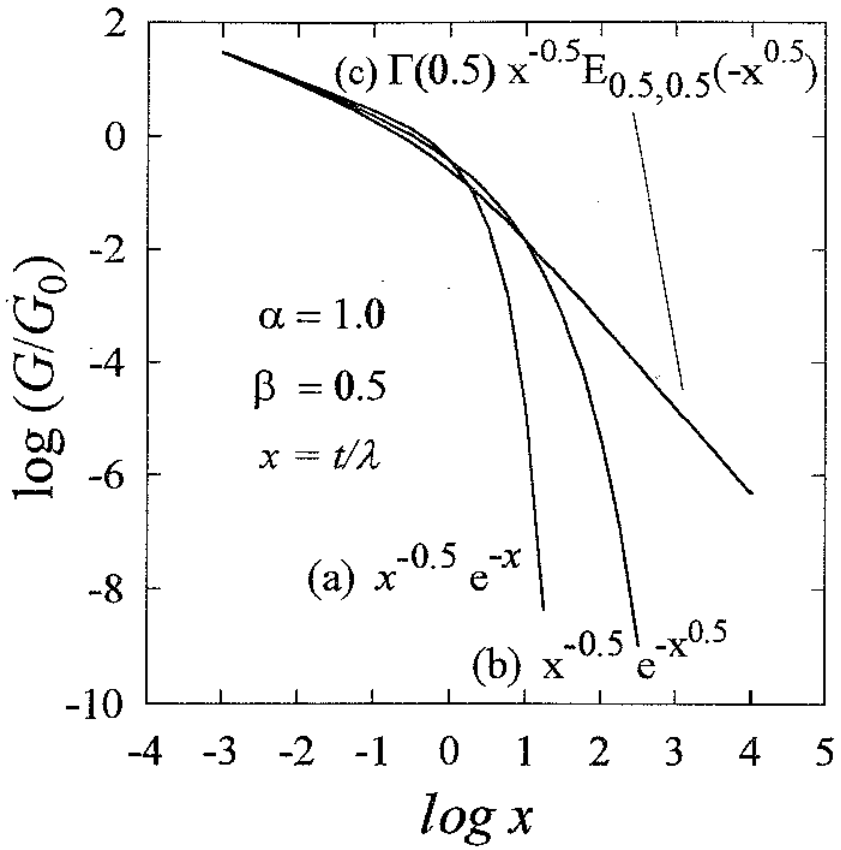
But better fit for

$$\gamma(t) = \exp[-(t/t_0)^\beta]$$



The glass transition literature is rife with power laws & stretched exponentials

$$G(t) = G_0\left(t/\lambda_m\right)^A \exp[-\left(t/\lambda_m\right)^B]$$



G Williams and DC Watts, Trans. Farad. Soc. 66, 80 (1970)
G/G0 from Paper by: Friedrich, Schiessel & Blumen,

Mechanical & Dielectric Response: Basics

Application of electric field E on a non-conducting sample leads to Polarization, P

$$P = \varepsilon_0(\varepsilon - 1)E \qquad D = \varepsilon_0 E + P = \varepsilon_0 \varepsilon E = \varepsilon_0(1+\chi)E$$

We can think of complex dielectric function, ε or susceptibility, χ as analogous to a ratio of a field (stress or E) and its response (strain or P): though here locally medium is polarized!

For an arbitrary time dependent force, ψ(t), the time dependent displacement, x(t) is related through a response function, μ(t), such that

$$x(t) = \int_{-\infty}^{t} \mu(t-t')\psi(t')dt$$

The integral follows two fundamental properties of such linear systems

1) Casuality: x(t) depends only on the forces in past, hence the choice of these limits!
2) Superposition principle: An arbitrary time dependent forces is same as applying multiple forces as small pulses, and the total displacement is given by the integral in both cases. Boltzmann assumed that the stress at time t depends not only on the strains at that instant, but also on previous times. But as t-t' increases, the relative effect of the past contributions becomes less significant than present strains.

The relaxation of polymers, seen through dielectric spectroscopy, is manifestation of reorientation of individual polar units; the mechanical measurement is result of aggregate relaxation through motion of one or more bead-springs, each mode has a different relaxation time.

Q: Why do the retardation time & relaxation time from J(t) and G(t)or Tg measured by dielectric spectroscopy and mechanical response differ in their values?

A good discussion is given in Chapter 5 of G. Strobl, The Physics of Polymers, Springer Verlag, (1997)

Response functions, symmetry and lack of it!

