Quiz 8 Polymer Properties 5/22/01

Rubber elasticity is based on an ideal chain subject to only entropic effects just as an ideal gas is subject to only entropic effects.

a) **Write** the ideal gas law in terms of the number of atoms, n.
Write a similar law for a ideal chain where pressure is written F/R where R is the chain extension.
How are the degree of polymerization and the number of gas atoms related?

b) Consider a tank of n ideal gas molecules (N = 1) with volume V at temperature T. A reaction occurs that bonds all of the gas molecules in to dimers (N = 2), then tetramers (N = 4) etc.
How does the pressure depend on N?
Explain how this relates to question a.

c) **Describe** the deformation gradient tensor $\mathbf{E}_{ij}$.
Why is this tensor insufficient for the calculation of the stress strain behavior of an elastomer?

d) **How** can deformations that lead to stress be calculated?
Give and expression for the Cauchy tensor, $\mathbf{C}_{jk}$.
How can the Cauchy tensor be related to deformations that lead to stress?

e) For uniaxial extension in the z-direction in an incompressible material
give $\mathbf{E}_{ij}$ and $\mathbf{C}_{ij}$.

Answers: Quiz 8 Polymer Properties 5/22/01

a) PV = n k T where n is number of molecules or atoms
For an ideal chain $F/R = k_{spr} = 3kT/(Nl_p^2)$ where N is the DOP
N ~ 1/n

b) P ~ 1/N since n ~ 1/N
This shows the similarity between an ideal gas and an ideal rubber, that is the number of molecules decreases with the degree of polymerization. We expect that the ideal chain is acting with a single relaxation time and mean free path as verified theoretically in the Rouse model which predicts a single mode relaxation that dominates chain dynamics of this type.

c) and d) Consider a bulk sample of rubber composed of tens of millions of single chains connected by crosslink sites. For such systems it is appropriate to consider a continuum view and define a deformation by the displacement of a material element at position **R** in the unstressed state to a position **R'** in the stressed state. The deformation gradient tensor, $E_{\iota\phi}$, describes the defomation in terms of a tensor expression $E_{\iota\phi} = \delta R'_i/\delta R_j$, where i and j are any combination of Cartesian coordinates 1,2,3. Then E_{ij} is a 3x3 matrix describing the relative positions of material elements on deformation.

> Consider that the position of a material element in the deformed state R' is a function of the initial , undeformed position R, R'(R). This is the displacement function. Not all deformations dR'(R)/dR lead to stress. Rigid body rotations and translations, for example, do not lead to the development of stress. Then the question is how can we consider only deformations that lead to stress. Take R' and R' + dR', two neighboring positions in the deformed state. Then release stress so the two positions go to R and R+dR. The relative change in position is given by the square root of dR'•dR' - dR•dR, and this must have a value different from 0 for the development of stress. We have that dR = (dR/dR') dR' and $(dR/dR')_{ij} = (dR_i/dR_j)$. If you substitute in these expressions you obtain,
>
> $$dR_i'\bullet dR_i' - dR_i\bullet dR_i = dR'_j\,(C_{jk} - \delta_{jk})\,dR'_k$$
>
> where C_{jk} is the Cauchy tensor that gives deformations that lead to stress. $C_{jk} = (dR_i/dR'_j)(dR_i/dR'_k)$

e) For uniaxial extension,

$$E_{\alpha\beta} = \begin{pmatrix} 1/\sqrt{\lambda} & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & \lambda \end{pmatrix}$$

and B_{ij} is given by,

$$B_{\alpha\beta} = \begin{pmatrix} 1/\lambda & 0 & 0 \\ 0 & 1/\lambda & 0 \\ 0 & 0 & \lambda^2 \end{pmatrix}$$

$$C_{\alpha\beta} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & 1/\lambda^2 \end{pmatrix}$$