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Excluded Volume in Macromolecules

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SUMMARY

The excluded volume in macromolecules has been discussed in an elementary way, and has been compared with that of the real gases. The excluded volume has been classified into two categories, namely, inter- and intramolecular excluded volumes, and have been discussed in greater length in terms of their origin and their influence on configurational and hydrodynamic properties. It is concluded that the calculation of intermolecular excluded volume is not difficult, while the intramolecular excluded volume requires detailed knowledge about the nature and the various interactions between the polymer segments.

The subject of macromolecular chemistry is analogous to the theory of gases. For gases, one comes across two kinds of theories, namely, the ideal gas theory and the nonideal or the real gas theory. The nonideality in gases arises mainly due to the perturbations created by the attractive or the repulsive forces. Similar problems also arise in macromolecular chemistry.

The vast subject of macromolecular chemistry as far as the theoretical interest is concerned, may be divided into two categories: 1) the non-excluded volume or the Markoffian problem, which is similar to the problem of ideal gases; 2) the excluded volume or non-Markoffian problem, which is

similar to the problem of real gases. In random walk terminology, these two problems are equivalent to the normal random walk (Gaussian problem) and to the excluded random walk (non-Gaussian problem). Therefore the excluded volume problem can be treated in a similar way as the theory of real gases. The excluded volume originates due to perturbations exercised by the interactions. These interactions arise from many angles and are classified broadly into two classes: 1) intermolecular interactions and 2) intramolecular interactions. The intermolecular interactions are common among gases, liquids, and solids, while intramolecular and intermolecular interactions are common among high polymers and polyelectrolytes. Besides these two kinds of interactions, there are also solvent-solute interactions. These interactions can be minimized or reduced to a smaller magnitude by choosing dilute solution. If the system is under the influence of external forces, then the interaction between the system and the external forces may take place.

The excluded volume is of two kinds: 1) the excluded volume between the molecules which is known as intermolecular excluded volume and exists in gases, especially in dense gases; and 2) the excluded volume within a molecule which is known as intramolecular excluded volume and is common in nonionic polymers. The concept of excluded volume is not new. This concept was originated along with the Van der Waal's theory of real gases. According to this theory, the atoms are associated with finite mass. This association of finite mass leads to the fact that two atoms cannot occupy the same volume element of the space with a result of mutual exclusion. Hence, the excluded volume is the result of inherent inability of two atoms to occupy the same volume element. To illustrate this concept, we consider the following example. Let A and B be two spherical particles with hard cores and let them be in contact with each other. Let the radius of the sphere be r . Then the volume of a single sphere is $\frac{4}{3}\pi r^3$ (Fig. 1). Due to the finite mass of A and B, the excluded volume exists and is described by the dotted circle (in three dimensions this dotted circle is a sphere). This excluded volume is shared by both particles and is equal to $\frac{4}{3}\pi\sigma^3$, where σ is the radius of the dotted circle or the diameter of the single sphere. This value of excluded volume is exact if and only if the excluded volume is spherical. But in reality this is not the case due to the local fluctuations in the density and moreover, the gas particles have soft cores instead of hard cores. Therefore, we may consider that the calculated value for excluded volume is an average over local fluctuations. The excluded volume for a single sphere is $\frac{2}{3}\pi\sigma^3$, which is just four times the volume of a single particle.

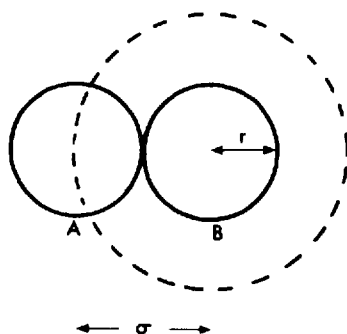


Figure 1

ORIGIN OF THE EXCLUDED VOLUME

In the previous section it was mentioned that the excluded volume arises due to the fact that two particles (atoms or molecules) cannot occupy the same volume element of the space at the same time. In other words, the electron densities associated with the particles cannot be placed in the same volume element at the same time. This inability of the particles is inherent. Every particle which exists in nature is allowed a certain residual energy which is an inherent character. By virtue of this character the attractive or repulsive forces exist. The attractive forces are dominant at a considerably long distance compared to the radius of the particle, and the repulsive forces are dominant only at short distances. As two particles approach each other, the repulsive forces begin to dominate and become enormous at the point of contact (note here that the repulsive potential wall extending to infinity as described by the hard core potential is meaningless). This enormous energy prevents two particles from approaching closer than the point of contact. Hence the possibility of two particles occupying the same volume element is excluded. Therefore, the origin of the excluded volume results from the repulsive forces. However, the repulsive forces are not solely responsible for excluded volume. In addition to these forces, the attractive forces to a certain extent contribute toward excluded volume [1].

