090116 Quiz 2 Polymer Properties

1) Balankin et al. (*Phys. Rev. E* **75** 051117 (2007)) describe the scaling properties of randomly folded balls of aluminum foil (left below). They determine density versus size plots (right) where h is the sheet thickness and R is the ball diameter.

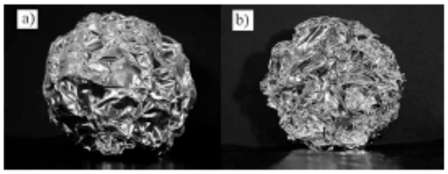


FIG. 1. Images of (a) balls folded from an aluminum sheet of thickness h=0.06 mm and edge size L=60 cm and (b) the cut through this ball.

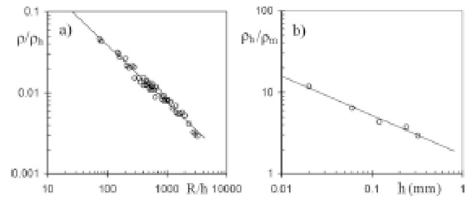


FIG. 3. (a) Data collapse for ρ/ρ_h versus R/h (the slope of the fitting line is $3-D$=0.7009, R^2=0.98); and (b) log-log plot of ρ_h/ρ_m versus h (straight line is given by $y=1.728x^{-0.4816}$, R^2=0.98).

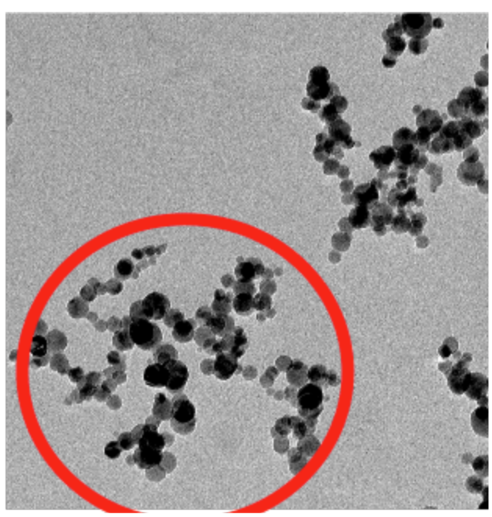
a) Write a general scaling law between mass and size. Name the scaling exponent associated with this scaling law.

b) What values would you expect this exponent to display for i) a rod, ii) a Gaussian chain, iii) a self-avoiding walk, iv) a sheet of paper and v) a crumpled sheet of paper that is 75% air?

c) For the scaling law you propose in 1a) how do you expect density to scale with size? If the slope in the first plot (a log-log plot of reduced density versus reduced size) above is -0.7 what is the scaling exponent from question 1a? Does this agree with your values of question 1b)?

d) What is the connectivity dimension, c, for crumpled aluminum foil?

e) The following ceramic aggregate displays the same dimension as the aluminum foil above. By roughly counting the beads and calculate d_f, c, d_{min}, z, p and s.



2) Real polymer chains show two main categories of divergence from the Gaussian state.

a) List these two categories and give a brief description.

b) Explain how the characteristic ratio C_∞ is related to the Kuhn length, l_k.

c) Define the packing length in terms of the molecular weight and the density.

d) How is the packing length related to the entanglement molecular weight, M_e.

e) In the following plot of Lohse commercial polyolefin samples are considered with polydispersity indicies of greater than 10 in some cases. How would polydispersity affect the packing length?

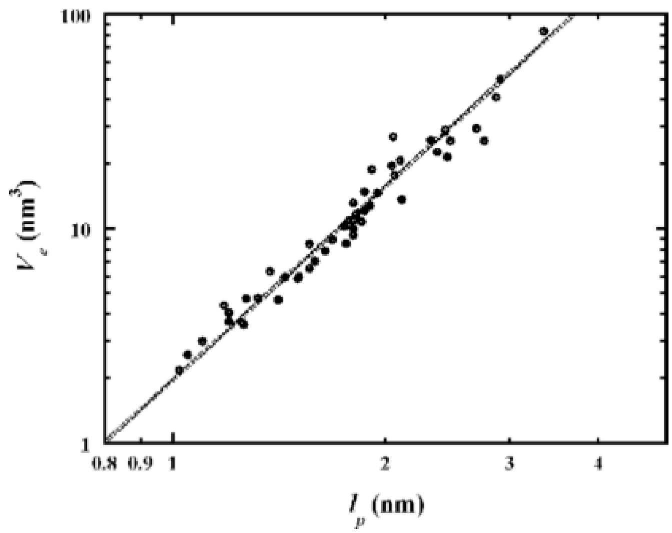


Figure 1. Plot of V_e vs. l_p^3 for polyolefins. Solid line is from Eq. (10).

The Influence of Chemical Structure on Polyolefin Melt Rheology and Miscibility Lohse DJ *J. Macromol. Sci. Part C: Polym. Rev.* **45** 289 –308 (2005).

3) Consider a polyethylene chain.

a) The Kuhn length is 13Å, calculate how many monomer units are in a Kuhn step.a)

b) Hydrogenated polybutadiene (HPB) has the same chemical structure as polyethylene. How many monomer units are in a Kuhn step for HPB?

c) Explain the importance of the monomer composition on the Kuhn length.

d) If the Kuhn length is larger than a monomer, what determines its size?

e) Does the Kuhn length depend on the polymer molecular weight? What about the packing length?

