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Diffusion - how to measure friction

Ref: Van Holde Ch 4-5
Tanford Sec. 21
Yamakawa Sec. 30

We begin with fluxes

Flux = rate at which some material is transported across a unit area or "hypothetical wall."

e.g. $J = \frac{\text{gm}}{\text{cm}^2 \text{ s}}$

There are two views

1) Flux is product of a mobility and a gradient in some potential
(The usual force-susceptibility thing)

2) Flux is product of diffusion coefficient and concentration gradient

1) $J = -L_i \frac{dU_i}{dx}$

$L =$ like conductivity
in electricity

expect $L \sim \frac{1}{\text{friction}}$ $f =$ like resistance
in electricity

- sign: flow away from high potential

Guess what the potential is?

chemical potential - i.e. entropy mostly
or chemical potential plus gravity
(centrifuge)

or chemical potential plus electric
(electrophoresis)

$$2) \quad J = -D \frac{dc}{dx} \quad (\text{Fick's Law})$$

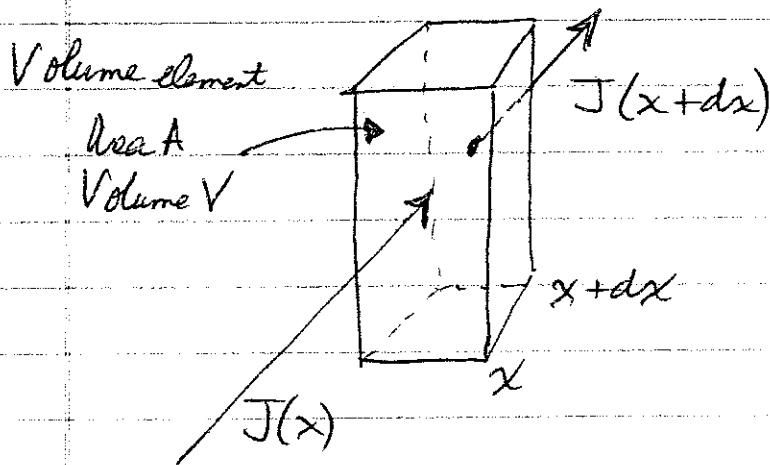
In this view we are more phenomenological:
concentration gradients just fade
away.

$$\begin{aligned} \text{Units of } D &= \frac{\text{flux units}}{\left(\frac{\text{conc}}{\text{distance}}\right)} = \frac{\left(\frac{g}{\text{cm}^2 \cdot s}\right)}{\left(\frac{g}{\text{cm}^3}\right)} \\ &= \frac{\text{cm}^2}{s} \end{aligned}$$

Note: The units hint at a molecular view of diffusion as the mean square displacement per unit time $D = \frac{\langle x^2 \rangle}{2t}$.

Now we have to connect these 2 viewpoints & it will turn out that D relates to f . But D also reflects... you guessed... Thermodynamics & nonideality.

We begin: Equation of continuity (conservation)



What is change in solute mass, q , inside the volume element per unit time?

$$\frac{dq}{dt} = A [J(x) - J(x+dx)]$$

Concentration change per unit time is $\frac{1}{V} \frac{dq}{dt}$

$$\text{i.e. } \frac{dc}{dt} = \frac{A}{V} [J(x) - J(x+dx)]$$

\uparrow
 $\frac{1}{dx}$

$\approx -dJ$

In other words...

$$\boxed{\frac{dc}{dt} = -\frac{dJ}{dx}}$$

Continuity
= Conservation
of Mass

{ Note: This one dimensional view has
the 3-D extension $\frac{dc}{dt} = -\nabla \cdot \underline{J}$ }

Use the definition of D (Fick's Law) $J = -D \frac{dc}{dx}$

$$\Rightarrow \boxed{\frac{dc}{dt} = D \frac{d^2c}{dx^2}}$$

FICK'S 2nd Law
= definition of D + continuity

In words: rate change of concentration is proportional
to the curvature in concentration

