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Kinetic and Equilibrium Aspects of Floc Coagulation

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Abstract

The kinetics of colloid flocculation are examined within the framework of a modified Gouy-Chapman model, and the rate of flocculation formulated as a time constant for passage over a barrier in the floc–floc interaction potential. Equilibrium considerations are investigated theoretically by viewing flocculation as a phase change involving cooperative interactions. Critical temperatures and colloid concentrations necessary for flocculation are found to depend on ionic strength, particle size, and zeta potential.

INTRODUCTION

The rapid and complete flocculation of colloidal suspensions is an important objective to sewage, industrial waste, and drinking water treatment plant designers and operators. It is also of interest in the recovery of metals from leachates. Biological colloids must be removed in the clarifier following biological oxidation of municipal sewage and many industrial wastes (*1*). Insoluble metal hydroxides and salts must be removed in the separation of metals, fluoride, and phosphate from wastewaters (*2*), and aluminum hydroxide flocs must be removed from drinking water during its treatment. A discussion of the problem and a good summary of present models, theory, and practice are given in the recent elegant papers of Grutsch and Mallatt (*3–5*).

An early and lucid treatment of the theoretical aspects of colloid stability was given by Verwey and Overbeek (*6*), who built on the Gouy-Chapman model of the electric double layer. Devereux and deBruyn's book contains a great deal of helpful numerical data (*7*). Sonntag and Strenge give an analysis of the interaction of the repulsive electrical forces and attractive dispersion forces to yield a resultant floc–floc interaction potential which may or may not exhibit a barrier; coagulation is said to occur when conditions are such that there is no barrier (*8*).

Here we extend this general model to examine the rate of agglomeration of floc particles in the presence of a barrier in the interaction potential. We also examine the effect of potential well depth on the critical particle concentration necessary for flocculation to occur. The approaches used derive from some of our earlier work on foam flotation (*9–11*), and we shall draw heavily from these papers in the analysis which follows.

KINETICS OF FLOC COAGULATION

We wish to consider the rate at which floc particles agglomerate together, attracted by dispersion forces and repelled by electrical forces. We examine a one-dimensional model for diffusion in a potential field. We let:

$2r_0$ = effective length of a floc particle
η = viscosity of medium
$V(x)$ = potential energy of two floc particles separated by a distance x
$P(x, t)\,dx$ = probability of finding a distance between the two floc particles in the range $(x, x + dx)$ at time t

The evolution of $P(x, t)$ is given by the usual driven diffusion equation,

$$\frac{\partial P}{\partial t} = \frac{KT}{6\pi\eta r_0}\frac{\partial^2 P}{\partial x^2} + \frac{\partial}{\partial x}\left[\frac{1}{6\pi\eta r_0}\frac{dV}{dx}P(x, t)\right] \tag{1}$$

As we shall see shortly, $V(x)$ is given only in numerical form, so we must integrate Eq. (1) numerically. We obtain a finite-difference representation for Eq. (1) as follows. Let

$$P(m, n) = P(m\Delta t, n\Delta x)$$

Then for interior points ($n \neq 1$ or $n_{\max}$), we have

$$\begin{aligned}\frac{\partial P(m, n)}{\partial t} = {} & \frac{kT}{6\pi\eta r_0 \Delta x^2}[P(m, n + 1) - 2P(m, n) + P(m, n - 1)] \\ & + \frac{1}{6\pi\eta r_0 \Delta x^2}\{[V(n + 1) - V(n)][P(m, n) + P(m, n + 1)]\cdot 1/2 \\ & - [V(n) - V(n - 1)][P(m, n) + P(m, n - 1)]\cdot 1/2\}\end{aligned} \tag{2}$$

When $n = 1$ (left end of interval), our boundary condition (reflecting) is given by

$$\frac{\partial P(m,1)}{\partial t} = \frac{kT}{6\pi\eta r_0 \Delta x^2}[P(m,2) - P(m,1)] + \frac{1}{6\pi\eta r_0 \Delta x^2}[V(2) - \mathrm{H}V(1)][P(m,2) + P(m,1)]\cdot 1/2 \tag{3}$$