EXCLUDED VOLUME IN MACROMOLECULES

The excluded volume in macromolecules is of two kinds: the intramolecular excluded volume and the intermolecular excluded volume. The

first kind exists among different parts of the same molecule and the second kind exists between the molecules themselves. The intramolecular excluded volume is very important and is the center of attraction for many workers. The intermolecular excluded volume is not so important and is easily minimized by considering dilute solutions. However, the intramolecular excluded volume cannot be minimized since it is the inherent capacity of the molecule and moreover exists in the same molecule.

Let us discuss the first kind in detail. A polymer molecule contains a number of atoms (or segments) associated with attractive and repulsive forces due to their finite mass and residual energy. In a poor solvent, the attractive forces are more dominant than the repulsive forces. Hence two segments can occupy the same volume element, which means that two segments are allowed to overlap. In reality, this situation does not exist due to the finite mass of the individual segments. Hence any two segments in a molecule cannot overlap. Such situation also arises in the non-Gaussian problem or the excluded volume problem. This mutual exclusion problem is very attractive to work with but is more difficult to treat theoretically. Due to this reason very little progress has been made in this direction.

Windwer [2] has introduced a very interesting concept to analyze the intramolecular excluded volume in detail. His concept is as follows: The restriction of keeping an atom in the chain from passing a certain volume in space occupied by another atom in the chain gives two effects. The first effect, labeled "intrinsic excluded volume" (IEV), prohibits two atoms in the same molecule from simultaneously occupying the same position in space, resulting in an expansion of the molecule (here space is considered to be discontinuous). The second effect is really a resultant feature of the first. When a series of positions are excluded from the molecule, they encompass certain regions in space which become bounded by these impenetrable atoms (diminution in the accessibility of these regions in space). They also become excluded from the remainder of the molecules and tend to expand the system relative to the amount of volume excluded. This factor is termed the "excess excluded volume" (EEV). Then the total excluded volume is the sum of these two effects:

$$\text{total excluded volume} = \text{IEV} + \text{EEV} \quad (1)$$

CALCULATION OF EXCLUDED VOLUME

The excluded volume between two molecules is easily calculated. The polymer molecule assumes different configurations due to thermal agitation

and flexibility. These configurations are equivalent in the sense that they have the same molecular weight and identical energy content. Since the molecule extends in space, it has a tendency to occupy a certain fraction of space. This fraction of space is known as the volume occupied by the polymer molecule. We assume that equivalent configurations have identical volumes because it is very difficult to evaluate the volume associated with the individual equivalent configurations as it requires a detailed knowledge of the nature of the molecule. We may simplify this problem by considering the molecule lying on the surface of a sphere with center of mass as origin. Therefore, the volume described by the molecule is equivalent to the volume of the sphere and the mean square radius of the molecule is equivalent to the radius of the sphere. So the excluded volume is evaluated as follows:

Let $\langle S^2_N \rangle$ be the mean square radius of a polymer molecule in an arbitrary unit. Then the volume of a molecule is $\frac{4}{3}\pi \langle S^2_N \rangle^{3/2}$. The excluded volume per pair is $8\frac{4}{3}\pi \langle S^2_N \rangle^{3/2}$, and the excluded volume per molecule is $4\frac{4}{3}\pi \langle S^2_N \rangle^{3/2}$, which is four times the volume of a molecule.

