Guinier law (interpretation w/o a model)

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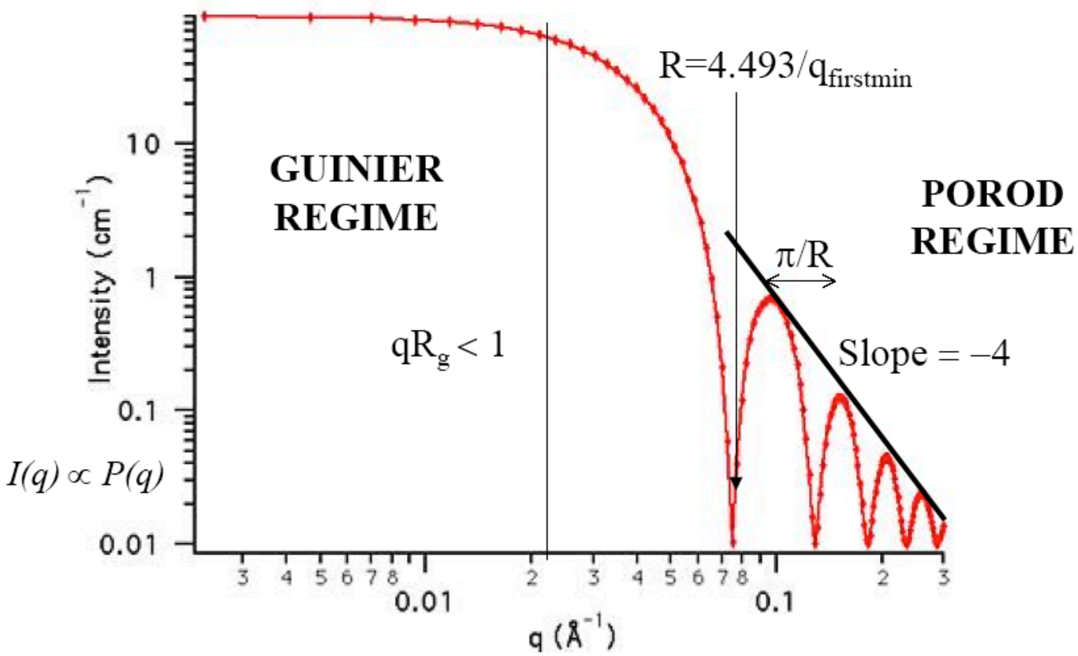
Dilute monodisperse spheres



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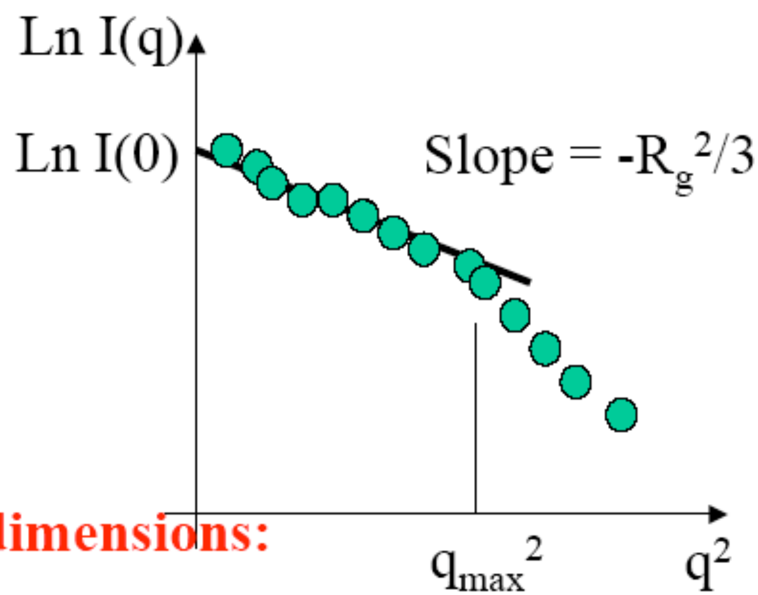
$$P(q)_{q\to 0} \cong P(0)\exp\left(-\frac{1}{3}R_g^2 q^2\right)$$

$$q_{\max} R_g \le 1$$

$R_g \neq R$ = rms distance from 'centre of scattering density'



Constants relate R_g to particle dimensions:

R = 100 Å $\qquad R_g = \sqrt{\frac{3}{5}}R = 77.5\ \text{Å}$

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Only holds if:

a. $q < 1/R_g$

b. dilute

c. Isotropic

d. matrix or solvent scattering is removed

Guinier law (outline of derivation)

$\rho(\mathbf{r})$ is scattering length distribution

$$A(\mathbf{q}) = \int \rho(\mathbf{r}) \exp(-i\mathbf{qr})\, d\mathbf{r}$$

Expand as a power series:

$$A(\mathbf{q}) = \int \rho(\mathbf{r})\, d\mathbf{r} - i \int \mathbf{qr}\, \rho(\mathbf{r})\, d\mathbf{r} - (1/2!) \int (\mathbf{qr})^2 \rho(\mathbf{r})\, d\mathbf{r} + \ldots$$