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Again for single relaxation

$$\gamma(t) = \exp[-(t/\tau)] \qquad \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau}$$

KWW relaxation

$$\gamma(t) = \exp[-(t/t_0)^\beta]$$

Unsolved problems:

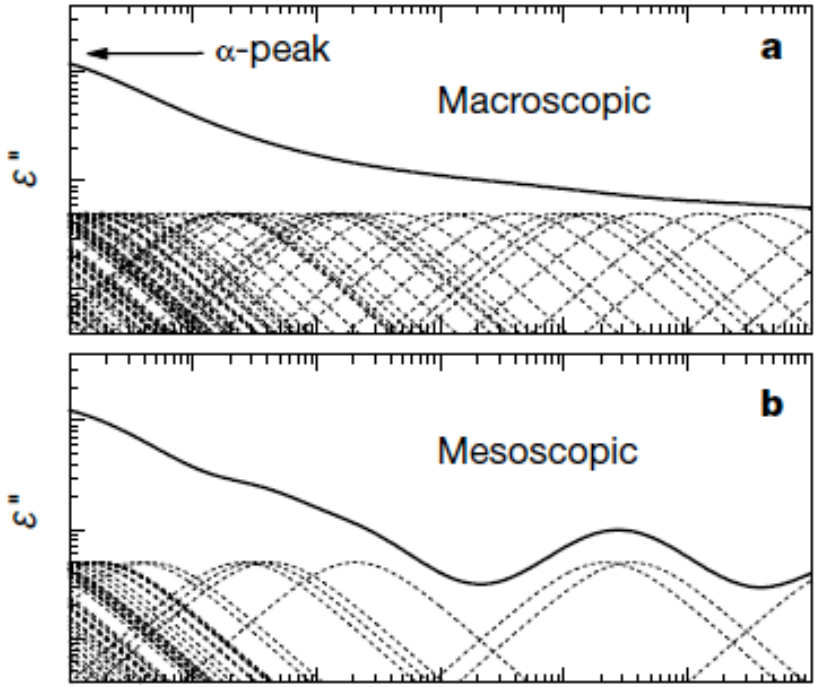
Temperature dependence of segmental motion differs from chain motion

Blend & solution dynamics show anomalies unexplained by coupling and free volume models

