

Stability Ratios for Doublet Formation and for Deposition of Colloidal Particles with Arbitrary Interaction Potentials: An Analytical Approximation

Thomas Gisler* and Michal Borkovec

*Institute of Terrestrial Ecology,
Federal Institute of Technology (ETH),
Grabenstrasse 3, CH-8952 Schlieren, Switzerland*

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Unlike in fast (diffusion-limited) aggregation, the rate of doublet formation in slow (reaction-limited) coagulation is intimately linked to the details of the interaction potential between the colliding monomers. The classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory states that this total interaction potential¹ can be expressed as a sum of two contributions, namely

$$V(h) = U_W(h) + U(h) \quad (1)$$

where h is the distance between the surfaces of the particles. The first contribution U_W is due to van der Waals attraction which can be approximated for spherical particles as $U_W(h) = -Aa/12h$ for $h \ll a$, where a is the particle radius and A the Hamaker constant. The second contribution is the electrostatic potential $U(h)$ which depends on parameters such as the charge Z and the size of the particles, its surface potential Φ_s , and the inverse Debye screening length κ . The overall potential $V(h)$ itself has a maximum at $h = h_s$ for ionic strengths below the critical coagulation concentration.

The doublet formation rate constant k is defined by Smoluchowski's equation² $dc_2/dt = kc_1^2$, where c_1 and c_2 are the number densities of monomers and dimers, respectively. In the limit of fast aggregation where $V(h) = 0$, the rate constant is given by $k^{\text{fast}} = 8\pi aD$, where D is the single particle diffusion coefficient. The actual coagulation rate constant k^{slow} is commonly expressed in terms of the stability ratio $W = k^{\text{fast}}/k^{\text{slow}}$. When the dynamics of the motion of the spherical particles is described by pure diffusion, Fuchs has shown that^{1,3}

$$W = 2a \int_0^\infty e^{\beta V(h)} (h + 2a)^{-2} dh \quad (2)$$

where $1/\beta = k_B T$ is the thermal energy unit. In the slow aggregation regime the structure of the DLVO potentials makes the integrand in eq 2 a sharply peaked function, and therefore only values in the neighborhood of the maximum of the potential $V(h)$ at $h = h_s$ contribute to the integral. In this case a steepest descent approximation allows eq 2 to be written as a Gaussian integral giving the result⁴

$$W \simeq \pi^{1/2} e^{\beta V(h_s)} (2a^2 \beta |\partial^2 V / \partial h^2|_{h=h_s})^{-1/2} \quad (3)$$

We have used the fact that $a\kappa \gg 1$ for all realistic systems. In order to proceed, one has to solve for the barrier location $h_s(\kappa)$ given by

$$\left. \frac{\partial V(h)}{\partial h} \right|_{h_s} = 0 \quad (4)$$

This is a transcendental equation for most potentials. Reerink and Overbeek⁴ have circumvented this rather uncomfortable situation by expanding $W(\kappa)$ around a reference point κ_0 for one special case of the electrostatic potential. The reference point κ_0 was chosen such that the potential barrier $V(h_s)$ vanishes. In the following we generalize their approach to arbitrary electrostatic potentials of the form $U(x, \kappa)$ where $x = \kappa h$. Using this form in eqs 1 and 4 we obtain

$$Aa\kappa/12 = -x_s^2 U'(x_s, \kappa) \quad (5)$$

where the prime denotes a partial differentiation with respect to x . This equation determines $x_s = h_s \kappa$ as a function of κ . At the reference point κ_0 introduced above x_s has the value of x_0 ; the two quantities κ_0 and x_0 are determined by the following set of nonlinear equations

$$x_0 = -U_0/U_0' \quad (6)$$

$$a\kappa_0 = 12x_0 U_0/A \quad (7)$$

The subscript indicates evaluation at x_0 and κ_0 .

