Effect of Interaction Energy on Floc Structure

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The means for predicting possible floc configurations have until now been mainly numerical simulations of floc growth (Vold, 1963; Sutherland and Goodarz-Nia, 1971; Goodarz-Nia and Sutherland, 1975; Goodarz-Nia, 1977). An analytical scheme, although limited to calculating the probability of finding various configurations of chainlike flocs, has also been proposed (Sutherland, 1970). All these studies, along with experimental evidence (Klimpel and Hogg, 1986; Medalia, 1967, 1970), indicate that, in general, the density decreases with increasing floc size.

A majority of the simulations involve the single-particle addition model, in which one particle at a time is introduced and attaches at only one point to the floc structure. A study by Sutherland and Goodarz-Nia (1971) led to the improved Smoluchowski model in which no restriction is set on the number of particles added at any one time; however, the single contact point assumption is strictly imposed. In addition, reference is made to the work of Meakin (1986) in which computer simulation of floc growth involves cluster-cluster aggregation rather than single-particle addition. The work, however, is based on two-dimensional formations and is primarily devoted to the measurement of fractal geometry. Relation of flocs to fractals also appears in Witten and Sander (1983), where scale invariance is applied to study growth, gelation, and the structure factor of aggregates. In addition, it is worthwhile to mention the paper by Seaton and Glandt (1986) in which spatial correlation functions regarding flocs formed by computer simulations are deduced.

Furthermore, it is important to note that all previous works consider specifically interparticle interaction energies of the types shown in Figure 1. The repulsive barrier present in curve II of Figure 1 simply reduces the rate of flocculation (Ruckenstein and Prieve, 1973). In both cases I and II, however, as a result of Van der Waals forces, an infinite negative interaction energy at zero point of contact exists. This basically leads to the situation where the particle sticks rigidly and permanently, and in some cases fuses, to another particle. Consequently, once a particle is positioned on a floc, it will not vary its relative orientation, and hence, this increases the chances of forming chainlike configurations.

This paper deals with interaction energies of the type presented in Figure 2. It is observed that in addition to the primary energy well, a secondary well with finite energy exists. Here, V^* represents the magnitude of the energy at the secondary well. For the sake of convenience, the interaction energy, V, is made dimensionless with respect to kT (see ordinates in Figures 1 and 2) and denoted by ϕ, so that $\phi = V/kT$. Subsequently, the dimensionless energy at the secondary well is represented by ϕ^*, where $\phi^* = V^*/kT$. This form of energy curve can be attained by careful control of the electrolyte concentration of the colloidal solution. Accordingly, particles that acquire the above-mentioned energy curve will coagulate at the secondary minimum, since the barrier hinders entrance into the primary well. The relatively low value of ϕ^* indicates that contact is not rigid, so that two attached particles will have the freedom to rotate relative to each other. This increases the chances of forming two or more contacts on each particle, thus leading to higher probabilities for obtaining close-packed structures, as opposed to the interaction energies illustrated in Figure 1.

Floc Characterization

A new approach to characterizing a floc is presented. The parameters involve the number of particles forming a floc (floc size), i, and the number of contact points, j, within the floc. For example, the simple loose-packed flocs, including chain configurations, shown in Figure 3a have $i = 5$ and $j = 4$. These formations represent single-contact arrangements where a newly introduced particle attaches to the floc at only one point. Figure 3b, on the other hand, illustrates flocs of size $i = 5$ with 6 and 7 contact points. Some three-dimensional flocs of size $i = 5$ are illustrated in Figure 3c where the number of contact points has increased to 8 and 9. Figures 3b and 3c represent situations where the single contact restriction is lifted.

It is important to mention the difference between the above-

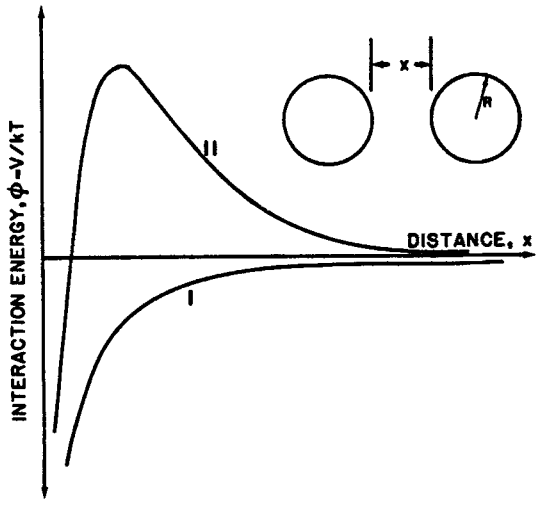

Figure 1. Typical interaction energy curves.