When $n = N$ ($n_{\max}$, right end of interval),

$$\frac{\partial P(m,N)}{\partial t} = \frac{kT}{6\pi\eta r_0 \Delta x^2}[P(m,N-1) - P(m,N)] - \frac{1}{6\pi\eta r_0 \Delta x^2}[V(N) - V(N-1)][P(m,N-1) + P(m,N)]\cdot 1/2 \tag{4}$$

We integrate Eqs. (2), (3), and (4) forward in time using a predictor-corrector method:

$$P_1(m+1,n) = P(m,n) + \Delta t \frac{\partial P(m,n)}{\partial t} \tag{5}$$

$$P_2(m+1,n) = P(m,n) + \frac{\Delta t}{2}\left[\frac{\partial P(m,n)}{\partial t} + \frac{\partial P_1(m+1,n)}{\partial t}\right] \tag{6}$$

$$P(m+1,n) = P(m,n) + \frac{\Delta t}{2}\left[\frac{\partial P(m,n)}{\partial t} + \frac{\partial P_2(m+1,n)}{\partial t}\right] \tag{7}$$

We found no difficulty with instabilities using Eqs. (2), (3), and (4) with this algorithm; the rather simple difference approximations to the space derivatives conserve probability exactly, and, combined with the predictor-corrector method, do not seem to introduce spurious large eigenvalues into the system.

The potential energy due to the dispersion force (attractive) is given by (*12*)

$$V_D(x) = \frac{-A}{48\pi}\left[\frac{1}{\frac{1}{2}x^2} + \frac{1}{(\frac{1}{2}x + 2r_0)^2} - \frac{2}{(\frac{1}{2}x + r_0)^2}\right]\cdot 4r_0^2 \tag{8}$$

$$A \simeq 10^{-13}\ \text{erg}$$

The potential energy due to the electrical force (repulsive) is given by (*10*)

$$V_E(x) = \frac{-Dr_0{}^2C^{1/2}}{\pi}\int_{\psi_m(x)}^{\psi_1} \log\left[\frac{(1 + B\cosh w)^2}{(1 + B)(1 + B\cosh w_m)}\right] \cdot\left\{\log\left[\frac{1 + B\cosh w}{1 + B\cosh w_m}\right]\right\}^{-1/2} d\psi - V_E(\infty) \tag{9}$$

$$V_E(\infty) = \frac{-Dr_0{}^2C^{1/2}}{\pi}\int_0^{\psi_1} 2\left\{\log\left[\frac{1 + B\cosh w}{1 + B}\right]\right\}^{1/2} d\psi \tag{10}$$

$C = 2A/\beta ezB$

$A = \dfrac{8\pi zec_\infty}{(1 - 2c_\infty/c_{\max})D}$

$B = 2c_\infty/(c_{\max} - 2c_\infty)$

$\beta = 1/kT$

$w = \beta ez\psi$

$w_m = \beta ez\psi_m$

$|z|$ = |charge| of ions in the electrolyte solution in which the floc particles are dispersed (a 1–1 electrolyte)

e = electronic charge

c_∞ = electrolyte concentration, "molecules" per cm^3

$c_{\max}$ = maximum possible electrolyte concentration (corrects for the finite volumes of the ions)

D = dielectric constant of the solution

$\psi_m(x)$ = electric potential midway between two floc particles separated by a distance x, calculated as shown below

ψ = electric potential at a point ξ cm from the left particle when the two floc particles are x cm apart

We calculate $\psi_m(x)$ from the relationship

$$\frac{d\psi}{d\xi} = \left[C\log\frac{1 + B\cosh\beta ez\psi}{1 + B\cosh\beta ez\psi_m}\right]^{1/2} \tag{11}$$

the first integral of our Poisson-Boltzmann equation. Here $x/2 \leq \xi \leq x$, $(d\psi/d\xi)\ (x/2) = 0$, and $\psi(x) = \psi_1$, the surface potential of the floc particles; we use the numerical method outlined earlier (*10*).

We wish to find a measure of the longest time constant, τ (associated with the nonzero eigenvalue of smallest magnitude), of Eq. (1) and its boundary conditions. This should give us a measure of the rate of diffusion together of the two floc particles. We anticipate that this time constant will become quite large (and the colloidal system metastable) as the potential energy barrier between the particles becomes significantly larger than *kT*, but that agglomeration of the particles should be rapid (colloidal system unstable) when there is no barrier or the barrier is of the order of *kT*. We obtain a measure of the desired time constant as follows.

