Experimental Techniques to Measure Properties of Glasses

Jaydeep Basu

Department of Physics

IISc Bangalore

International School on Glass Formers & Glasses, Jan 2010, Bangalore

Lecture Plan - Day 1

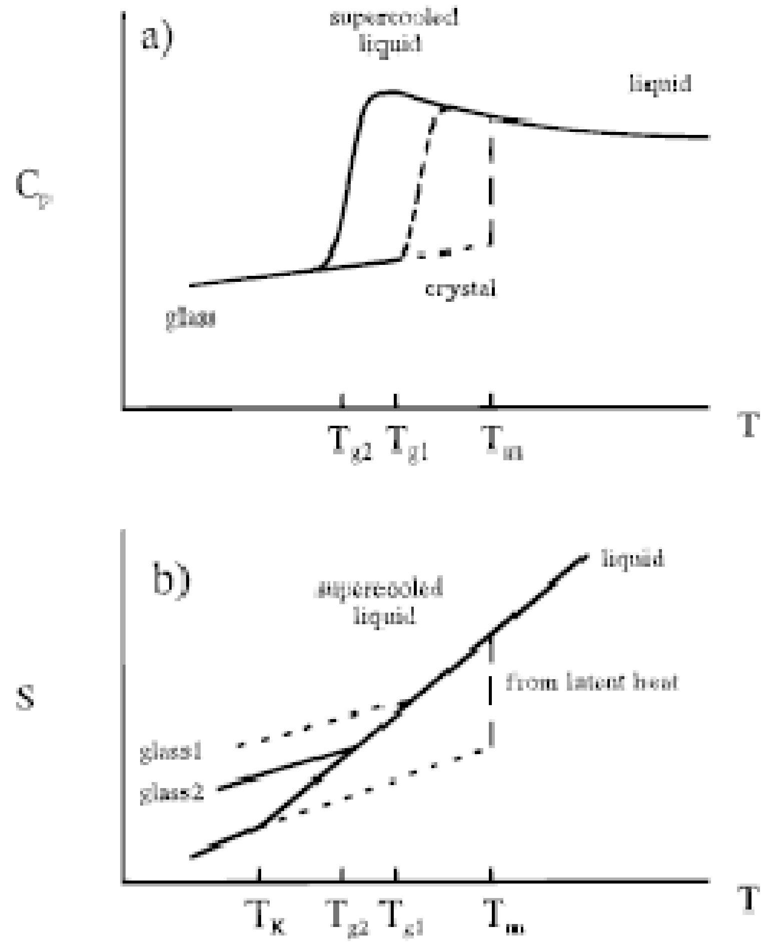
- Basics of Differential Scanning Calorimetry (DSC)
- Modulated DSC (MDSC)
- Examples

- Basics of Laser scanning confocal microscopy
- Single Molecule Spectroscopy
- Examples

Differerential Scanning Calorimetry

ICTAC definition: A technique in which the heat flow rate to the sample is monitored against time or temperature while the temperature is programmed. (International Confederation for Thermal Analysis and Calorimetry)

- Why is it a popular technique to study
- glasses?
- Can measure heat capacity, **CP**, which can
- be used to estimate the glass transition
- temperature **TG**.



Ediger et al JPC (1996)

Some Basic Thermodynamic Definitions

$$C_V \equiv \frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_{V,n}$$

$$H \equiv U + pV$$

$$H = \int C_p \, dT$$

$$C_p \equiv \frac{dQ}{dT} = \left(\frac{\partial H}{\partial T}\right)_{p,n}$$

$$\frac{dQ_{reversible}}{T} \equiv dS$$

$$S = \int (C_p/T)\, dT$$

$$\frac{dH}{dt} = C_P \frac{dT}{dt}$$

$$H = \int_0^T C_p \, dT + \Delta H_f$$

$$dU = TdS + dF$$

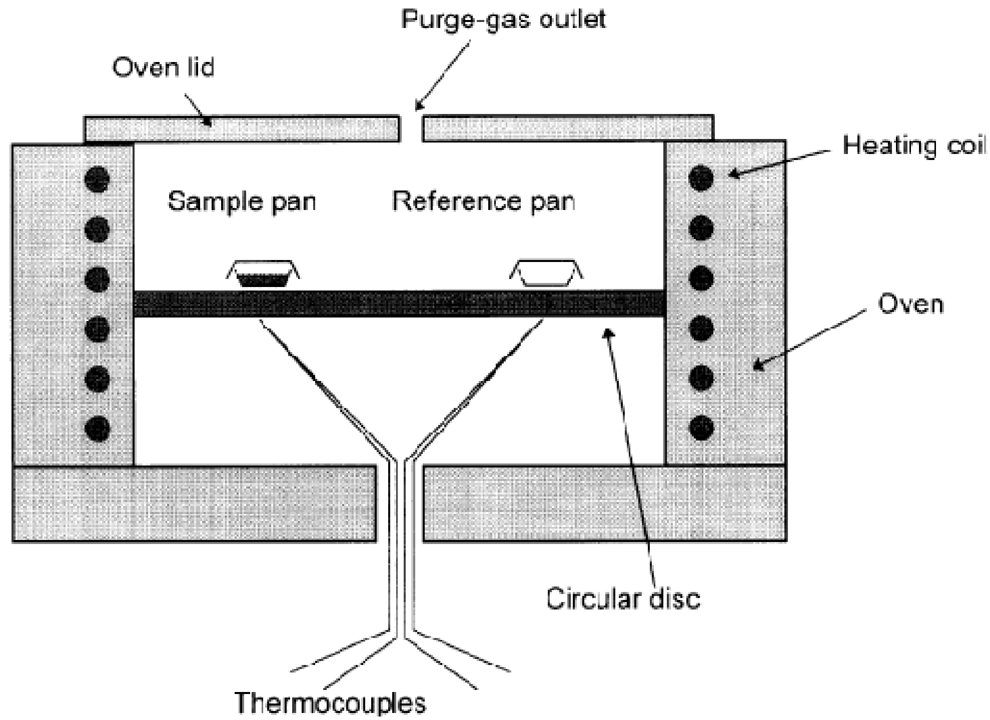
$$S = \int_0^T \frac{C_p}{T} \, dT + \Delta S_f$$

$$G = H - TS$$

Modes of DSC

- **Heat Flux**
- **Power Compensation**

Heat Flux Calorimeter



Theory of heat flux calorimeter

Biot-Fourier Eqn. of steady state heat conduction

$$\frac{\phi}{A} = -\sigma.\nabla T$$

ϕ is heat flow rate; A is area of pans; $\sigma$is thermal conductivity; T is temperature

$$\frac{\phi_{FS}}{A} = \frac{\sigma(T_F - T_S)}{\Delta l}$$

and

$$\frac{\phi_{FR}}{A} = \frac{\sigma(T_F - T_R)}{\Delta l}$$

Δl – distance between temp measurement point and furnace

Theory of heat flux calorimeter

T_F, T_R, T_S are the furnace, reference and sample temperatures, respectively.

If a constant (exothermic) heat flow rate ($\phi_r < 0$) is produced in the sample, T_S increases by ΔT_S , the temperature difference T_F-T_S and thus heat flow rate ϕ_{FS} decreases. Here, ϕ_r is the reaction heat flow rate consumed/produced by the sample. In the steady state, $\Delta\phi_{FS} = \phi_r$

$$\Delta\phi_{FS} = \phi_r = -\frac{A\sigma}{\Delta l}\Delta T_S = -K.\Delta T$$

Newton's Law

$$dQ_s/dt = K(T_b - T_s)$$
$$dQ_r/dt = K(T_b - T_r)$$

Theory of heat flux calorimeter

Since there is no change on the reference pan, $\Delta T_S = \Delta T_{SR} = T_S - T_R$ and $\phi_r = \Delta\phi_{SR} = \phi_{FS} - \phi_{FR}$

Hence,

$$\phi_r = -\frac{A\sigma}{\Delta l}\Delta T_{SR} = -K.\Delta T$$

Theory of heat flux calorimeter

Finally,

$$\Delta\phi_{SR} = \beta(C_S - C_R) = -K.\Delta T$$

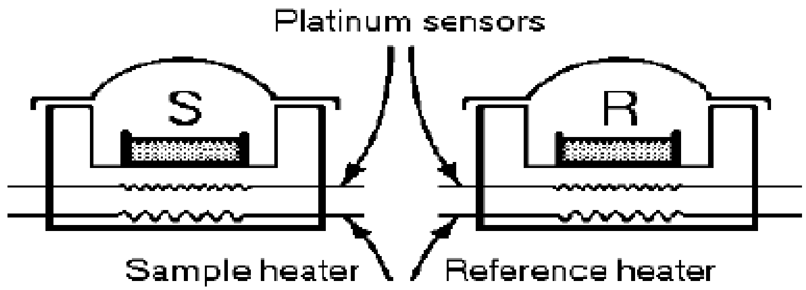
where, $\beta = \frac{dT}{dt}$ and $C_S and\ C_R$ are the respective specific heats. Thus for empty pan reference

$$C_S = -K\frac{\Delta T}{\beta}$$

while for a pan with reference material

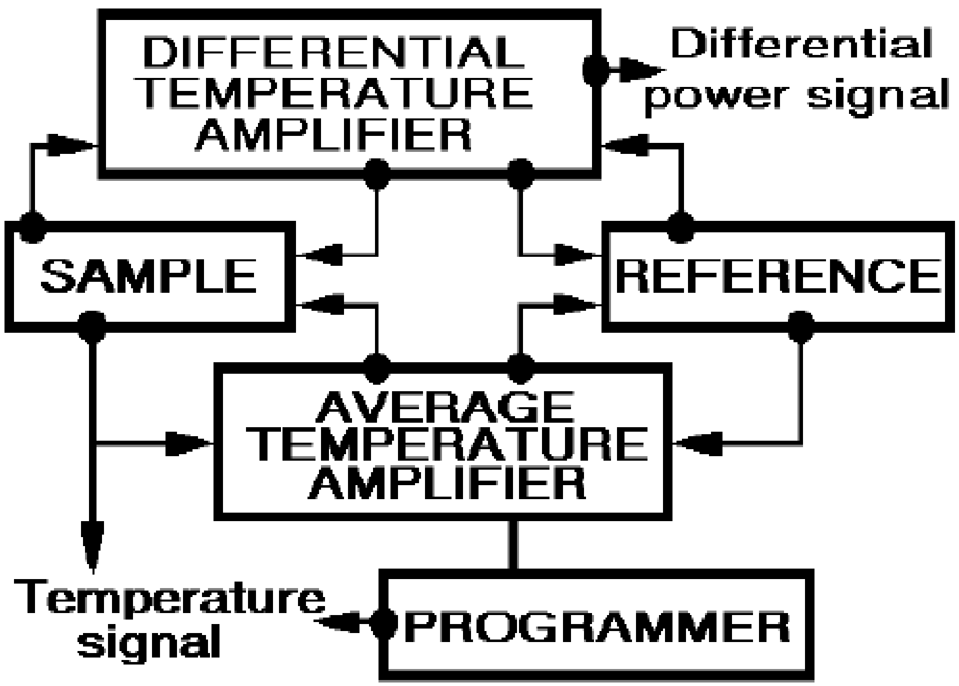
$$C_S = C_R - K\frac{\Delta T}{\beta}$$

Power Compensation Calorimeter



110-1000 K   0.1-500 K/min

noise ±4 μW   sample size up to 75 mm^3



PC Calorimeter – Steps in Measurement

- Individual micro-furnaces heated separately
- Programmer supplies same power to the sample and reference micro-furnaces
- In case of thermal symmetry same heating power for sample and reference
- For sample thermal transitions involving heat exchange the sample's heating power is regulated by a proportional controller
- $\Delta P = k_1 * \Delta T$ and $\phi_m = k_2 * \Delta T$
- Measured ΔT thus directly gives heat flow rate in sample

