Dynamic Light Scattering (aka QLS, PCS)

Oriented particles create interference patterns, each bright spot being a speckle. The speckle pattern moves as the particle move, creating flickering.

All the motions and measurements are described by correlations functions

- $G_2(\tau)$- intensity correlation function describes particle motion
- $G_1(\tau)$- electric field correlation function describes measured fluctuations

Which are related to connect the measurement and motion

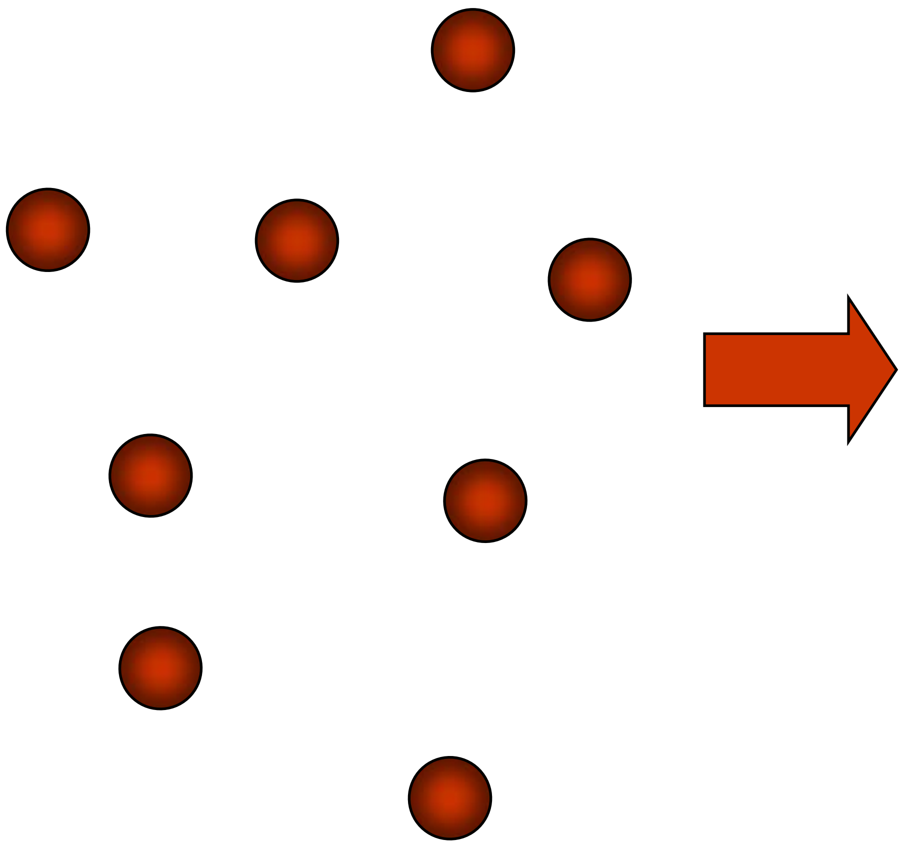
$$G_2(\tau) = B\left[1 + \beta \left| g_1(\tau) \right|^2 \right]$$

Analysis Techniques:

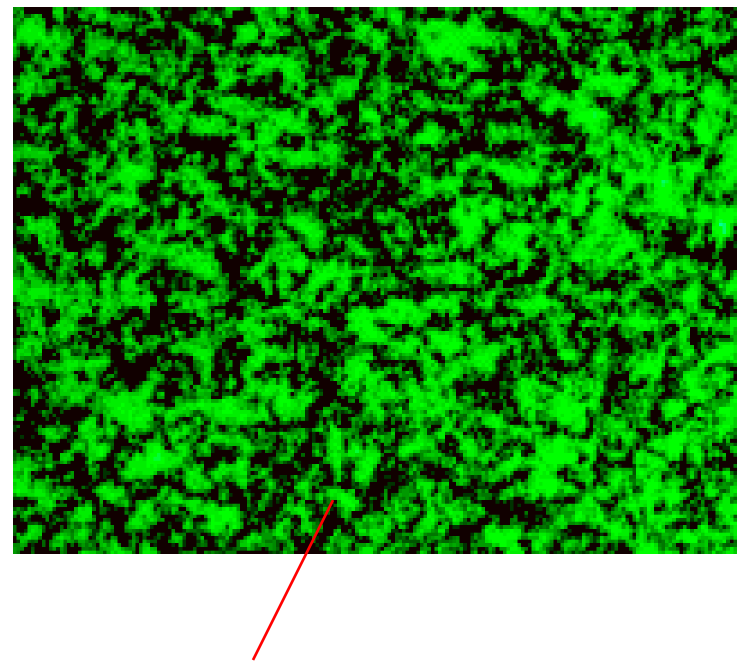
- Treatment for monomodal distributions: linear and cumulant fits
- Treatment for non-monomodal distributions: Contin fits

It is also possible to measure other motions, such as rotation.

Particles behave like 'slits', the orientation of which generates interference patterns

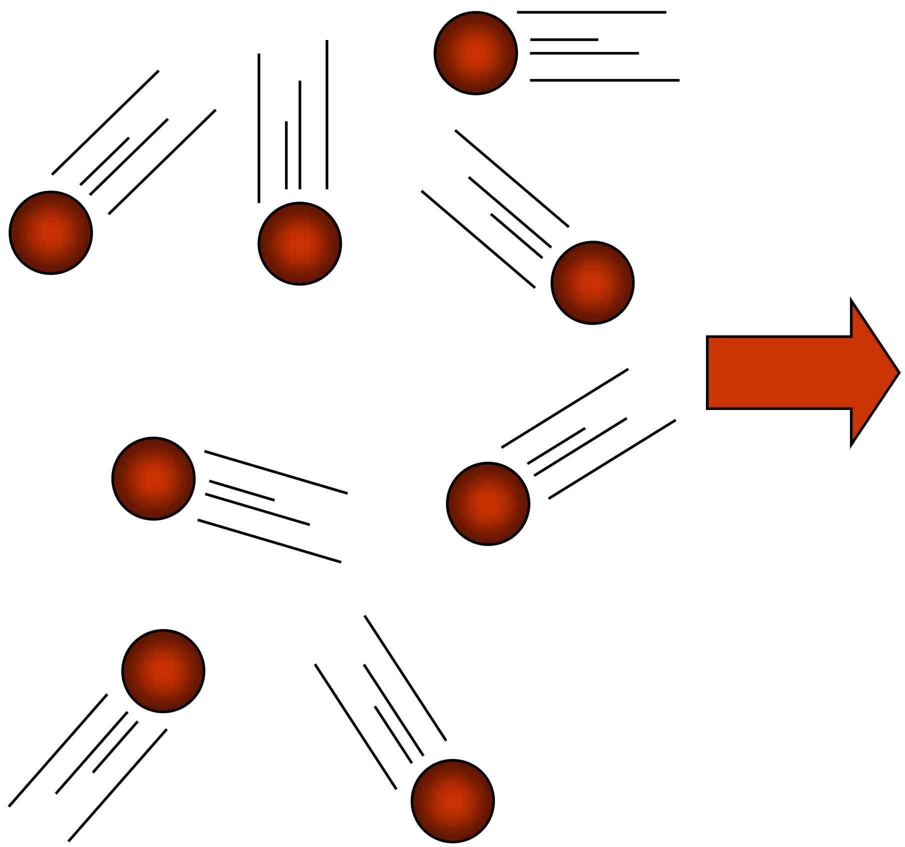


Generates a 'speckle' pattern

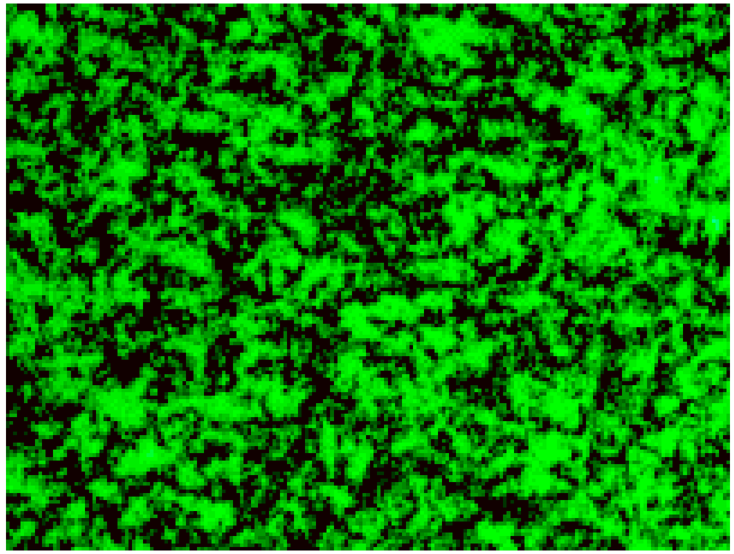


Various points reflect different scattering angles

Movement of the particles cause fluctuations in the pattern

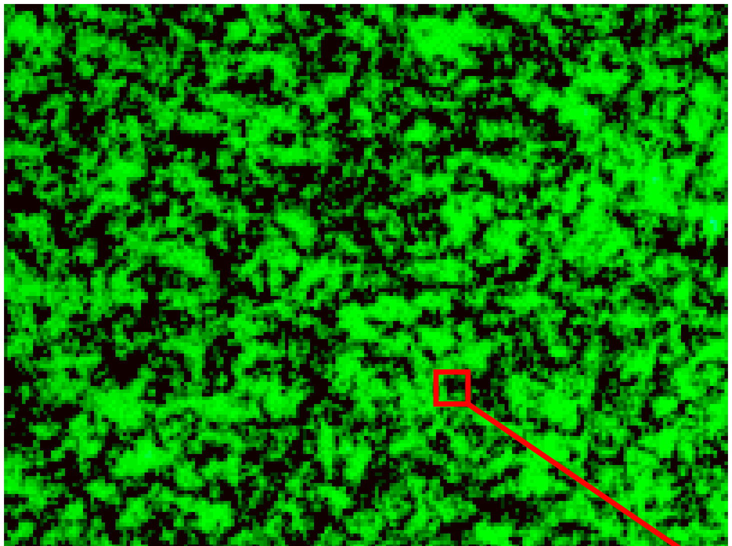


The pattern 'fluctuates'