ANSWERS: 090116 Quiz 2 Polymer Properties

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1) a) $z = \alpha \left(\frac{R}{\ell}\right)^{d_f}$

z = mass

R = size

ℓ = step size

α = lacunarity

d_f = mass fractal dimension

b)

	d_f
rod	1
Gaussian Chain	2
SAW	5/3
Paper	2
Crumpled Paper	~2.5

c)

$$\rho = \frac{z}{R^3} \sim z^{1-\frac{3}{d_f}}$$

$$R \sim z^{\frac{1}{d_f}}$$

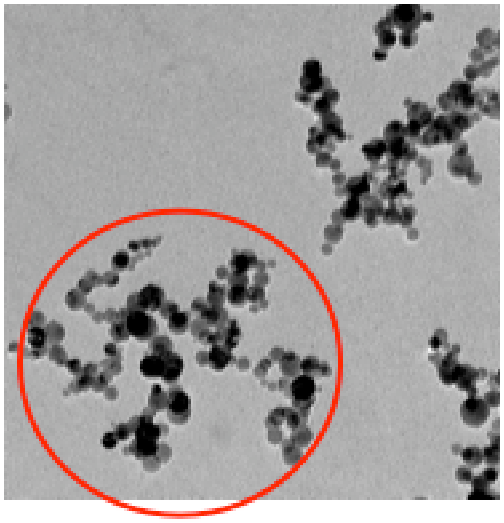
$$\rho = R^{d_f - 3}$$

$$d_f - 3 = -0.7$$

$$d_f = 2.3$$

d) c = 2 because it is a sheet structure.

e)



Nano-titania from Spray Flame

$$\mathbf{R/d_p = 10,\ \alpha \sim 1,\ z \sim 220}$$
$$\mathbf{d_f = \ln(220)/\ln(10) = 2.3}$$

$d_{min} = 1.47$; $c = 1.56$; $s = 39.2$; $p = 31.7$

2) a) Short range and long range interactions. Short range interactions involve short chain index differences and lead to changes in the Kuhn length. Long range interactions involve large differences in the chain index and lead to changes in chain scaling.

b) $$C_\infty = \frac{\langle R^2 \rangle_{Experimental}}{n_{\text{mer units}} l^2_{\text{mer units}}} = \frac{n_{\text{Kuhn}} l^2_{\text{Kuhn}}}{n_{\text{mer units}} l^2_{\text{mer units}}}$$

characteristic ratio (in polymers)
The ratio of the mean-square end-to-end distance, $\langle r^2 \rangle_0$, of a linear polymer chain in a theta state to $N \cdot L^2$, where N is the number of rigid sections in the main chain, each of length L; if all of the rigid sections are not of equal length, the mean-square value of L is used, i.e.

$$L^2 = \sum_i L_i^2 / N$$

In simple single-strand chains, the bonds are taken as the rigid sections. The recommended symbol is: C_N (C_∞ when $N \to \infty$).
P.B. 49

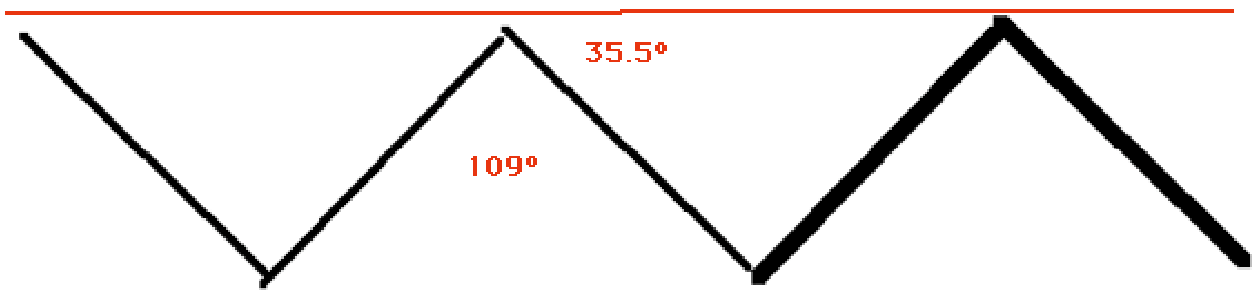
IUPAC Compendium of Chemical Terminology 2nd Edition (1997)

c) $p = \dfrac{M}{\rho N_A \left\langle R^2 \right\rangle_{Experimental}}$

d) $M_e \sim \rho p^3$

e) Since the packing length does not depend on the molecular weight of the chain it is probably not sensitive to polydispersity in the molecular weight of the chains.

3) a)



Each C-C bond is 1.54 Å in length and occurs at an angle of 35.5° to the planar zig-zag axis so each bond contributes 1.54*cos(35.5) = 1.25Å. Each ethylene unit contributes two bonds so the number of ethylene units in a Kuhn step is 13/2.5 = 5.2.

b) Each butadiene unit has 4 bonds so there are 13/5 = 2.6 butadiene monomer units in a Kuhn step.

c) The monomer unit is arbitrary, it does not effect the Kuhn length.

d) The Kuhn length is determined by the bond rotation energies.

e) The Kuhn length does not depend on the polymer molecular weight. There may be some association between the packing length and the Kuhn length. The question isn't resolved.