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Equilibrium State of Aggregation in Suspensions Comprising Linear Clusters

Ruben D. Cohen[1]

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The final state of aggregation in a suspension containing nonbranching, one-dimensional (linear) flocs is investigated. Allowing coagulation to occur at a finite secondary minimum of magnitude V^* rather than the infinite primary well, it is realized that the system eventually reaches steady state where a relatively large number of flocs coexist at equilibrium. It is shown that, under this condition, the number of flocs $\bar{N}$ expected to result is exponentially related to $-V^*$ and directly proportional to $\sqrt{N_0}$, where N_0 is the initial number of individual particles in the suspension.

KEY WORDS: Equilibrium aggregation; linear flocculation; one-dimensional clusters; secondary-well aggregation; flocculation at secondary well.

1. INTRODUCTION

Following Smoluchowski's theories of coagulation, there has appeared an extensive literature regarding transient size distributions (ref. 4 and references therein) and structural properties of the aggregates (refs. 1, 6, and 8 and references therein) undergoing flocculation. Additional models of flocculation in the presence of a variety of interparticle interaction energy curves have also been developed. Figure 1 depicts, for example, the typical forms of interaction energy curves that have until recently been considered in most cases. Both represent irreversible flocculation at an infinite primary energy well. The energy barrier that appears in curve II of Fig. 1 simply reduces the rate of coagulation.[7] However, in both situations, coagulation persists at an unsteady rate until all the particles in the suspension converge to eventually form one large cluster.

[1] Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77251.

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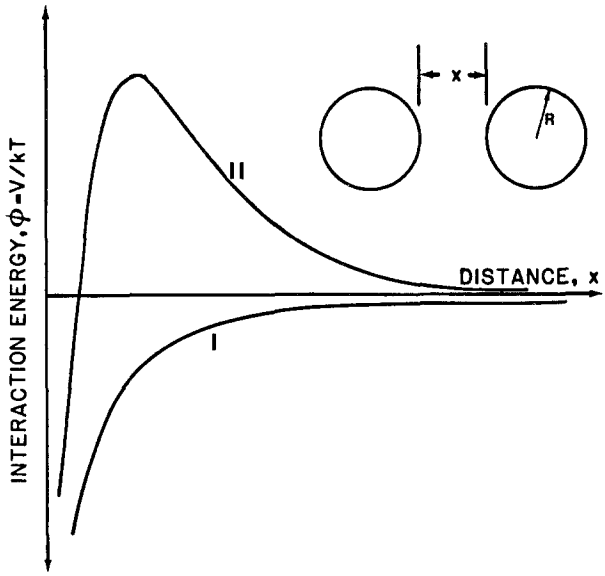

Fig. 1. Typical interaction energy curves.[2]

It is well known that under certain conditions, energy curves similar to that illustrated in Fig. 2 can be produced. This paper mainly focuses on aggregation in the presence of a secondary minimum with a finite value equal to V^* where particle attachments occur. The dynamics of floc growth for this situation has been recently investigated by Dickinson,[3] who, by means of numerical simulations, showed that secondary wells tend to establish more compact clusters, as opposed to coagulation due to curves shown in Fig. 1. An analysis involving floc configurations at equilibrium,[2] which incorporates the ideas of statistical mechanics for structural considerations, firmly supports the conclusion reached by Dickinson.[3] This behavior is simply due to the minimization of potential energy, which, in principle, governs the formation of densely packed clusters.

It should be emphasized that in systems where particles coagulate at finite-valued energy wells, the influence of thermal energy, characterized by kT, where k is the Boltzmann constant and T is the absolute temperature, becomes substantial in prohibiting continuous and ever-unsteady aggregation. Subsequently, the system is carried to a final state, where a relatively large number of flocs coexist in equilibrium. In what follows, an analysis of such a system containing flocs at steady state is presented.