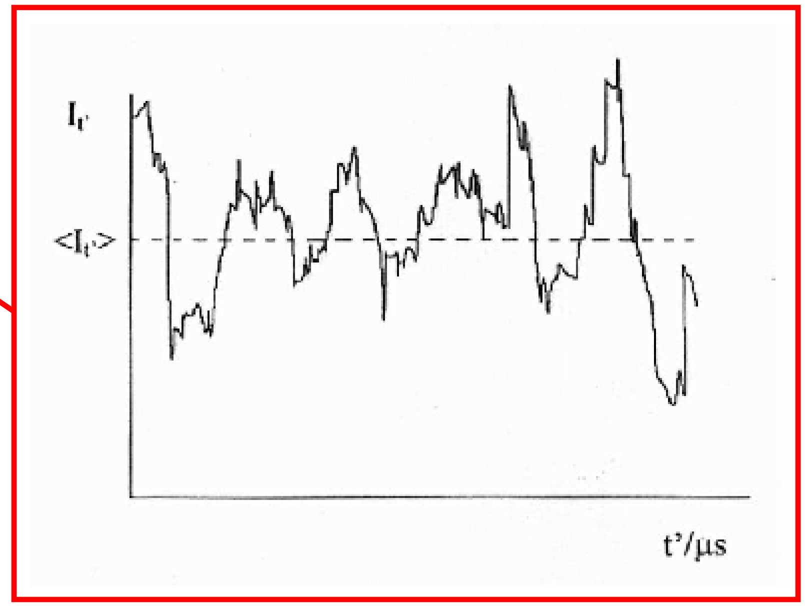


Movement is defined by the rate of fluctuation

Measure the intensity of one speckle



Experimentally, the intensity of one 'speckle' is measured



Order of magnitude for time-scale of fluctuations

fluctuations occur on the time-scale that particles move about one wavelength of light…

$$\Delta x \approx \lambda$$

Assuming Brownian motion of the particles…

$$(\Delta x)^2 = Dt$$

The time-scale is:

λ ~ 500 nm

Change on the msec time frame

$$t \approx \frac{\left(5x10^{-5}\,cm\right)^2}{2.5x10^{-8}\,cm^2/s} \approx 100\,m\,sec$$

D for ~ 200 nm particles

How is the time scale of the fluctuations related to the particle movement?

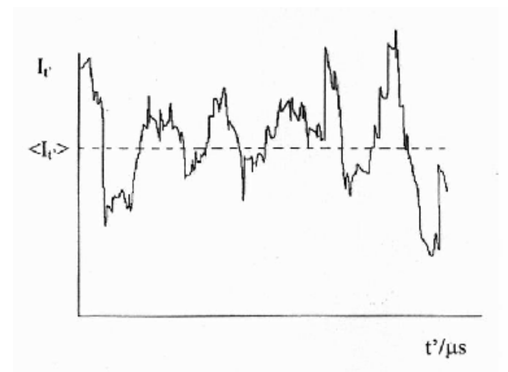
Requires several steps:

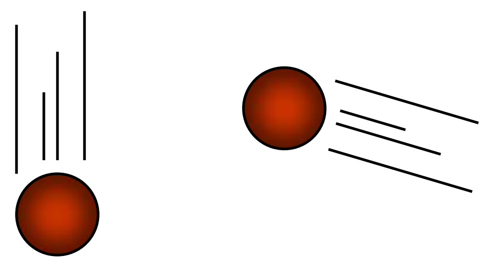
1. Measure fluctuations an convert into an Intensity Correlation Function

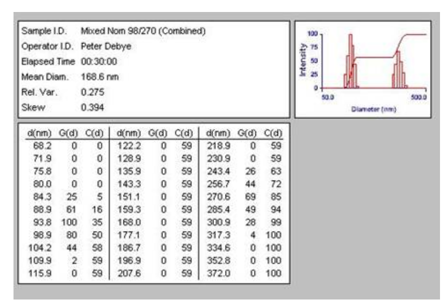
2. Describe the correlated movement of the particles, as related to particle size into an Electric-Field Correlation Function.

3. Equate the correlation functions, with the Seigert Relationship

4. Analyze data using cumulants or CONTIN fitting routines







Sample I.D. Mixed Nom 98/270 (Combined)
Operator I.D. Peter Debye
Elapsed Time 00:30:00
Mean Diam. 168.6 nm
Rel. Var. 0.275
Skew 0.394

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
68.2	0	0	122.2	0	59	218.9	0	59
71.9	0	0	128.9	0	59	230.9	0	59
75.8	0	0	135.9	0	59	243.4	26	63
80.0	0	0	143.3	0	59	256.7	44	72
84.3	25	5	151.1	0	59	270.6	69	85
88.9	61	16	159.3	0	59	285.4	49	94
93.8	100	35	168.0	0	59	300.9	28	99
98.9	80	50	177.1	0	59	317.3	4	100
104.2	44	58	186.7	0	59	334.6	0	100
109.9	2	59	196.9	0	59	352.8	0	100
115.9	0	59	207.6	0	59	372.0	0	100

- **Math/Theory**

- Application/Optics

- Data Analysis

2 texts:

'Light scattering by Small Particles' by van de Hulst

'Dynamic Light Scattering with applications to Chemistry, Biology and Physics' by Berne and Pecora

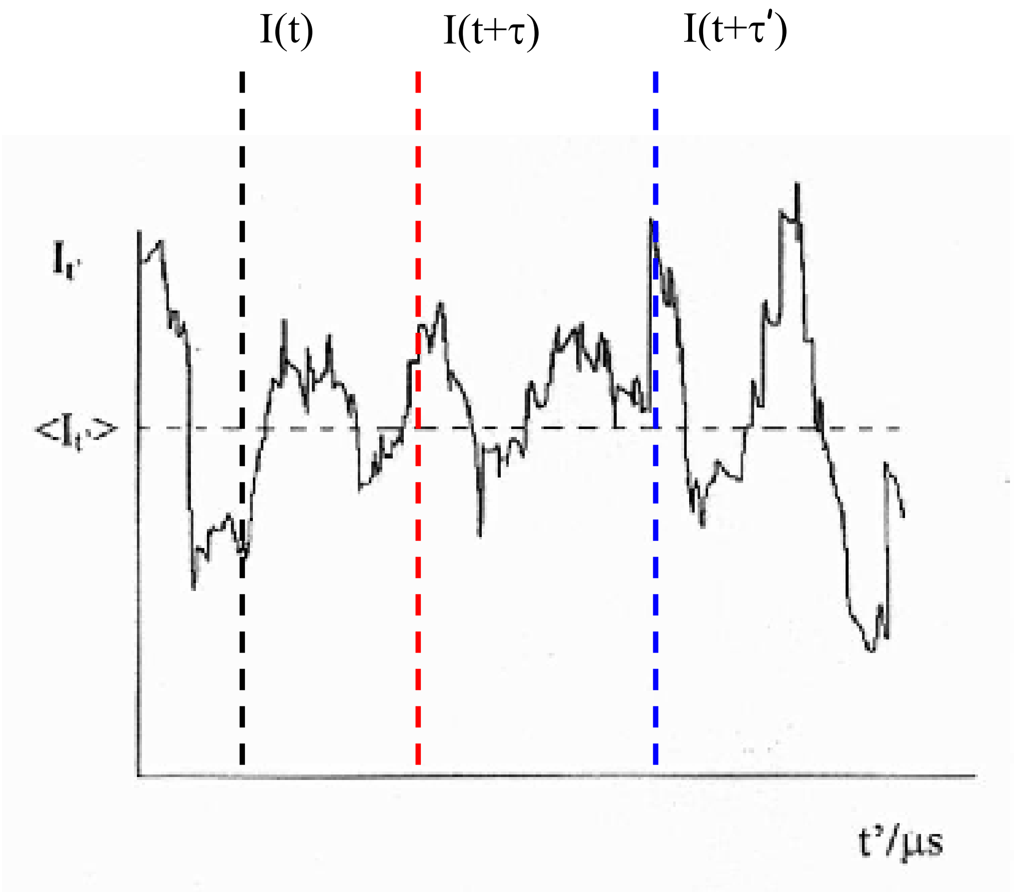
First, the Intensity Correlation Function, $G_2(\tau)$

Describes the rate of change in scattering intensity by comparing the intensity at time t to the intensity at a later time ($t + \tau$), providing a quantitative measurement of the flickering of the light

Mathematically, the correlation function is written as an integral over the product of intensities at some time and with some delay time, τ

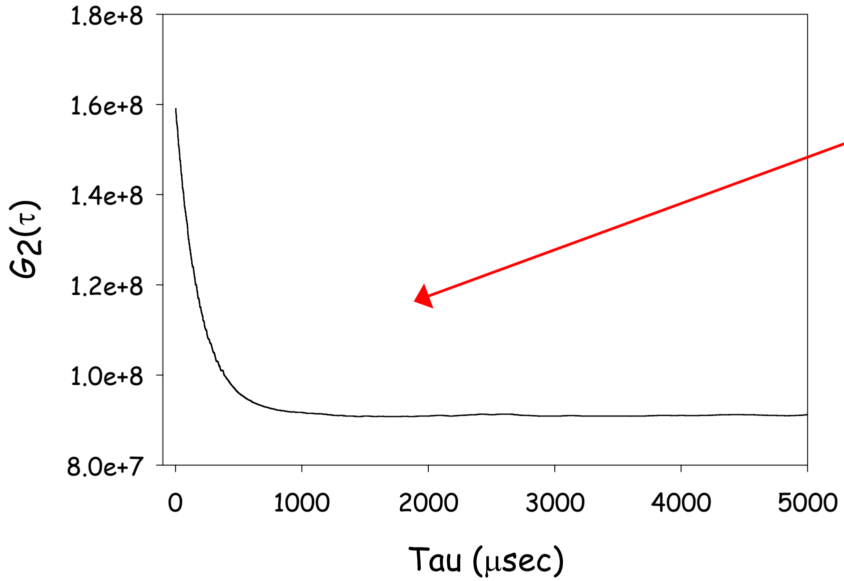
$$G_2(\tau) = \frac{1}{T}\int_0^T I(t)I(t+\tau)d\tau$$

Which can be visualized as taking the intensity at I(t) times the intensity at I(t+τ)- red), followed by the same product at I(t+t')- blue, and so on…



