030418 Quiz 3 Properties
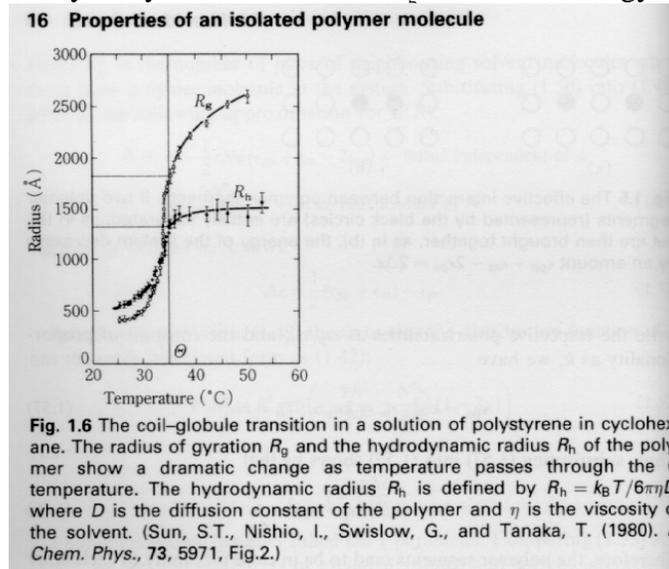
1) The partition function, Z, gives the number of configurational states accessible to a molecule at a given temperature. For a polymer, a state relates to a given set of bond rotations.
   a) Write an expression for the partition function for a polymer chain.
   b) Calculate the partition function near absolute 0, T => 0.
   c) What is the partition function at a very high temperature, T=> ?
   d) The probability of a polymer being in a certain state is given by the Boltzmann probability,

$$P(_i) = \frac{\exp{-u_i/kT}}{Z}$$

   Explain this from what you know about the partition function and what is given above.
   e) How is the potential energy diagram for bond rotation related to the partition function?

2) The binary auto-correlation function describes the spatial correlation of structure.
   -Sketch the correlation function, g(r) as a function of r
   -and **explain** the curve for:
   a) A space filling material (relative to the size-scale of observation, r) such as water.
   b) A crystal.
   c) A Gaussian Polymer Coil.

3) The following figure from Doi, *Introduction to Polymer Physics*, shows the relative behavior of R_g and R_H near the theta temperature. At T = , $d_f = 2$, below , $d_f = 3$ and above , $d_f = 1.67$. (R_H is the hydrodynamic radius and R_g is the radius of gyration)

16 Properties of an isolated polymer molecule

Fig. 1.6 The coil–globule transition in a solution of polystyrene in cyclohexane. The radius of gyration R_g and the hydrodynamic radius R_h of the polymer show a dramatic change as temperature passes through the θ temperature. The hydrodynamic radius R_h is defined by $R_h = k_B T/6\pi\eta D$, where D is the diffusion constant of the polymer and η is the viscosity of the solvent. (Sun, S.T., Nishio, I., Swislow, G., and Tanaka, T. (1980). J. Chem. Phys., **73**, 5971, Fig.2.)

   a) Explain why the $R_g < R_H$ below the theta temperature.
   b) Explain why $R_g > R_H$ at and above the theta temperature.
   c) Explain why R_H is roughly constant above the theta temperature.
   d) Why is the relationship between R_H and R_g different for dynamic light scattering and rheology for a non-draining Gaussian Coil? (Give the relationships if you know them).

1) a) $Z = \sum\limits_{\{i\}} \exp\dfrac{-u\{_i\}}{kT}$

b) Near T =>0 the exponential is 0 for all states except the lowest energy state where u = 0.
   Then the chain can only have one state at absolute 0, all trans for polyethylene, and Z = 1.

c) At high temperature the argument to the exponentials are all 0 so each state contributes 1 and
   Z is the number of possible states which are equally populated.

d) Z is the total number of states. Terms like exp(-u_i/kT) are summed to obtain Z. Each state, i,
   contributes exp(-u_i/kT) to Z so the probability of state i is the ratio of this contribution to
   the whole.

e) The potential energy diagram gives the difference between the lowest energy state, the all
   trans configuration for alkane chains, and the configuration of interest, i. This difference
   in energy is u_i in the above equations.

2)
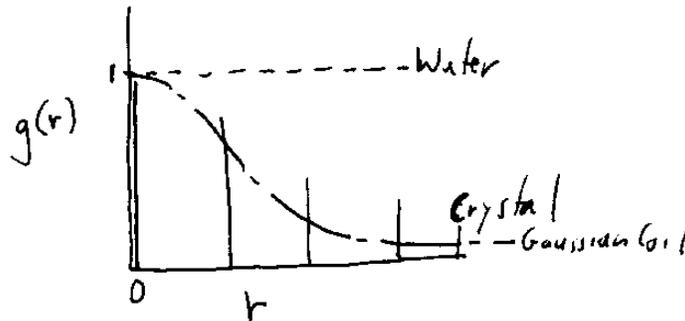
a) For water the probability from a given point to hit a point at any accessible distance r is
always 1. Summing over all possible initial points and normalizing also yields 1 for all r.

b) For a crystal starting at a lattice site the probability is a series of delta functions spaced at the
d-spacing. Normalization for the probability fraction leads to decaying peaks spaced at the d-
spacing.

c) For the Gaussian coil there is a probability of 1 at r = 0 and a decaying probability until you
reach the extended chain length, r=nl, where the probability goes to 0.

3) a) Below the theta temperature the chain is collapsed, d_f = 3, so we could consider a sphere.
The hydrodynamic radius of a sphere is the sphere radius, R. The radius of gyration is smaller
than the radius, 1.3 R_g = R.

b) At the theta point and above the theta point the chain is a linear (C=1) mass-fractal object
with dimension 2 at the theta point and 1.67 above the theta point. For a mass-fractal object the
hydrodynamic radius is smaller than R_g. Additionally, a coil in a good solvent (and any mass-
fractal with a dimension less than 2) is an asymmetric object (on the road to a rod). For an
asymmetric object the hydrodynamic radius is dominated by the smaller size dimension of the
object (i.e. radius of a rod) while the radius of gyration is governed by the mass distribution

which weights the larger size dimension, the length, greater than the hydrodynamic radius does (see notes).

c) R_H is roughly constant above the theta temperature probably because the polymer dimension is constant above the theta temperature and the asymmetry of the coil and the smaller size dimension remains roughly constant in the range observed.

d) For a linear Gaussian coil in DLS $(R_H/R_g) = 2/3$ while for an intrinsic viscosity measurement $(R_H/ R_g) = 7/8$. ("According to theory" as reported in Strobl p. 291 to 295). It would seem the most logical approach is that the DLS measurement looks at essentially the unperturbed coil subjected to weak thermally driven Brownian motion of such a coil while the intrinsic viscosity measurement involves application of an external shear force to the coil resulting in a larger perturbation of the coil structure. This line of reasoning would indicate that DLS should have a larger ratio, R_H/R_g, however, a smaller ratio is seen. The second obvious approach is to consider the solvent penetration of the coil. Apparently, in a low perturbation measurement, DLS, the solvent penetrates further into the coil leading to a smaller ratio of R_H/R_g.

The actual answer to this question is probably quite involved.