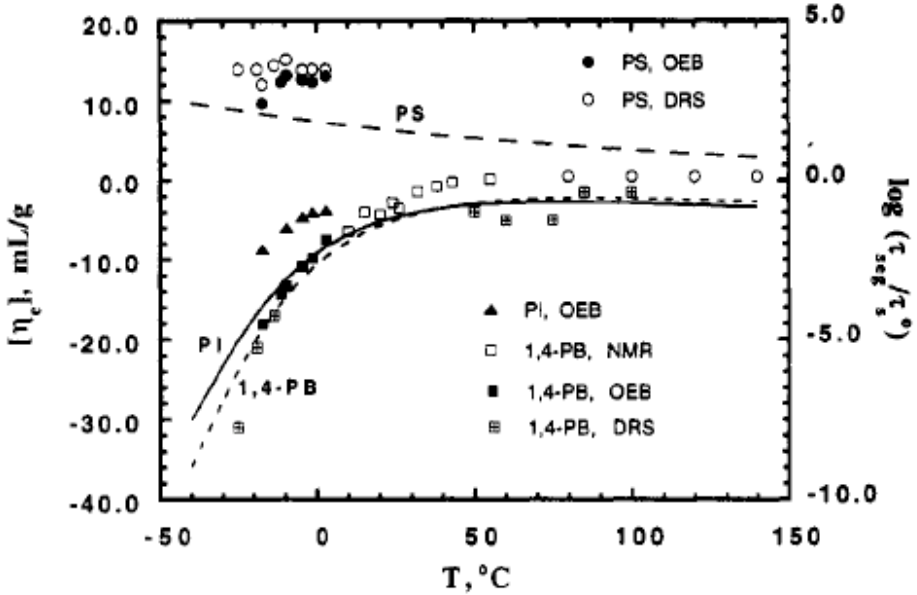
Thermorheological complexity

Breakdown of Stokes-Einstein relationship

Alpha process

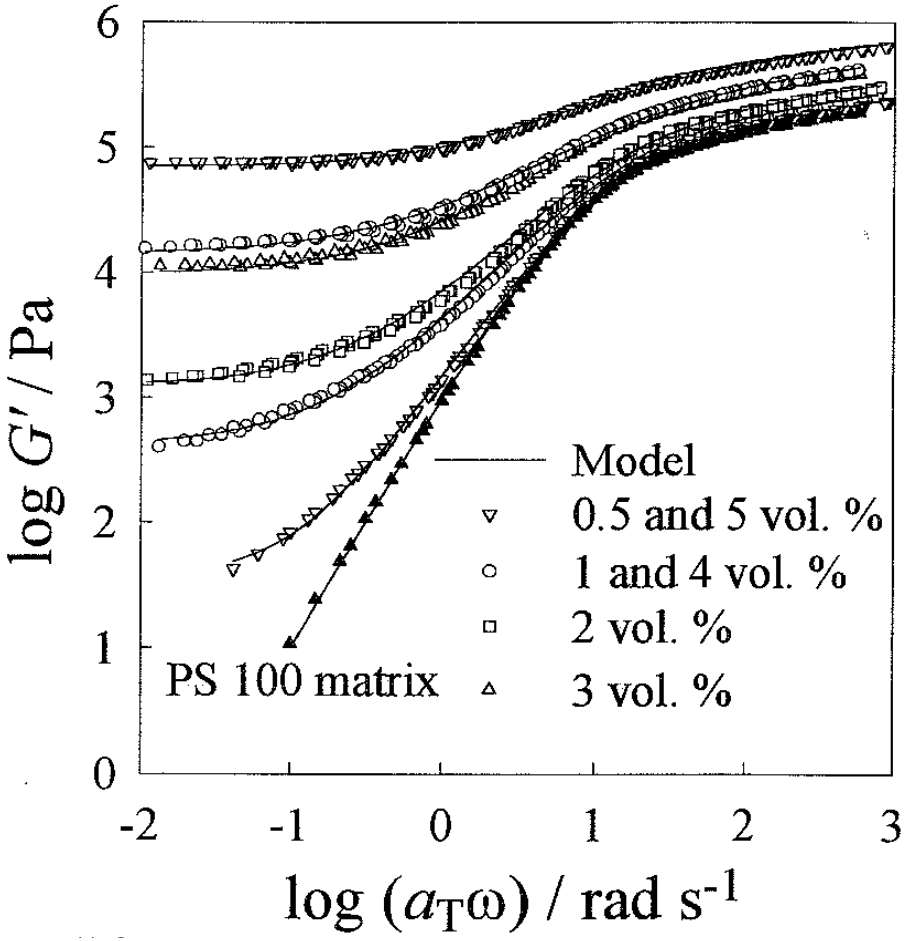


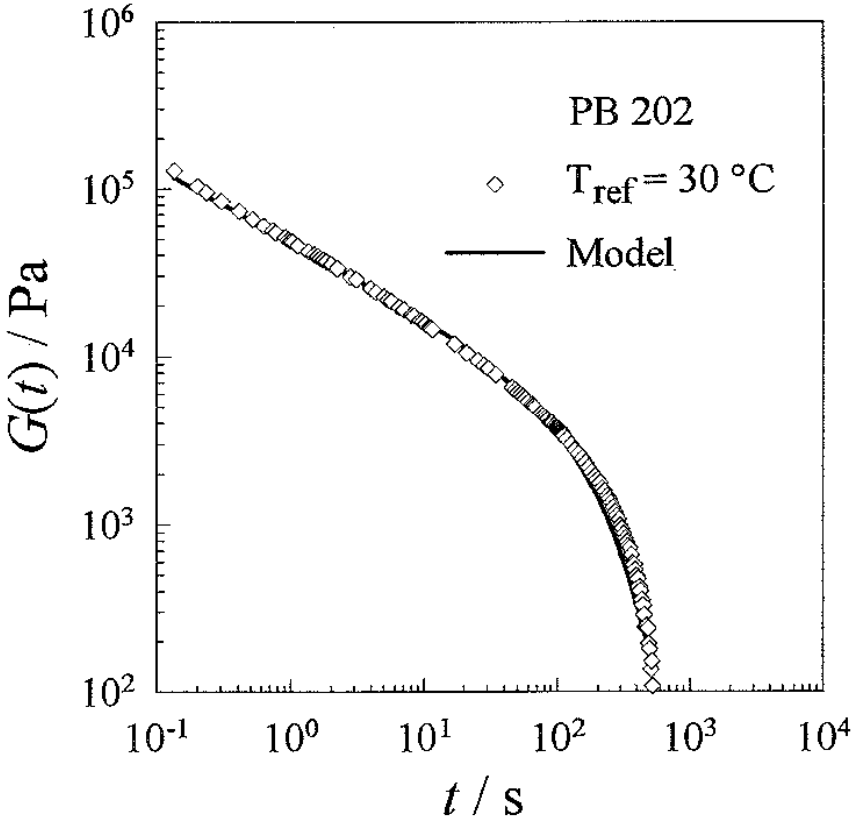
EV Russell and NE Israeloff, *Nature,* 408, 695 (2000)



Adding polymer speeds up solvent dynamics see review TP Lodge, *J. Phys. Chem,97, 1480* (1993); Personal views: My MS thesis showed that in rheology solution viscosity is lower than solvent!