{ Note: The 3-D extension is
 $\frac{dc}{dt} = D \nabla^2 c$ }

We now connect general driving force picture to thermodynamics

$$\text{We had } J = -L \frac{dU}{dx}$$

$$\text{let } U = \frac{\mu_2}{N} = \frac{\text{energy}}{\text{molecule}}$$

$$\text{So... } J = -L \frac{d\mu_2}{dx}$$

work on this for awhile

$$\frac{d\mu_2}{dx} = \frac{d\mu_2}{dc} \frac{dc}{dx} = \frac{d\mu_2}{dn_2} \frac{dn_2}{dc} \frac{dc}{dx}$$

$$\text{But } d\mu_2 = -\frac{n_1}{n_2} d\mu_1 \quad \text{Gibbs-Duhem}$$

$$\Rightarrow \frac{d\mu_2}{dn_2} = -\frac{n_1}{n_2} \frac{d\mu_1}{dn_2}$$

$$\text{So... } \frac{d\mu_2}{dx} = \frac{-n_1}{n_2} \frac{d\mu_1}{dn_2} \frac{dn_2}{dc} \frac{dc}{dx} = \frac{-n_1}{n_2} \frac{d\mu_1}{dc} \frac{dc}{dx}$$

$$\text{But } \frac{d\mu_1}{dc} = -\bar{V}_1 \frac{d\pi}{dc}$$

$$\text{So... } \frac{d\mu_2}{dx} = \left(\frac{n_1 \bar{V}_1}{n_2} \right) \left(\frac{dT}{dc} \right) \left(\frac{dc}{dx} \right)$$

now work on this term

$$\text{Recall } V = n_1 \bar{V}_1 + n_2 \bar{V}_2$$

$$\Rightarrow n_1 \bar{V}_1 = V - n_2 \bar{V}_2$$

$$\Rightarrow \frac{n_1 \bar{V}_1}{n_2} = \left(\frac{V}{n_2} \right) - \bar{V}_2$$

inverse of molarity, [2]

$$\text{but } n_2 = \frac{g_2}{M_2}$$

$$\text{and } \frac{g_2}{V} = c$$

$$\text{So... } \frac{V}{n_2} = \frac{M_2}{c}$$

$$\Rightarrow \frac{n_1 \bar{V}_1}{n_2} = \frac{M_2}{c} - \bar{V}_2$$

$$\begin{aligned} \hookrightarrow \frac{\text{volume}}{\text{mole}} &= \frac{\text{volume grams}}{\text{gram mole}} \\ &= \tilde{v}_2 M_2 \end{aligned}$$

$$= \frac{M_2}{c} - \tilde{v}_2 M_2$$

$$\frac{n_1 \bar{V}_1}{n_2} = \frac{M_2}{c} (1 - \tilde{v}_2 c)$$

$$\text{So... } \frac{d\mu_2}{dx} = \frac{M_2}{c} (1 - \tilde{n}_2 c) \left(\frac{d\pi}{dc} \right) \left(\frac{dc}{dx} \right)$$

$$\text{We had } J = -\frac{L}{N} \frac{d\mu_2}{dx}$$

$$\text{or... } J = -\frac{L}{N} \frac{M_2}{c} (1 - \tilde{n}_2 c) \left(\frac{d\pi}{dc} \right) \left(\frac{dc}{dx} \right)$$

evidently all this is D
according to our phenomenological
definition of $D = -J / \left(\frac{dc}{dx} \right)$

Earlier we said $L \sim \frac{1}{f}$ but we need to complete

that to provide the constant of proportionality. Friction
is defined in terms of velocity

$$f = \frac{\text{force}}{\text{velocity}} = \frac{-\frac{1}{N} (d\mu/dx)}{\left(\frac{J}{c} \right)} = \frac{-\frac{1}{N} (d\mu/dx)}{\frac{-\frac{1}{N} (d\mu/dx)}{c}}$$

