Quiz 6 Properties of Materials CME 300
November 4, 2011

1) The following three images are the result of a simulation of a polymer chain.

a) The programmer thinks that there is a problem with the simulation code since the last image shows an almost linear structure that would seem to be impossible for a random walk. Also the second structure doesn't seem to be evenly distributed about the center. Comment on this by suggesting what the programmer should do.

b) For the random walks, examples of which are shown above, what is the value of <R>? Why?

2) -Give the value (or expression) for <R^2> for a random walk (define the parameters),
-the 3-d Gaussian function for P(R), the probability of an end-to-end distance R, and
-the Boltzman function describing a thermally activated probability function P(R) for a given end-to-end distance.
-How can these be used to determine the energy as a function of chain end-to-end distance R for a random polymer chain?

3) When a rubber ball is frozen to below -60°C it bounces and when it is warmed to room temperature it bounces, however when it reaches about -60°C it does not bounce.

a) Why does the ball bounce when very cold?
b) Why does the ball bounce when warm?
c) At -60°C why does the ball not bounce?
(Give an answer that is more than two sentences for each. That is, propose a molecular mechanism for the observed behavior. One of the answers may involve a time constant τ, the relaxation time.)

ANSWERS: Quiz 6 Properties of Materials CME 300
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1) a) The programmer thinks that there is a problem with the simulation code since the last image shows an almost linear structure that would seem to be impossible for a random walk. Also the second structure doesn't seem to be evenly distributed about the center. Comment on this by suggesting what the programmer should do.

The program is working fine, random walks are random so any result is possible from a fully collapsed chain on the starting point to a fully extended chain. Both of these cases are unlikely since they both have 0 conformational entropy, that is, they both have only one state and ln(1) = 0. The most probable end-to-end distance is 0. Random walks are expected to display a wide range of different structures.

b) For the random walks, examples of which are shown above, what is the value of <R>? Why?

It is just as likely that a walk will go a given distance in +x as in –x. The same is true for y and z so the average value of all of these directions is 0, $\langle R \rangle = 0$.

2) *-Give the value (or expression) for $\langle R^2 \rangle$ for a random walk,*

$\langle R^2 \rangle = nl^2$ $\langle R^2 \rangle$ is the mean square of the end to end distance, n is the number of steps and l is the step length.

-the 3-d Gaussian function for P(R), the probability of an end-to-end distance R, and

$$P(R) \sim \exp\left(\frac{-3R^2}{2nl^2}\right)$$

-the Boltzman function describing a thermally activated probability function P(R) for a given end-to-end distance.

$$P(R) \sim \exp\left(\frac{-E(R)}{kT}\right)$$ E(R) is the energy for the polymer chain as a function of end-to-end distance R, k is the Boltzman constant and T is the absolute temperature.

-How can these be used to determine the energy as a function of chain end-to-end distance R for a random polymer chain?

We can equate the two probability functions, equating the argument to the exponential, and solve for E(R). $E(R) = \frac{3R^2kT}{2nl^2}$

3) When a rubber ball is frozen to below -60°C it bounces and when it is warmed to room temperature it bounces, however when it reaches about -60°C it does not bounce.

a) Why does the ball bounce when very cold?

When very cold the polymer chains cannot move in a coordinated motion and the structure forms a glass. In a glass the mechanical response is due to compression of atomic distances and the response due to atomic repulsion. This is identical to the behavior seen in ceramic glasses such as silica glass. The response is hard but brittle behavior.

b) Why does the ball bounce when warm?

When warm the polymer would be a liquid if the chains were not crosslinked. The crosslinks create a condition that when a mechanical stress is applied the chains are stretched between crosslinks and the material responds as a Hookean elastic following the ideal rubber law. The molecular mechanism is that the thermal motion of the atoms in the chain generate a retractive force that counteracts applied stress.

c) At -60°C why does the ball not bounce?

(Give an answer that is more than two sentences for each. That is, propose a molecular mechanism for the observed behavior. One of the answers may involve a time constant τ, the relaxation time.)

At the glass transition the polymers inherent relaxation time matches the time associated with impact of the ball with the table or floor. At this point all of the energy associated with the impact has the same frequency as the resonant frequency or 1/relaxation time for the polymer. The energy can be transferred to the chains and the chains can dissipate the energy as heat. Below the glass transition temperature the impact is much faster than the relaxation time so the chains can not move and the ball responds like an inorganic glass, above the glass transition the energy is at a lower frequency so that it leads to motion of the entire chain and deformation of the chain with a response associated with rubber elasticity.