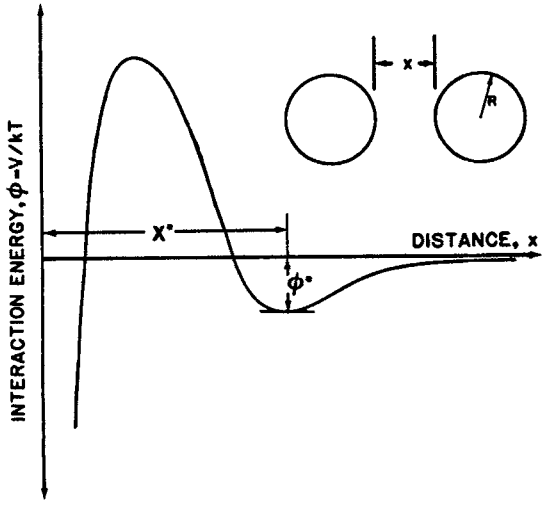

Figure 2. Typical interaction energy curve having a secondary minimum.

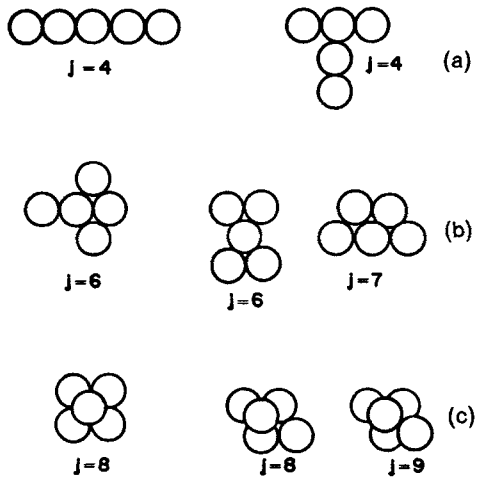

Figure 3. Possible floc structures for $i = 5$.

mentioned approach and the well-established lattice theory (Guggenheim, 1954) that is used to study the somewhat physically related phenomenon of polymer structures, in addition to modeling liquids, crystals, and percolation. Lattice theory, in general, conceptualizes space as being subdivided into an array of lattices. The array follows a specified lattice coordination number, z, defined as the number of nearest neighbors that any lattice space would acquire. As an example, for the simple cubic or von Neumann lattice $z = 6$, whereas for the close-packed lattice $z = 12$ (Kumar *et al.*, 1987). Consequently, adopting a specific coordination number would restrict the array to follow a certain spatially periodic sequence.

Applications of lattice theory abound in existing literature; therefore, carrying on an in-depth description is deemed unnecessary. Altogether, the important point is that lattice theory is based on spatial periodicity and hence does not allow random combinations of different coordination numbers to occur simultaneously. As a result, modeling and simultations of floc formations, which otherwise demand random positioning of particles, cannot be accommodated by lattice theory.

Returning to the present approach, it can be shown that configurations leading to minimum contact points per number of particles in a floc are the loose-packed arrangements shown in Figure 3a. In this case

$$j = j_{\min} = i - 1 \tag{1}$$

On the other hand, maximum contact points per number of particles in the floc can be achieved only when a newly introduced particle comes in contact with three particles that are already in a triangular arrangement, thus forming a tetrahedron; see for example the structure $i = 5$ and $j = 9$ in Figure 3. As a result, for every new particle that is added, a set of three new contact points is established, of course provided that $i > 3$. Thus, for most dense close-packed structures, j is given by

$$j = j_{\max} = 3i - 6 \quad i > 2 \tag{2a}$$

It can easily be shown, however, that Eq. 2a is valid for $i \leq 12$. As i exceeds 12, $j_{\max}$ attains the more general form

$$j_{\max} = \alpha(i)i - \beta(i) \quad i > 12 \tag{2b}$$

where $\alpha(i)$ and $\beta(i)$ are constants within certain ranges of floc sizes that are different, but not much, from their respective values of 3 and 6 that appear in Eq. 2a. In reality, Eq. 2b expresses the general functional form of $j_{\max}$ in relation to i for all floc sizes, a function that varies linearly with i. As an example, for $i \leq 2$, $\alpha(i) = 1$ and $\beta(i) = 1$, and for $2 < i \leq 12$, $\alpha(i) = 3$ and $\beta(i) = 6$. $\alpha(i)$ and $\beta(i)$ are expected to quickly reach asymptotic values as $i \gg 1$.