\swarrow e.g. $\frac{\left(\frac{g}{\text{cm}^2 \text{ s}} \right)}{\left(\frac{g}{\text{cm}^3} \right)} = \frac{\text{cm}}{\text{s}} = \text{velocity}$

$$\text{Thus } \boxed{f = \frac{c}{L} \quad \text{or} \quad L = \frac{c}{f}}$$

$$\text{So... } J = - \underbrace{M_2 (1 - \tilde{n}_2 c)}_{\text{if}} \underbrace{\left(\frac{d\pi}{dc} \right) \left(\frac{dc}{dx} \right)}_D$$

i.e.
$$D = \frac{M_2}{Nf} (1 - \tilde{v}_2 c) \left(\frac{d\pi}{dc} \right)$$

This term came from converting \bar{v}_1 to \bar{v}_2

Note: Some people seem $(1 - \tilde{v}_2 c)^2$
 hard to tell why - everyone still confused.

Vintz (1985)	$(1 - \tilde{v}_2 c)^2$
Schurr	$(1 - \tilde{v}_2 c)$
Pelosa	$(1 - \tilde{v}_2 c)$

Now, we already know that

$$\pi = cRT \left[\frac{1}{M} + B_2 c + \dots \right]$$

$$\frac{\partial \pi}{\partial c} = RT \left[\frac{1}{M} + 2B_2 c + \dots \right]$$

Thus

$$D = \frac{RTM_2}{Nf} (1 - \alpha_2 c) \left(\frac{1}{M_2} + 2B_2 c + \dots \right)$$

$$D = \frac{kT}{f} (1 - \alpha_2 c) (1 + 2B_2 M_2 c + \dots)$$

$$D^0 = \frac{kT}{f}$$

at $c=0$

Note: appearance of $(1 - \alpha_2 c)$ term still debated. Appears to depend on how $(\partial \pi / \partial c)$ is measured.

at time:
 This is a good piece
 of paper. Also
 Also Deutsch
 Paper very thin
 doesn't give
 to LS

Now it turns out $f = f(c)$, as you would expect! This dependence is due to intermolecular H I; other attractions, etc

$$D = \frac{kT(1 - \bar{v}_2 c)(1 + 2B_2 Mc + \dots)}{f^0(1 + k_f c)}$$

$$= \frac{D^0(1 - \bar{v}_2 c)(1 + 2B_2 Mc + \dots)}{(1 + k_f c)}$$

You can write $1 + k_f c \approx 1 - k_f c$, multiply it all out and get:

$$D = D^0(1 + k_D c + \dots)$$

k_D can be \oplus or \ominus

Generally, in a good solvent it is \oplus

Must say something about general diffusion:

We have used:

$$J_i = L_i \frac{\partial \mu_i}{\partial x}$$

In general....

$$J_i = \sum_j L_{ij} \frac{\partial \mu_j}{\partial x}$$

Now proceed with Van't Hoff

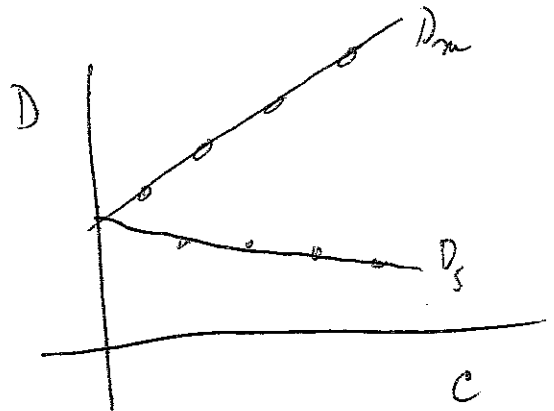
Caveat! The derivation here proceeds mostly from classical Thermo. The theory of irreversible Thermo is done by Schurr and also by Vink - Both approaches seem sensible - but they do differ!