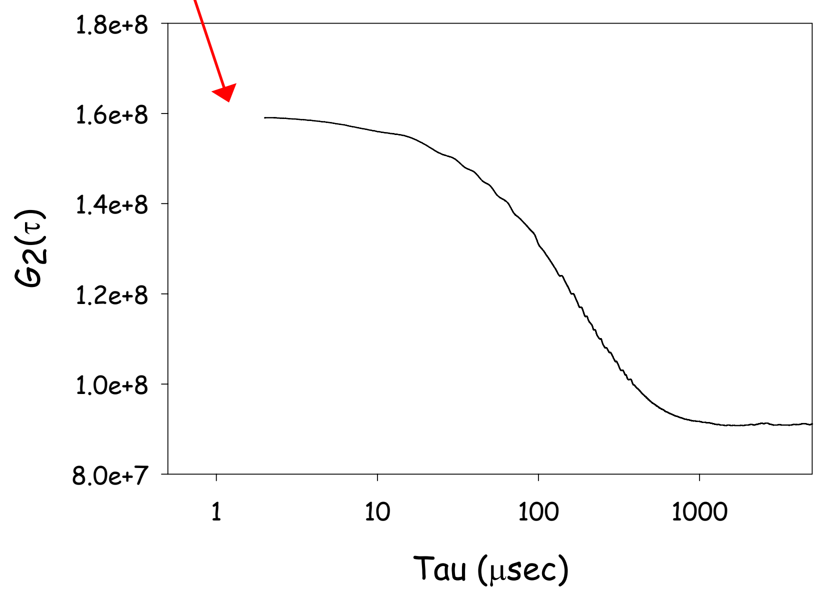
The Intensity Correlation Function has the form of an exponential decay

plot linear in τ



The correlation function typically exhibits an exponential decay

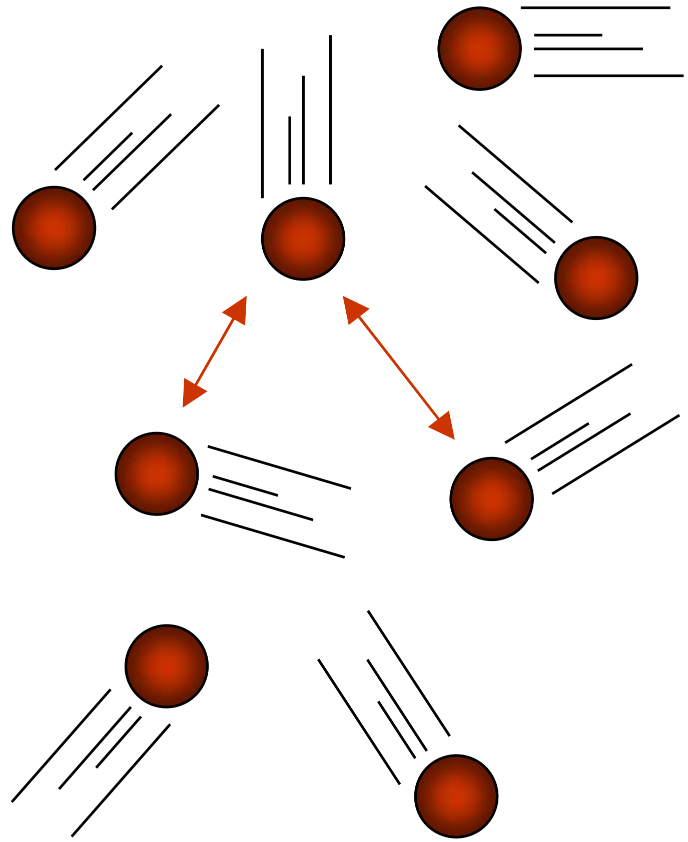
plot logarithmic in τ



Second, Electric Field Correlation Function, $G_1(\tau)$

It is Not Possible to Know How Each Particle Moves from the Flickering

Instead, we correlate the motion of the particles relative to each other



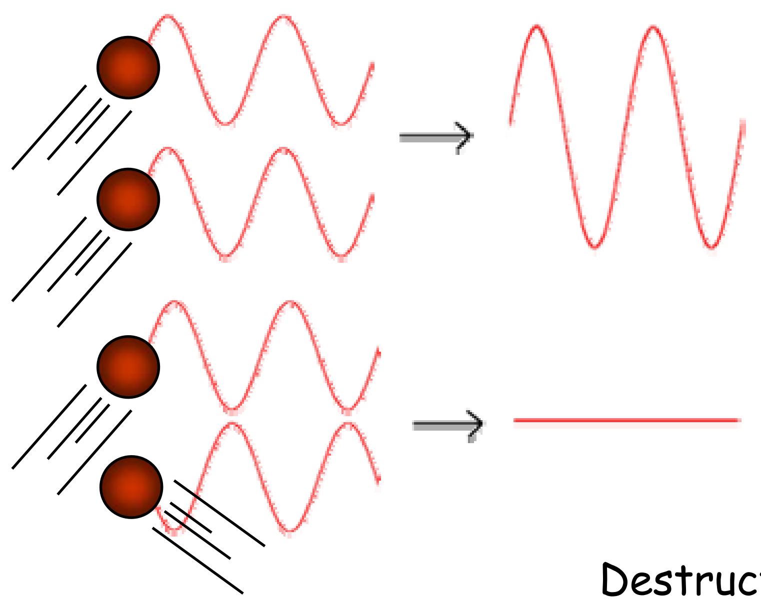
Integrate the difference in distance between particles, assuming Brownian Motion

The electric field correlation function describes correlated particle movement, and is given as:

$$G_1(\tau) = \frac{1}{T}\int_0^T E(t)E(t+\tau)d\tau$$

G_1(t) decays as and exponential with a decay constant Γ, for a system undergoing Brownian motion

$$G_1(\tau) = exp^{-\Gamma\tau}$$

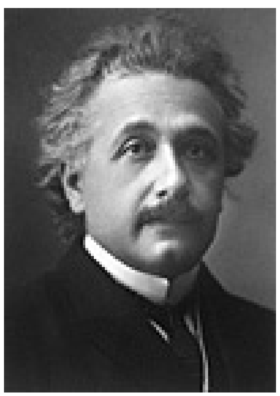


The decay constant is re-written as a function of the particle size

The decay constant is related by Brownian Motion to the diffusivity by:

$$\Gamma = -Dq^2 \qquad q = \frac{4\pi n}{\lambda} sin\left(\frac{\theta}{2}\right)$$

with q^2 reflecting the distance the particle travels … and the application of Stokes-Einstein equation



Boltzmann Constant

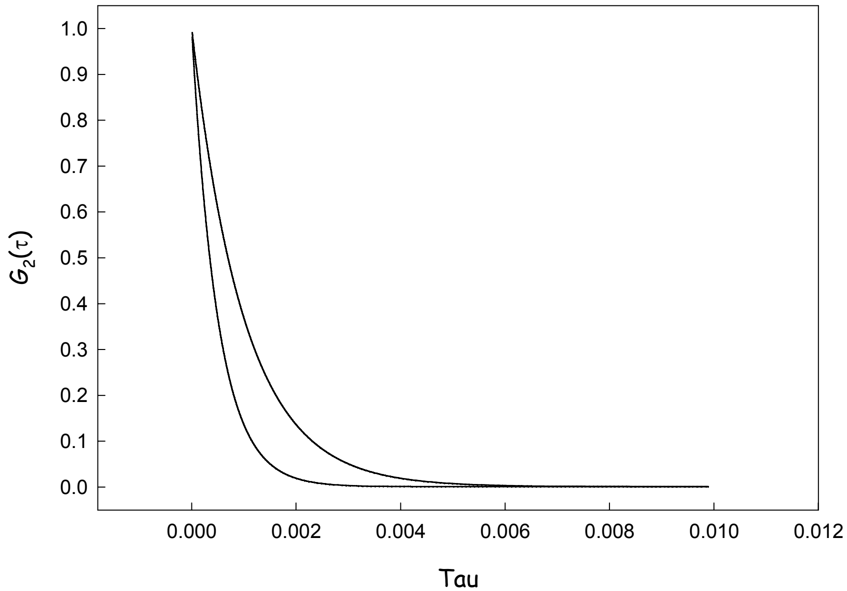
temperature

$$D = \frac{kT}{6\pi\mu r} = \frac{\text{thermodynamic}}{\text{hydrodynamic}}$$

viscosity

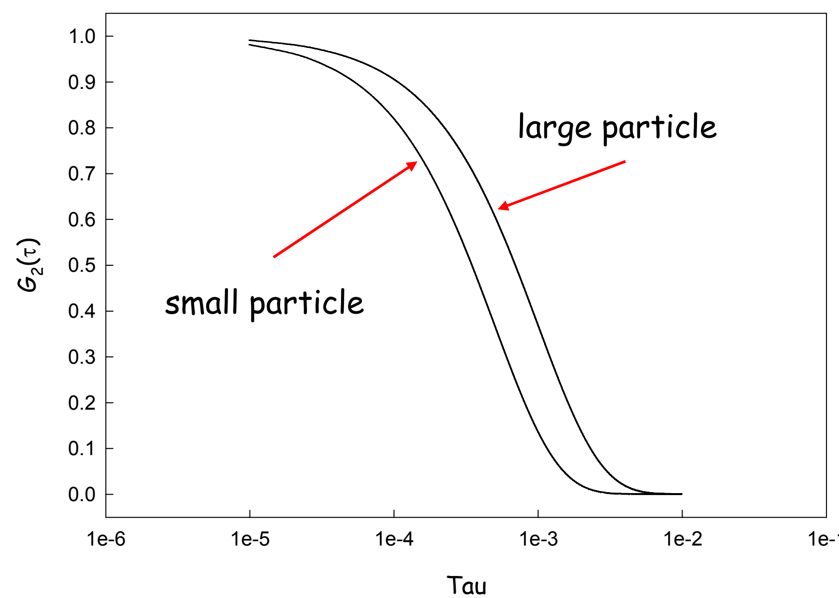
particle radius

Rate of decay depends on the particle size



large particles diffuse slower than small particles, and the correlation function decays at a slower rate.

and the rate of other motions (internal, rotation...)



