

particles, a number of triple particles and perhaps some larger aggregates. Whether the double, triple, etc., particles are molecules in the act of collision or whether they are groups of molecules that have been joined for a long period of time, we have no way of knowing from this frame. That is, we do not know the life-time of these pairs or triplets; time here is not a variable; a stationary frame has no time axis. Let us examine another frame further on in the film. Here the array of particles in the picture is different, but the frames bear quite a resemblance to each other; again, single molecules are present (1-mers), double molecules (2-mers), 3-mers, etc. The resemblance consists in not only the same species (1-mer, 2-mer, 3-mer, etc.) appearing; on counting we find (if enough molecules appear on a frame) that the number of each species on each frame is the same. This follows from the fact that we have taken a gas at equilibrium and each sample must have the same macro-properties as any other. Hence we have a gas at equilibrium that apparently consists of a mixture of 1-mers, 2-mers, 3-mers, etc. We say the gas is associated with a degree of association given by

$$Z_n = \frac{\sum_i i N_i}{\sum_i N_i} \quad (1)$$

where $\sum N_i$ is the number of individual particles, in units of moles per unit mass, while $\sum i N_i$ is the number of unimers in a given mass. (A particle or cluster of size j , a j -mer, contains j unimers; a 1-mer contains one unimer.)

Since the particles present are in equilibrium, this means that the species are individually in equilibrium with each other. The number of each species present at equilibrium is regulated by the value of the equilibrium constants of the system. The reactions can be written as



with an equilibrium constant of $K_{r,s}$ for all values of r and s . Actually, we do not have to consider all these equilibrium constants, but can restrict ourselves to a single set containing $j-1$ constants that refer to the reactions with the 1-mer, namely



whose equilibrium constant is $K_{1,r}$, r having any value. The rest of the equilibrium constants can be formed as

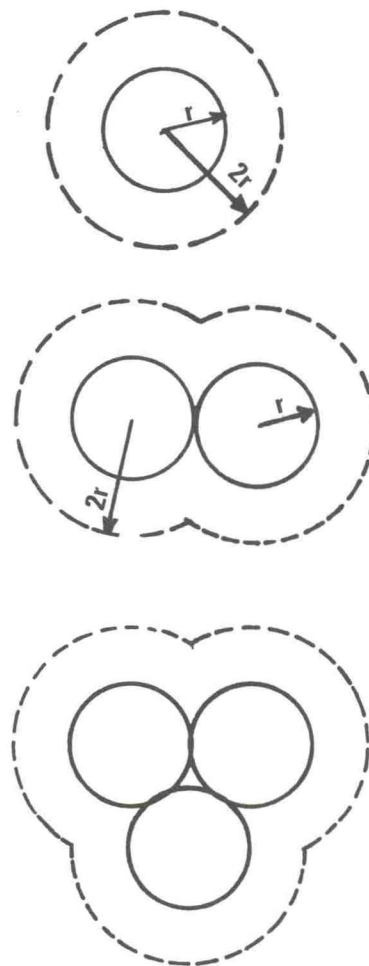


Figure 1. The covolumes of the lower j -mers. The dotted line encloses the covolume or excluded volume. It can be seen that the covolume of a 2-mer is not twice that of a 1-mer.

combinations of this set. The relationship between the numbers of each species is quite simple, namely

$$C_j = K_j C_1^j \quad (2)$$

where

$$K_j = \frac{1}{2} \prod_{x=1}^{j-1} K_{1,x}; j \geq 2 \quad (2a)$$

$$K_1 = 1 \quad (2b)$$

$$C_j = N_j/v$$

and where v = total volume and C_j is the concentration of the species of size j . K_j is the concentration equilibrium constant and is independent of the size of the sample. This follows from the fact that changing the size of the sample in Equation 2 does not change the value of C_j or C_1 . These relationships can be derived both by a kinetic process and an equilibrium process.