We now expand $\ln W$ into a Taylor series in $\ln \kappa$ around the reference point $\ln \kappa_0$, keeping terms up to first order

$$\ln W \simeq \ln W_0 + \left. \frac{d \ln W}{d \ln \kappa} \right|_0 (\ln \kappa - \ln \kappa_0) \quad (8)$$

The zero-order term follows from inserting eqs 6 and 7 into eq 3 and can be expressed as

$$W_0 = \pi^{1/2} \frac{x_0}{2a\kappa_0} (\beta U_0 - x_0^2 \beta U_0''/2)^{-1/2} \quad (9)$$

Since the linear coefficient in eq 8

$$s_0 = - \left. \frac{d \ln W}{d \ln \kappa} \right|_0 > 0 \quad (10)$$

the stability ratio given by eq 8 decreases as κ increases and becomes unity at

$$\kappa_c = \kappa_0 W_0^{1/s_0} \quad (11)$$

The value of $\kappa = \kappa_c$ determines the critical coagulation concentration. In several textbook discussions¹ this condition is identified with $\kappa = \kappa_0$. As $\kappa_0 > \kappa_c$ this holds only in a first approximation.

Figure 1 explains the general features of the present approximation scheme for the calculation of stability ratios where $\ln W$ is plotted as a function of $\ln a\kappa$. The exact stability ratio shows a crossover from slow to fast aggregation with increasing κ (thin line A). The thick line B is the linear Taylor series approximation (eq 8) around the reference point κ_0 . The value of the stability ratio at the reference point is given by eq 9 and the negative slope s_0 . The critical κ_c given by eq 11 is located where the Taylor approximation equals zero.

Our analytical approximation of eq 2 can therefore be written as

$$\ln W \simeq \begin{cases} -s_0 \ln (\kappa/\kappa_c) & \text{for } \kappa < \kappa_c \\ 0 & \text{for } \kappa \geq \kappa_c \end{cases} \quad (12)$$

The two basic parameters s_0 and κ_c which enter eq 12 can be evaluated analytically. The slope s_0 is calculated by taking the derivative of eq 3 with respect to κ and making use of eqs 5-7. We obtain the result

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(2) von Smoluchowski, M. *Z. Phys. Chem.* 1917, 92, 129.

(3) Fuchs, N. *Z. Phys.* 1934, 89, 736.

(4) Reerink, H.; Overbeek, J. Th. G. *Discuss. Faraday Soc.* 1954, 18, 74.

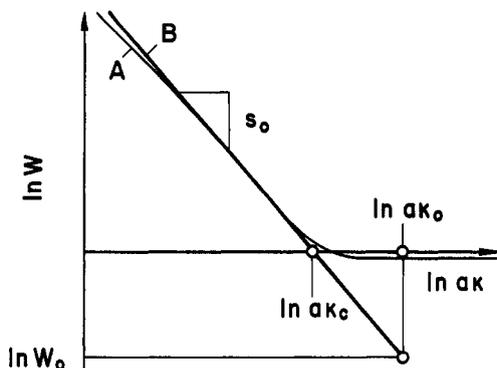


Figure 1. Schematic doubly logarithmic plot of the stability ratio W for colloidal doublet formation as a function of dimensionless inverse Debye length $a\kappa$ (a being the particle radius). Thin line A is the exact stability ratio. Note that in the definition of W we used $V(h) = 0$ for the reference interaction. Since the van der Waals attraction is the actual interaction driving fast coagulation, $\ln W$ reaches a negative limiting value at high salt concentrations. Line B is the present analytical approximation and is given by κ_c which determines the critical coagulation concentration and its slope s_0 .

$$s_0 = \beta U_0 - \kappa_0 (\partial U / \partial \kappa)_0 + 1 + \frac{2U_0 - \kappa_0 x_0^2 (\partial U'' / \partial \kappa)_0}{2(2U_0 - x_0^2 U_0'')} - \frac{[6U_0 + x_0^3 U_0'''] [U_0 + x_0 \kappa_0 (\partial U' / \partial \kappa)_0]}{2(2U_0 - x_0^2 U_0'')} \quad (13)$$

By use of eqs 12 and 9 in eq 11 the critical coagulation condition can be shown to be

$$\kappa_c = \kappa_0 \left(\frac{4a^2 \kappa_0^2 (\beta U_0 - x_0^2 \beta U_0'' / 2)}{\pi x_0^2} \right)^{-1/(2s_0)} \quad (14)$$

Equations 6, 7, 12, 13, and 14 represent the central results of this note.

