Interaction between Particles Suspended in Solutions of Macromolecules

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I. Introduction

Most of the theories which have been presented on forces acting between suspended colloidal particles are concerned with van der Waals’ force and a force caused by electric double layers on particles.1,2 These theories can explain many phenomena observed in experiments relating to the stability of suspended particles. Forces of other origins, however, can also act between the particles.3 In this paper we derive an attractive force acting between particles suspended in a solution of macromolecules where there is neither direct interaction between two particles nor between particles and solute macromolecules.4 The magnitude of this force is of the order of osmotic pressure of the solution of macromolecules and the range is of the order of diameter of macromolecules. This force becomes strong in solutions of chain macromolecules or dissymmetrical macromolecules and is greatly intensified by giving electric charges to the macromolecules. In such a case, a macroscopic aggregation of suspended particles can take place. We give some numerical examples of the critical concentration at the macroscopic aggregation. Even a minute change in the condition of solute macromolecules can completely change the state of particles. Direct experimental proof of the reality of the force derived here has not yet been obtained. Some phenomena, however, suggest that this force actually acts between suspended particles.

II. Interaction in Solution of Spherical Macromolecules

Let us consider two large parallel plates immersed in a solution of rigid spherical macromolecules. When the distance between the inner surfaces of these two plates is smaller than the diameter of solute macromolecules, none of these molecules can enter the space between the plates and this space becomes a phase of the pure solvent. Therefore, a force equivalent to the osmotic pressure of the solution of macromolecules acts on the outer surfaces of these plates. Such a force also appears between two spherical particles suspended in this solution.

When the concentration of macromolecules is sufficiently low, the force $P$ between two particles suspended in the solution is given by
\[ P = kTN \Delta \ln Q/\Delta a \]  
\[ Q = \int_1^r \exp \left(-\left(\phi(x,a)/kT\right) \right) dx \]

where \( N \) denotes the total number of solute macromolecules, \( V \) the total volume of the solution, and \( a \) the distance between the centers of two particles. The quantity \( \phi(x,a) \) is the potential energy of a macromolecule situated at \( x \) generated by its interaction with the suspended particles or, more rigorously, \( x \) is the average free energy of a macromolecule at \( x \) when two particles are fixed at distance \( a \). The negative value of \( P \) corresponds to the attraction between particles.

If macromolecules are rigid spheres with no interaction between them and suspended particles, then \( Q \) is equal to the volume of space in which each macromolecule can move freely. In other words, we can obtain \( Q \) by subtracting from the total volume of the solution the volume into which the centers of macromolecules cannot enter owing to hindrance by the particles. When particles are also spherical, we have:

\[ Q = V - \pi(x/4)(D + d)^3/2 + (D + d) \Delta a = \frac{1}{2}(D + d)a^2 \]

\[ D \leq a \leq D + d \]

\[ V = \left(\pi(x/4)(D + d)/2\right)^3 \]

\[ D + d \leq a \]

where \( D \) and \( d \) are diameters of suspended particles and solute macromolecules, respectively. Consequently, we obtain:

\[ P = -\mu S \]

where

\[ S = \frac{(\pi/4)D^2}{(\pi/4)(D + d)^3/2 - a^2} \]

\[ D \leq a \leq D + d \]

\[ D + d \leq a \]

and

\[ \mu = kTN/V \]

When two particles approach each other, two-spherical volumes of diameter \( D + d \) which enclose macromolecules begin to overlap at mutual distance \( a \) equal to \( D + d \). With further decrease of the volume of the overlapping region increases and therefore the attraction acts between particles. The quantity \( S \) in (3.1) is an area of the circular cross section of the overlapping region at the middle of \( a \), and \( \mu \) is the osmotic pressure of the solution of macromolecules. Since the interaction between macromolecules was neglected in deriving the above result, \( \mu \) was expressed by van't Hoff's formula.