Finally, the two correlation function can be equated using the Seigert Relationship

Based on the principle of Guassian random processes – which the scattering light *usually* is

The Seigert Relationship is expressed as:

$$\text{Intensity I} = |\overline{\mathrm{E}}|^2 = E * E^*$$

$$G_2(\tau) = B\left[1 + \beta |g_1(\tau)|^2\right]$$

Intensity Correlation Function
(recall: this is measured)

Electric Field Correlation Function
(recall: this is what the particles are doing)

where B is the baseline and β is an instrumental response, both of which are constants

- $G_2(\tau)$ intensity correlation function measures change in the scattering intensity

- $G_1(\tau)$ electric field correlation function describes correlated particle movements

- The Seigert Relationship equates the functions connecting the measurable to the motions

$$G_2(\tau) = B\left[1 + \beta \left| g_1(\tau) \right|^2\right]$$

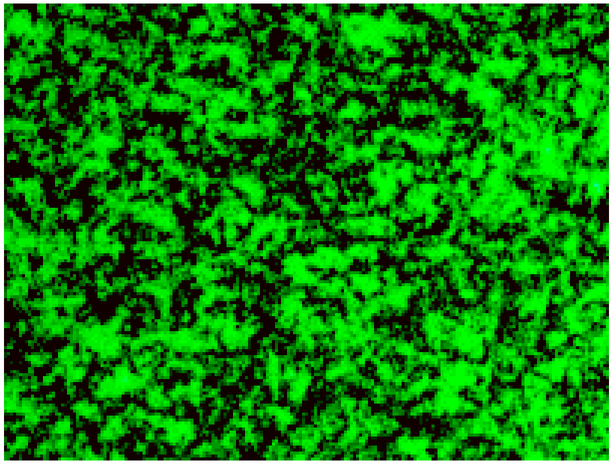
- Math/Theory

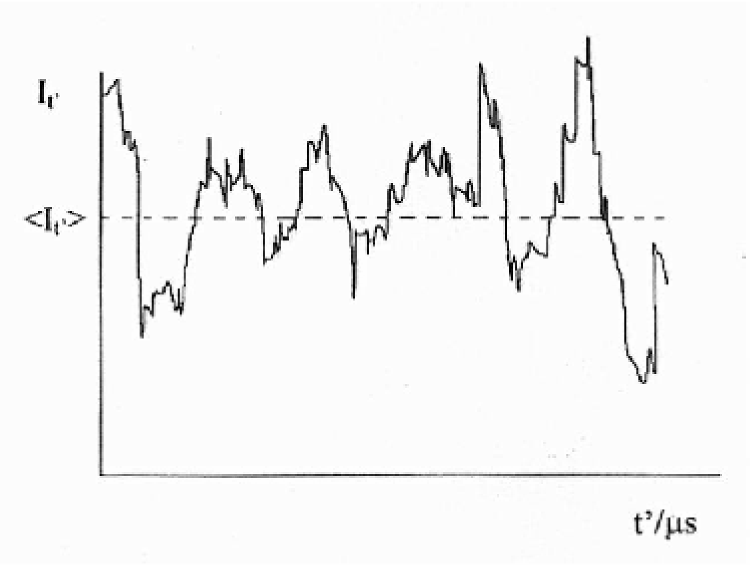
- **Application/Optics**

- Data Analysis

So, consider a simple example of the process

Measure the intensity fluctuations from a dispersion of particles.





Commercial Equipment

- Need laser, optics, correlator, etc…
- Commercial Sources
  - Brookhaven Instruments
  - Malvern Instruments
  - Wyatt Instruments
    (multiangle measurements, HPLC detectors)
  - ALV (what we have)
- Costs range $50K to $100K

Instrumental Considerations

- Light Source
  - Monochromatic, polarized and continuous (laser)
  - Static light scattering goes as $1/\lambda^4$, suggests shorter wavelengths give more signal
    - typical Ar^+ ion laser at 488 nm
  - Dynamic light scattering S/N goes as λ, while detector sensitivity goes as $1/\lambda$, so wavelength is not too critical. HeNe lasers are cheap and compact, but weaker (λ = 633 nm)
  - Power needed depends on sample (but there can be heating!)
  - Calculation of $G(\tau)$ depends on two photons, and so on the power/area in the cell. Typically focus the beam to about 200 μm
  - Sample can be as small as 1 mm in diameter and 1 mm high. Typical volumes 3-5 ml.

Instrument Considerations

- Need to avoid noise in the correlation functions
  - Dust!
    - Usually adds an unwanted (slow) component
    - See in analysis – some software help
    - AVOID by proper sample preparation when possible
  - Poisson Noise
    - counting noise, decreases with added counts, important to have enough counts; typically 10^7 over all with 10^6 at baseline
  - Stray light
    - adds an unwanted heterodyne component ($\exp(-\Gamma)$ instead of $\exp(-2\Gamma)$). Avoid with proper design

Correlators

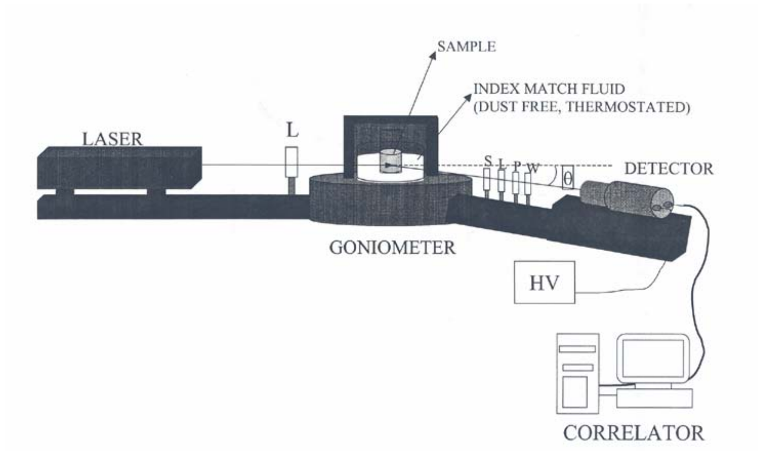
- Need to calculate $G_2(\tau) = \frac{1}{T}\int_0^T I(t)I(t+\tau)d\tau$

which is approximated by $$G_2(\tau) \approx \frac{1}{N}\sum_{i=1}^{N(large)} I(t_i)I(t_i+\tau)$$

so calculate by recording I(t) and sequentially multiplying and adding the result. To do in real time requires about ns calculations thus specialized hardware

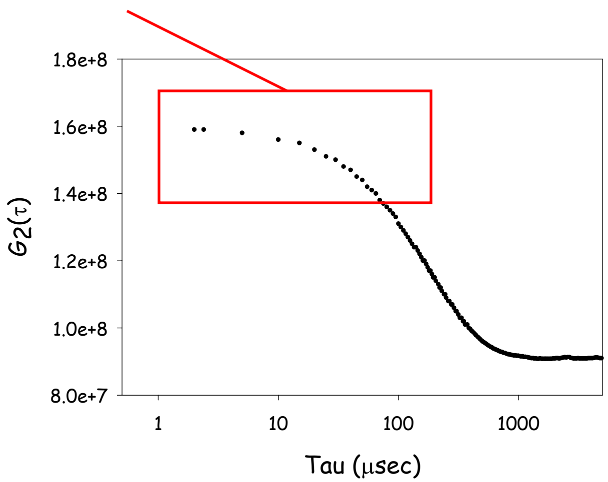
- Pike – 1970s (Royal Signals and Radar Establishment, Malvern, England)
- Langley and Ford (UMASS) $\Rightarrow$ Brookhaven
- 1980's Klaus Schatzel, Kiel University $\Rightarrow$ ALV

Autocorrelation function is collected



The auto-correlator collects and integrates the intensity at the different delay times, τ, all in real time

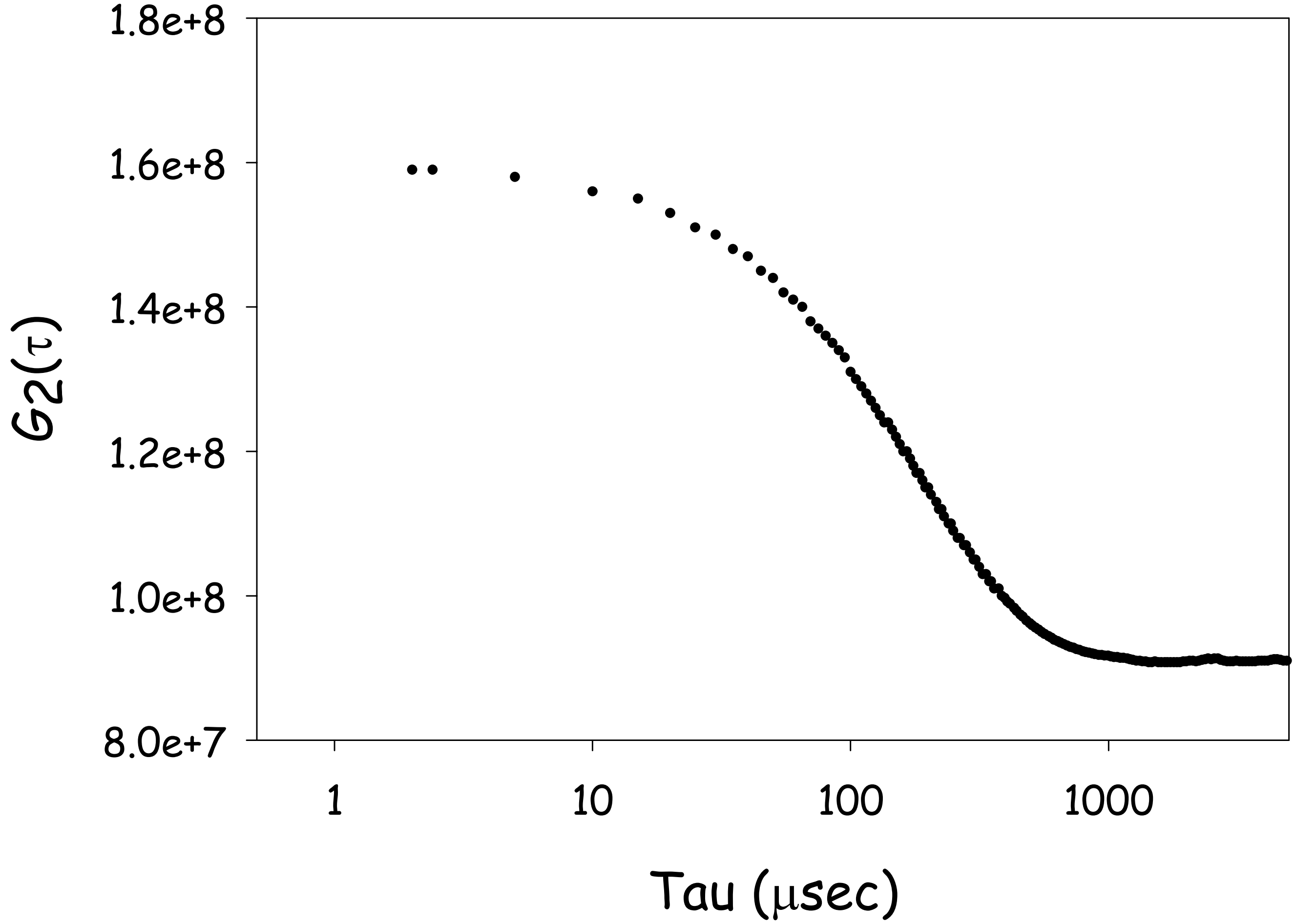
Each point is a different τ.