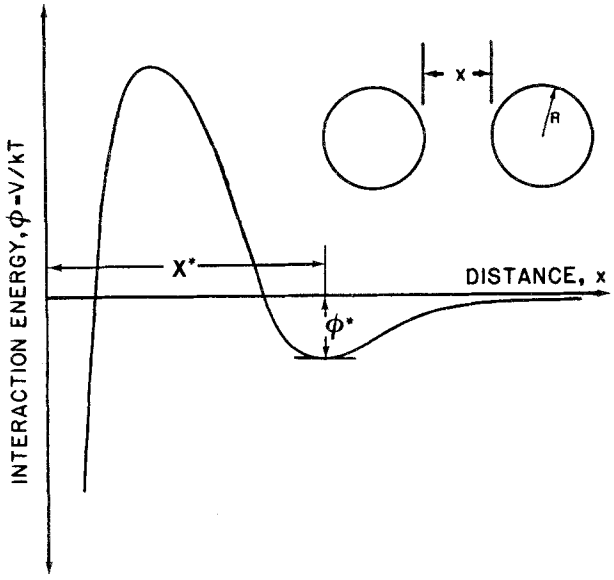

Fig. 2. Typical interaction energy curve having a finite secondary minimum.[2]

2. PROBLEM FORMULATION AND SOLUTION

The interest here is to study the effects of interaction energies of the type shown in Fig. 2 on the final state of flocculation. Of primary concern is the subsequent influence that V^* may have in determining the ultimate number of clusters at equilibrium. For the purpose of the analysis, it is assumed that:

1. The system initially holds a dilute, monodisperse suspension of N_0 individual particles.
2. Upon carefully adding a flocculant, an energy curve similar to that shown in Fig. 2 is produced. This therefore carries the system through a rapid phase of coagulation where particles attach at the secondary well V^* while the energy barrier acts to resist entrance into the infinite primary well.
3. Flocculation is allowed to continue until the system reaches equilibrium with the surroundings. In this final state, the solution contains a number of flocs equal to N, and subsequently a *total* of j interparticle contacts. As a result, the system's potential energy is reduced by an amount equal to jV^* in relation to its initial state.

In consequence of the above, one may assume that the probability

$p(N, j)$ of finding the final system with a total of N clusters and j interparticle contacts follows the Boltzmann distribution given by

$$p(N, j) = A\Omega(N, j)\, e^{j\phi^*} \tag{1}$$

where ϕ^* $(= V^*/kT)$ is the dimensionless value of the secondary well, $e^{j\phi^*}$ is the Boltzmann factor, A is a proportionality constant, and $\Omega(N, j)$ is the degeneracy or the total number of ways that are possible for the system of N aggregates to contain a total of j interparticle contacts.

It is therefore noted that calculation of $p(N, j)$ requires a knowledge of the degeneracy $\Omega(N, j)$. The task of determining $\Omega(N, j)$ in general is quite difficult, especially when flocs of two and three-dimensions are considered. Consequently, this paper is restricted to analyzing one-dimensional (linear) aggregates, where related complications are substantially reduced. Although it is understood that, in view of real systems, this merely represents a hypothetical case, the results that are derived here may subsequently be extended to more complex structures. In addition, the similarity of the present work to polymers, where linear formations are indeed feasible, can lead to actual applications.

Returning to the analytical formulation, if N represents the final number of clusters in the system, then

$$N = \sum_{i=1}^{i_{\max}} n(i) \tag{2}$$

where i is the floc size, $i_{\max}$ is the maximum floc size, and $n(i)$ is the number of flocs with size equal to i. Also

$$N_0 = \sum_{i=1}^{i_{\max}} in(i) \tag{3}$$

where N_0 is the total number of particles in the system. Furthermore, by restricting the aggregates to acquire linear and nonbranching formations, it follows that the number of interparticle contacts in a single floc of size i is simply equal to $i-1$. This thereby leads to an expression for the total number of contacts j in the final state of the system that is given by

$$j = \sum_{i=1}^{i_{\max}} (i-1)\, n(i) \tag{4}$$

which by virtue of Eqs. (2) and (3) reduces to

$$j = N_0 - N \tag{5}$$

independent of i_{max}. Eliminating j from Eq. (1) leads to

$$p(N, N_0) = A\Omega(N, N_0)\, e^{(N_0 - N)\phi^*} \tag{6}$$

where $p(N, N_0)$ denotes the probability for the system of N_0 particles to reduce to a final state containing N chains. In addition, $\Omega(N, N_0)$ represents the possible number of ways in which N flocs can form out of N_0 distinguishable particles. To clarify the matter, Table I serves as an example in order to illustrate all the possible arrangements that three distinct particles can acquire after flocculation.