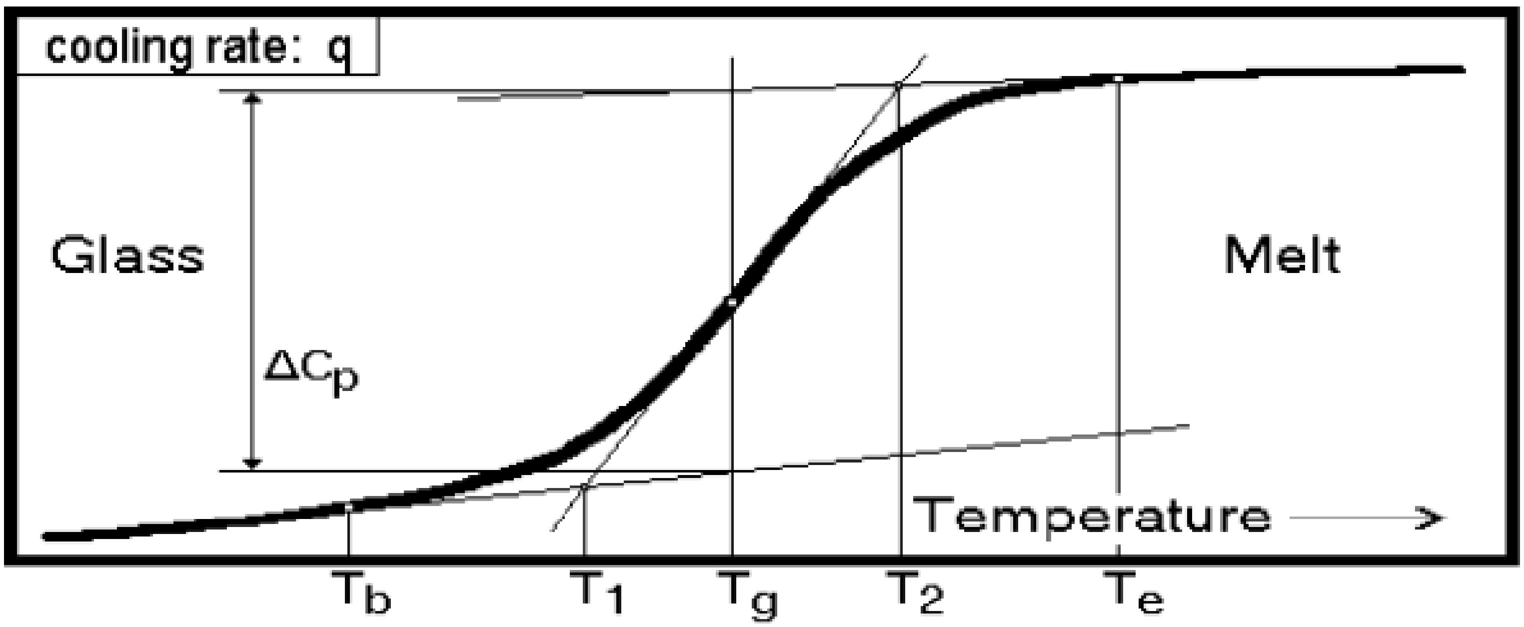
Advantages of PC Calorimeter

- Fast heating/cooling rate
- Differential heating power directly measures heat flow

What can you measure using DSC?

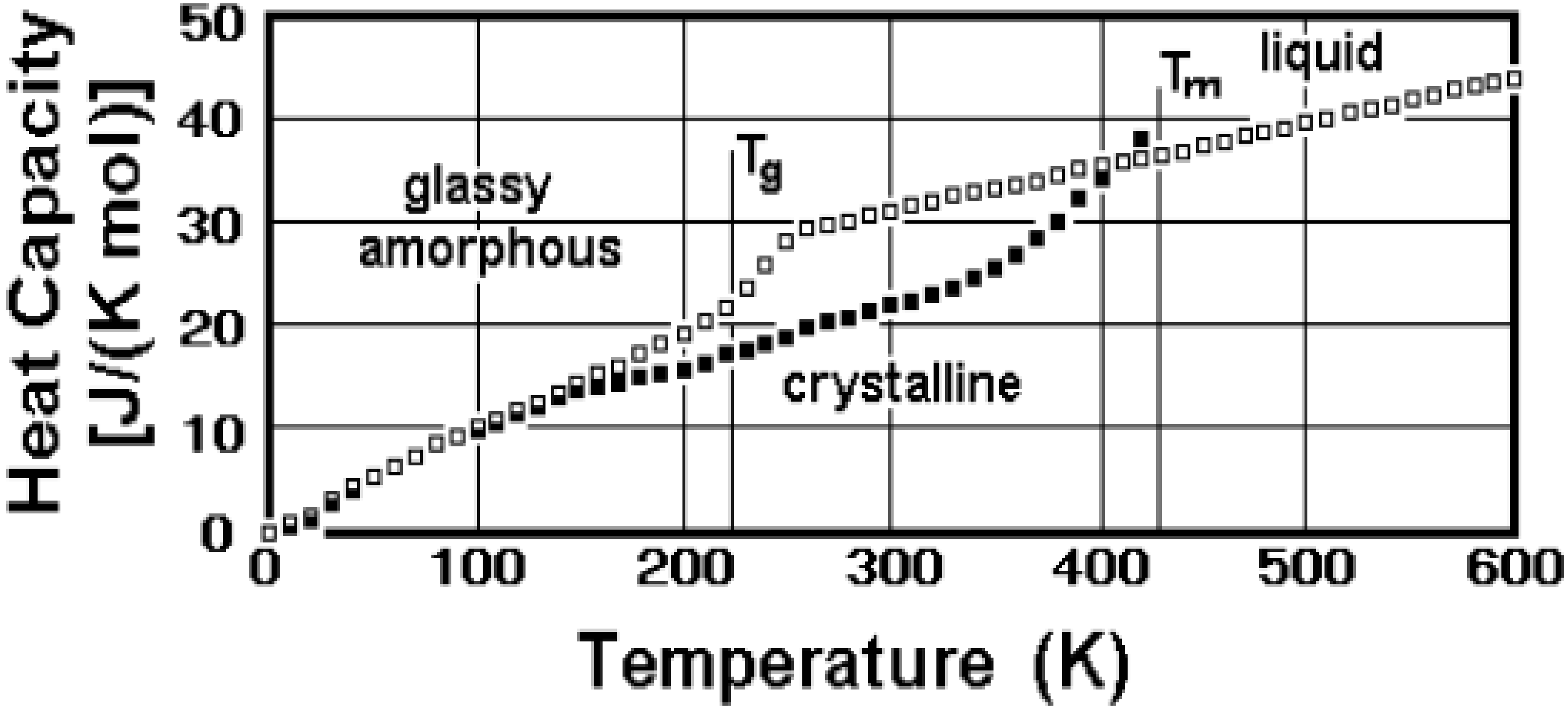
- Specific Heat (C_P)
- Entropy, S $S = \int (C_p/T)\,dT$
- Enthalpy, H $H = \int C_p\,dT$

Measurement of Glass Transition by DSC



Wunderlich, Thermal Analysis of Polymers (Springer)

Measurement of Glass Transition by DSC



Wunderlich, Thermal Analysis of Polymers (Springer)

Fictive Temperature

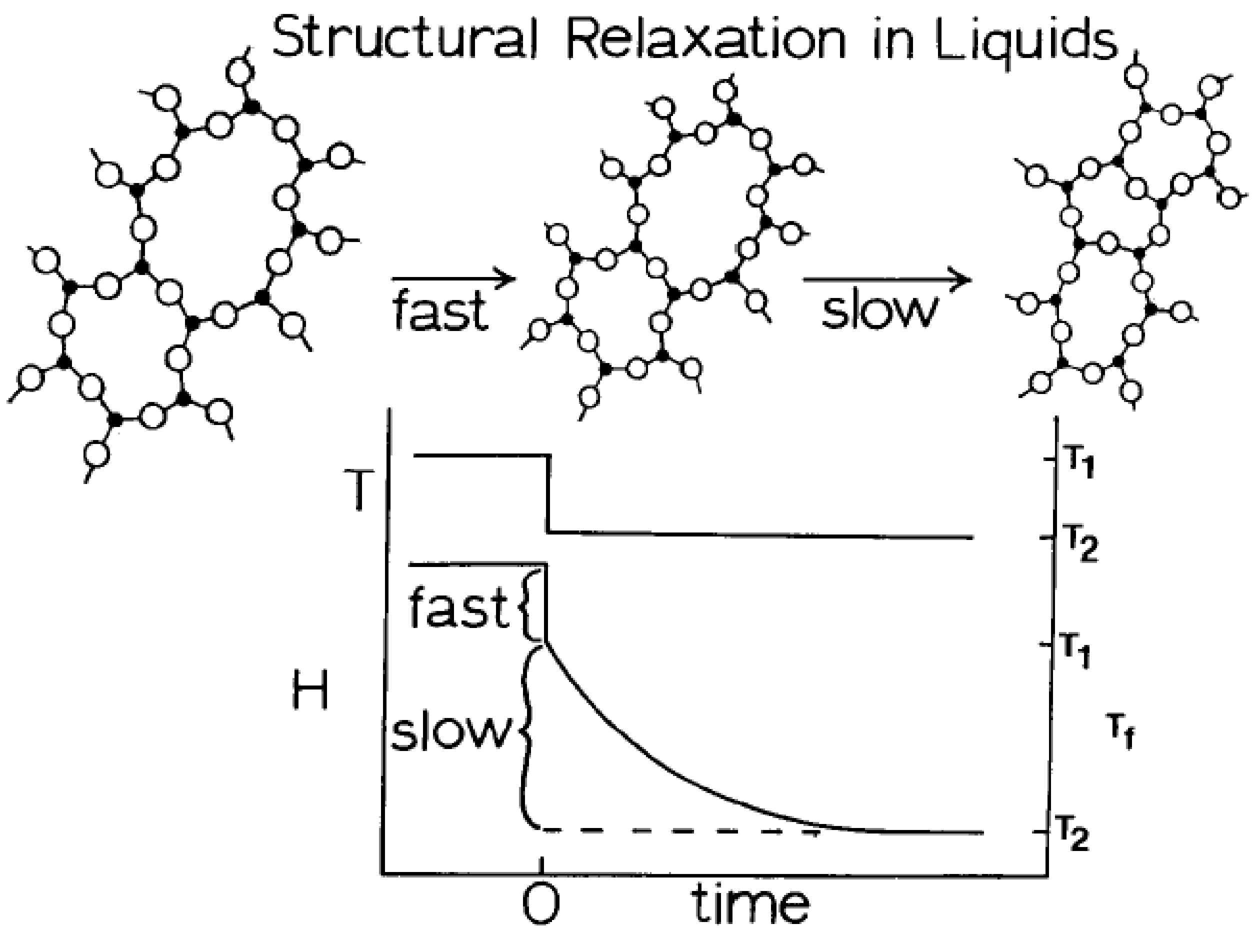


Fig. 1. Schematic plot of enthalpy H and fictive temperature T_f versus time during isothermal structural relaxation following a step change in temperature.