τ (μsec)	$G_2(\tau)$
2.000000000E+000	1.593461120E+008
2.400000095E+000	1.590897440E+008
5.000000000E+000	1.582029760E+008
1.000000000E+001	1.564198880E+008
1.500000000E+001	1.546673760E+008
2.000000000E+001	1.529991520E+008
2.500000000E+001	1.513296000E+008
3.000000000E+001	1.497655360E+008
3.500000000E+001	1.482144000E+008
4.000000000E+001	1.466891040E+008
4.500000000E+001	1.452316800E+008
5.000000000E+001	1.438225120E+008
…	
6.000000000E+00	4 9.100139200E+007

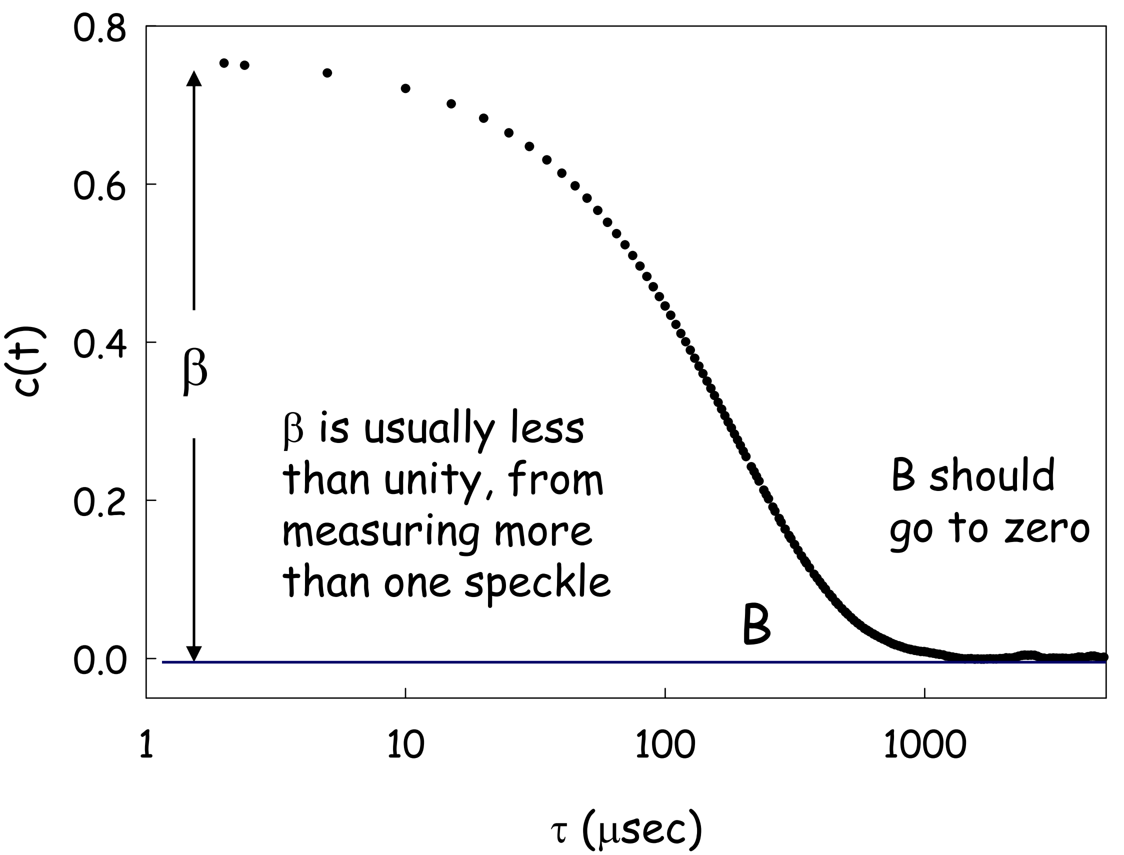
… then, create the raw correlation function

Evaluate the autocorrelation function from the intensity data

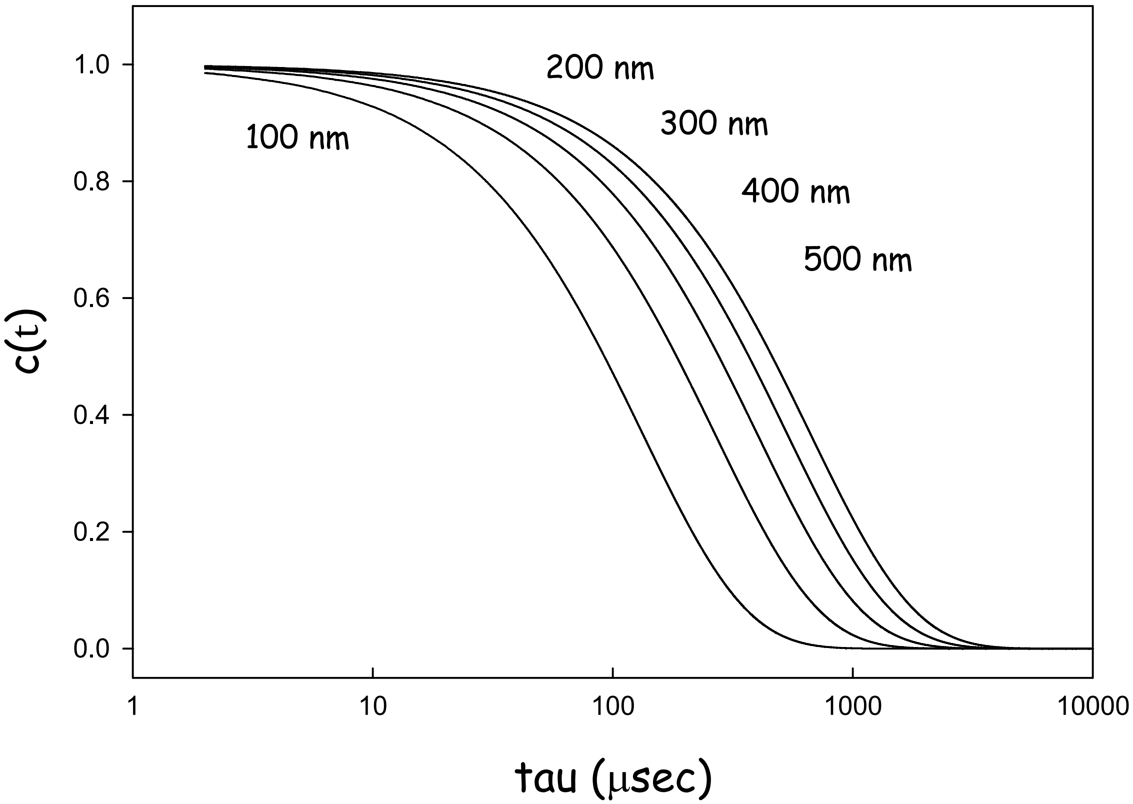


… then, normalize the raw correlation function through some simple re-arrangements

$$C(\tau) = \frac{G_2(\tau) - B}{B} = \beta e^{-2\Gamma\tau}$$



General principle: the measured decay is the *intensity-weighted* sum of the decay of the individual particles



Recall that different size particles exhibit different decay rates.

Expressed in mathematical terms

$g_1(\tau)$ can be described as the movements from individual particles; where $G(\Gamma)$ is the intensity-weighted coefficient associated with the amount of each particle.

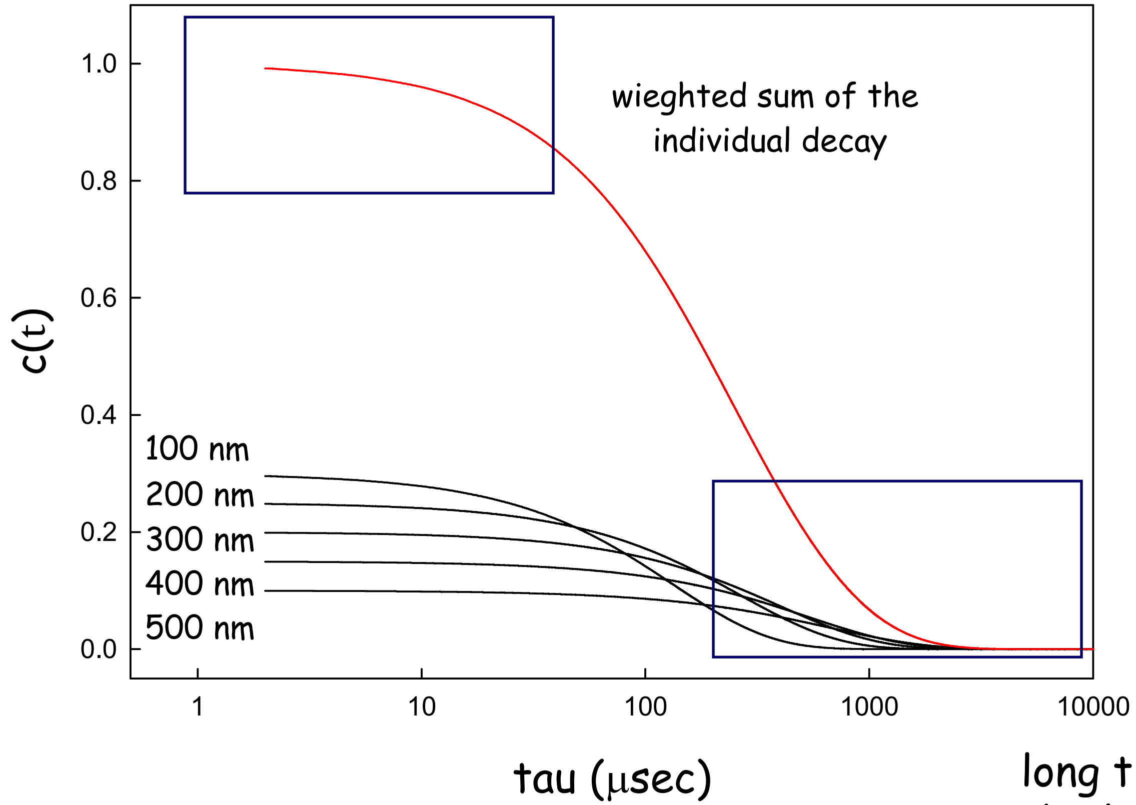
$$g_1(\tau) = \sum_i G_i(\Gamma) e^{-\Gamma_i \tau}$$

For example, consider a mixture of particles:

0.30 intensity-weighted of 100 nm particles,
0.25 intensity-weighted of 200 nm particles,
0.20 intensity-weighted of 300 nm particles,
0.15 intensity-weighted of 400 nm particles,
0.10 intensity-weighted of 500 nm particles.