Define

$$f(t) = \int_{x_{\min}}^{x_1} [P_{\text{equil}}(x) - P(x, t)]^2 \, dx \tag{12}$$

where

$x_{\min}$ = distance of closest possible approach of the two floc particles
$V(x_1)$ = maximum

$$P_{\text{equil}}(x) = \exp[-\beta V(x)] \Big/ \int_{x_{\min}}^{x_{\max}} \exp[-\beta V(x')] \, dx' \tag{13}$$

$x_{\max}$ = maximum distance between floc particles

We plot $\log_e f(t)$ versus time; the slope of the plot gives us an upper bound to $2/\tau$. The slope approaches $2/\tau$ in the limit as t becomes very large, provided that $x_{\max}$ is bounded (so that the eigenvalues of the system form a discrete set). A reasonable value for $x_{\max}$ would be of the order of the average distance between colloidal particles in the initial suspension.

EQUILIBRIUM ASPECTS OF FLOC COAGULATION

The above analysis yields information on whether potential barrier heights do or do not permit flocculation to occur at a rate sufficiently rapid to be feasible. We next address ourselves to the question of whether the equilibrium conditions in the suspension are favorable for floc formation; both kinetic and equilibrium factors must be favorable for flocculation to occur.

Flocculation is basically a phase change—a condensation of the colloidal particles from what is in essence a gaseous (dispersed) state to a condensed agglomeration. Such a cooperative phenomenon is readily amenable to analysis by an approximate method described years ago by Fowler and Guggenheim (*13*) and recently used by us in connection with foam flotation (*11*). The analysis is as follows.

We let

z = maximum number of nearest neighbors a floc particle can have
θ = packing fraction; $\theta \to 1$ corresponds to a solid array of floc particles

$2w/z$ = interaction energy of one pair of floc particles which are in adjacent cells; takes into account van der Waals attractions and electrical repulsions modified by the ionic atmospheres of the floc particles. It is proportional to the surface area the two floc particles present to each other

We define

$$\beta = \left\{1 - 4\theta(1-\theta)\left[1 - \exp\left(\frac{-2w}{zkT}\right)\right]\right\}^{1/2} \tag{14}$$

and let $c(\theta)$ be the concentration of single particles (in terms of average number per cell) in the suspension:

$$c(\theta) = c_0 \frac{\theta}{1-\theta}\left(\frac{2-2\theta}{\beta + 1 - 2\theta}\right)^z \tag{15}$$

Now as $\theta \rightarrow 0$, we should have $c(\theta) \rightarrow \theta$. Since $\lim_{\theta \rightarrow 0} \beta = 1$ and $\lim_{\theta \rightarrow 0} c(\theta) = c_0\theta$, we evidently choose $c_0 = 1$, and

$$c(\theta) = \frac{\theta}{1-\theta}\left(\frac{2-2\theta}{\beta + 1 - 2\theta}\right)^z \tag{16}$$

The isotherms computed from Eqs. (15) and (16) exhibit a critical temperature given by Ref. *13*; below this temperature

$$T_c = \frac{-w}{kz}\log_e(z/z - 2) \tag{17}$$

values of θ near one-half are unstable, and the system separates into a condensed floc phase and a more dilute suspension. The values of θ for these two phases are the two roots (other than $\theta = 1/2$) of the equation

$$c(\tfrac{1}{2}) = \exp\left(\frac{w}{kT}\right) = \frac{\theta}{1-\theta}\left[\frac{2-2\theta}{\beta(\theta) + 1 - 2\theta}\right]^z \tag{18}$$

as shown by Fowler and Guggenheim (*13*). So if on calculating $c(\theta)$ from Eq. (16) we find $c(\theta) > c(\tfrac{1}{2})$ for $\theta < \tfrac{1}{2}$, we set $c(\theta) = c(\tfrac{1}{2})$; if $c(\theta) < c(\tfrac{1}{2})$ for $\theta > \tfrac{1}{2}$, we set $c(\theta) = c(\tfrac{1}{2})$. This is the same sort of situation which arises with van der Waals isotherms for nonideal gases when the temperature is below the critical value.

