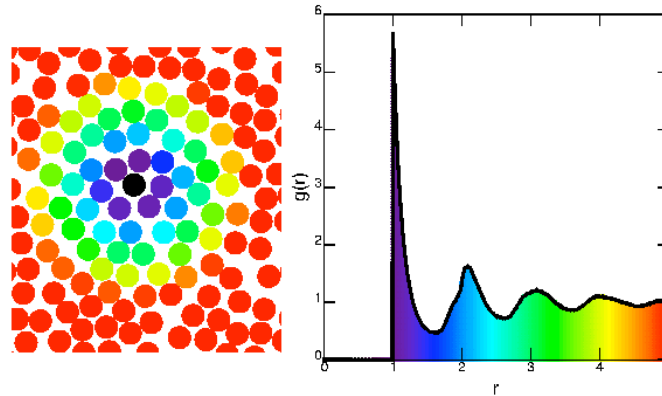


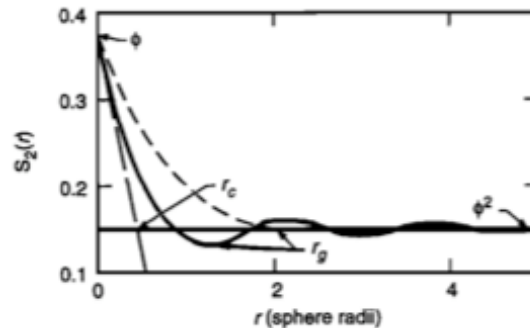
## 090204 Quiz 4 Polymer Properties

- 1) The following figure shows a 2D correlation function calculated by Eric Weeks of Emory University:



2D Correlation function from <http://www.physics.emory.edu/~weeks/idl/gofr.html> (John C. Crocker and Eric Weeks Emory University).

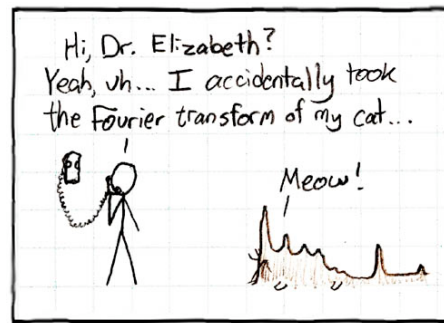
- a) Explain how this correlation function might be calculated.
  - b) Why is there a “correlation hole” below  $r = 1$ ?
  - c) Why does the function display multiple maximum with the first being the largest?
  - d) The first maxima has a value close to 6, explain the significance of 6 for spherical packing.
  - e) What would the Fourier Transform of this correlation function look like?
- 2) The correlation function is sometimes described by a “rod throwing” exercise. In this description we randomly toss a rod of length  $r$  into a material (such as a polymer coil) and  $g(r)$  represents the probability that both ends of the rod land in the phase of interest (the polymer). The following graph shows the correlation function for a porous rock calculated from micrographs.



**Figure 1.** Two-point correlation functions for fully penetrable (short dashed curve) and impenetrable (solid curve) sphere models [after Berryman and Blair, 1986]. Porosity is 0.38 for both curves. Parameter  $r_c$  gives an estimate of mean pore diameter;  $r_g$  gives estimate of spherical particle size. Slope near origin is shown by long-dashed line.

Using two-point correlation functions to characterize microgeometry and estimate permeabilities of sandstones and porous glass. Blair SC, Berge PA, Berryman JG *J. Geophys. Res.* **101** 20,359-75 (1996).

- a) Explain what physical feature of the system is represented by  $g(0)$  in this context and explain why.
  - b) Explain what is the value of  $g(r \Rightarrow \infty)$  for a disordered system and explain why.
  - c) The initial slope of  $g(r)$  intercepts  $g(r \Rightarrow \infty)$  at the Sauter mean diameter,  $d_p = \langle V \rangle / \langle S \rangle = R_3 / R_2$ . Explain what  $R_3$  and  $R_2$  are and why  $d_p$  might be found at this location in the plot.
  - d) Blair indicates that  $R_g$  is found where the first maxima crosses  $g(r \Rightarrow \infty)$ . Define  $R_g$ .
  - e) What is the advantage of a statistical measure of size such as  $R_g$  or  $d_p$  for porous rock structure over discrete measures such as the pore diameter or end to end distance of rock particle clusters?
- 3) The scattered intensity is the Fourier transform of the pairwise correlation function.
- a) What is a Fourier transform? (pictures below from Google may help)



- b) Debye calculated the Debye function for Gaussian polymer coils by performing a Fourier transform of an exact solution for the pairwise correlation function for a random coil,

$$g(q) = \frac{2N}{Q^2} (Q - 1 + \exp(-Q)) \quad \text{where } Q = q^2 R_g^2$$

Show that this function extrapolates to Guinier's Law at low- $Q$  ( $Q \ll 1$ ).

- c) Show that the function extrapolates to the scattering function for a 2-d object at high  $Q$  ( $Q \gg 1$ ).