A sample correlation function would look something like this…

Short times emphasize the intensity weighted-average



Recall sizes
0.30 (100 nm)
0.25 (200 nm)
0.20 (300 nm)
0.15 (400 nm)
0.10 (500 nm)

long times reflected the larger particles

- Math/Theory
- Application/Optics
- **Data Analysis**

Finally, calculate the size from the decay constant

Γ = ??? in sec^{-1} (experimentally determined)

D = ??? in $cm^2\ sec^{-1}$

r = ??? in cm

$$D = \frac{\Gamma}{q^2}$$

Diffusivity is determined... need refractive index, wavelength and angle

$$q = \frac{4\pi n}{\lambda} sin\left(\frac{\theta}{2}\right)$$

$$r = \frac{kT}{6\pi\mu D}$$

Calculate the radius, but need the Boltzmann constant, temperature and viscosity

What is left?
Need a systematic way to determine Γ's

the distribution of particle sizes defines the approach to fitting the decay constant

Monomodal Distribution	→	Linear Fit Cumulant Expansion
Non-Monomodal Distribution	→	Exponential Sampling CONTIN regularization

What is left?
Need a systematic way to determine Γ's

First, consider the monomodal distribution, where the particles have an average mean with a distribution about the mean (red box, first)

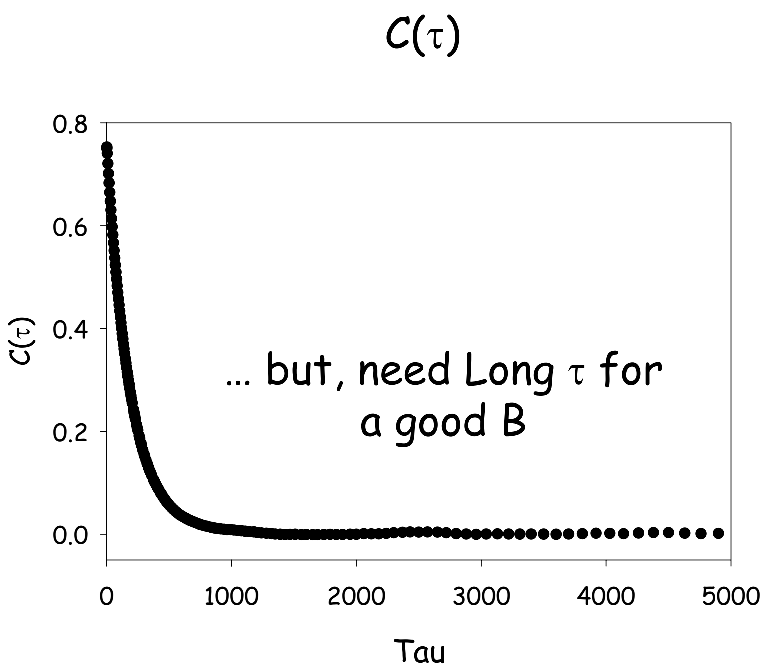
Monomodal Distribution	→	Linear Fit Cumulant Expansion
Non-Monomodal Distribution	→	Exponential Sampling CONTIN regularization

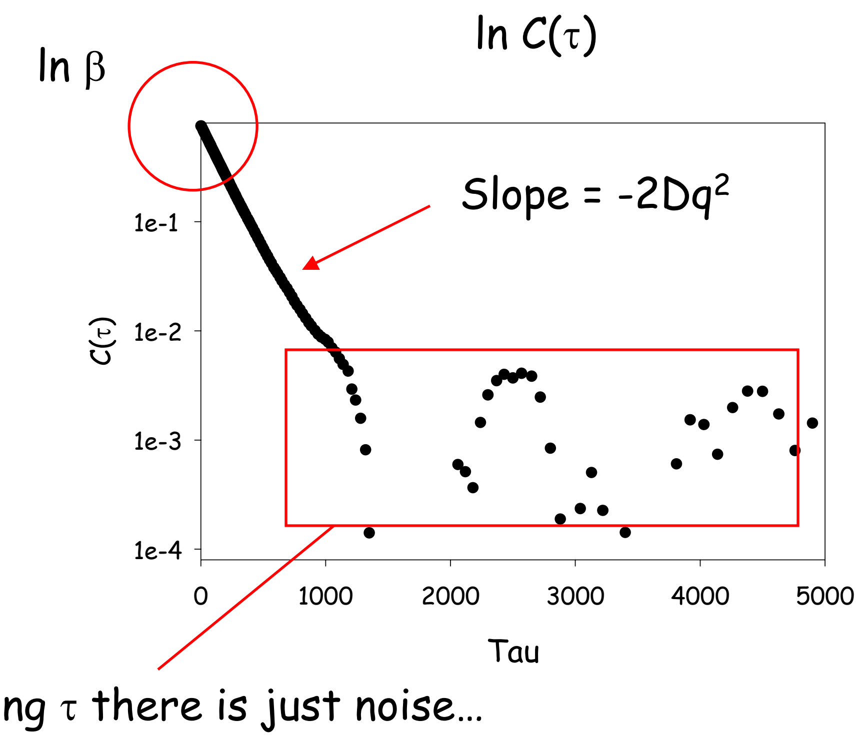
Simplest- the 'basic' linear fit

Assumes that all the particles fall about a relatively tight mean

Take the logarithm of the normalized correlation function

$$ln\left(\frac{G_2(\tau)-B}{B}\right)=ln\,\beta-2q^2D\tau$$





Cumulant expansion

Assumes that the particles distribution is centered on a mean, with a Gaussian-like distribution about the mean.

Where to start…

$$g_1(\tau) = \int_0^{\infty} G(\Gamma) e^{-\Gamma \tau} d\Gamma$$ ← Integral sum of decay curves

Larger particles are 'seen' more…

Probability Density Function
(Coefficients of Expansion)

$$G(\Gamma) = M^2 P(q) S(q)$$

Intraparticle Form Factor
And Interparticle Form Factor
that both DEPEND ON q

$$G(\Gamma) \approx N(R) R^6 : \text{ solid}$$

$$G(\Gamma) \approx N(R) R^4 : \text{ hollow shell (vesicle)}$$

Then, re-arrange the Seigert Relationship in terms of a cumulant expansion

Recall that the correlation function can be expressed as

$$ln\, c(\tau) = ln\left[\frac{G_2(\tau) - B}{B}\right] = ln\,\beta - 2\, ln\, g_1(\tau)$$

Cumulant expansion is a rigorous defined tool of re-writing a sum of exponential decay functions as a power series expansion… so, that the sum from the previous page is replaced by the expansion (GET BACK HERE IN A FEW MINUTES)

$$g_1(\tau) = \int_0^\infty e^{i\Gamma\tau} P(\Gamma) d\Gamma \qquad ln\, g_1(\tau) \equiv \sum_{n=0}^{\infty} k_n \frac{(i\tau)^n}{n!} = \int_0^\infty k_n \frac{(i\tau)^n}{n!} d\tau$$

http://mathworld.wolfram.com/cumulant.html

… need to carry through some mathematics

First, define a mean value

$$g_1(\tau) = e^{-\overline{\Gamma}\tau} e^{-(\Gamma - \overline{\Gamma})\tau}$$

$\overline{\Gamma}$ is the mean 'gamma'

Note: power series expansion $e^{-x} \approx 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \ldots$

Second, substitute the power series for the difference term (second term)

$$g_1(\tau) = \int_0^\infty G(\Gamma) e^{-\Gamma\tau} d\Gamma = \int_0^\infty G(\Gamma) e^{-\overline{\Gamma}\tau} \left[1 - (\Gamma - \overline{\Gamma})\tau + \frac{(\Gamma - \overline{\Gamma})^2}{2!}\tau - \ldots \right] d\Gamma$$

Cumulant Expansion (more)

$$g_1(\tau) = \int_0^\infty G(\Gamma) e^{-\Gamma\tau} d\Gamma = e^{-\overline{\Gamma}\tau} \int_0^\infty G(\Gamma) \left[1 - (\Gamma - \overline{\Gamma})\tau + \frac{(\Gamma - \overline{\Gamma})^2}{2!}\tau - \ldots \right] d\Gamma$$

Working through the integrals…

$$g_1(\tau) = e^{-\overline{\Gamma}\tau} \left(1 - 0 + \frac{k_2{}^2}{2!}\tau^2 - \frac{k_3{}^3}{3!}\tau^3 + \ldots \right)$$

Such that k_2 is the second moment, k_3 is the third moment, …

$$k_2 = \int_0^\infty G(\Gamma)(\Gamma - \overline{\Gamma})^2 d\Gamma \qquad k_3 = \int_0^\infty G(\Gamma)(\Gamma - \overline{\Gamma})^3 d\Gamma$$

Cumulant Expansion (even more)

$$\frac{1}{2}ln\left[\frac{G_2(\tau)-B}{B}\right]=\frac{1}{2}ln\,\beta+ln\left[\underbrace{e^{-\overline{\Gamma}\tau}}_{a}\underbrace{\left(1+\underbrace{\frac{k_2{}^2}{2!}\tau^2-\frac{k_3{}^3}{3!}\tau^3}_{x}+\dots\right)}_{b}\right]$$

a b x

Note: ln of products $ln(ab)=ln\,a+ln\,b$

Note: power series expansion $ln(1+x)\approx x-\frac{1}{2}x^2+\dots$

Note that x terms >> x^2 terms, so that x^2 are negligible

Cumulant Expansion (more…)

$$ln\left[\frac{G_2(\tau)-B}{B}\right]=ln\,\beta-2\overline{\Gamma}\,\tau+K_2{}^2\tau^2-\ldots$$