To illustrate the applicability of the general results, let us first consider the potential

$$U(x, \kappa) = C e^{-x} \quad (15)$$

where $C \propto a \tanh^2(\beta \Phi_s / 4)$. This interaction potential has been used in the study by Reerink and Overbeek.⁴ The solution of eqs 6 and 7 yields $x_0 = 1$ and $\kappa_0 = 12C / (eaA)$. Using these results and $\partial U / \partial \kappa = 0$ in eqs 9, 13, and 14, we obtain $W_0 = [\pi e^3 A^2 / (288 \beta C^3)]^{1/2}$. The slope turns out to be

$$s_0 = \beta C / e - 1/2 \approx 0.37 \beta C - 0.50 \quad (16)$$

whereas the critical coagulation concentration is determined by

$$\kappa_c = \frac{12C}{eaA} \left(\frac{\pi e^3 A^2}{288 \beta C^3} \right)^{1/(2s_0)} \approx 4.42 \frac{C}{aA} \left(\frac{0.073 A^2}{\beta C^3} \right)^{1/(2s_0)} \quad (17)$$

Note that by virtue of $a\kappa_0 \gg 1$, the electrostatic coupling constant C must be assumed to be much larger than the Hamaker constant A . Reerink and Overbeek⁴ have obtained for the slope $s_0 = \beta C / e$, which is the leading term of eq 16. These analytical results agree well with numerical calculations (see Figure 2, graph A).

As a second example consider the Derjaguin approximation of the interaction potential obtained by solving the linearized Poisson-Boltzmann equation with constant potential boundary conditions¹

$$U(x, \kappa) = C \ln(1 + e^{-x}) \quad (18)$$

where $C \propto a \Phi_s^2$. An analogous calculation yields the

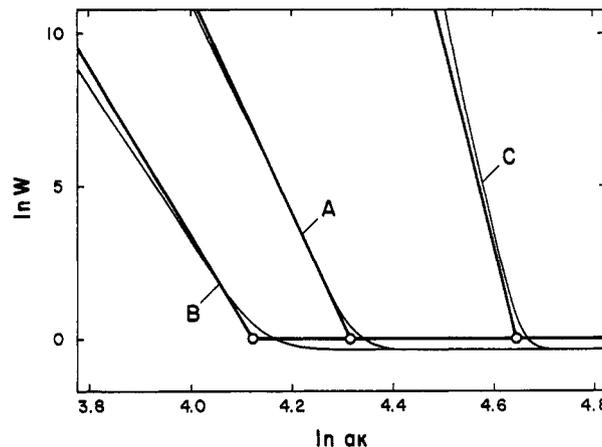


Figure 2. Comparison of exact stability ratios (thin lines) with the present analytical approximation (thick lines) for different interaction potentials: exponential potential eq 15 (A), constant electrostatic potential interaction eq 18 (B), and constant charge boundary condition eq 21 (C). In all three cases $\beta A = 5$ and $\beta C = 100$. The barrier height at the critical concentration has the value $\beta V_c \approx 6$.

following slope and critical coagulation condition

$$s_0 \approx 0.28 \beta C - 0.26 \quad (19)$$

$$\kappa_c \approx 3.79 \frac{C}{aA} \left(\frac{0.457 A^2}{\beta C^3} \right)^{1/(2s_0)} \quad (\text{for } C \gg A) \quad (20)$$

A comparison with the exact result is shown in Figure 2 (graph B). The linear approximation intersects the exact stability curve at $\ln W \approx 2$. The exact stability ratio has an inflection point at $\ln W \approx 5$.