Moynihan (1996)

Fictive Temperature

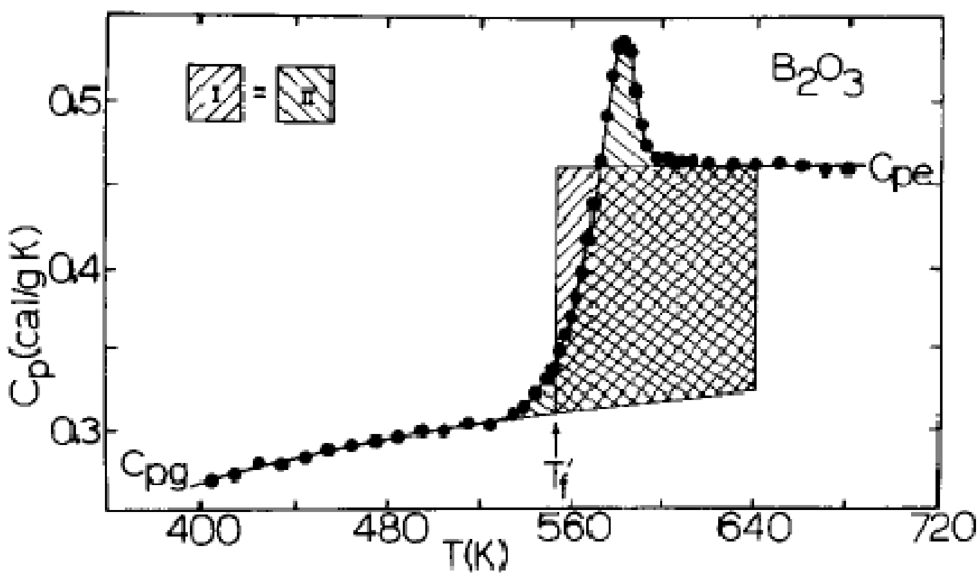
$$\phi(t) = \frac{T_f(t) - T_2}{T_1 - T_2} = \sum_i g_i \exp\left(-\int_0^t dt'/\tau_i\right)$$

$x \ (0 \leq x \leq 1)$

Non-linearity parameter

$$\ln \tau_i = \ln \tau_{i0} + \frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f}$$

TNM Eqn



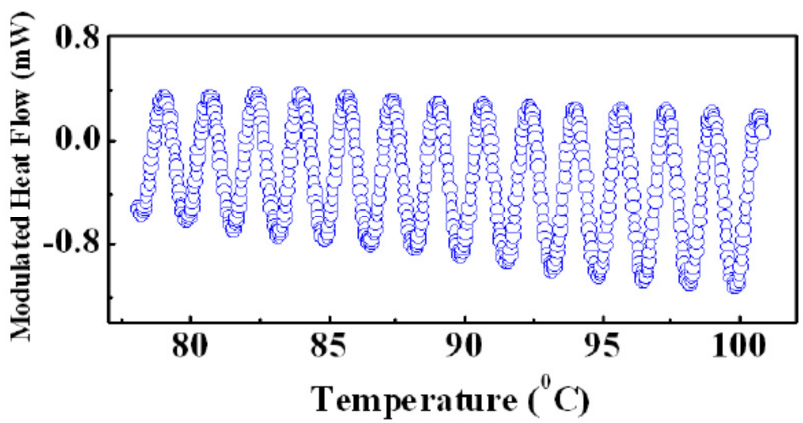
Moynihan (1996)

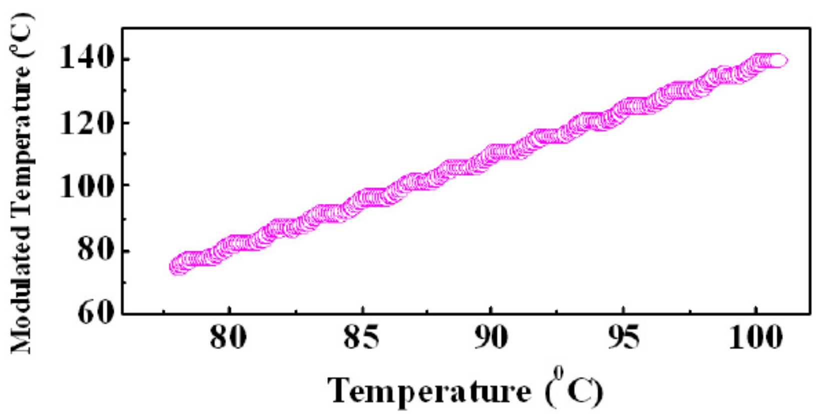
Modulated Differential Scanning Calorimetry (MDSC)

- In MDSC, a sinusoidal heating profile is overlaid on the standard linear ramp
- From this experiment, the standard Heat Flow curve is separated into two components called the Reversing Heat Flow and the Non-Reversing Heat Flow
- Total Heat Flow is the same as in standard DSC
- Reversing Heat Flow is the Cp component
- Non-Reversing Heat Flow is the Kinetic Component
- Available frequency range 2-200 mHz

Principle of MDSC

$$T(t) = T_0 + \beta_0 t + T_a \sin(\omega_0 t)$$





Theory of MDSC

Linear Response theory - FDT

$$X(t) = \alpha_{\mathrm{st}} F(t) + \frac{d}{dt}\int_{-\infty}^{\infty} \alpha(t - t')F(t')\,dt'$$

$$\lim_{t\to 0} \alpha(t) = \alpha_{\mathrm{st}}$$

$$\alpha(\omega) = \alpha_{\mathrm{st}} + \int_{-\infty}^{\infty} \dot{\alpha}(t)e^{-i\omega\tau}\,dt$$

$$\alpha(\omega) = \alpha'(\omega) - i\alpha''(\omega)$$

$$\langle X^2\rangle_\omega = \frac{kT}{\pi\omega}\alpha''(\omega)$$

$$dS(t) = \frac{C_{\mathrm{st}}}{T}\Delta T(t) - \int_{-\infty}^{t} \frac{\dot{C}_{\mathrm{dyn}}(t - t')}{T}\Delta T(t')dt'$$

ΔT(t) = F(t) and ***dS(t) = X(t)***.

Schawe, J Poly Phys (1998)

Theory of MDSC ..

$$C(t) = C_{\mathrm{st}} + C_{\mathrm{dyn}}(t)$$

$$C(\omega) = C_{\mathrm{st}} + \int_0^\infty \dot{C}_{\mathrm{dyn}}(t')e^{-i\omega t'}dt' = C'(\omega) - iC''(\omega) = C_{\mathrm{st}} + C'_{\mathrm{dyn}}(\omega) - iC''(\omega)$$

Often the measured heat capacities are also interpreted in terms of *reversing* and *non-reversing* heat capacities.
The reversing heat capacity is given by

$$|C(\omega_0)|$$

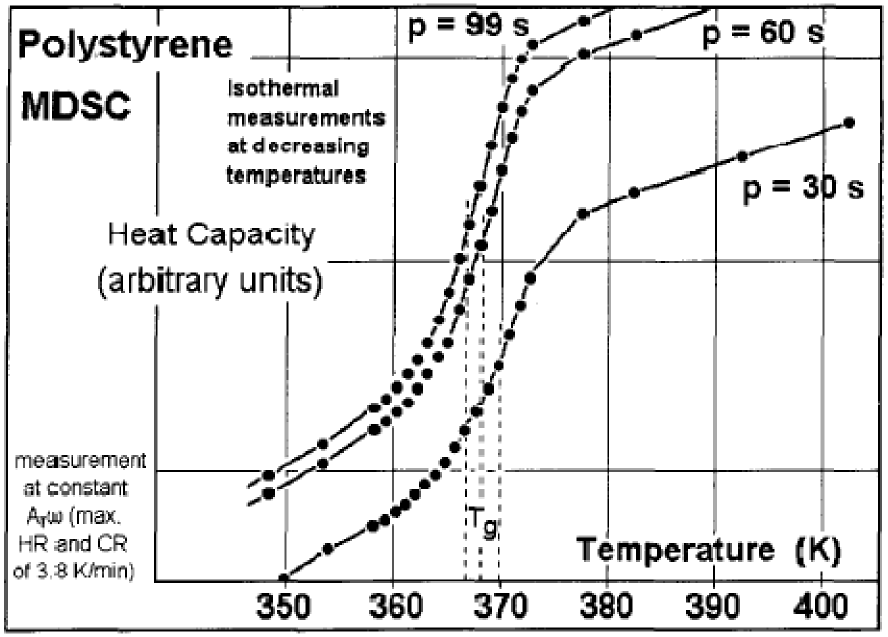
$$|C_p^*(\omega)| = \frac{A_{HF}}{A_q}$$

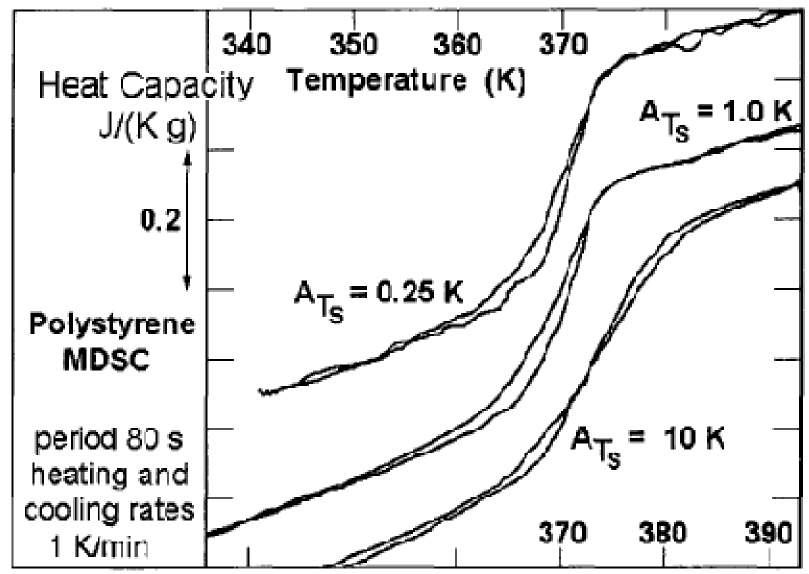
A_{HF} is the ampl of modulation of the heat flow (response)
A_q is the ampl of modulation of the heating rate (Force)

