Chapter 33 - **SCATTERING FROM FRACTAL SYSTEMS**

Consider a system of interacting particles in a medium. The particles could have fractal (rough) surfaces or they could form a mass fractal structure through clustering. In general terms, the scattering cross section is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = \phi \Delta\rho^2 V_P P(Q) S_I(Q) . \qquad (1)$$

$\overline{N} = (N/V) = \phi/V_P$ is the particle number density, V_P is the particle volume, ϕ is the particle volume fraction, P(Q) is the form factor, $\Delta\rho^2$ is the contrast factor and $S_I(Q)$ is the structure factor. The two types of fractal behavior (mass fractal and surface fractal) have been investigated (Bale-Schmidt, 1984; Teixeira, 1988) and will be discussed in turn.

1. MASS FRACTAL

A mass fractal is a structure containing branching and crosslinking to form a 3D network.

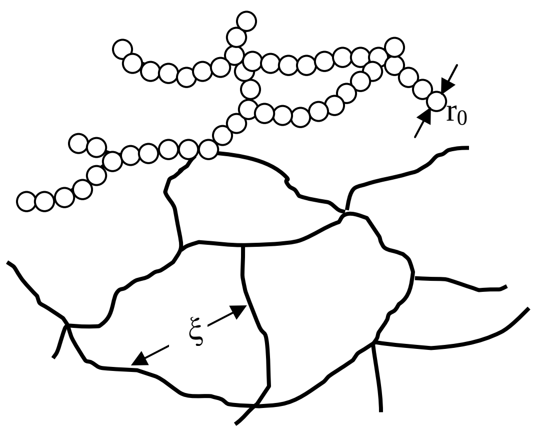

Figure 1: Schematic representation of a mass fractal structure containing branching points and crosslinks. This structure is made out of monomeric units or small particles that are clustered.

The inter-particle structure factor is given by:

$$S_I(Q) = 1 + 4\pi\overline{N}\int_0^\infty dr\, r^2 \left[g(r) - 1\right] \frac{\sin(Qr)}{Qr} . \qquad (2)$$

Here g(r) is the pair correlation function. It is the probability of finding another scatterer at position $\vec{r}$ given that there is a scatterer at the origin. Defining a mass fractal dimension D_m, g(r) can be modeled as follows:

$$\overline{N}[g(r)-1]=\frac{D_m}{4\pi r_0^{D_m}} r^{D_m-3} \exp\left(-\frac{r}{\xi}\right). \qquad (3)$$

This comes from a particle number density that varies like a mass fractal:

$$N(r)=\overline{N}\int_0^r dr\, g(r) 4\pi r^2 = \left(\frac{r}{r_0}\right)^{D_m}. \qquad (4)$$

The parameter ξ is a characteristic size for the mass fractal and r_0 is the radius of the individual particles making up the fractal object. Performing the Fourier transform, one obtains:

$$S_I(Q)=1+\frac{1}{(Qr_0)^{D_m}}\frac{D_m\Gamma(D_m-1)}{\left[1+1/\left(Q^2\xi^2\right)\right]^{(D_m-1)/2}}\sin\left[(D_m-1)\tan^{-1}(Q\xi)\right]. \qquad (5)$$

Note that $\tan^{-1}(z)$ is also called arctan(z). The small-Q limit is obtained using standard expansions:

$$\tan^{-1}(z\to 0)=z-\frac{z^3}{3}... \qquad (6)$$

$$\sin(z\to 0)=z-\frac{z^3}{3!}...$$

$$S_I(Q\to 0)=1+\Gamma(D_m+1)\left(\frac{\xi}{r_0}\right)^{D_m}\left\{1-\frac{D_m(D_m+1)}{6}Q^2\xi^2\right\}.$$

This gives an estimate of the radius of gyration for a mass fractal as:

$$R_g^{\,2}=\frac{D_m(D_m+1)\xi^2}{2}. \qquad (7)$$

The high-Q limit is obtained using the following expansion which yields the asymptotic Q-dependence:

$$\tan^{-1}(z\to\infty)=\frac{\pi}{2}-\frac{1}{z}... \qquad (8)$$

$$S_I(Q\to\infty)=1+\frac{1}{Q^{D_m}r_0^{D_m}}D_m\Gamma(D_m-1)\left\{\sin\left[(D_m-1)\frac{\pi}{2}\right]-\cos\left[(D_m-1)\frac{\pi}{2}\right]\frac{(D_m-1)}{Q\xi}\right\}.$$

for $\xi^{-1}\le Q\le r_0^{-1}$. This is a modified $1/Q^{D_m}$ behavior. The mass fractal dimension D_m varies between 2 and 3 and is equivalent to the Porod exponent. Note that when $D_m = 2$, $\cos\left[(D_m-1)\frac{\pi}{2}\right]=0$ so that the asymptotic behavior varies with a Porod exponent D_m. When $D_m = 3$, $\sin\left[(D_m-1)\frac{\pi}{2}\right]=0$ instead and the Porod exponent is D_m+1.

