090109 Quiz 1 Polymer Properties

1) In class we noted that when many polymer chains are considered or when a single chain is considered averaged as a function of time, the average distance between the ends of a polymer coil should equal 0, $\langle R \rangle = 0$.

   a) Explain why this is the case.

   b) What is Brownian motion and how is it related to a polymer coil? Does an average Brownian walk display $\langle R \rangle = 0$

   c) If $\langle R \rangle = 0$ does this mean that the probability function describing the Brownian walk must be symmetric? Explain what a symmetric probability function is and give an example of such a function.

   d) Give the 1d and the 3d normalized Gaussian probability functions and explain the three differences between the two functions.

   e) What is the value of $\langle R^2 \rangle$ in terms of the number of steps in a Gaussian Chain. If $\langle R^2 \rangle = \sigma^2$, where σ is the standard deviation, how does the standard deviation or the width of the Gaussian distribution function (in a plot of $P_G(R)$ versus R) depend on n?

2) Probability functions, such as the Gaussian distribution function, are used to calculate moments such as the second moment of size, $\langle R^2 \rangle$.

   a) Show that the first moment of size is 0 for a 1d Gaussian distribution. (You need to calculate the first moment knowing the Gaussian function).

   b) A normalized probability function has an integral value of 1. Normalize the probability function: $P(R) = 1 - R^2/k^2$ given that the maximum value of R is nl and the minimum value is –nl. (The function is symmetric about 0 so you need only integrate from 0 to the maximum value and multiply by 2.)

   c) Use the probability function of b to calculate $\langle R^2 \rangle$.

   d) How does the result of part c compare with $\langle R^2 \rangle$ for the 1d Gaussian distribution function, $P_G(R) = \exp\left(-R^2/k^2\right) = \exp\left(-R^2/2nl^2\right)$?

3) The Gaussian polymer coil was the first structure that was well described as a mass-fractal structure.

a) What is the mass fractal dimension, d_f, for a polymer coil?

b) Name another object that displays this mass-fractal dimension. Discuss this briefly.

c) Calculate the density of a polymer coil as a function of size, r.

d) For dirt that is composed of aggregates and pores between aggregates the cumulative mass per fixed volume of the dirt, M, follows,

$$M = k\left(\frac{r}{L}\right)^{d_f + 1 - d} \qquad (26)^*$$

where r is the size of observation and L is a systemic size constant, and d is the spatial dimension (Perrier EMA, Bird NRA *Soil & Tillage Research* **64** 91-99 (2002) eqn. 26). The figure below shows a slope of 0.88. What is the mass fractal dimension of the Ariana dirt if d = 3, i.e. for a 3d sample?

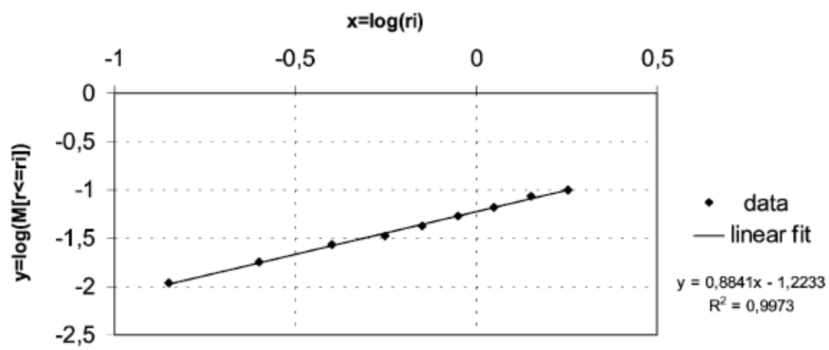

Fig. 3. Test of Eq. (26) from linear regression of $y = \log(M[r \le r_i])$ versus $x = \log(r_i)$ using the Ariana data (Table 1, r (mm), M (kg)).

e) Cumulative mass is the integral of mass below a certain size (from 0 to r) such as you would measure using a sieve. How does Perrier's equation (26) relate to your calculation in part c?