Typical Parameters for MDSC

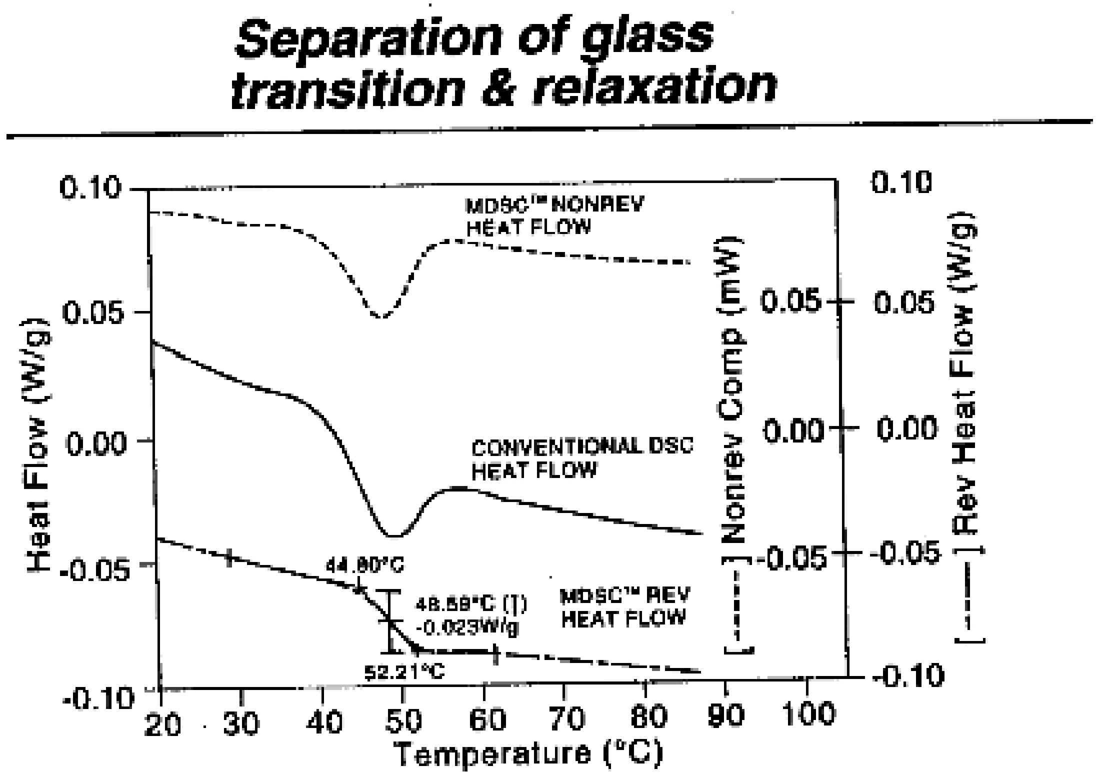
- Modulation Periods – 10 – 200 secs
- Amplitude – 0.1- 2.0 K

MDSC - Examples

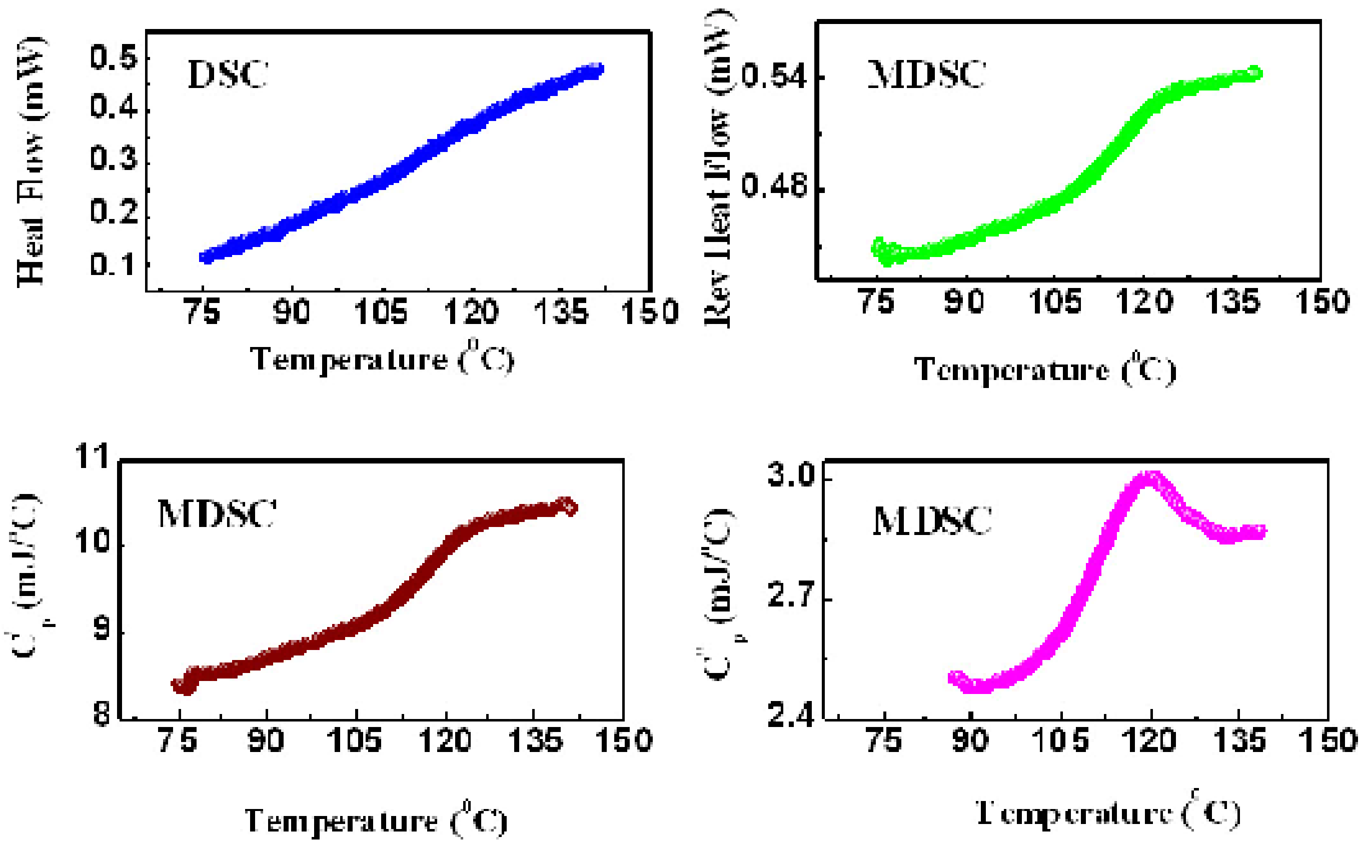




MDSC - Examples



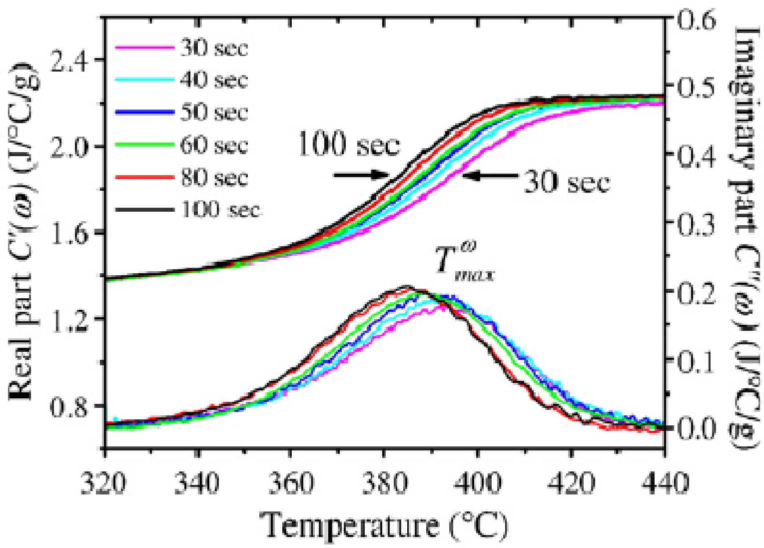
MDSC - Examples

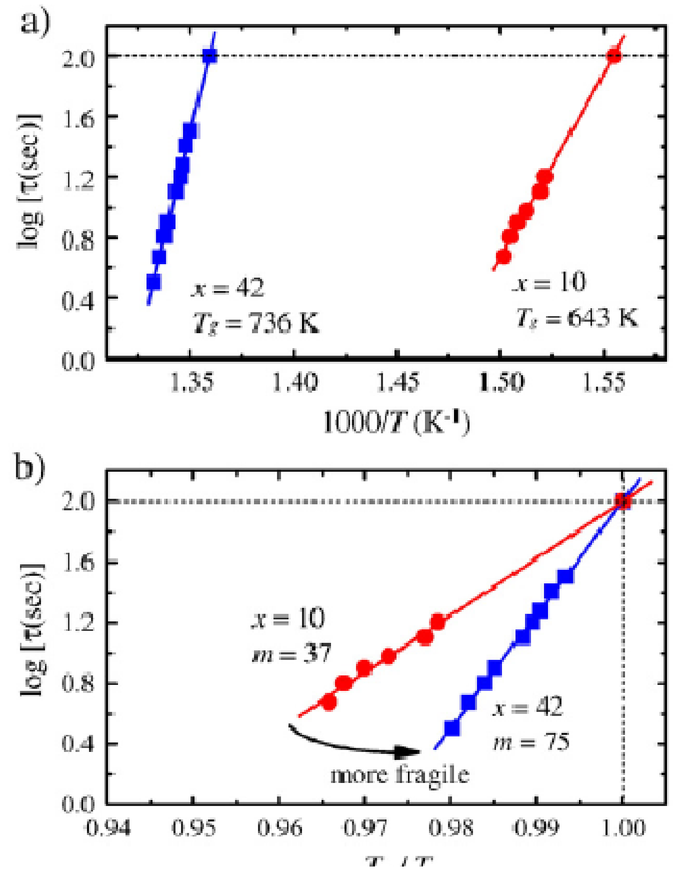


Glass Transition of Polymethyl methacrylate

Srivastava and Basu, Phys Rev Lett 98 (2007)

MDSC –Spectroscopy





Matsuda Solid State Ionics (2008)

$$\tau = \frac{P}{2\pi} = \frac{1}{\omega}$$

$$m = \lim_{T \to T_g} \left| \frac{d \log \tau}{d(T_g/T)} \right|$$

Heat Capacity Spectroscopy

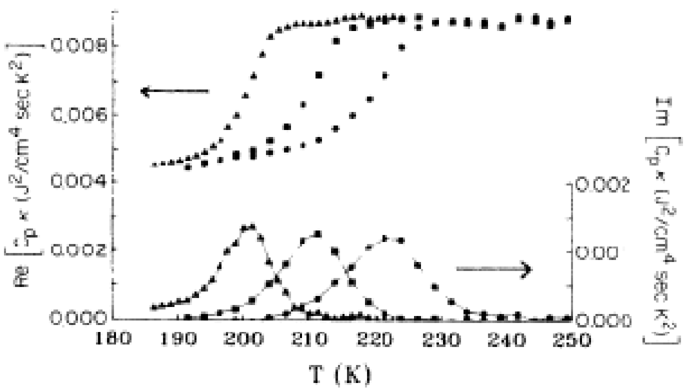


FIG. 1. The real and imaginary parts of $c_p\kappa$ (units of $J^2/cm^4 \sec K^2$) for glycerol as a function of temperature. The measurement frequencies are $f=0.62$ Hz (▲), $f=34$ Hz (■), and $f=1100$ Hz (●). This figure is taken from Ref. 4, but with the vertical scale corrected.

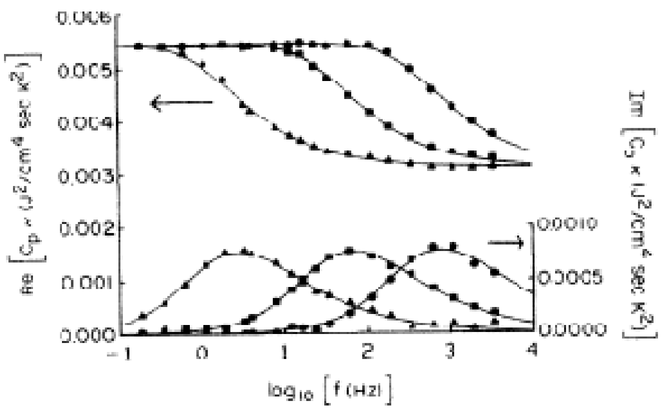


FIG. 3. The real and imaginary parts of $c_p\kappa$ (units of $J^2/cm^4 \sec K^2$) for propylene glycol as a function of frequency. The temperatures are $T=180.5$ K (▲), $T=188$ K (■), and $T=195.5$ K (●). The solid lines are fits to the data with a Kohlrausch-Williams-Watts function with $\beta=0.61$.