The arguments stated above thereby suggest that the number of contact points j in a unit floc of size i is bounded by

$$i - 1 \leq j \leq \alpha(i)i - \beta(i) \tag{3}$$

for $i > 2$. This is illustrated in Figure 4 for the specific case of $2 < i \leq 12$, which shall be denoted "small floc region," with α and β known to equal 3 and 6, respectively.

Following floc characterization, two parameters specifying the number of flocs in the system are $n(i, j)$ and $N(i)$. These are

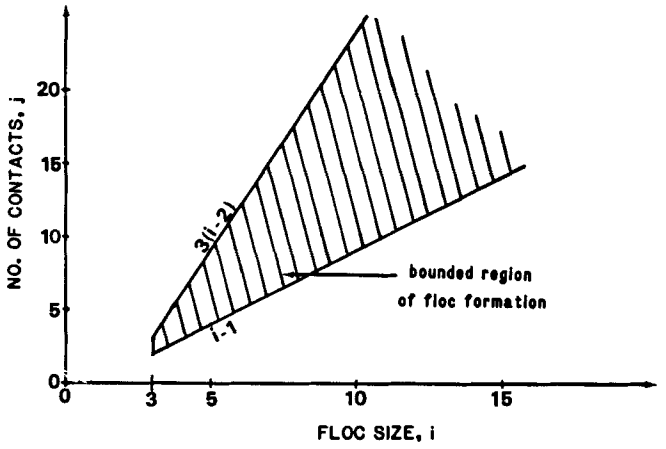

Figure 4. Upper and lower bounds of floc formation.

defined as

$$n(i,j) \equiv \text{number of flocs of size } i \text{ and } j \text{ contacts} \quad (4a)$$

and

$$N(i) \equiv \text{total number of flocs of size } i = \sum_{j=j_{\min}}^{j_{\max}} n(i,j) \quad (4b)$$

In addition to the above, the degeneracy, $\Omega(i,j)$, is defined to be the number of distinguishable arrangements for a floc of size i that contains j attachment points. To clarify the matter, several values of $\Omega(i,j)$ for $i = 3$ and 4 are illustrated in Table 1. Although degeneracy-related calculations have been carried out for several types of linear and branching chain configurations (Sutherland, 1970), the general task of calculating $\Omega(i,j)$ to account for the aggregates considered here proves to be difficult and therefore will not be attempted. It is important, however, to observe that in general $\Omega(i,j_{\max})$ is always a minimum, therefore indicating

$$\Omega(i,j)/\Omega(i,j_{\max}) \geq 1 \quad j_{\min} \leq j \leq j_{\max} \quad (5)$$

Table 1. Possible Floc Configurations for $i = 3, 4$

i	j	CONFIGURATION	Ω(i, j)
3	2		1
	3		1
4	3		2
	4		2
	5		1
	6		1

Problem Formulation

The purpose of this paper is to introduce a means for calculating the probability of finding certain possible floc structures. It is assumed that:

1. The system is in thermal equilibrium with the surroundings
2. Particle size distribution is unimodal
3. Interparticle attachments occur at the secondary minimum with magnitude of dimensionless energy equal to ϕ^*
4. All flocs in the system have size equal to i (unimodal floc size distribution)

Furthermore, the restriction of very thin double layers, and hence attachment distance (x^* in Figure 2) as illustrated in Figure 5 will be imposed. This leads to the assumption that electric interactions between different contact points on a single particle will have minimal effects on each other, suggesting that interaction energies can be linearly summed. Consequently, a floc containing j contact points will have its total free energy reduced by an amount equal to $j\phi^*$, corresponding to the energy level of the floc.