Within the framework of this approach, flocculation can take place if two criteria are satisfied. First, the temperature must be below the critical temperature, and second, the concentration of individual particles c must equal or exceed $c(\tfrac{1}{2}) = \exp(w/kT)$. We require the effective size of the floc particles, $2r_0$, and $2w/z$, the interaction energy (negative) of two floc particles in adjacent cells. The particle size is determined by the conditions of particle formation; the particle surface potential by the identity of the particles and the concentrations of potential-determining ions in the solution. We calculate the interaction energy from

$$\frac{2w}{z} = V_D(x_{\min}) + V_E(x_{\min}) \tag{19}$$

where V_D is given by Eq. (8), and V_E by Eq. (9).

RESULTS

A number of runs were made in which $f(t)$, w, T_{crit}, and the critical floc concentration were computed. A typical run took approximately 2 min on an XDS Sigma 7 machine. Plots of $\log_e f(t)$ versus time are shown for various surface potentials ψ_1 at a concentration of 1–1 electrolyte of 0.1 mole/l. (See Fig. 1.) Under the conditions of these runs the floc–floc potential exhibits no barrier if $|\psi_1|$ is less than 25 mV. We found that log $f(t)$ plots showed considerable curvature in the range $0 < t <$

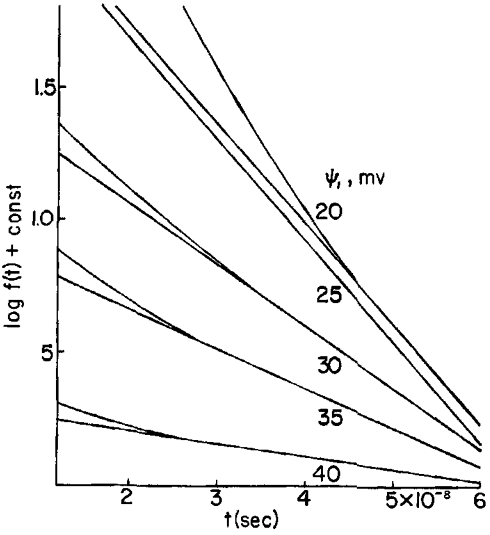

FIG. 1. Effect of surface potential ψ_1 on the rate of decay of $f(t)$. $c_\infty = 10^{-4}$ mole/cm^3, $c_{\max} = 10^{-2}$, $T = 298$ °K, $r_0 = 50$ Å, $\eta = .01$ poise, $A_D = 5 \times 10^{-13}$ erg, $n_z = 6$, $z = 1$.

TABLE 1

Dependence of Flocculation Parameters on Surface Potentials ($kT = 4.114 \times 10^{-14}$ erg)[a]

ψ_1 (mV)	τ (sec)	$V_{\max}$ (erg)	w (erg)	T_c (°K)	c_{floc} (particles/cm^3)
20	$\sim 1.80 \times 10^{-8}$	(No barrier)	-1.463×10^{-12}	716.4	3.54×10^2
25	1.79×10^{-8}	(No barrier)	-1.201×10^{-12}	587.8	2.10×10^5
30	2.91×10^{-8}	9.16×10^{-15}	-8.810×10^{-13}	431.3	5.01×10^8
35	4.68×10^{-8}	6.223×10^{-14}	-5.046×10^{-13}	247.0	3.77×10^{13})
40	13.9×10^{-8}	1.429×10^{-13}	-7.440×10^{-14}	36.4	(1.31×10^{18})

[a] $c_\infty = 10^{-4}$ mole/cm^3, $c_{\max} = 10^{-3}$ mole/cm^3, $r_0 = 50$ Å, $\eta = 0.1$ P, $A_D = 5 \times 10^{-13}$ erg, $n_z = 6$, $z = 1$, $T = 298$°K.

10^{-8} sec, but that in the range $2 \times 10^{-8} < t < 6 \times 10^{-8}$ sec the plots were quite linear and the limiting slope could readily be obtained provided that $|\psi_1| > 20$ mV. If $|\psi_1| \leq 20$ mV, the decay toward equilibrium is very rapid and the plot is nonlinear out to $t = 6 \times 10^{-8}$ sec. Evidently if there is no potential barrier, the lowest nonzero eigenvalue may not be well-separated from the other nonzero eigenvalues—a hardly surprising result.

We note that the lowest eigenvalue of our differential equation must be zero, corresponding to the time-independent equilibrium state. If a barrier is introduced into the potential energy, one of the other eigenvalues decreases in size; at sufficiently high barrier heights it is associated with the time constant for diffusion over the barrier, and would be expected to show the usual Boltzmann-type dependence on barrier height.