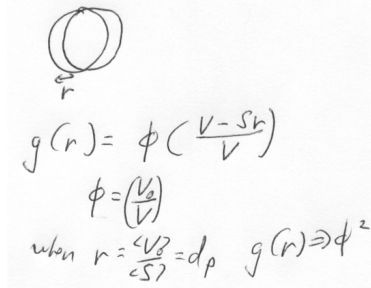
- d) The Lorentzian function,  $I(q) = \frac{N}{1 + Q/2}$ , is sometimes used as a simple substitute for the Debye equation. Show if this is appropriate by finding the large  $Q$  and small  $Q$  limits for this function. (You may want to use the expansion  $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$  for  $x \ll 1$ .)

- e) The radius of gyration for a sphere is calculated from an integral of  $R^2$  times the surface area of a spherical shell  $4\pi R^2 dR$  from 0 to the radius of the sphere normalized by the same surface area function integral. Calculate the radius of Gyration for a sphere as a function of the sphere radius.

## ANSWERS: 090204 Quiz 4 Polymer Properties

- 1) a) We begin at a point in a particle and count the number of particles at a distance “r” from the first particle. We then average this value over all of the starting particles in the system, N particles, dividing by N to normalize the result.
- b) It is not possible for two particles to intersect each other. The value of 0 below  $r = 1$  indicates that the system displays “Excluded Volume” and the gap between 0 and 1 is called a “correlation hole”.
- c) The correlation decays with distance from a particle with the first nearest neighbors being fairly well correlated, but with further orders of correlation weaker. This is typical of liquid state ordering. At a long enough distance (beyond the correlation length) there is no correlation between particles. Because of this the first peak is large and nearly of value 6 and the subsequent peaks are broader and of lower amplitude until the peaks vanish into the square of the volume fraction at longest distances.
- d) 6 represents the nearest neighbor coordination number for spheres in a hexagonal packing which is the closest packing arrangement. This is the (111) closest packed plane in FCC structures or the (1000) or (100) plane in HCP structures.
- e) The Fourier transform would display a single broad peak. This is a liquid like structure showing disorder. If it were a perfect closest packed plane the Fourier transform would be a sharp peak.

- 2) a)  $g(0)$  is the probability that a single point will fall in the rock phase. This is 1- the porosity of the rock or the occupied volume fraction.
- b) As  $r \Rightarrow \infty$  for a disordered structure there is no correlation for the two points at the end of the rod so the value of  $g(0)$  goes to  $(1 - \text{porosity})^2$ .
- c)  $R_3$  is the third moment of size so the integral of the particle size distribution function times  $R^3$ . At low size we see a linear region where the volume fraction decays because small shifts in  $r$  lead to a loss of the observed volume by a fraction  $Sr$  as shown below. When  $r = d_p$  we observe the volume fraction squared for  $g(r)$  following the linear function.



$$g(r) = \phi \left( \frac{V - Sr}{V} \right)$$

$$\phi = \left( \frac{V_2}{V} \right)$$

when  $r = \frac{V_2}{S} = d_p$   $g(r) \Rightarrow \phi^2$

- d)  $R_g^2$  is the second moment of size with respect to the center of mass for an object.

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (R - COM)^2$$

- e)  $R_g$  and  $d_p$  exist even when the particles have odd shapes such as rock aggregates and pores. In such cases a micrograph or photograph is of little use in quantifying the structure.

- 3) a) For an arbitrary function we consider that the function can be constructed by summing cosine waves of different amplitudes and frequencies. The Fourier transform of a function is a

plot of the unique set of amplitudes versus the frequencies that can reconstruct the arbitrary function. This can be achieved through the muscle of the equation shown in the first figure. The transform of a familiar shape like a cat can become unfamiliar in the frequency (or  $q$ ) domain as schematically shown in the second figure.

b) At  $Q \ll 1$  the exponential term can be expanded to  $1 - Q + Q^2/2 - Q^3/6$ . When this is combined with the first two terms in the brackets and divided by  $Q^2$  from the first term we have  $N(1 - Q/3)$ . The same exponential expansion, in reverse, yields Guinier's law,  $N \exp(-Q/3)$ .

c) At high- $q$  the exponential term goes to 0 and  $Q \gg 1$  so we have  $Q$  for the term in parentheses. The function becomes  $2N/Q$  where  $Q$  scales with  $q^2$ . The fractal scaling law is  $I(q) \sim q^{-df}$  so  $df = 2$ .

d) At large  $Q$ ,  $Q/2$  is much larger than 1 so the function becomes  $2N/Q$  so this is the same as the Debye Function at high- $q$ . However, at low- $q$  we use the sum of powers rule to convert the function to  $N(1 - Q/2 + \dots)$  which, using the exponential expansion becomes  $N \exp(-Q/2)$ . This differs from both Guinier's law and from the Debye function so the Lorentzian function is not a good approximation for the Debye function at low- $q$ .

e)  $R_g^2 = 3/5 R^2$  show the math.