Thus, for given ϕ^*, the probability, $p(i,j)$, of finding aggregates of type (i,j) in a system of unimodal floc size distribution, will follow the Boltzmann distribution given by

$$p(i,j) = n(i,j)/N(i) = A\Omega(i,j)e^{j\phi^*} \quad (6)$$

where A is a proportionality constant, $e^{j\phi^*}$ is the Boltzmann factor, and $N(i)$ represents the total number of flocs in the system. ϕ^* is the dimensionless magnitude of energy at the secondary well and therefore is given as a positive quantity. The exponent in Eq. 6 is positive due to the fact that $p(i,j)$ is expected to increase with increasing number of contact points per floc, which in effect specifies ϕ^* as "negative potential energy."

The constant A in Equation 6 can be evaluated via the normalization condition. With $j_{\min}$ and $j_{\max}$ available from Eqs. 1 and 2, Eq. 4b is incorporated to reduce Eq. 6 to

$$p(i,j) = \frac{n(i,j)}{N(i)} = \Omega(i,j)e^{j\phi^*} \Big/ \sum_{j=i-1}^{\alpha i-\beta} \Omega(i,j)e^{j\phi^*} \quad (7)$$

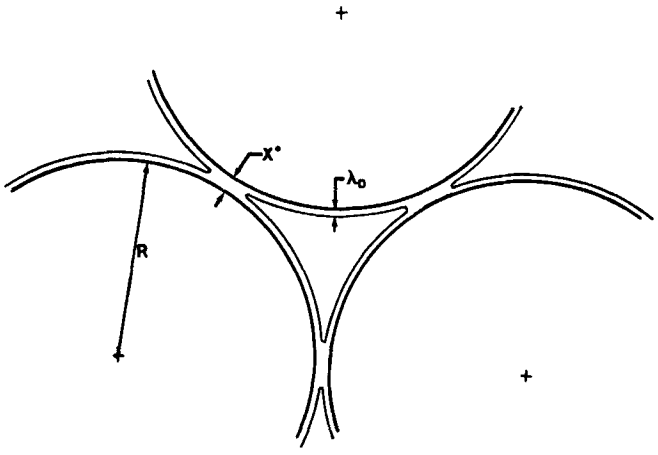

Figure 5. Very thin particle attachment distance.
Electric interaction between contact points because $x^*/R \ll 1$

Hence, exact calculation of $p(i, j)$ requires a knowledge of the degeneracy, $\Omega(i, j)$. As previously mentioned, calculation of $\Omega(i, j)$ becomes increasingly complex as i increases. Consequently, an attempt will be made to calculate conservative limiting upper bounds below which $p(i, j_{max})$ lies.

Conservative Upper Bound Estimates for $p(i, j_{max})$

The expression represented by Eq. 7 leads to the calculation of $p(i, j)$, of course provided that $\Omega(i, j)$ is known. To bypass this difficulty, the inequality given by Eq. 5 will be utilized in order to obtain a rough estimate of the limiting upper bound to the probability, $p(i, j_{max})$, of finding dense and close-packed configurations.

To achieve such dense structures, each particle when introduced must come in contact with at least three touching particles. Consequently, the floc will be composed of tightly packed groups of tetrahedral unit cells; see for example Figure 3c, $j = 9$. The number of contacts per number of particles in this type of arrangement approaches a maximum of $j = j_{max} = \alpha i - \beta$. Therefore, by Eq. 7

$$p(i, j_{max}) = \Omega(i, j_{max}) \exp(j_{max}\phi^*) \Big/ \sum_{j=i-1}^{\alpha i-\beta} \Omega(i, j) e^{j\phi^*} \quad (8)$$

$$p(i, j_{max}) = \Omega(i, j_{max}) \exp(j_{max}\phi^*)/[\Omega(i, j_{min}) \exp(j_{min}\phi^*) + \cdots + \Omega(i, j) \exp(j\phi^*) + \cdots + \Omega(i, j_{max}) \exp(j_{max}\phi^*)] \quad (9)$$