Equation of state

To connect these equations with the external variables P , v , and T , we carry out a classical derivation of particles moving in a box and rebounding from the walls, except that for the number of particles in the classical derivation we substitute the number of particles in the mixture of species we have described above. Actually we consider the various sized particles to have no attraction to each other but to have a volume. The attractive forces in the gas are considered to yield the various species. Thus we think of the gas as a mixture of species, each behaving ideally except that each has a volume. The derivation is quite straightforward and the equation of state derived is

$$P \left(1 - \frac{\bar{v}}{v} \right) = RT \sum_i C_i \quad (3)$$

In this equation of state, which is quite simple, there are two more variables than in the simple gas equation, but there are *no arbitrary constants*. The two new variables are $\sum C_i$, which comes from association theory, and \bar{v} , the covolume of the particles, which comes from this derivation. It must be recognized that the covolume, or excluded volume as it is sometimes called, of a 2-mer cannot be twice that of a 1-mer. This can readily be seen from Figure 1. Hence it follows that the total covolume should be defined as

$$\bar{v} = \bar{v}_1 N_1 + \bar{v}_2 N_2 + \bar{v}_3 N_3 + \dots = \sum \bar{v}_j N_j \quad (4)$$

It can be shown that this equation of state is the closed form of the virial equation of state, which is

$$\frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots \quad (5)$$

by inserting the definitions of \bar{v} and $\sum C_j$ into Equation 3 and expanding. Since it has been shown empirically that the virial equation of state represents quite exactly the P - v - T properties of real gases, this derivation puts a theoretical foundation under the virial equation of state and simultaneously confirms the validity of this equation of

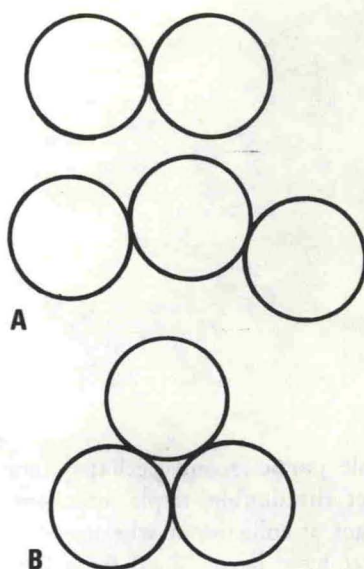


Figure 2. The 2-mer and the 3-mers
A, linear form; B, closely packed form

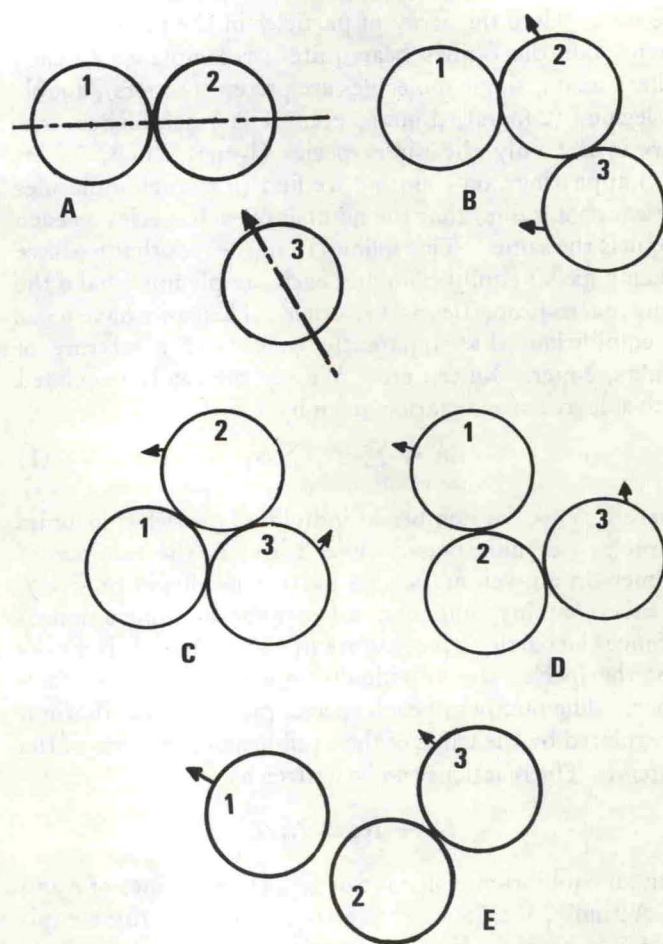


Figure 3. Formation and degradation of a 3-mer
A, just before collision; B, Moment of collision. First bond forms. Unimer #3 imparts momentum to unimer #2. #3 has component of momentum which carries it toward unimer #1; C, Second bond forms. If energy of collision is small, all the kinetic momentum is converted to rotational momentum. If energy of collision is large, goes to D; D, If momentum is great, first bond breaks. If momentum is not too great, goes to C and then back to D and repeats; E, Great momentum, second bond breaks