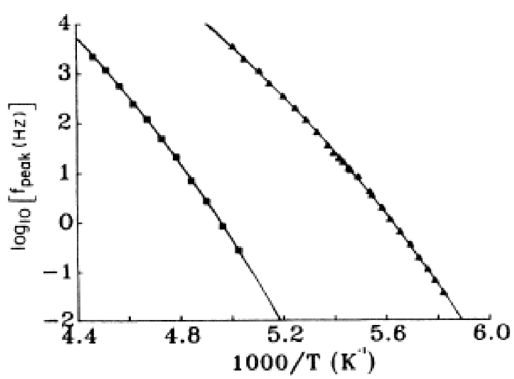
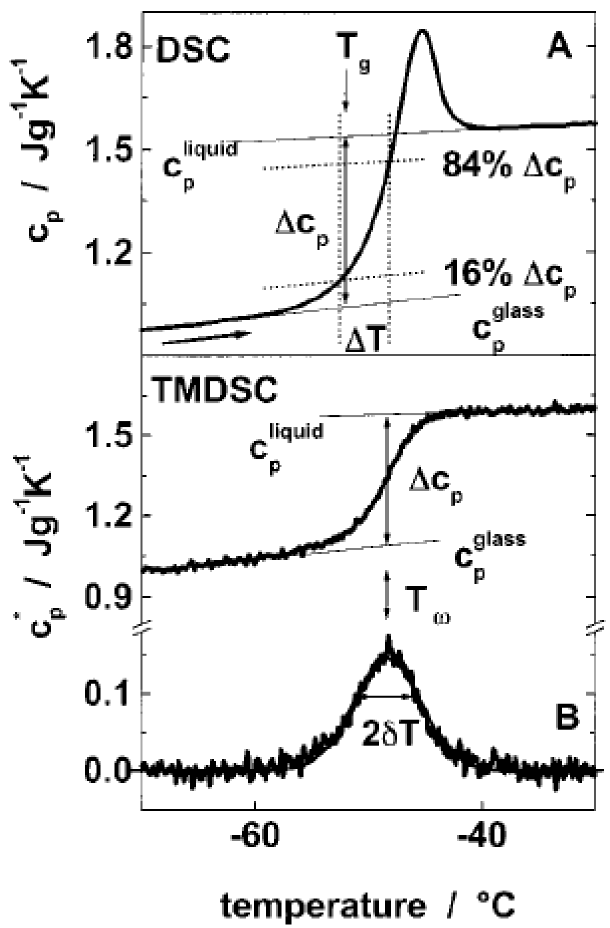


FIG. 4. The peak frequency, on a log scale, versus inverse temperature for glycerol (■) and for propylene glycol (▲). The solid lines in both cases are two indistinguishable fits to the data with a Vogel-Fulcher-Tammann law and with a scaling law. The parameters for the fits are given in Table II.

Birge, PRB (86)

Dynamic heterogeneity or CRR from DSC



$$V_\alpha = \xi_\alpha^3 = k_B T^2 \Delta(1/c_V)/\rho\delta T^2$$

$$N_\alpha = V_\alpha \rho/M_0$$

Hempel et al, J Phys Chem B 104, 2460 (2000).

Assumptions

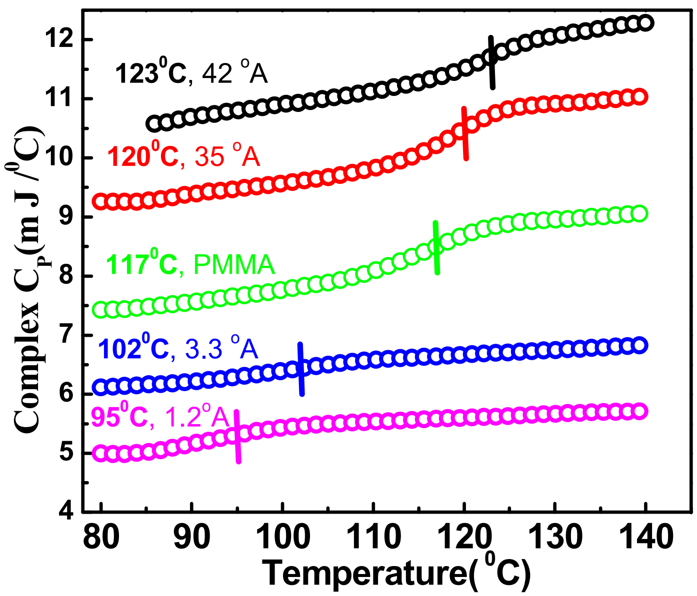
- δT is the temperature fluctuation of one CRR
- T fluctuation is obtained from FDT
- Central part of imaginary C_P is Gaussian

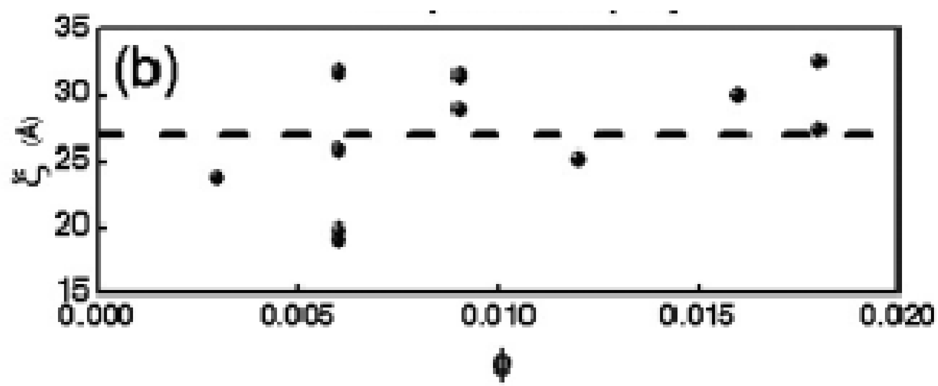
- $dT/d\ln\omega$ is constant across the dispersion zone

TABLE 1: Summary of the Investigated Substances

				DSC				TMDSC				
no.	substance, abbreviation	M_0, g/mol	fullname	T_g, °C	δT, K	Δc_p, J/g K	$\xi_\alpha(T_g)$, nm	T_ω (t_p/s), °C	δT, K	Δc_p, J/g K	$\xi_\alpha(T_\omega)$, nm	rem.
1	PMMA	100	poly(methyl methacrylate)	95	5.1	0.25	1.5	97.5 (60)	8.5	0.23	1.1	*e, g*
2	PEMA	114	poly(ethyl methacrylate)	70	3.8	0.26	1.8	75.5 (60)	7.5	0.22	1.1	*g*
3	PPrMA	128	poly(*n*-propyl methacrylate)	51	4.8	0.20	1.4	56.5 (60)	10.0	0.18	0.9	*g*
4	P*n*BMA	142	poly(*n*-butyl methacrylate)	25	5.4	0.19	1.2	32.5 (60)	8.0	0.16	0.9	*g*
5	P*n*PenMA	156	poly(*n*-pentyl methacrylate)	7	7.0	0.29	1.0	8.5 (60)	11.3	0.20	0.8	*g*
6	P*n*HMA	170	poly(*n*-hexyl methacrylate)	−20	8.8	0.29	1.0	−12 (60)	12.1	0.33	0.9	*g*
7	BIBE	268	benzoin isobutyl ether	−52	2.1	0.49	3.2	−48.5 (60)	2.8	0.49	2.7	
8	AMPEK	196	poly(ether ketone) from ICI	153	2.0	0.25	3.2	153 (600)	2.2	0.24	3.0	*a, g*
9	PS	104	poly(styrene) PS168N BASF	100	2.3	0.28	3.0	103.5 (60)	3.4	0.28	2.5	*a, g*
10	PVAC	86	poly(vinyl acetate)	40	2.3	0.44	3.2	45.5 (24)	3.6	0.39	2.3	*b, g*
11	CKN	126	$40Ca(NO_3)_2\ 60KNO_3$	64	2.4	0.55	3.2	68.5 (60)	2.9	0.46	2.6	*b, g*
12	$Na_2O{\cdot}SiO_2$	91	natrium disilicate	458	8.0	0.27	1.8	470 (750)	12.1	0.28	1.4	*b, g*
13	DGG	59	standard glass 1 from DGG[45]	538	12.1	0.25	1.4	576 (120)	14.0	0.23	1.3	*b, g*
14	$2SN_4$	954	liquid sulfur bridged twin crystal[45]	78	2.5	0.45	1.1	84 (100)	2.7	0.42	1.1	*b, g*
15	SBR1500	61	styrene−butadiene−rubber, 23% styrene	−58	2.4	0.46	2.7	−56 (60)	3.2	0.45	2.2	*g*
16	P(*n*BMA-*stat*-S) 2%S	141	poly(*n*-butyl methacrylate-*stat*-styrene) 2% styrene	30	4.3	0.22	1.5	34.5 (48)	10.7	0.22	0.9	*a, f, g*
17	$Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$	78	metallic glass	373	6.3	0.24	2.6	389 (60)	13.4	0.18	1.6	*d, h*
18	MAG	65	mixed alkali glass	477	10.8	0.22	1.5					*c*,[52] *i*
19	glycerol	92		−84	2.5	1.02	2.9	−80 (60)	2.6	0.97	2.6	*i*
20	salol	214	phenyl salicylate	−54	1.8	0.53	3.1	−51 (60)	2.3	0.55	3.3	*a*
21	OTP	230	*o*-terphenyl	−24	2.3	0.46	3.0					*c, i*
22	sorbitol	182	D(−) sorbitol	−12	2.0	1.04	3.6					*c, i*
23	BMPC	296	bis(methoxy phenyl)cyclohexane	−31	2.1	0.41	3.0	−26.5 (60)	2.5	0.36	3.1	*a*
24	selenium	79		37	2.7	0.38	3.0					*c*,[53] *i*
25	PVC	62	poly(vinyl chloride)	80	2.4	0.31	3.1					*c*,[44] *i*
26	silicate glasses	30...58		476−545	17.6 ± 5.3	0.27 ± 0.05	1.2					*c*,[54] *i*
27	cyclohexanol	100	phase I (ODIC)	−124	2.0	0.26	2.4					*c*,[55] *i*
28	B_2O_3	70	bortrioxid	274	8.1	0.50	1.5	305 (60)	12.5	0.61	1.3	*i*