Table 1 shows the dependence of time constant on surface potential. We see that as the barrier height rises significantly above kT, the expected increase in the time constant for flocculation occurs. In this solution (ionic strength = 0.1 mole/l), evidently flocculation will become quite slow at surface potentials of the order of 40 to 45 mV, and the colloid will be metastable at higher surface potentials.

The effect of varying the ionic strength (c_∞) on the time dependence of $\log f(t)$ is shown in Fig. 2. As the ionic strength increases, the rate of the system's approach to equilibrium increases markedly. The time constants determined from these plots are listed in Table 2. Evidently as the ionic

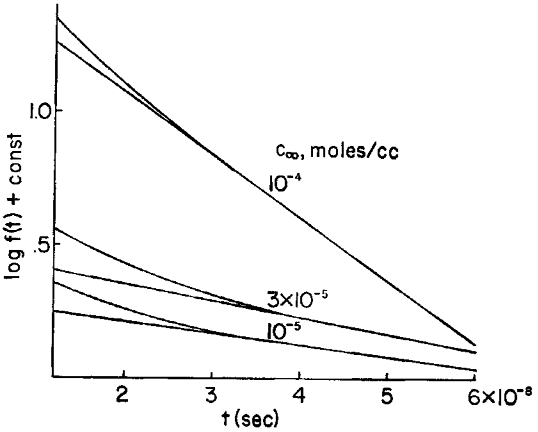

FIG. 2. Effect of ionic strength on the rate of decay of $f(t)$. $\psi_1 = 30$ mV, c_∞ as indicated, other parameters as in Fig. 1.

TABLE 2

Dependence of Flocculation Parameters on Ionic Strength ($kT = 4.114 \times 10^{-14}$ erg)[a]

c_∞ (mole/cm^3)	τ (sec)	$V_{\max}$ (erg)	w (erg)	T_c (°K)	c_{floc} (particles/cm^3)
10^{-5}	1.51×10^{-7}	5.879×10^{-14}	-1.402×10^{-12}	686.3	1.59×10^3
3×10^{-5}	1.02×10^{-7}	5.328×10^{-14}	-1.147×10^{-12}	561.5	7.76×10^5
10×10^{-5}	2.91×10^{-8}	0.916×10^{-14}	-8.810×10^{-13}	431.3	5.01×10^8

[a] $\psi_1 = 30$ mV, $c_{\max} = 10^{-3}$ mole/cm^3, $r_0 = 50$ Å, $\eta = 0.01$ P, $A_D = 5 \times 10^{-13}$ erg, $n_z = 6$, $z = 1$, $T = 298$ °K.

TABLE 3

Dependence of Flocculation Parameters on Temperature[a]

T (°K)	τ (sec)	$V_{\max}$ (erg)	w (erg)	T_c (°K)	c_{floc} (particles/cm^3)
298	1.51×10^{-7}	5.879×10^{-14}	-1.402×10^{-12}	686.3	1.59×10^3
320	1.44×10^{-7}	5.906×10^{-14}	-1.417×10^{-12}	694.0	1.15×10^4
340	1.39×10^{-7}	5.888×10^{-14}	-1.431×10^{-12}	700.4	5.77×10^4

[a] $\psi_1 = 30$ mV, $c_\infty = 1 \times 10^{-5}$ mole/cm^3, $c_{max} = 10^{-3}$ mole/cm, $t_0 = 50$ Å, $\eta = 0.01$, $A_D = 5 \times 10^{-13}$ erg, $n_z = 6$, $z = 1$.

TABLE 4

Dependence of Flocculation Time Constant on Particle Size[a]

r_0 (Å)	τ (sec)	$V_{\max}$ (erg)	w (erg)	T_c (°K)	c_{floc} (particles/cm^3)
40	0.79×10^{-7}	3.747×10^{-14}	-7.164×10^{-13}	350.7	5.34×10^{10}
50	1.02×10^{-7}	5.328×10^{-14}	-1.147×10^{-12}	561.5	7.76×10^5
60	1.44×10^{-7}	7.193×10^{-14}	-1.675×10^{-12}	819.9	1.20

[a] $\psi_1 = 30$ mV, $c_\infty = 3 \times 10^{-5}$ mole/cm^3, $c_{\max} = 10^{-3}$ mole/cm, $T = 298$ °K, $\eta = 0.01$ P, $A_D = 5 \times 10^{-13}$ erg, $n_z = 6$, $z = 1$.

strength decreases much below 0.01 mole/l, the potential barrier increases to the point where the colloidal system flocculates sufficiently slowly that it can be regarded as metastable.