The intermolecular excluded volume is also calculated by using the interaction potential [3]. Let U be the interaction potential for a pair of molecules. Then the excluded volume for this pair is given by,

$$v = \int [1 - \exp(-U/kT)] d^3r \quad (2)$$

The volume v is the effective size of molecules as in the second virial coefficient. The parameter v can be most conveniently evaluated by assuming a particular form of molecule-molecule interaction. For simplicity we assume that a polymer molecule describes a hard sphere of diameter σ . Then the interaction potential for a pair of hard spheres is

$$\begin{aligned} U &= \infty & \text{for } r < \sigma \\ &= 0 & \text{for } r \geq \sigma \end{aligned} \quad (3)$$

Substituting this potential in the following integral and evaluating

$$v = \int_0^{\infty} [1 - \exp(-U/kT)] 4\pi r^2 dr \quad (4)$$

the integral, we obtain $v = \frac{4}{3}\pi\sigma^3$, which is eight times the volume of either

sphere. The effective size per molecule is half of this volume, i.e., four times the volume of the sphere.

The calculation of the excluded volume due to two segments (intramolecular excluded volume) in the same molecule is more difficult as it requires detailed knowledge of the interactions between two segments.

EFFECT OF EXCLUDED VOLUME

We now briefly discuss the effect of excluded volume on configurational, thermodynamic, and hydrodynamic properties. The magnitude of the excluded volume depends on the nature of the solvent. In a poor solvent, the attractive forces are dominant over the repulsive forces, thus making the excluded volume negative. In a good solvent, the repulsive forces are more predominant than the attractive forces, thus making the excluded volume positive. As we pass from a poor solvent to a good solvent, the excluded volume increases. At a certain temperature both attractive and repulsive forces balance each other, thus making the excluded volume vanish. This point known as the "Flory θ -point," which is similar to the Boyle point in real gases. Let us denote the most probable property by X_N^* and its square by X_N^{*2} . Like thermodynamic properties, the configurational and hydrodynamic properties are additive since these properties increase with molecular weight. These properties are expressed through the following equation:

$$X_N^{*2} \equiv \langle X_N^2 \rangle \simeq aN^\gamma + b \quad (5)$$

where a and b are constants, and N is the number of atoms (or segments) in a molecule. The constant a depends on the detailed nature of the molecule and b is assumed to be a function of chain stiffness. The γ is assumed to be 1 for configurational properties and $\frac{1}{2}$ for hydrodynamic properties. Now we consider the polymer molecule under the influence of the excluded volume force. Under these circumstances, Eq. (5) is invalid for the γ values given above. Further, we assume that the system under study is a dilute solution so that we can neglect the intermolecular excluded volume. Due to the imposed excluded volume the distance (absolute) between any two segments increases by a small amount. This effect results in expanding the volume of a molecule. The molecule becomes less dense in the sense that the probability density of any two segments in a given volume

decreases. Hence the given properties increase or decrease in their magnitude. This condition is represented by

$$\lim_{\substack{\text{excluded} \\ \text{volume}}} \langle X^2_N \rangle \rightarrow \langle X^2_N \rangle' \quad (6)$$

where $\langle X^2_N \rangle'$ is the property in the perturbed state. This expansion of the molecule is usually scaled by the exponent of the molecular weight or the number of atoms in a molecule. The excluded volume properties are represented by the following general equation:

$$\langle X^2_N \rangle' \simeq a'N^\epsilon + b' \quad (7)$$

where $\epsilon > 1$ for configurational properties, $\epsilon \neq \frac{1}{2}$ for hydrodynamic properties, and again a' and b' are constants. With the help of Eqs. (5) and (7) we can calculate the excess volume which arises due to excluded volume effect. This property defined as

$$V^E = \frac{4}{3}\pi [\langle X_N \rangle'^{3/2} - \langle X^2_N \rangle'^{3/2}] \quad (8)$$

where $\langle X^2_N \rangle'$ and $\langle X^2_N \rangle$ are the mean square radii in the perturbed and unperturbed states, respectively.

In conclusion we summarize that the effect of excluded volume is to increase or decrease the magnitude of the properties under consideration. We have discussed only nonionic polymers. The effect of excluded volume in ionic polymers depends on the number of charges. If the molecule is highly charged, the excluded volume may be insignificant due to the like forces between the charges. However, the excluded volume may be more significant in low charged polymers. In addition to these systems, a considerable interest has also been developed to investigate the effect of excluded volume on helix-to-random coil transition polynucleotides [4]. The effect of excluded volume does not alter the order of phase transition. However, such an effect increases the value of the ring closure index by a small amount. The order of phase transition may be altered if the excluded volume is combined with chain stiffness [5].

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