Examples

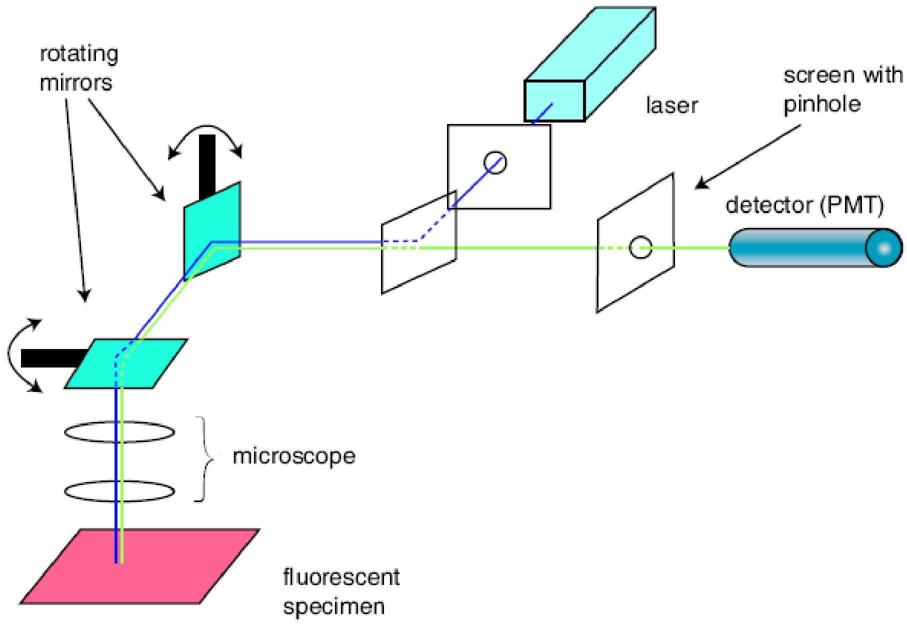


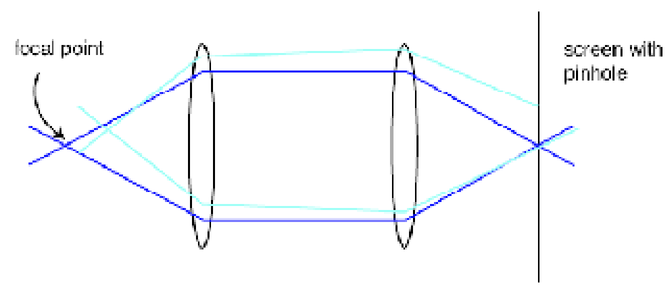


Srivastava and Basu, PRL, 98 165701 (07)

However DSC *does not* provide the *spatio-temporal* picture of the glass formation

Imaging and Particle Tracking in Glasses





Schematic of a Laser Scanning Confocal Microscope (LSCM)

Prasad, Weeks et al J Phys Cond Matt 19, 113102 (2007)

LSCM - Applications

Advantages over conventional fluorescence microscope

- Rejection of out-of-focus light – better visibility
- Ability to perform depth resolved measurements

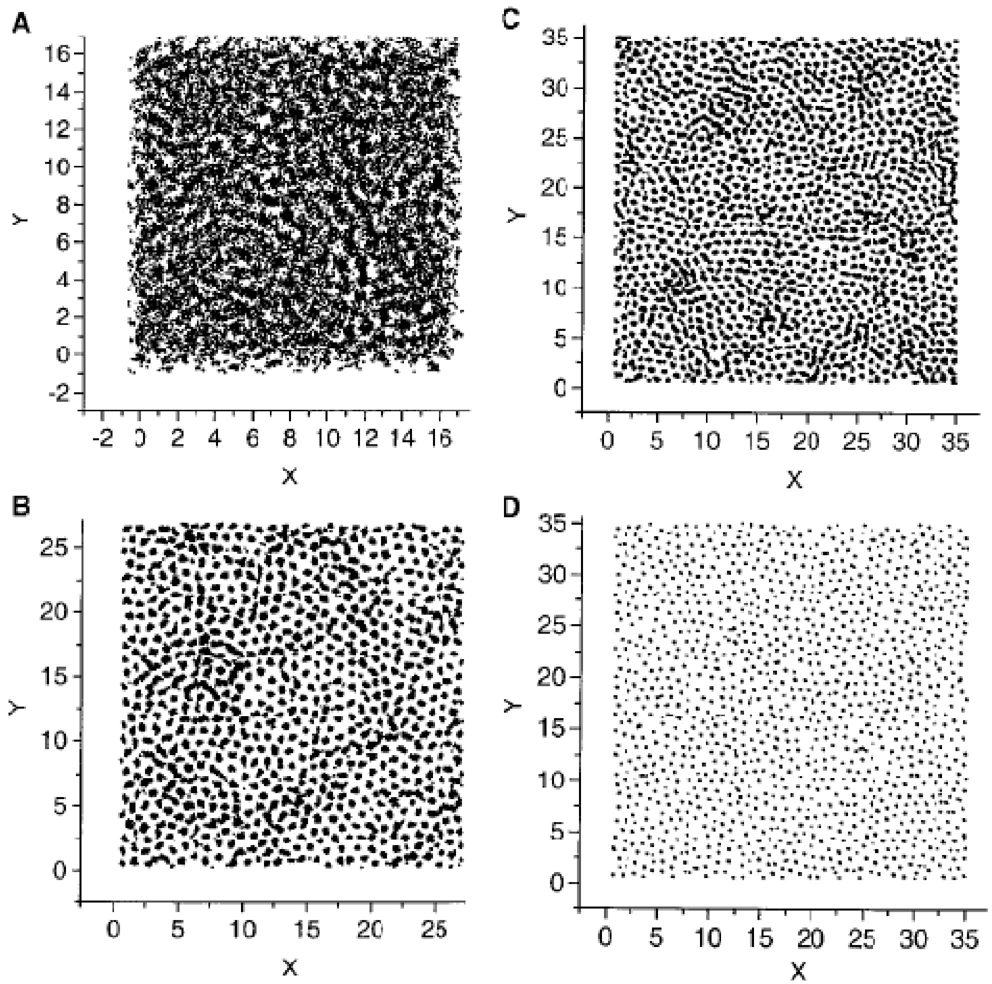
Disadvantages

- Image acquisition rate slower than video rate

Systems which can be studied

- Colloids and nanoparticles

LSCM - Examples



Kegel et al Science 287, 290 (2000)

What can you measure?

Van Hove Correlation function,

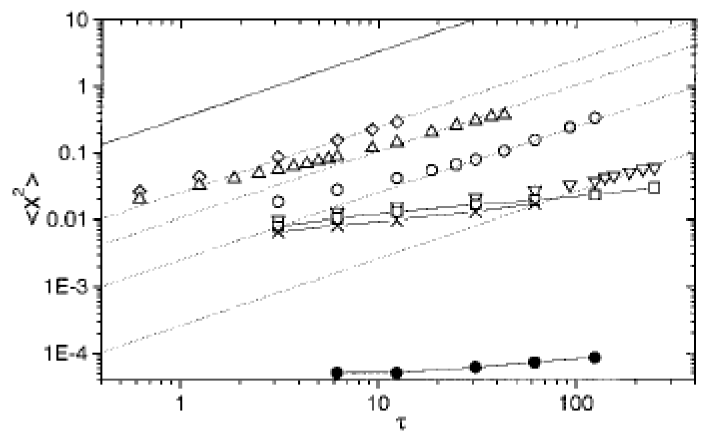
$$G_s(x,\tau) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \delta[x + x_i(0) - x_i(\tau)] \right\rangle$$

$$= \frac{N(x,\tau)}{N}$$

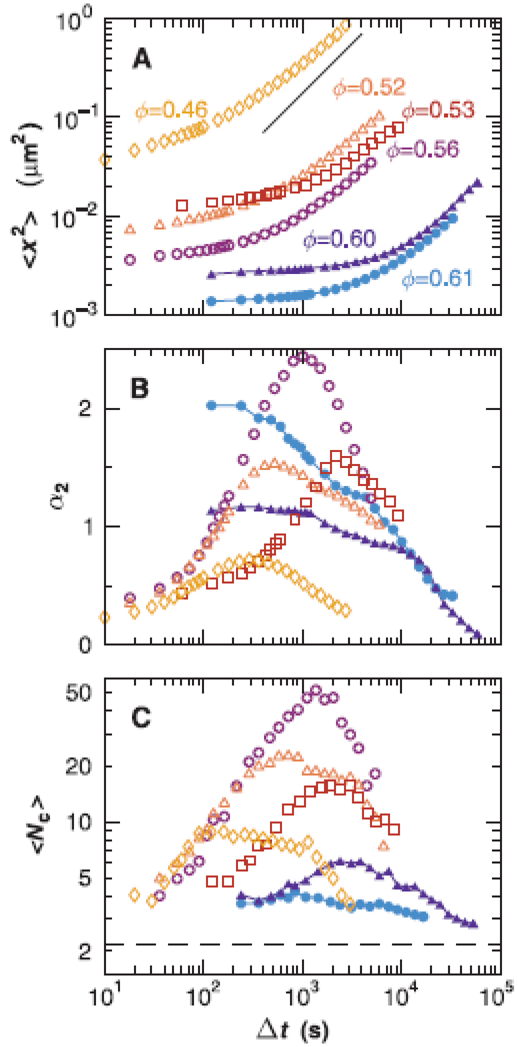
Non-Gaussian parameter,

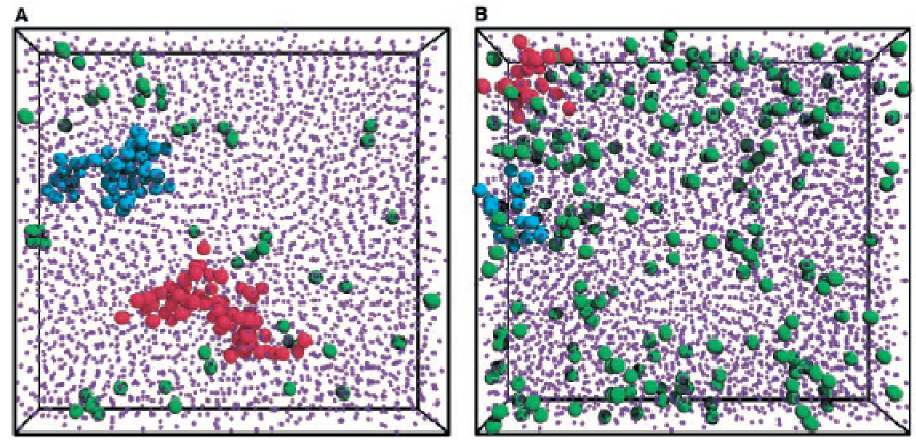
$$\alpha_2(\tau) = \frac{\langle x^4(\tau)\rangle}{3\langle x^2(\tau)\rangle^2} - 1$$

Mean Squared Displacement,



What can you measure?