It is clear that, at equilibrium, the system contains N clusters, where N may vary within $1 \leqslant N \leqslant N_0$. Therefore, the constant A in Eq. (6) can be evaluated by implementing the normalization condition given by

$$\sum_{N=1}^{N_0} p(N, N_0) = 1 \tag{7}$$

Incorporating Eq. (6) into (7) results in

$$1/A = e^{N_0} \sum_{N=1}^{N_0} \Omega(N, N_0) e^{-N\phi^*} \tag{8}$$

Substitution of the above expression into Eq. (6) gives

$$p(N, N_0) = \Omega(N, N_0) e^{-N\phi^*} \Big/ \sum_{N=1}^{N_0} \Omega(N, N_0) e^{-N\phi^*} \tag{9}$$

Since the denominator in Eq. (9) is analogous to the partition function, which is commonly represented by Q in statistical mechanics literature, then

$$p(N, N_0) = \Omega(N, N_0) e^{-N\phi^*}/Q \tag{10}$$

Table I. All Distinct Final States and Their Respective Degeneracies Achievable from Linear Aggregation of Three Particles in Suspension

Initial state, $N_0 = 3$	All Possible Final States	N	$\Omega(N, 3)$
① ② ③	① ② ③	3	1
	①② ③ ① ②③ ①③ ②	2	3
	①②③ ①③② ③①②	1	3

where

$$Q \equiv \sum_{N=1}^{N_0} \Omega(N, N_0) e^{-N\phi^*} \tag{11}$$

By definition, the expected number of flocs $\bar{N}$ that is most likely to appear at equilibrium is

$$\bar{N} = \sum_{N=1}^{N_0} Np(N, N_0) \tag{12}$$

which reduces to

$$\bar{N} = \sum_{N=1}^{N_0} N\Omega(N, N_0) e^{-N\phi^*}/Q \tag{13}$$

after utilizing the expression for $p(N, N_0)$ given by Eq. (10). By virtue of Eq. (11), Eq. (13) is rewritten as

$$\bar{N} = \frac{-\partial Q/\partial \phi^*}{Q} = -\frac{\partial \ln Q}{\partial \phi^*} \tag{14}$$

Evidently, calculation of $\bar{N}$ strictly depends on Q, which in turn requires $\Omega(N, N_0)$ to be explicitly known. Derivation of the degeneracy as applied to this case is quite involved and therefore is not presented here. It is shown, however, that

$$\Omega(N, N_0) = \frac{N_0!}{(N_0 - N)\, N!} \sum_{m=0}^{m_{\max}} mB(N_0 - N, m)\, B(N, m) 2^{-m} \tag{15}$$

where

$$m_{\max} = \begin{cases} N, & 2N \leqslant N_0 \\ N_0 - N, & 2N > N_0 \end{cases} \tag{16}$$

and $B(n, m)$ is the binomial coefficient given by

$$B(n, m) \equiv \frac{n!}{(n-m)!\, m!} \tag{17}$$

Substituting Eq. (15) into Eq. (11) yields

$$Q = N_0! \left\{ \sum_{N=1}^{N_0/2} \Omega_1(N, N_0, \phi^*) \sum_{m=0}^{N} \Omega_2(m, N, N_0) 2^{-m} + \sum_{N=1+N_0/2}^{N_0} \Omega_1(N, N_0, \phi^*) \sum_{m=0}^{N_0 - N} \Omega_2(m, N, N_0) 2^{-m} \right\} \tag{18}$$

where

$$\Omega_1(N, N_0, \phi^*) \equiv \frac{e^{-N\phi^*}}{(N_0 - N)\, N!} \tag{19a}$$

and

$$\Omega_2(m, N, N_0) \equiv mB(N, m)\, B(N_0 - N, m) \tag{19b}$$

It can further be shown that when N_0 is large ($N_0 \gg 1$), which is typical of suspensions, the first double summation appearing in Eq. (18) far outweighs the second one. Consequently, Eq. (18) simplifies to

$$Q = N_0! \sum_{N=1}^{N_0/2} \Omega_1(N, N_0, \phi^*) \sum_{m=0}^{N} \Omega_2(m, N, N_0) 2^{-m} \tag{20}$$

in order to give

$$\bar{N} = \frac{-\partial}{\partial \phi^*} \ln \left\{ \sum_{N=1}^{N_0/2} \Omega_1(N, N_0, \phi^*) \sum_{m=0}^{N} \Omega_2(m, N, N_0) 2^{-m} \right\} \tag{21}$$

by virtue of Eq. (14).