The effect of varying the temperature (with the viscosity and surface potential held constant) is indicated in Table 3. Under the conditions of these runs the barrier height appears to be little affected by the temperature, despite the fact that the ionic atmosphere becomes more diffuse with increasing temperature. As the temperature increases we find the time constant of the system decreasing—the approach to equilibrium is accelerated as one would expect. The extent of the acceleration is rather small, due to the fact that the potential barrier height (the "activation energy" in chemical kinetic terms) is only of the order of kT.

The effect of the particle size ($2r_0$ = length of particle) is indicated in Table 4. In all of these runs a potential barrier existed as indicated; since the potential energy of floc–floc interaction is approximately proportional to r_0^2, we expect and find that the time constant for flocculation increases markedly with increasing particle size. At higher surface potentials or lower ionic strengths, the barrier heights would be even larger, and the time constants would be expected to increase with r_0 even more rapidly. Under conditions of low $|\psi_1|$ and/or high ionic strength, the barrier may be eliminated entirely, in which case τ would still be expected to increase slowly with r_0 since viscous drag increases with r_0.

It is somewhat more difficult to assess the equilibrium criteria for flocculation [that $T < T_c$ and $c > c(\theta = \frac{1}{2})$]. Calculation of T_c from Eq. (17) and $c(\frac{1}{2})$ from Eq. (18) both require a knowledge of $2w/z$, the interaction energy of two floc particles at their distance of closest approach. This quantity approaches $-\infty$ if we let the distance x between the two surfaces approach zero (V_D is singular, while V_E remains finite as $x \to 0$). The extent to which hydration shells prevent extremely close approach is uncertain, so one must make a rather arbitrary choice of this distance of closest approach. We choose 10 Å, emphasizing the arbitrary nature of the choice.

From Table 1 we see the expected decrease in binding energy with increasing surface potential and note that at surface potentials above 30 to 35 mV flocculation will not occur no matter how high the floc concentration if the temperature is maintained at 298 °K. T_c, the temperature above which flocculation does not occur, decreases with increasing surface potential, and c_{floc}, the minimum particle concentration at which flocculation may occur, increases with increasing $|\psi_1|$.

In Table 2 we find a rather surprising result. As ionic strength increases, the binding energy of floc particles to each other decreases in magnitude, T_c decreases, and c_{floc} increases. Presumably at sufficiently high ionic strengths the colloid would be thermodynamically stable and flocculation would never occur. This appears to be due to the increased stabilization of the separated surfaces as ionic strength increases.

Table 3 exhibits a weak temperature dependence of T_c, a weak dependence on T of the floc–floc binding energy, and a substantial increase of c_{floc} with T, as one would expect.

The effects of particle size ($2r_0$) on T_c and c_{floc} are as expected; increasing r_0 increases $|w|$ and results in very marked increase in T_c and decrease in c_{floc} as seen in Table 4. We note here that the *increase* of τ with increasing r_0 (due to increased barrier height and noted earlier) means that colloids of fairly large particle size and finite surface potentials are especially likely to be metastable; capable of forming stable flocs, but at an extremely slow rate.

In summary, we note that surface potential, ionic strength, particle size, temperature, and particle concentration are significant variables in flocculation, and that their kinetic and equilibrium effects can be examined by the methods described here. The constant A_D in Eq. (8) (the attractive van der Waals component of the interaction energy) is also a significant parameter, but cannot be varied; we have used a value of 5×10^{-13} erg taken from Sonntag and Strenge (*8*). The distance of closest approach, assigned arbitrarily in this work, might be estimated by experimental measurement of c_{floc} at a given temperature or of T_c for well-characterized colloidal particles.

We note that the presence of a barrier in the interaction potential does not prevent flocculation unless the barrier height is substantially greater than kT. Either kinetic or equilibrium considerations may be critical in determining whether flocculation occurs; equilibrium factors depend strongly on the distance of closest approach of the floc particles, which is poorly characterized at present.

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