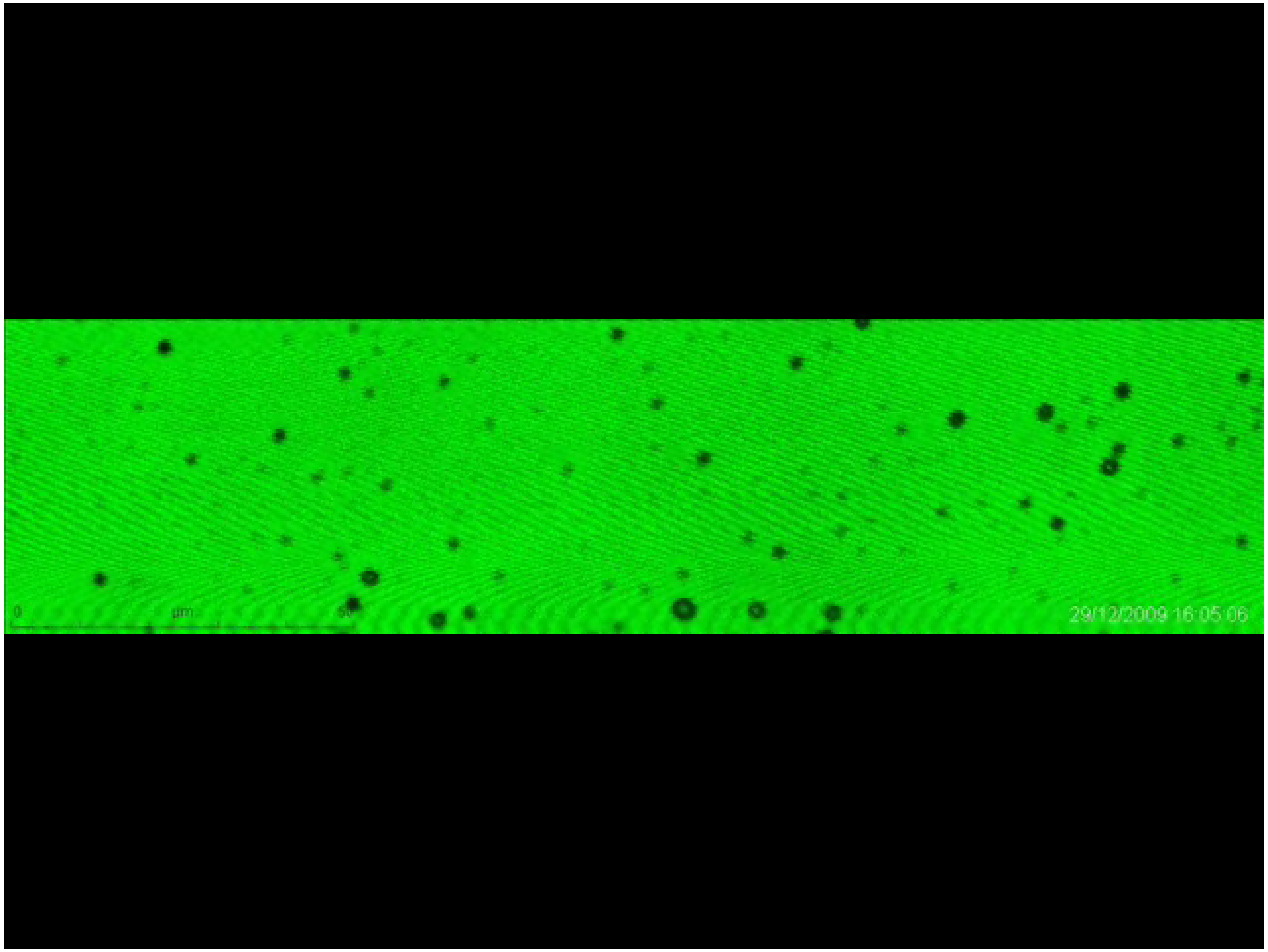


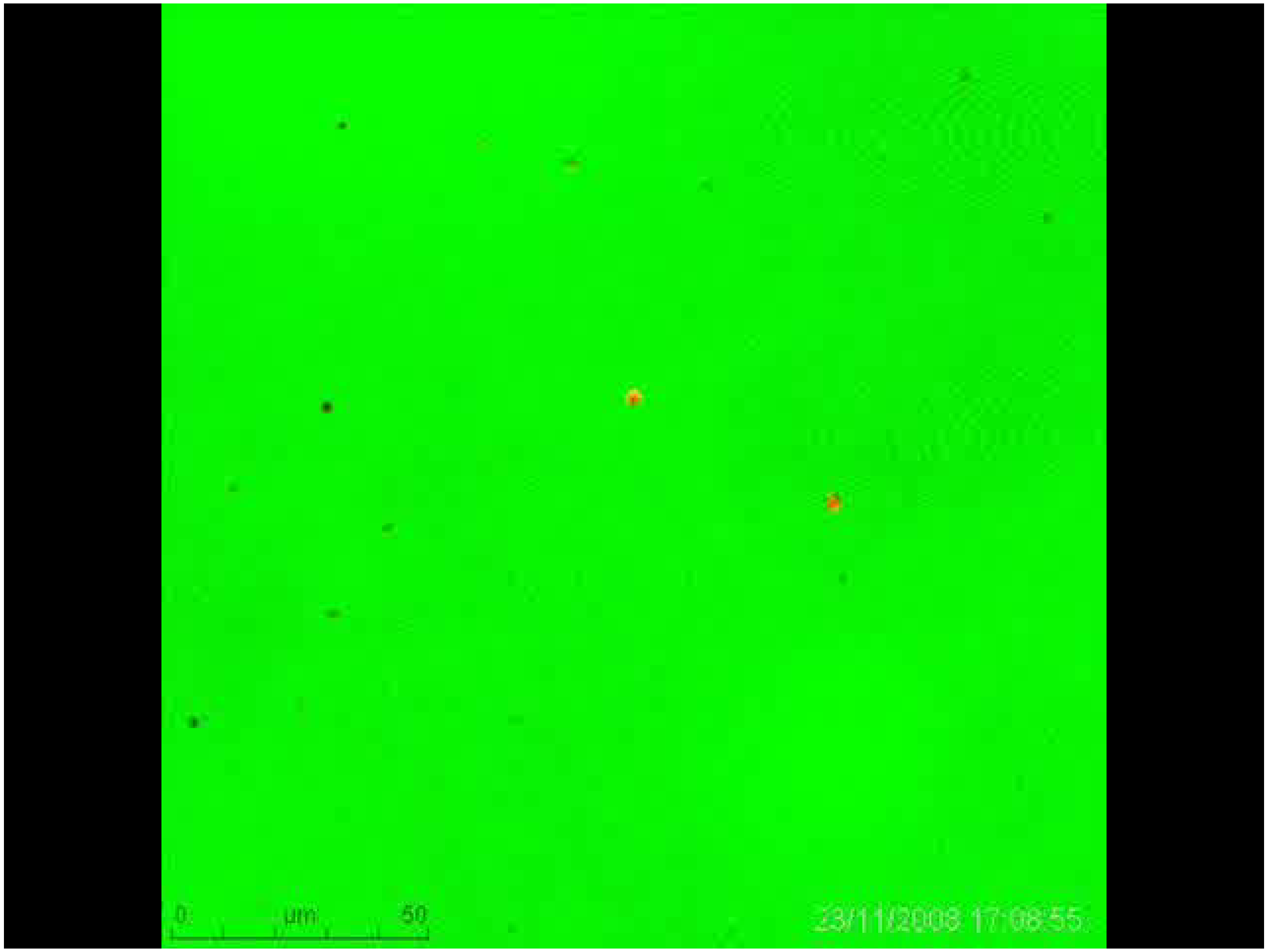


Big Particles – *fast*; small particles – *slow*

5-Jan-10

Weeks et al Science 287, 627 (2000)

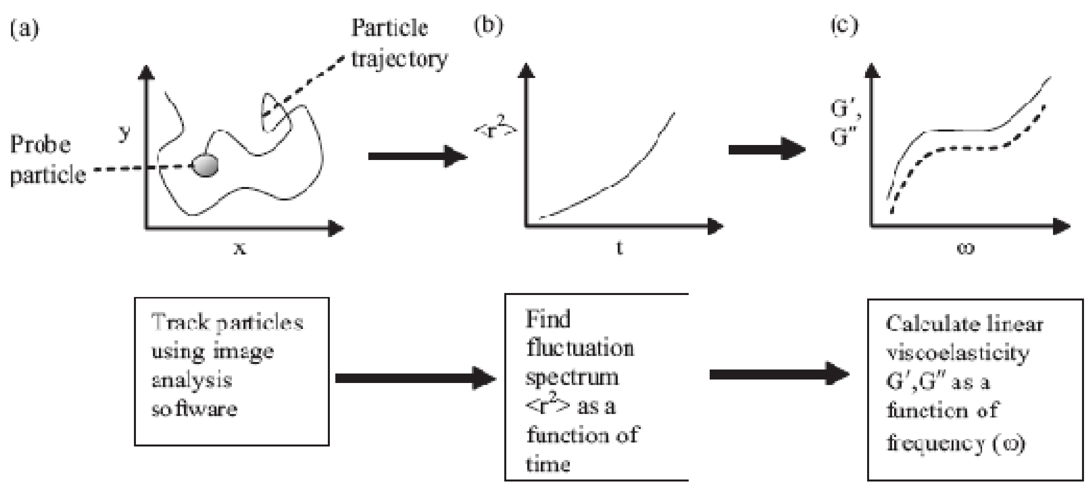

29/12/2009 16:05:06


0 um 50
23/11/2008 17:08:55

Other applications..

Particle Tracking Micro-rheology (MR)

Tom Waigh (2005)



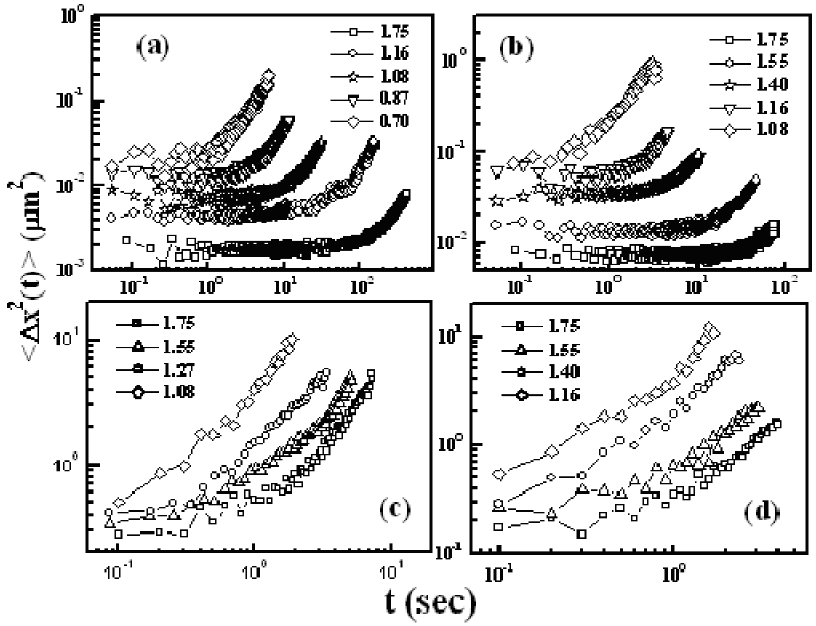
Generalised Stokes-Einstein relation

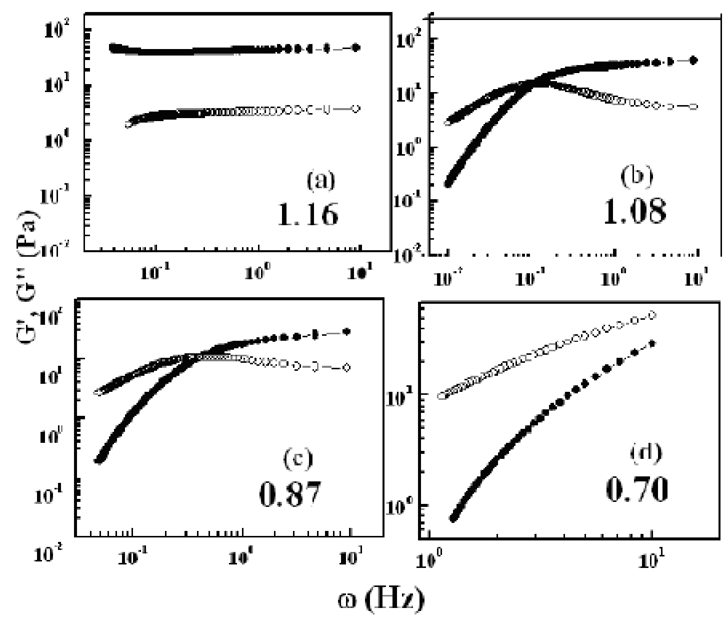
$$\tilde{G}(s) = \frac{2K_BT}{3\pi Rs\left\langle \Delta\tilde{x}^2(s)\right\rangle},$$

Mason & Weitz, PRL (95)

You can now connect to conventional Rheology discussed by Ranjini – but MR can be done with _spatial resolution_.