After all this, we still have not said much about how we would measure diffusion.

Two general categories exist

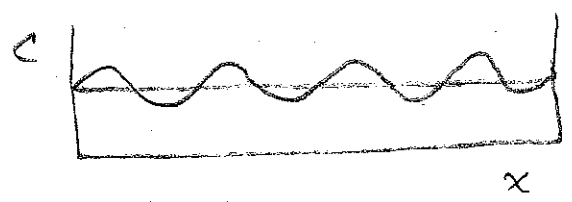
- * Mutual diffusion - measurements of conc. vs. position - The thermodynamic viewpoint
- * Self diffusion - measurement of $\langle x^2 \rangle$ vs. t - The molecular viewpoint, valid even when no perceptible gradient exists

$$D_m \neq D_s$$



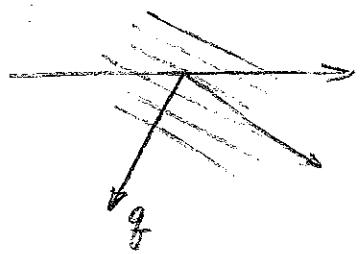
Diffusion with periodic boundary conditions

Why it matters: our little coke/ice experiment was a bust because it is so hard to create a layer with a sharp boundary. When you do succeed, things are still pretty hard because the shape of the core profile is complex. There are 3 experimental methods where it is "easy" to create a spatial oscillation of concentration (DLS, FPR, FRS)



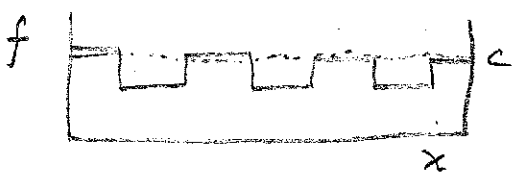
How: These methods "create" the oscillating core profiles differs greatly.

DLS



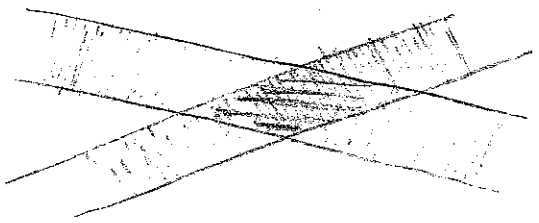
Any scattering apparatus naturally selects that Fourier component of the spontaneous fluctuations which satisfies Bragg's law.

FPR (pattern FPR)



Same fluctuations in c as present in DLS but does not respond to these. Responds instead to "large" ($\sim 5\%$) fluctuations in fluorescence.

FRS



Same situation as FPR but smoothly oscillating optical pattern, not sharp stripes.

D14

Exercise: show that $c(x,t) = A \sin qx e^{-\gamma t}$ is a solution of Fick's 2nd law if $\gamma = q^2 D$.

Ans: $\frac{dc}{dt} = -\gamma A \sin qx e^{-\gamma t} = -\gamma c(x,t)$

$\frac{d^2c}{dx^2} = -q^2 c(x,t)$ (each deriv brings out a q
two sin/cos derivs causes
sin change)

Remember
Fick's 2nd law
 $\frac{dc}{dt} = D \frac{d^2c}{dx^2}$

$\rightarrow -\gamma c(x,t) = -Dq^2 c(x,t)$

$\gamma = q^2 D$ makes a solution

How did they come up with that "damped wave" solution?

Solution of Fick's 2nd Law by Fourier transform.
{ ref. Cantor & Schimmel, Part II, Ch. 10, p. 578 }
but there is an error

Fourier methods allow complex waveforms to be represented as a sum of normal sine waves.

$$\begin{aligned}
 c(x,t) &= \text{[Complex waveform]} \\
 &= \text{[Sine wave } k_1 = \frac{2\pi}{\lambda_1}] + \text{[Sine wave } k_2 = \frac{2\pi}{\lambda_2}] + \dots \\
 &\quad \updownarrow \bar{c}(k,t)
 \end{aligned}$$

Each component has a different wavevector k and amplitude.
We call the amplitudes $\bar{c}(k,t)$.