Realizing that, due to $N_0 \gg 1$, Ω_1 and Ω_2 are sharply peaking functions, the ln term in the above equation can readily be evaluated by the classical asymptotic approach (see, for example, ref. 5). Without going through the details, it can be shown that the ln term acquires a maximum at

$$N = N^* = (N_0/2)^{1/2} e^{-\phi^*/2} \tag{22}$$

which satisfies the relation

$$N_0 \gg N^* \gg 1 \tag{23}$$

Therefore, substituting N^* from Eq. (22) for N into Eq. (21) and differentiating with respect to ϕ^* leads to

$$\bar{N} = (N_0/2)^{1/2} e^{-\phi^*/2} \tag{24}$$

which again implies that $N_0 \gg \bar{N} \gg 1$, in accordance with the inequality given by Eq. (23). Equation (24) is a surprisingly simple expression that represents the number of linear aggregates expected to form in a flocculated suspension that originally contained N_0 individual particles. The influence of ϕ^*, and hence V^*, is observed to be exponential.

For the purpose of comparison, Fig. 3 illustrates the range of validity of Eq. (24) in relation to the exact numerical solution of Eq. (13) in con-

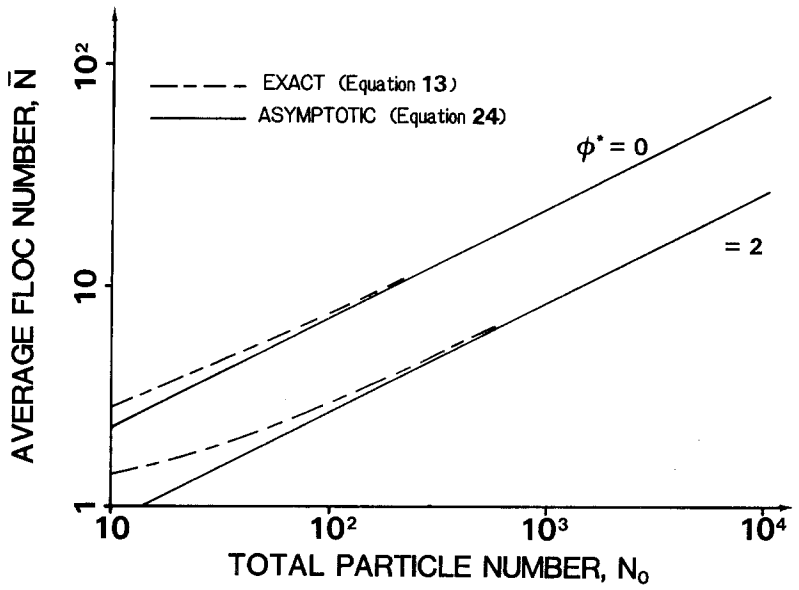

Fig. 3. Comparison of asymptotic and exact solutions depicting the number of flocs $\bar{N}$ expected to result from N_0 individual particles having undergone linear flocculation.

junction with Eqs. (15) and (18). It is evident that the asymptotic solution provided by Eq. (24) agrees very well with the exact solution above a cutoff point of $\bar{N} = 7$.

The simplicity of Eq. (24) allows ϕ^* to be determined in terms of N_0 and $\bar{N}$. Hence,

$$\phi^* = \ln \frac{(N_0/\bar{N})^2}{2N_0} \tag{25}$$

so that the interaction energy can indirectly be determined by obtaining the ratio of initial to final concentrations or number densities $N_0/\bar{N}$, given the total number of particles N_0 in the system.

3. CONCLUSIONS

The problem of equilibrium aggregation as influenced by interaction energy curves containing finite energy wells, shown in Fig. 2, is investigated. Assuming that flocculation occurs at the secondary minimum of magnitude V^*, it follows that for every interparticle contact that is

established in the process of coagulation, the potential energy of the system is reduced by V^*, which in turn carries the system to a lower energy state. As a result, Boltzmann statistics is implemented to determine the final or equilibrium state of the clusters in the suspension.

Although at this stage the study is preliminary in that it essentially is restricted to linear and nonbranching conformations, it is foreseen that the model may help pave the way for predicting the equilibrium states of solutions containing more complex aggregates of higher dimensions. In addition, the similarity of the configurations considered here to those of linear polymers may further justify its practical applications in that field.

It is also important to mention that the model is expected to fail when highly concentrated dispersions are considered. In this situation, near-neighbor collisions will obviously dominate. Subsequently, this would yield degeneracies that may best be computed using lattice theory.

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