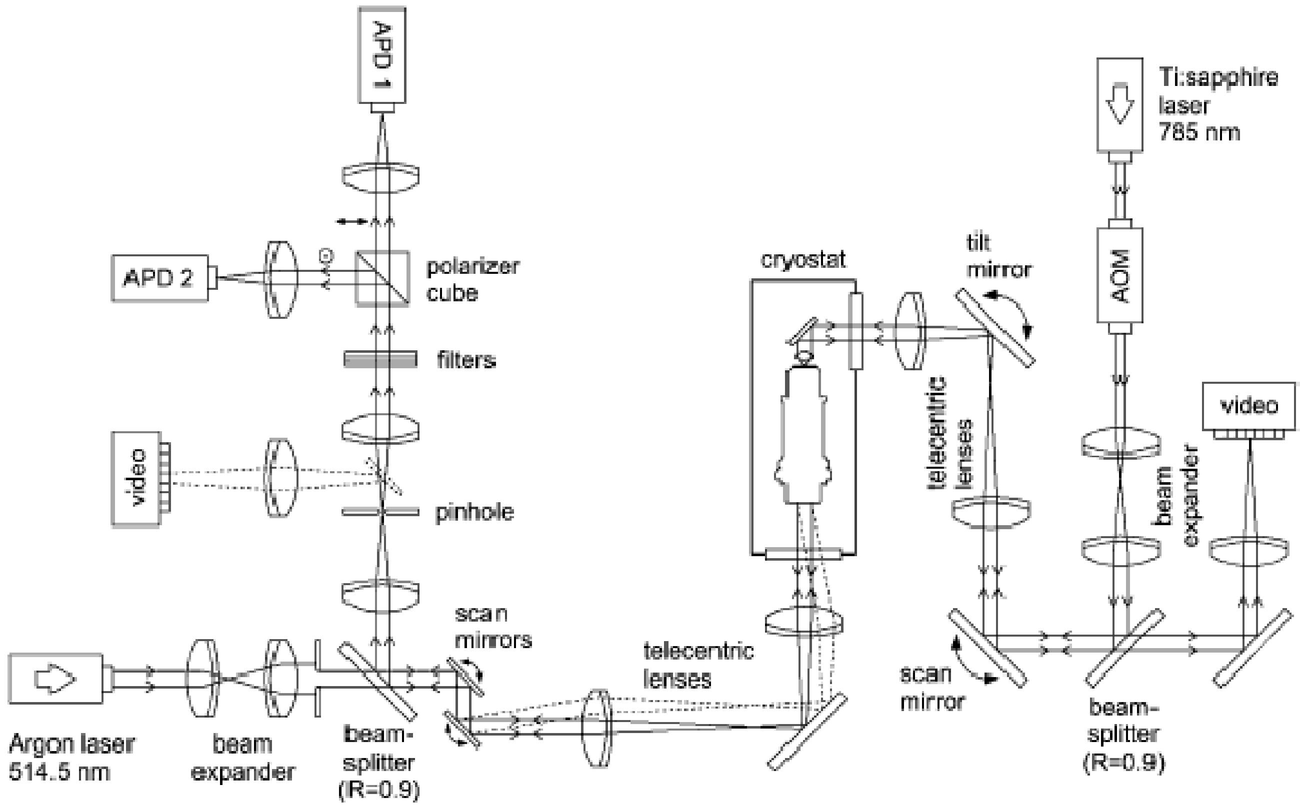
MR - Examples





Kandar et al (submitted, 2009)

Dynamic Heterogeneity from Spatially resolved single molecule dynamics (SMD)



Schematic of a SMD experiment configuration

Specifications of SMD

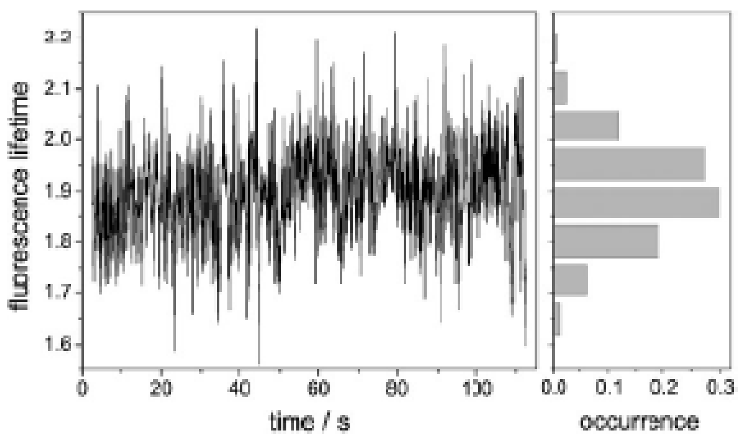
- Fluorescence lifetime fluctuations and their time autocorrelations
- Fluorescence intensity anisotropy and its time autocorrelations
- Measurements are usually made with dyes or quantum dots in glasses within a temperature range TG $\pm$ 10-15K.

SMD – Lifetime Fluctuations

For lifetime fluctuations one can write

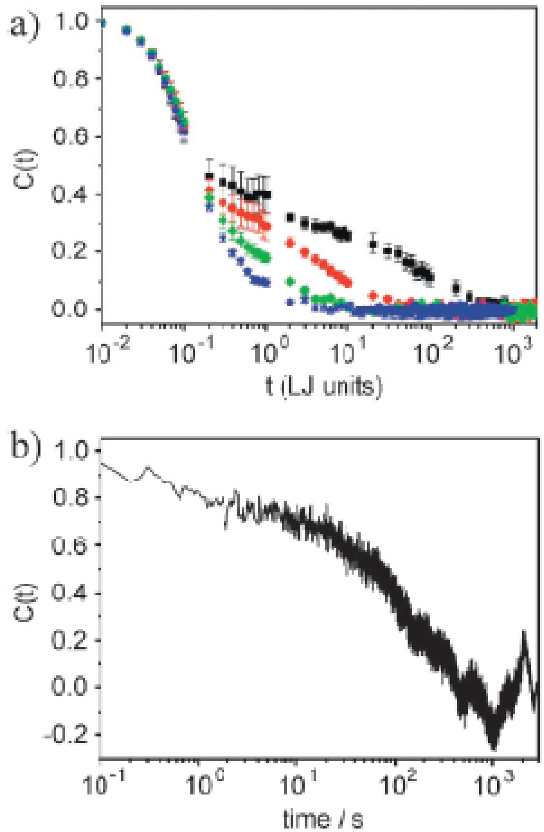
$$C(\tau) = \frac{\langle A(t+\tau)A(t)\rangle}{\langle A(t)A(t)\rangle}$$

where A(t) is the Fluorescence lifetime at time t.



Vallee et al PRL 91, 038301 (2003)

SMD – Lifetime Fluctuations



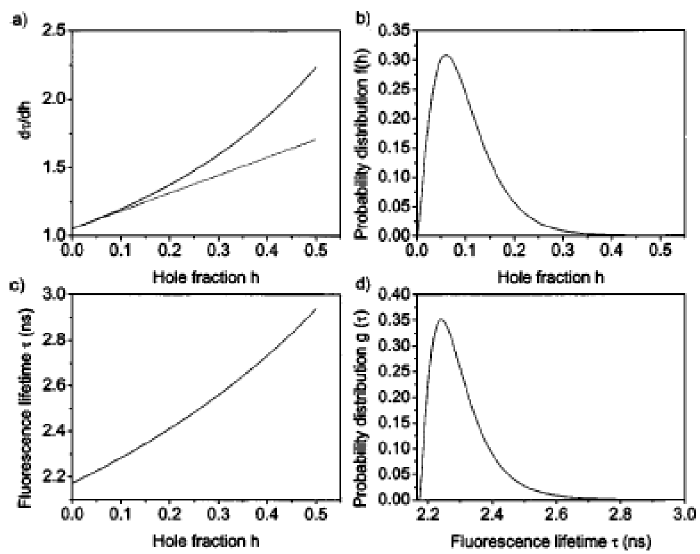
$$\Gamma = \frac{2\pi}{\hbar}|\langle e|H_{int}|g\rangle|^2\rho(\omega),$$

$$\Gamma_0 = \frac{\omega_0^3|\vec{\mu}|^2}{3\pi\epsilon_0\hbar c^3} = \frac{1}{\tau_0},$$

$$\epsilon = h\epsilon_{vac} + (1-h)\epsilon_{pol},$$

h is the fraction of holes and
ε is dielectric constant.

Correlate fluctuation in fraction of holes to fluctuation of lifetime!!



$$g(h) = f(\tau)\left|\frac{d\tau}{dh}\right|$$

RAL Vallee, J Chem Phys, 127 154903 (2007)

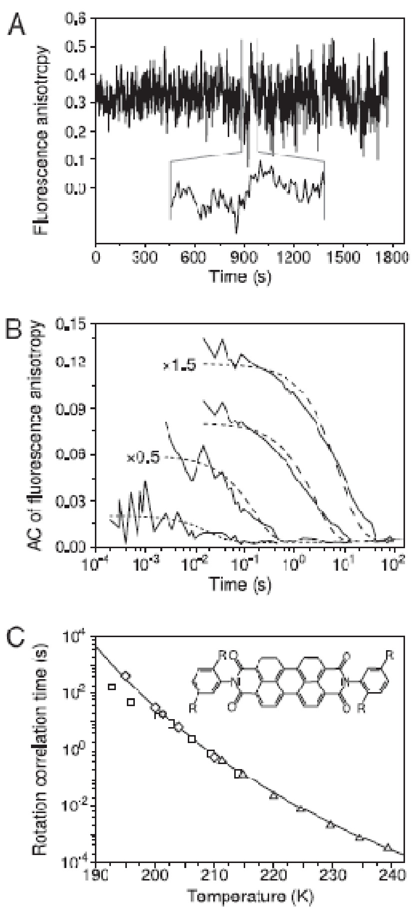
SMD using Fluorescence Intensity Anisotropy

$$r = \frac{F_{\parallel} - F_{\perp}}{F_{\parallel} + 2F_{\perp}}.$$

$$C_r'(t) = \frac{\langle r(t' + t) r(t') \rangle}{\langle r(t') \rangle^2} - 1 \approx \frac{\langle c_{SM} \rangle}{N} \exp\left(- \frac{t}{\langle \tau_R \rangle} \right)$$

$$A = \frac{F_{\parallel} - F_{\perp}}{F_{\parallel} + F_{\perp}}.$$

$$C_A'(t) = \frac{\langle (A(t' + t) + 1)(A(t') + 1) \rangle}{\langle A(t') + 1 \rangle^2} - 1 \approx \frac{1}{2} \exp\left(-\frac{t}{\tau_R} \right)$$



Zondervan et al PNAS 104, 12628 (2007)