It is convenient to replace the sum with integral & switch

() to complex exponential notation for the wave.

$$c(x,t) = \int_{-\infty}^{\infty} e^{ikx} c(k,t) dk$$

This works both ways* $\bar{c}(k,t) = \int_{-\infty}^{\infty} e^{ikx} c(x,t) dx$

(* Things like π and $-$ maybe missing; check a text)

So $c(x,t)$ and $\bar{c}(k,t)$ are F.T. pairs.

In general, you could define a Fourier operator $\int_{-\infty}^{\infty} e^{ikx} dx$

Now consider Fick's 2nd law

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

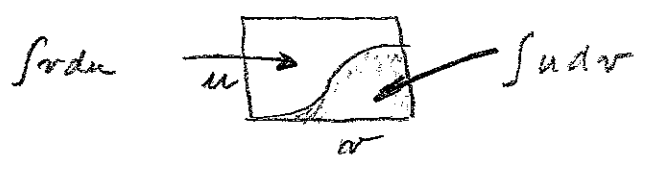
Apply the Fourier operator to both sides.

$$\frac{d}{dt} \int e^{ikx} c(x,t) dx = D \int e^{ikx} \frac{d^2}{dx^2} c(x,t) dx$$

The left side is easy; it's just $\frac{d}{dt} \bar{c}(k,t)$

The RHS is harder by far. To reduce it, we will twice use integration by parts. You remember it:

$$\int u dv = uv - \int v du$$



RHS

D16

$$D \int_{-\infty}^{\infty} e^{ikx} \frac{d}{dx} \left(\frac{d}{dx} c(x,t) \right) dx$$

$$u; du = ik u dx \quad dv; v = \frac{d}{dx} c(x,t)$$

$$\Rightarrow uv - \int v du$$

$$\Rightarrow D \left[e^{ikx} \frac{d}{dx} c(x,t) - \int dx \frac{d}{dx} c(x,t) \underbrace{ik e^{ikx}}_{u; du = ik^2 e^{ikx}} \right]$$

$$\Rightarrow D \left[e^{ikx} \frac{d}{dx} c(x,t) \right]_{-\infty}^{\infty} - D \left[ik e^{ikx} c(x,t) \right]_{-\infty}^{\infty} + D \int_{-\infty}^{\infty} c(x,t) i^2 k^2 e^{ikx} dx$$

We stipulate that $c(-\infty, t) = c(+\infty, t)$ and the same for the derivatives, so 1st two terms drop off.

$$\text{Thus RHS} = -Dk^2 \int c(x,t) e^{ikx} \quad (i^2 = -1)$$

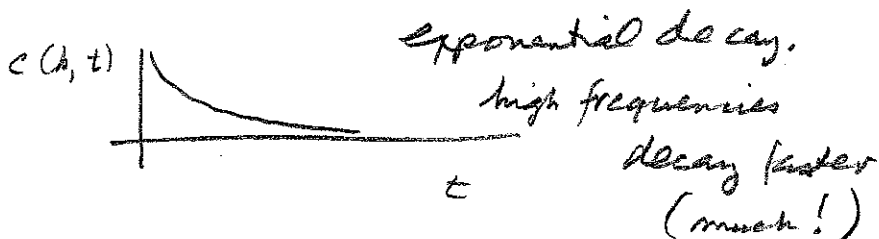
$$\text{LHS} = \text{RHS}$$

$$\Rightarrow \frac{d}{dt} \bar{c}(k,t) = -Dk^2 \int_{-\infty}^{\infty} c(x,t) e^{ikx} dx$$