Origin at center of mass

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ρv 0

Origin at center of mass

$$(\mathbf{qr})^2 = (q_x x + q_y y + q_z z)^2$$

$$xy = (1/\rho v) \int xy\, \rho(\mathbf{r})\, d\mathbf{r}\text{ , etc......}$$

Guinier law (outline of derivation)

$q << \rho v$; average intensity/particle, for large # randomly oriented particles:

$$I(q) = (\rho v)^2(1- ((q_x x)^2 + (q_y y)^2 + (q_z z)^2 + 2q_x q_y xy)$$

Isotropic:

average x^2 = *average* y^2 = *average* $z^2 = R_g{}^2/3$
average xy = *average* yz = *average* $zx = 0$

$$I(q) = (\rho v)^2(1- ((q\ R_g)^2 /3+ \ldots)$$

$$I(q) = (\rho v)^2 \exp (-qR_g)^2/3$$

Guinier law (outline of derivation)

For non-identical particles, Guinier law gives an average R & average v

Model structures - effect of dense packing

For N spherical particles, radius R, scattering length density ρ

$$A(\mathbf{q}) = \sum_{j=1}^{N} A_1(q) \exp(-i\mathbf{q}\mathbf{r}_j)$$

$\mathbf{R}_j$ = location of center of jth sphere, $A_1(q)$ = form factor for single sphere

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$$I(\mathbf{q}) = I_1(q) \sum_{j=1}^{N}\sum_{k=1}^{N} \exp(-i\mathbf{q}\mathbf{r}_{jk})$$

$$I(\mathbf{q}) = I_1(q)(N + \sum_{j=1}^{N}\sum_{k\neq 1}^{N} \exp(-i\mathbf{q}\mathbf{r}_{jk}))$$

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independent scattering from particles

correlated scattering betwn particles

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$<n>\, g(\mathbf{r})\, d\mathbf{r}$ = probability of finding another particle in $d\mathbf{r}$ at distance $\mathbf{r}$ from a given particle   ($<n>$ = average # density of particles)

$$I(\mathbf{q}) = N\, I_1(q)(1 + <n> \int g(\mathbf{r}) \exp(-i\mathbf{q}\mathbf{r})d\mathbf{r})$$

Or:

$$I(\mathbf{q}) = N\, I_1(q)(1 + <n> \int (g(\mathbf{r}) - 1) \exp(-i\mathbf{q}\mathbf{r})d\mathbf{r})$$

Model structures - effect of dense packing

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Isotropic:

$$I(q) = N\, I_1(q)(1 + \langle n \rangle \int_0^\infty 4\pi r^2 (g(\mathbf{r}) - 1) (\sin(qr))/(qr)\, dr)$$

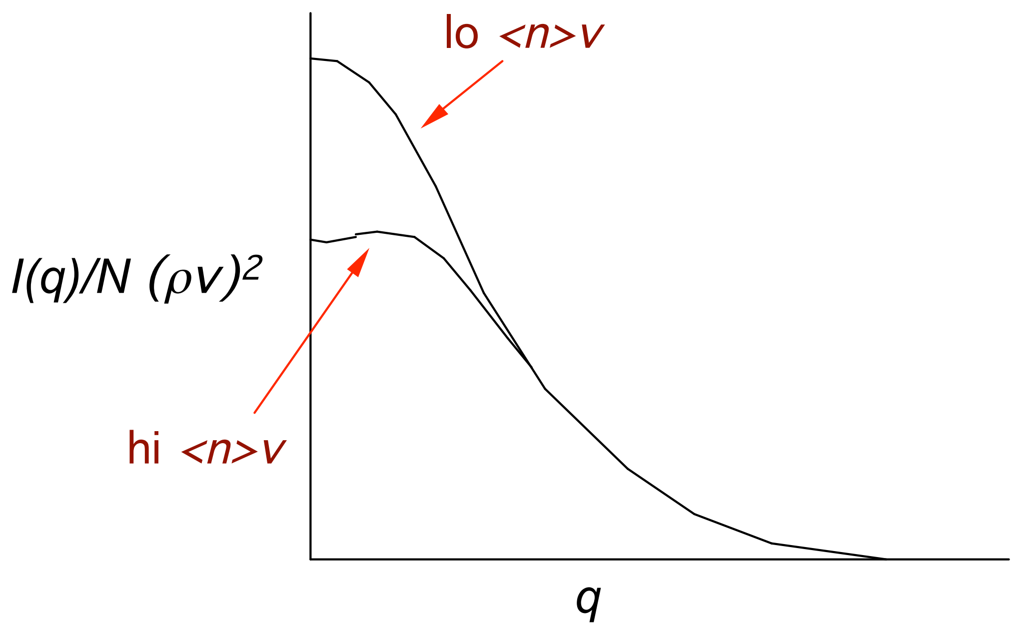
One result:

as fraction of volume occupied by spheres $\langle n \rangle v$ increases

Model structures - effect of dense packing

One result:

as fraction of volume occupied by spheres *<n>v* increases, low *q* intensity is suppressed.



Model structures - effect of dense packing

Anisotropic particles give similar result, altho more complicated.