Note:
Multiplied
by 2

intercept

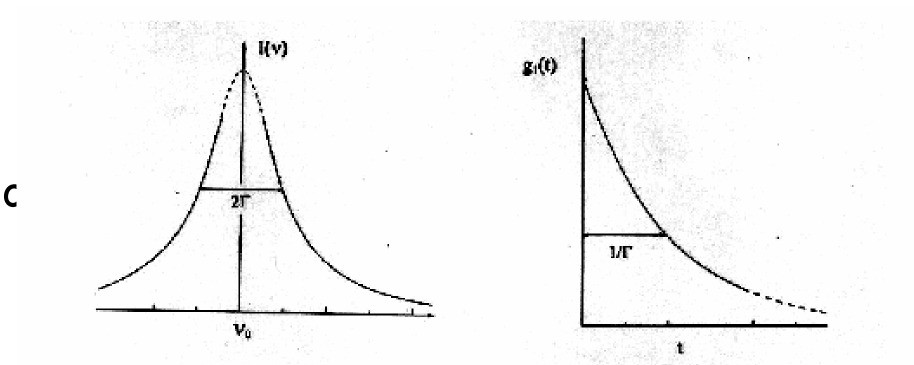
average decay

polydispersity

Polydispersity index $\gamma=\dfrac{k_2}{\overline{\Gamma}^2}$

… and indicates the width of the distributic

$\gamma = 0.005$ is mono-dispersed



Sample of Cumulant Expansion

390 nm Beads

	Gamma (s^{-1})	Diff. Coef. ($cm^2\ s^{-1}$)	Eff. Diam. (nm)	Poly	Skew	Kurtosis	RMS Error
Linear:	5.741e+02	1.078e-08	455.3				7.9000e-03
Quadratic:	6.498e+02	1.220e-08	402.3	0.241			2.6170e-03
Cubic:	6.588e+02	1.237e-08	396.8	0.284	0.27		1.4565e-03
Quartic:	6.647e+02	1.248e-08	393.2	0.330	0.76	3.63	1.2057e+00

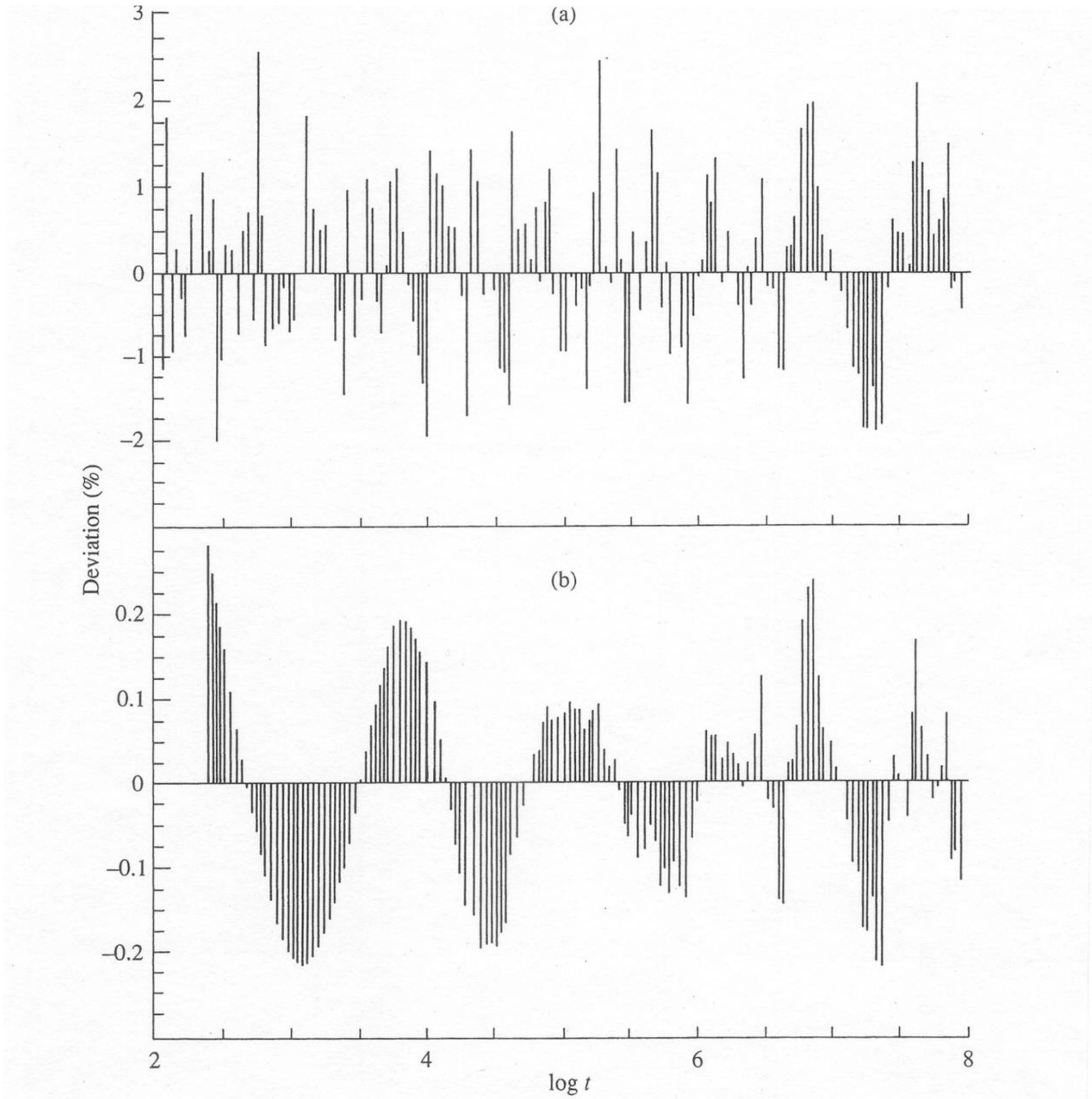
linear
$$\ln\left[\frac{G_2(\tau)-B}{B}\right] = \ln\beta - 2\overline{\Gamma}\tau$$
Gamma

quadratic
$$\ln\left[\frac{G_2(\tau)-B}{B}\right] = \ln\beta - 2\overline{\Gamma}\tau + K_2{}^2\tau^2$$
~ Poly

cubic
$$\ln\left[\frac{G_2(\tau)-B}{B}\right] = \ln\beta - 2\overline{\Gamma}\tau + K_2{}^2\tau^2 - \frac{K_3{}^3}{3}\tau^3$$
~ Skew

quartic
$$\ln\left[\frac{G_2(\tau)-B}{B}\right] = \ln\beta - 2\overline{\Gamma}\tau + K_2{}^2\tau^2 - \frac{K_3{}^3}{3}\tau^3 + \frac{K_4{}^4}{12}\tau^4$$
~ Kurtosis

Examine residuals to the fit



uncorrelated

correlated

What is left?
Need a systematic way to determine Γ's

Second, consider the different non-monomodal distribution, where the particles have a distribution no longer centered about the mean (red box, next)

Monomodal Distribution → Linear Fit

Cumulant Expansion

Non-Monomodal Distribution → Exponential Sampling

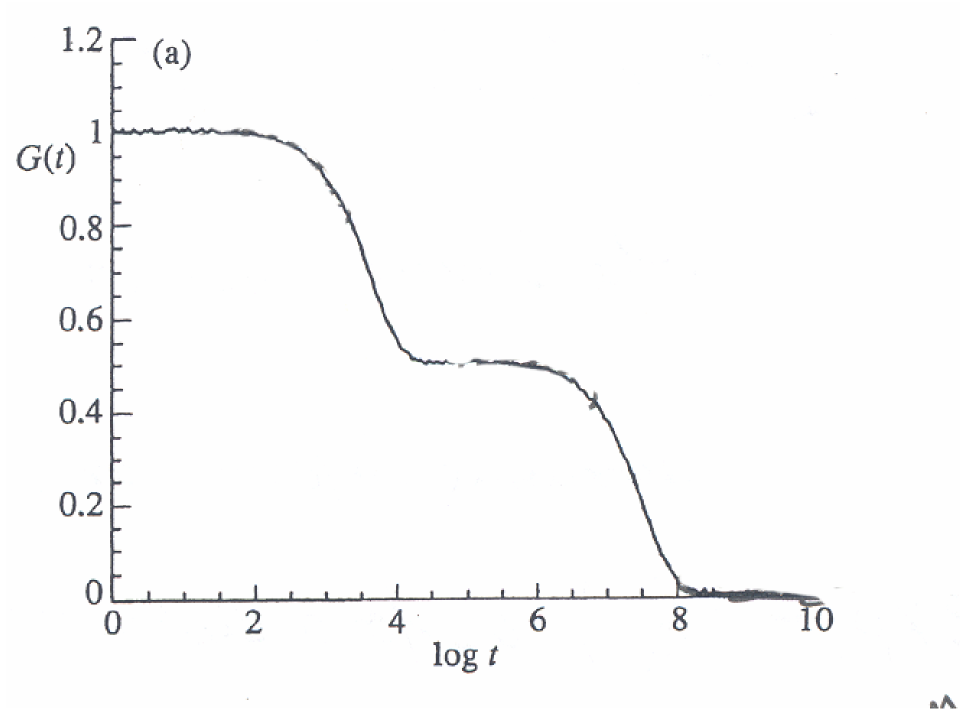
CONTIN regularization

Multiple modes because of polydispersity, internal modes, interactions… all of what make the sample interesting!