But This is just $\bar{c}(k,t)$

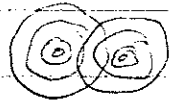
$$\text{So... } \frac{d}{dt} \bar{c}(k,t) = -Dk^2 \bar{c}(k,t)$$

$$\text{i.e. } \bar{c}(k,t) = \bar{c}(k,0) e^{-Dk^2 t}$$



Dynamic Light Scattering

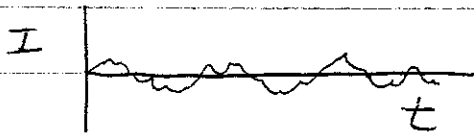
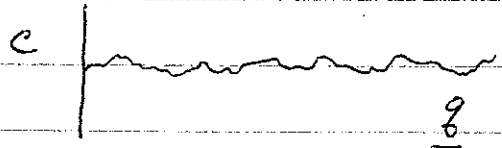
Particle Viewpoint *



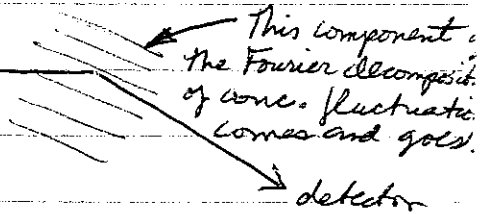
show overhead



Thermodynamic viewpoint *



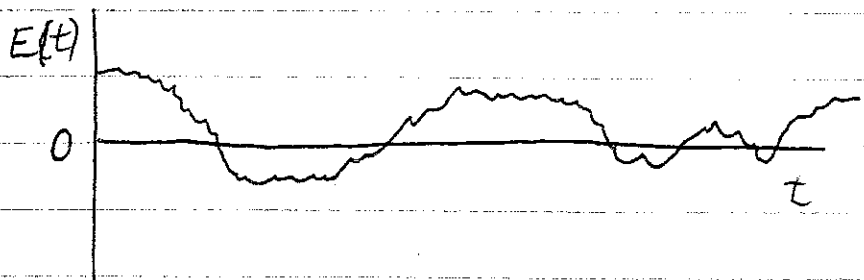
LASER



Two things needed: optics sufficient to see interference patterns and time resolution sufficient to follow the intensity changes.

Turns out these conditions are met fairly easily... to some degree by sacrificing instruments ability to do conventional LS intensity measurements. However, good machines can do both DLS and SLS.

Correlation



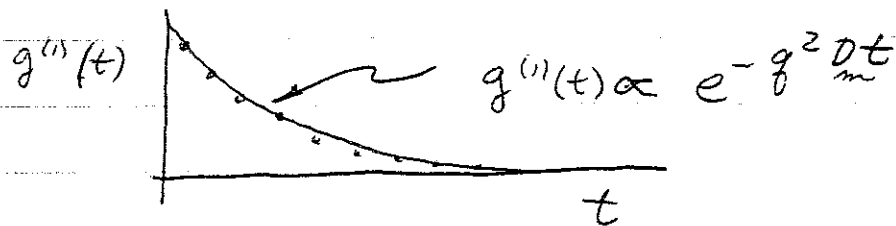
* There is another viewpoint of DLS based on Doppler broadening of laser light. From that point of view, DLS

define: $g^{(1)}(t) = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^{+T} E(t') E(t'+t) dt'$

@ $t=0$ get $g^{(1)}(t) = \langle E^2 \rangle$

@ $t=\infty$ get $g^{(1)}(t) = 0$

So obviously $g^{(1)}(t)$ decays. It turns out (and this takes a fair amount of development, which we will skip) that $g^{(1)}$ follows an exponential decay.