Aerosil filled PS and Relaxation of modified PB





$$G(t) = G_0 - (t/\lambda)^{\beta} \exp -(t/\lambda)$$

Filled system and relaxation of modified PB show examples of two systems that are very important for the industry. Fractional calculus fits data well, but what does it mean?

From Paper by: Friedrich, Schiessel & Blumen,

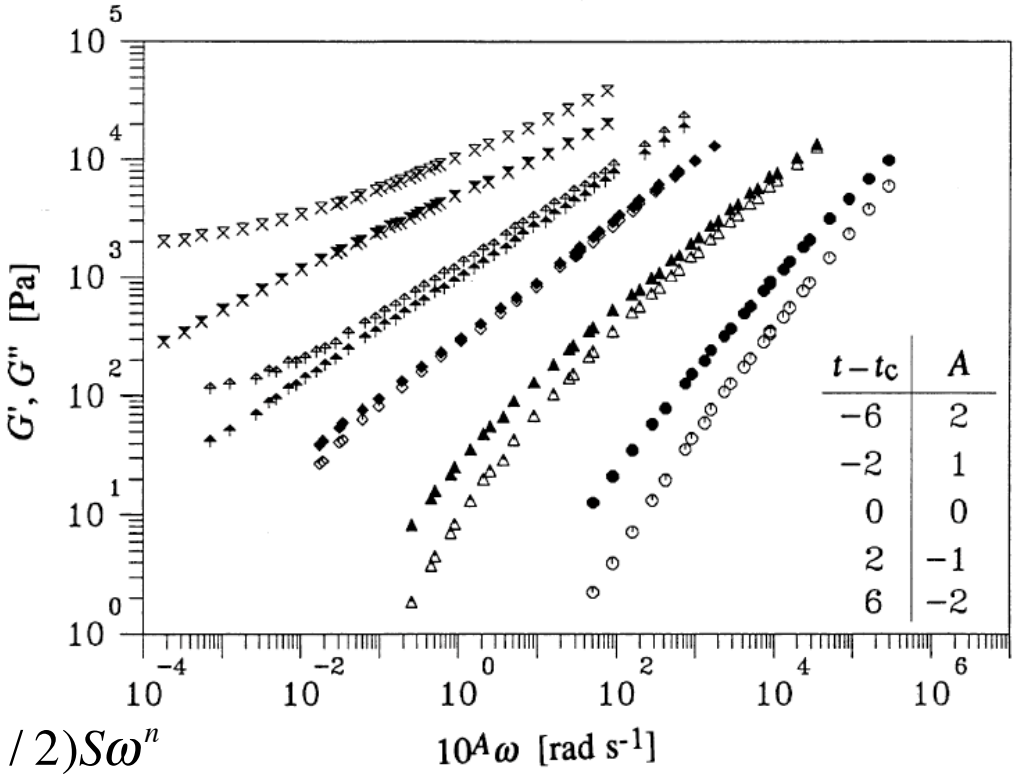
Weak gels, strong gels and physical gels

Strength of a gel

$$G(t) = St^{-n}$$

The data here is for PDMS samples that have been crosslinked to different extent:

When n > 0.5, G' < G"



Kramers-Kronig relation gives

$$G'(\omega) = \frac{G''(\omega)}{\tan(n\pi/2)} = \Gamma(1-n)\cos(n\pi/2)S\omega^n$$

"Power laws near gel point presumably arise from fractal scaling properties of gel clusters" (Larson's book)

UNSOLVED PROBLEMS, include associative polymers that I study!

$$G(t) - G_e = H_0 \int_0^\infty \left(\frac{\lambda}{\lambda_0}\right)^{-n} e^{-t/\lambda} \frac{d\lambda}{\lambda} = H_0 \Gamma(n) \left(\frac{t}{\lambda_0}\right)^{-n}$$

$$G'(\omega) = H_0 \Gamma(n)\Gamma(1-n)\cos\frac{n\pi}{2}(\lambda_0\omega)^n$$

$$G''(\omega) = H_0 \Gamma(n)\Gamma(1-n)\sin\frac{n\pi}{2}(\lambda_0\omega)^n$$

RG Larson, The Structure and Rheology of Complex Fluids, Oxford University Press, 1999

HH Winter and M. Mours, *Adv Polym Sci* 134, 165. *(1997)*