Quiz 1
Polymer Physics
January 17, 2018

The random walk model for a polymer chain has been associated with an ideal gas.

a) List similar assumptions involved in the ideal gas model and the random walk model.
b) Explain the statement: "*Both the ideal gas and the random walk chain are governed strictly by entropy.*"
c) Derive an expression for force as a function of chain end-to-end distance, R, and compare the expression to the ideal gas law by listing analogous terms, for example force and pressure, PV is energy or work, Fl is energy or work.
d) The ideal gas law is used to describe *non*-ideal behavior thorough a power-series in concentration (n/V) called the virial expansion. Propose a similar expansion for the ideal chain expression but not in terms of concentration. For the virial expansion concentration increases lead to more atomic interactions, what analogously happens in the *non*-ideal chain expression.
e) Most polymer melt rheological models rely both on random walk chain statistics and the concept of an entanglement. Discuss how these two models compare.

Answers: **Quiz 1**
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a) -The chain units can pass through each other just as the atoms of an ideal gas can pass through each other.
-Pressure arises due to totally elastic collisions with the wall, so the particles are invisible to each other but not to the wall. In the same way the chain is bonded so that it can transfer force from one unit to another through the chain bonds. So the chain units are invisible to each other but totally connected through the bonds. This brings up the contradiction in both models that the particles are totally randomly placed but totally excluded from certain places.

b) The absence of interactions means that there is no enthalpic component to the models.

c) Through comparison with the Boltzman expression,

$E = 3kT/2\ (R^2/nl^2)$

Ideal chain $l\ \mathrm{d}E/\mathrm{d}R = F\ l = 3kT\ (R/nl) = 3kT\ (R/L)$

Ideal gas law $\mathrm{PV} = \mathrm{kT}\ (\mathrm{n})$

(L is the chain contour length)

Analogous Terms:

Energy	PV	Fl
Number n	n	(R/L)

Both are dimensionless numbers reflecting the parameter of interest for the equation.

Force	P	F

d) Virial Expansion

$P = ckT\ (1+cA_2+ c^2A_3+\ldots)$

Proposed $\mathrm{F} = (R/nl^2)\ (3\mathrm{kT})\ (1+(R/nl^2)\ A_2+ (R/nl^2)^2A_3+\ldots)$

For the proposed expression the power-series is in chain extension. At high extensions (R/L) we see deviations form ideal chain behavior.

e) The entanglement model relies on chain-chain interactions that have a time dependence, $\tau_{\mathrm{entanglement}}$. The ideal chain model would seem to be in contradiction to this since the chain units have no interactions.