**There is some discrepancy between Perrier's eqn. (26) and that given above.*

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1) a) This is the case because it is equally likely to have the chain go in the +x direction as the – x direction. Similarly for the other coordinates so, on average, the chain ends up at 0.

b) Brownian motion is the random diffusive motion of particles or molecules subject to random thermal acceleration. Brownian motion is a characteristic of particles or molecules that follow Fick's law for diffusion. An average Brownian walk displays <R> = 0. The polymer chain can be modeled as if the path of a Brownian particle were connected with atoms to form a linear polymer chain of random structure. There are some problems with this model, the Brownian particle does not display discrete and uniform steps and the Brownian walk can cross itself, that is there is no exclusion of volume due to the presence of the chain itself for a Brownian walk.

c) If <R>=0 the probability function describing the Brownian walk must be symmetric, that is, it must show no preference for + or – x, y or z. A symmetric probability function will depend on only even powers of the argument, $P(R) = 1 - R^2/k^2 + \ldots$

d) $P_G(R) = \left(2\pi nl^2\right)^{-1/2} \exp\left(-\frac{R^2}{2nl^2}\right)$ and $P_G(R) = \left(2\pi nl^2/3\right)^{-3/2} \exp\left(-\frac{3R^2}{2nl^2}\right)$

The 1-d function probability function is cubed since x, y and z are independent for a random function so the 3d has a 3 in the exponential argument and a power 3 for the prefactor. The 3 in the prefator arises from normalization of the cubed exponential function.

e) $\langle R^2 \rangle = nl^2$ The width of the distribution depends on $n^{1/2}$.

2) a) $\langle R \rangle = \left(2\pi nl^2\right)^{-1/2} \int_{-\infty}^{\infty} R \exp\left(-\frac{R^2}{2nl^2}\right) dR = \left(nl^2/2\pi\right)^{1/2} \left[\exp\left(-\frac{R^2}{2nl^2}\right)\right]_{-\infty}^{\infty} = 0$

b) Calculate the integral as a normalization factor,

$$\int_{-nl}^{nl} \left(1 - R^2/k^2\right) dR = 2\int_0^{nl} \left(1 - R^2/k^2\right) dR = 2\left[R - R^3/3k^2\right]_0^{nl} = 2nl - 2n^3l^3/3k^2$$

Then divide the original function by this normalization factor,

$$P(R) = \frac{\left(1 - R^2/k^2\right)}{2nl\left(1 - n^2l^2/3k^2\right)}$$

c) $\left\langle R^2 \right\rangle = \int_{-nl}^{nl} R^2 \left(\frac{\left(1 - R^2/k^2\right)}{2nl\left(1 - n^2l^2/3k^2\right)} \right) dR = \frac{1}{nl\left(1 - n^2l^2/3k^2\right)} \int_0^{nl} \left(R^2 - \frac{3R^4}{k^2} \right) dR = \frac{2\left[\frac{R^3}{3} - \frac{3R^5}{5k^2} \right]_0^{nl}}{nl\left(1 - n^2l^2/3k^2\right)}$

$= \frac{2n^2l^2\left(1/3 - 3/5k^2\right)}{15\left(1 - n^2l^2/3k^2\right)}$

d) For the Gaussian function $\left\langle R^2 \right\rangle = nl^2$ so the two functions have different second moments and different scaling between mass and size.

3) a) 2

b) A disk. The mass fractal dimension does not fully describe an object.

c) $\rho \sim \frac{n}{r^3} = r^{d_f - 3} = \frac{1}{r}$

d) $d_f = 0.88-1+3 = 2.88$

e) Cumulative Mass/Volume $= M = k\int_0^r r^{d_f - d} dr = \frac{kr^{d_f - d + 1}}{\left(d_f - d + 1\right)}$