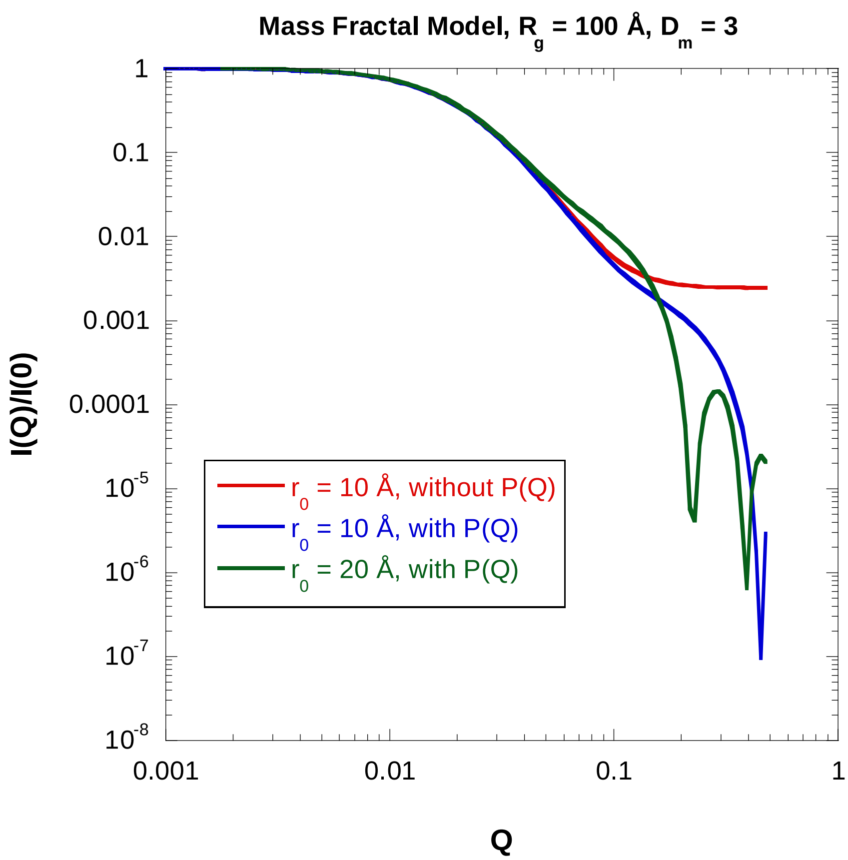

Figure 2: Normalized scattering intensity for the mass fractal model with and without the form factor P(Q) and with R_g = 100 Å and D_m = 3.

Note that the form factor P(Q) for the individual particles that make up the mass fractal was modeled here by spheres or radius r_0 with smooth surface. The case of particles with a fractal (i.e., rough) surface is considered next.

2. SURFACE FRACTAL

Consider a particle with fractal (rough) surface of fractal dimension D_s between 3 and 4.

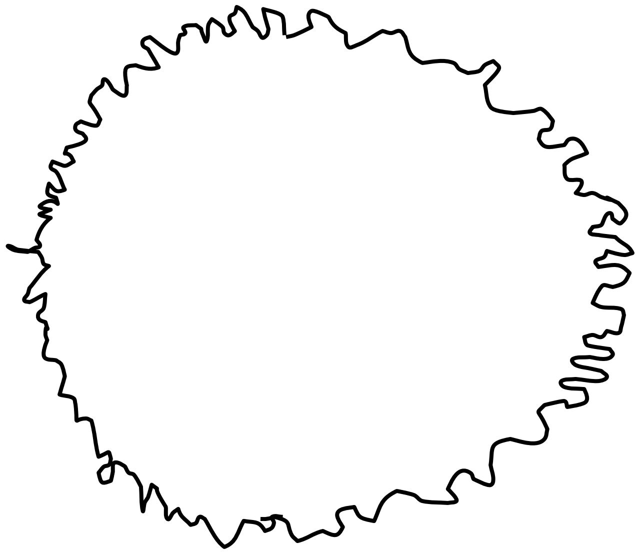

Figure 3: Schematic representation of a surface fractal structure of intermediate roughness.