Dividing numerator and denominator by $\Omega(i, j_{max})$ results in

$$p(i, j_{max}) = \exp(j_{max}\phi^*)/[b(i, j_{min}) \exp(j_{min}\phi^*) + \cdots + b(i, j) \exp(j\phi^*) + \cdots + \exp(j_{max}\phi^*)] \quad (10)$$

where

$$b(i, j) \equiv \Omega(i, j)/\Omega(i, j_{max}) \quad (11)$$

But, by virtue of the inequality provided by Eq. 5

$$b(i, j) \geq 1 \quad j_{min} \leq j \leq j_{max} \quad (12)$$

so that

$$p(i, j_{max}) \leq \exp(j_{max}\phi^*) \Big/ \sum_{j=i-1}^{\alpha i-\beta} e^{j\phi^*} \quad (13)$$

Due to the following relationship

$$\sum_{m=K}^{M} Z^m = (Z^{M+1} - Z^K)/(Z - 1) \quad (14)$$

Equation 13, for small flocs ($2 < i \leq 12$), reduces to

$$p(i, j_{max}) \leq \frac{1 - e^{-\phi^*}}{1 - e^{-2(i-2)\phi^*}} \quad 12 \geq i > 2 \quad (15)$$

since $\alpha = 3$ and $\beta = 6$. For general size flocs

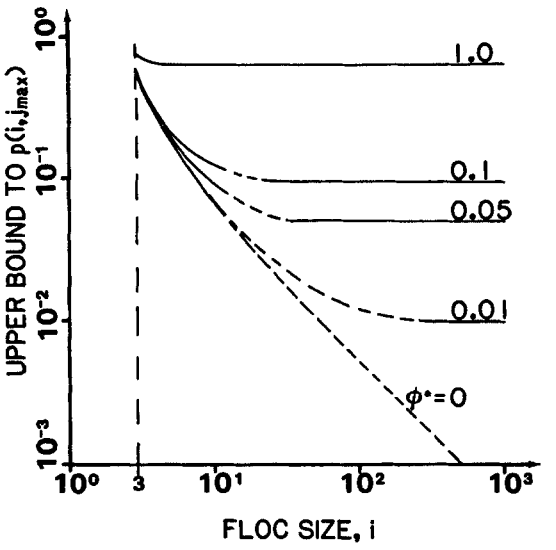

Figure 6. Upper bound estimates for probability function for several values of interaction energies.

$$p(i, j_{max}) \leq \frac{1 - e^{-\phi^*}}{1 - e^{-[(\alpha-1)i-(\beta-2)]\phi^*}} \quad (16)$$

thereby providing a limiting upper bound to $p(i, j_{max})$. Subsequently, for very large and dense ($i \gg 1, j = j_{max}$) flocs, Eq. 16 tends to

$$p(i, j_{max}) \leq 1 - e^{-\phi^*} \quad i \gg 1 \quad (17)$$

independent of floc size.

The behavior of Eqs. 15 and 17 is plotted in Figure 6. The solid lines represent the asymptotic solutions provided by the two equations, and the broken-line segments smoothly connecting them represent the intermediate floc sizes. It is evident that the probability of finding large flocs in dense close-packed arrangements increases dramatically with increasing interaction energy. The effect of ϕ^* on floc structure, however, reduces with decreasing aggregate size. It can also be concluded that smaller flocs are generally more dense than larger ones, an observation that is in good agreement with experimental findings.

Notation

$b(i, j)$ = Eq. 11
i = floc size
j = number of contacts in a single floc
j_{max} = maximum number of contacts possible in a floc, Eq. 2
j_{min} = minimum number of contacts possible in a floc, Eq. 1
k = Boltzmann constant
$n(i, j)$ = number of flocs of size i with j internal contacts
$N(i)$ = number of flocs of size i, Eq. 4b
$p(i, j)$ = probability function, Eqs. 6, 7
T = absolute temperature
V = interparticle interaction energy
V^* = interparticle interaction energy at secondary well
x^* = interparticle separation distance at secondary well
z = lattice coordination number

Greek letters

$\alpha = \alpha(i)$ – coefficient appearing in j_{max}, Eq. 2b
$\beta = \beta(i)$ – coefficient appearing in j_{max}, Eq. 2b
ϕ – dimensionless interaction energy – V/kT
ϕ^* – dimensionless interaction energy of secondary well – V^*/kT
$\Omega(i, j)$ – degeneracy or number of ways possible for forming size i flocs with j contacts

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