Exponential Sampling for Bimodal Distribution

$$g_1(\tau) = \sum a_i e^{-\Gamma_i \tau}$$

Assume a finite number of particles, each with their own decay

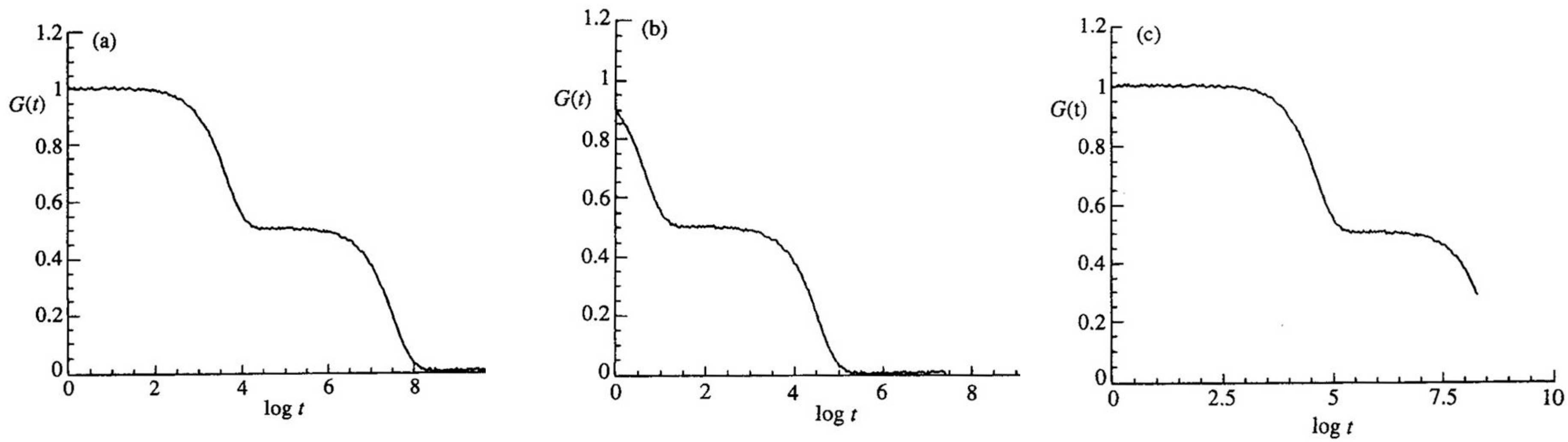


ribution

To be reliable the sizes must be ~5X different

Pitfalls

- Correlation functions need to be measured properly



a) Good measurements with appropriate delay times

b) Incomplete, missing the early (fast) decays

c) Incomplete, missing the long time (slow) decays

CONTIN Fit for Random Distribution

Laplace Transform of f(t)

$$F(s) = L[f(t)] = \int_0^\infty e^{-st} f(t)\,dt$$

Note: Fourier Transform

$$G(\omega) = \Im[f(t)] = \int_{-\infty}^{\infty} e^{-i\omega t} f(t)\,dt$$

In light scattering regime.

size distribution function

$$g_1(\tau) = L[G(\Gamma)] = \int_0^\infty e^{-\Gamma\tau} G(\Gamma)\,d\Gamma$$

So, to find the distribution function, apply the inverse transformation which is done by numerical methods, with a combination of minimization of variance and regularization (smoothing).

$$G(\Gamma) = L^{-1}[g_1(\tau)]$$

CONTIN

- Developed by Steve Provencher in 1980's
- Recognize that $g_1(\tau) = L[G(\Gamma)] = \int_0^\infty e^{-\Gamma\tau} G(\Gamma) d\Gamma$

is an example of a "Fredholm Integral" where

$$F(r) = \int K(r,s) A(s) ds$$

measured object of desire defines experiment

This is a classic ill-posed problem – which means that in the presence of noise many DIFFERENT sets of A(s) exist that satisfy the equation

CONTIN (cont.)

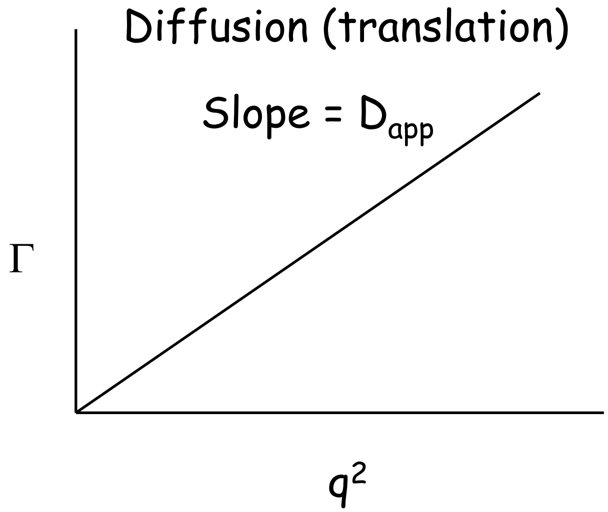
So how to proceed?

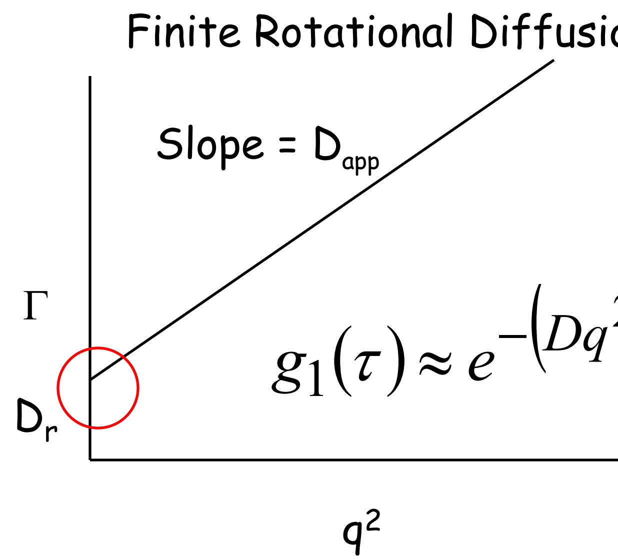
1. Limit information – i.e., be satisfied with the mean value (like in the cumulant analysis)
2. Use *a priori* information
   - Non-negative G(Γ) (negative values are not physical)
   - Assume a form for G(Γ) (like exponential sampling)
   - Assume a shape
3. Parsimony or regularization
   - Take the smoothest or simplest solution
   - Regularization (CONTIN)

     ERROR = (error of fit) +function of smoothness (usually minimization of second derivative)
   - Maximum entropy methods (+ p log (p) terms)

Analysis of Decay Times

First question: How do decay times vary with q?





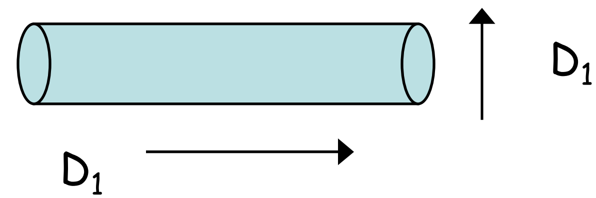
$$g_1(\tau) \approx e^{-\left(Dq^2 - 6D_r\right)\tau}$$

$\Gamma = D_{app}q^2$ where D_{app} is a collective diffusion coefficient that depends on interactions and concentration

Rotational diffusion can change the offset of the decay – can also observe with *depolarized* light

Not spheres... but still dilute, so D = kT/f

Cylinders $D = \frac{1}{3}\left(D_1 + 2D_2\right)$

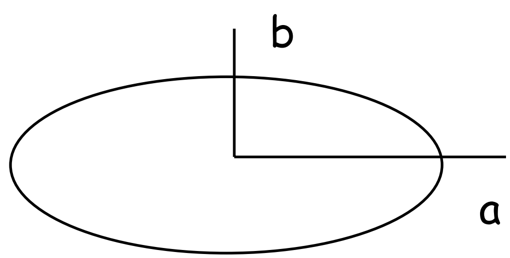


Worms $D = ln\left(L/D\right)\frac{KT}{3\pi\eta_o L}$

$$D = \frac{kT}{f}$$

Shape factor: A hydrodynamic term that depends on shape

Prolate



$$f = \frac{\left[1 - \left(b/a\right)^2\right]^{1/2}}{\left(b/a\right)^{2/3} \ln\left(\frac{1 + \left[1 - \left(b/a\right)^2\right]^{1/2}}{b/a}\right)}$$

Concentration Dependence

- In more concentrated dispersions (and can only find the definition of 'concentrated' generally by experiment'), measure a proper D_{app}, but because of interactions D_{app} (c)

- Again, $D = \langle thermo \rangle / \langle fluid \rangle =$

$$kT(1 + f(B) + \ldots)/f_o(1 + k_f c + \ldots)$$

So $D_{app} = D_0 \, (1 + k_D c + \ldots)$

like a second virial coefficient for diffusion

with $k_D = 2B - k_f - v_2$

partial molar volume of solute (polymer or micellar colloid)

Virial Coefficient

- Driving force = $\left(\frac{\partial \Pi}{\partial \rho}\right)_T = kT[1 + 4\pi\rho \int drr^2 (g(r) - 1]^{-1}$

at low density

$$\approx \mathrm{kT}[1 - 4\pi\rho \int (\mathrm{g}(\mathrm{r}) - 1)\mathrm{r}^2 dr + \ldots]$$

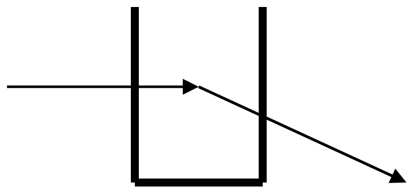
so for low density

$$\left(\frac{\partial \Pi}{\partial \rho}\right)_T \approx kT[1 + \rho B_2 + \ldots]$$

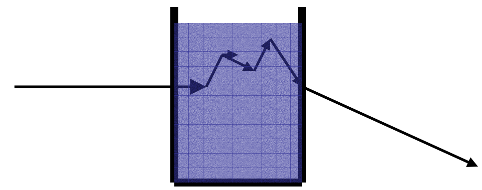
where

$$\mathrm{B}_2 = -4\pi \int (g(r) - 1) r^2 dr$$

Multiple Scattering



single scattering



multiple scattering

- Three approaches
  - Experimentally thin the sample or reduce contrast
  - Correct for the effects experimentally
  - Exploit it!

Diffusing Wave Spectroscopy (DWS)

- In an intensely scattering solution, the light is scattered so many times the progress of the light is essentially a *random walk* or *diffusive* process
- Measure in transmission or backscattering mode
- Probes faster times than QLS
- See Pine et al. J. Phys. France 51 (1990) 2101-2127

Summary

Oriented particles create interference patterns, each bright spot being a speckle. The speckle pattern moves as the particle move, creating flickering.

All the motions and measurements are described by correlations functions
- $G_2(\tau)$- intensity correlation function describes particle motion
- $G_1(\tau)$- electric field correlation function describes measured fluctuations

Which are related to connect the measurement and motion

$$G_2(\tau) = B\left[1 + \beta \left| g_1(\tau) \right|^2\right]$$

Analysis Techniques:
- Treatment for monomodal distributions: linear and cumulant fits
- Treatment for non-monomodal distributions: Contin fits
- Interactions, polydispersity, require careful modeling to interpret

Other motions, such as rotation, can be measured