The Porod law can be generalized to fractal surfaces through the following scaling for the surface:

$$S_P(r) \sim \left(\frac{r}{r_0}\right)^{D_s}. \qquad (9)$$

The form factor for the particle with fractal surface becomes at high-Q:

$$\phi V_P P(Q \to \infty) = \phi\pi \frac{S_P}{V_P} \Gamma(5 - D_s) \sin\left[\frac{\pi(D_s - 1)}{2}\right] \frac{1}{Q^{6-D_s}}. \qquad (10)$$

Note that this result yields zero for $D_s = 3$. In the case of the mass fractal model, a similar inconsistency was avoided by going to a higher term in the high-Q expansion.

A Porod plot (Log[I(Q)] *vs* Q) yields a slope of $-6+D_s$. A surface fractal dimension $D_s = 2$ corresponds to a smooth surface which, for high-Q, gives:

$$P(Q \to \infty) = \frac{3}{2r_0^{\,3}} \frac{S_P}{V_P} \frac{1}{Q^4}. \qquad (11)$$

S_P and V_P are the particle surface and volume. This is the well known Porod law for smooth surfaces.

3. FRACTAL POROD EXPONENTS

A figure summarizes the various fractal Porod law exponents for mass fractal systems such as polymer chains and networks and for fractal surfaces.

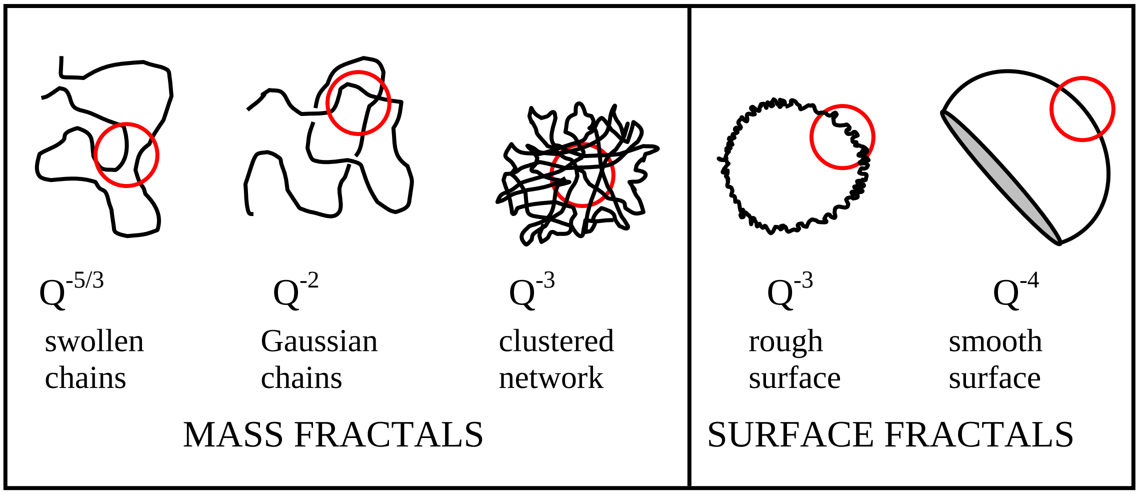

Figure 4: Assortment of fractal Porod exponents.

REFERENCES

H.D. Bale and P.W. Schmidt, "Small-Angle X-Ray-Scattering Investigation of Submicroscopic Porosity with Fractal Properties", Phys. Rev. Lett. 53, 596-599 (1984)

J. Teixeira, "Small-Angle Scattering by Fractal Systems", J. Appl. Cryst. 21, 781-785 (1988)

QUESTIONS

1. What is the Porod exponent for scattering from a fully swollen polymer coil?
2. What is the Porod exponent for scattering from a very rough surface? How about from a smooth surface?
3. What is the range of mass fractal Porod exponents for scattering from a clustered network?

ANSWERS

1. The Porod exponent for scattering from a fully swollen polymer coil is 5/3.
2. The Porod exponent for scattering from a very rough surface is 3. For a smooth surface, the Porod exponent is 4.

3. Scattering from a clustered network has a range of mass fractal Porod exponents between 2 and 3.