Now remember that photomultiplier tubes measure I , not E . As a result, we really measure

$$(*) \quad G^{(2)}(t) = B(1 + f |g^{(1)}(t)|^2)$$

$$G^{(2)} = \langle I(0) I(t) \rangle = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^{+T} I(t') I(t'+t) dt'$$

f = instrument parameter $0 < f < 1$

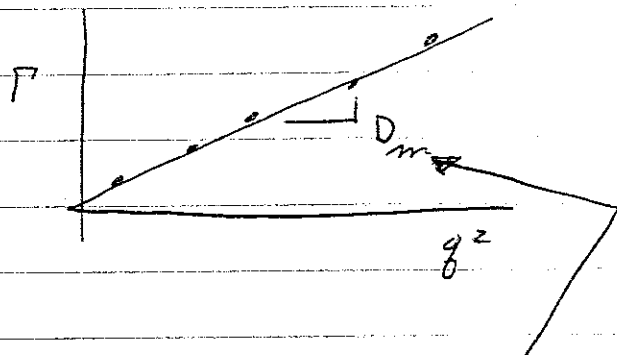
B = baseline, related to $\langle I \rangle^2$

Clearly, $g^{(1)}(t)$ can be obtained from $G^{(2)}(t)$

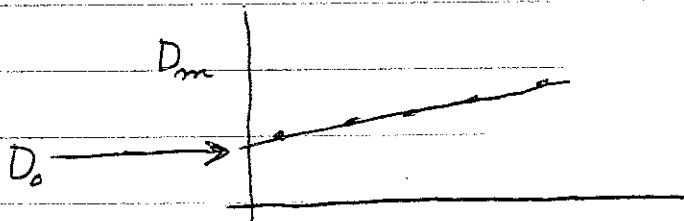
* This equation is called the Siegert relation, and it is usually valid in most DLS instruments.

So... we ultimately get $g^{(1)}(t) = e^{-q^2 D t}$

let $\Gamma = \text{decay rate} = q^2 D_m$



Since DLS senses mutual motions of many polymers in a gradient, it's a thermodynamic experiment, so with D_m



$$R_x = \frac{kT}{6\pi\eta D_0}$$

$$D_0 = \frac{kT}{6\pi\eta R_x} \approx 10^{-11} \text{ m}^2 \text{ s}^{-1}$$

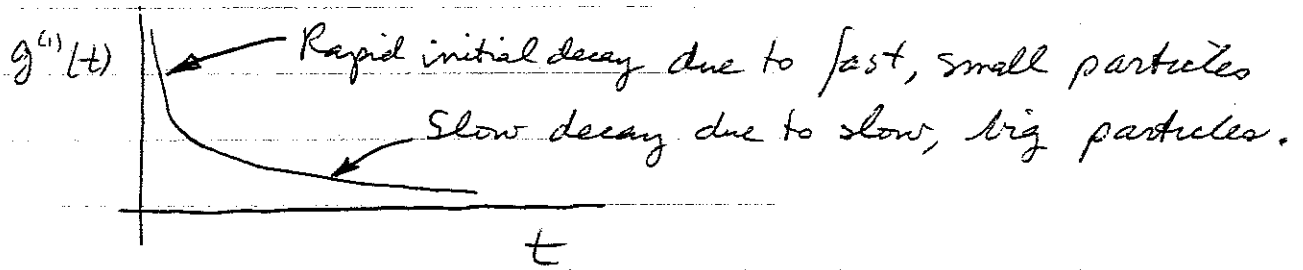
Particle Sizing

If several particles are present, $g^{(1)}$ becomes a sum of exponentials.

$$g^{(1)}(t) = \sum_i A_i e^{-q^2 D_i t}$$

The A_i are related to scattering power: $A_i = c_i M_i P_i(\theta)$

So... because it measures "speed" of molecules (in diffusion)
DLS can "sort" a mixture according to size.



Advantages of Sizing by DLS

- high temp (Teflon)
- corrosive solvents (PBT, Kevlar, etc.)
- easily changed from one system to another
- very robust, low-maintenance experiment

Disadvantages

- poor resolution
- sample must scatter
- hard to see small scatterers if large ones are also present