As the final example let us focus on the case of constant charge boundary condition¹

$$U(x, \kappa) = -C \ln(1 - e^{-x}) \quad (21)$$

where $C \propto aZ^2$. The results are

$$s_0 \approx 0.69 \beta C - 1.51 \quad (22)$$

$$\kappa_c \approx 5.77 \frac{C}{aA} \left(\frac{0.053 A^2}{\beta C^3} \right)^{1/(2s_0)} \quad (\text{for } C \gg A) \quad (23)$$

For this functional form of the interaction potential, the slope of our approximation (12) agrees well with the exact calculation (Figure 2, graph C). The critical coagulation condition, however, is slightly underestimated and the linear approximation is shifted from the exact stability plot toward smaller values of $\ln \kappa$. It is interesting to note that this effect goes along with the lack of an inflection point in the exact stability plot.

An analogous treatment can be applied to the situation of reaction limited particle deposition in a flow field past spherical collectors.⁶ Upon increasing ionic strength, a crossover from slow to fast deposition is observed which follows the same pattern as diffusive doublet aggregation.⁵ According to the analysis of Spielman and Friedlander the inverse collision efficiency $W^{(d)}$, which is defined as the ratio of fast and slow deposition rate constants, is given by^{6,7}

$$W^{(d)} \approx 0.6246 \left(\frac{u}{DA_s a_c^2} \right)^{1/3} \int_0^\infty (f(h) e^{\beta V(h)} - 1) dh \quad (24)$$

where D is the particle's diffusion coefficient, u the velocity

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(6) Spielman, L. A.; Friedlander, S. K. *J. Colloid Interface Sci.* 1974, 46, 22.

of the particle toward the collector of radius a_c , A_s a porosity-dependent dimensionless parameter,^{6,5} and $f(h)$ accounts for the hydrodynamic screening between particle and collector. This latter function can be approximated⁷ by $f(h) = 1 + a/h$. With the steepest descent approximation applied to eq 24, the deposition stability ratio takes the form of eq 12 if we make the following substitutions

$$W \rightarrow W^{(d)} \quad (25)$$

$$s_0 \rightarrow s_0^{(d)} = s_0 - 1 + \frac{U_0 + \kappa_0 x_0 (\partial U' / \partial \kappa)_0}{2U_0 - x_0^2 U_0''} \quad (26)$$

$$\kappa_c \rightarrow \kappa_c^{(d)} = \kappa_0 (a \kappa_0 B W_0 / x_0)^{1/s_0^{(d)}} \quad (27)$$

where W_0 is given by eq 9 and $B = 1.2491 [a^3 u / (a_c^2 A_s D)]^{1/3}$. The parameters x_0 and κ_0 are again determined by the solution of eqs 6 and 7.

We can illustrate these general results with the potential given by eq 15. The slope is

$$s_0^{(d)} = s_0 = \beta C / e - 1/2 \quad (28)$$

The critical deposition concentration is determined by

$$\kappa_c^{(d)} = \frac{12C}{eaA} \left(\frac{\pi e B^2}{2\beta C} \right)^{1/(2s_0)} \quad (29)$$

These equations should be compared with eqs 16 and 17 for the case of diffusive doublet aggregation. Note that for the exponential form of the electrostatic interaction potential, eq 15, the slope $s_0^{(d)}$ has the same value as for

diffusive doublet aggregation. On the other hand, the value for the critical deposition condition $\kappa_c^{(d)}$ can be either smaller or larger than the critical coagulation condition κ_c , depending on the relative size of a/a_c and the Peclet number $Pe = ua_c/D$.

In summary we have presented an analytical approximation for the stability ratios for diffusive doublet aggregation and deposition of colloidal particles for arbitrary electrostatic interaction potentials. For interparticle separations and Debye screening lengths small compared to the particle radius, we give explicit expressions for the critical coagulation conditions and slope in the stability plot. These are precisely the same quantities as determined in the experiment. Note that our prediction for the critical coagulation concentration is smaller than the textbook result obtained from the condition of vanishing barrier height. In our case the height of the potential barrier at the critical coagulation concentration is of the order of several thermal energy units. By use of interaction potentials which include size, charge, and structural polydispersity, the present approach might be useful in elucidating the long standing problem that experimental stability ratios are, in contrast to available theories, insensitive to particle size.

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