The physical interpretation of the simple result (3) can be obtained easily. Except on the part of the surface facing the phase of the pure solvent of cross section \( A \) between two particles, the osmotic pressure of the solution acts uniformly from every side on the surface of suspended particles. The total force acting on the outside half of one of the two particles is larger by \( 2\phi \), than the force acting on its inside half. Thus we can expect that the result (3.1) may be applicable even when the concentration of macromolecules is so high that the osmotic pressure cannot be expressed by van't Hoff's formula. Especially when the diameter \( D \) of the particles is very much larger than the diameter \( d \) of macromolecules and therefore the phase of the pure solvent between particles can be defined clearly, (3.1) can give the force almost exactly.

The potential energy \( U \) of this force \( P \) is written

\[ U(a) = -\mu(x/12)(D + d)^3 - 3(D + d)/a^2 \]

\[ D \leq a \leq D + d \]

\[ = 0 \]

\[ D + d \leq a \]

\[ (4) \]

If \( D \gg d \), (4) can be approximated by

\[ U(a)/kT = -(3/2)\mu(\Delta a)^2 \]

\[ 0 \leq a \leq 1 \]

(5)

where \( x = (D + d - a)/d \), \( \mu = kT/\Delta a^2 \) and \( \mu = (x/6)DN/V \); here \( \Delta a \) means the volume concentration of macromolecules. At \( a = 1 \) or \( a = 0 \), \( U \) takes the minimum value \(-3/2)\mu(\Delta a)^2 \) (\(-U_\infty \)).

For example, if \( \beta = 50 \) and \( \phi = 10^{-3} \), then \( U_\infty/kT = -0.75 \). The attractive potential between particles is of long range, but usually its absolute value is not very much larger than \( kT \) in dilute solutions of rigid spherical macromolecules.

III. Interaction in Solutions of Chain Macromolecules and of Dissymmetrical Macromolecules

Calculations have heretofore been made for particles in solutions of rigid spherical macromolecules. A similar method of calculation can be applied to particles in solutions of coiled chain macromolecules. In this case also, the essential feature of the relation between the potential \( U \) of particles and their mutual distance \( a \) is not altered, if we regard \( a \) as the apparent volume concentration of coiled macromolecules and \( d \) as their apparent diameter. It is remarkable that in solutions of chain macromolecules the apparent volume concentration can be large in very small net concentration. The aggregates are formed with competitive ease in solutions of chain macromolecules.

Assuming that the square of diameter \( d \) of chain macromolecules is proportional to their polymerization degree or molecular weight, we can prove from (5) that as the molecular weight of chain macromolecules is increased at a constant weight concentration, the range of force between suspended particles is increased and the value of \( U_\infty \) is kept nearly constant. Therefore, with increasing molecular weight we can expect an increasing number of aggregates.

Now, let us consider a solution of rigid ellipsoidal macromolecules of length \( A \) and diameter \( B \). By the same method as in the previous section, we can obtain the potential energy \( U \) between spherical particles suspended
\[ P = kTN \delta \ln Q/\delta a \]  
\[ Q = \int f(x) \exp \left[ -\frac{\alpha(x,a)}{kT} \right] dx \]

where \( N \) denotes the total number of solvent macromolecules, \( V \) the total volume of the solution, and \( a \) the distance between the centers of two particles. The quantity \( \alpha(x,a) \) is the potential energy of a macromolecule situated at \( x \) generated by its interaction with the suspended particles or, more rigorously, \( x \) is the average free energy of a macromolecule at \( x \) when two particles are fixed at distance \( a \). The negative value of \( P \) corresponds to the attraction between particles.

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\[ Q = V - \pi (1/3) [(D + d)^{3/2} + (D + d)u - (1/2)a^{3}] \]

\[ D \leq a \leq D + d \]

\[ V - 8\pi (1/3) [(D + d)^{3/2} - a^{3}] \]

\[ D + d \leq a \]

where \( D \) and \( d \) are diameters of suspended particles and soluble macromolecules, respectively. Consequently, we obtain

\[ P = -\mu S \]

\[ S = \left( \frac{4}{3} \right)D^{3} = \left( \frac{4}{3} \right) [(D + d)^{3} - a^{3}] \]

\[ D \leq a \leq D + d \]

\[ 0 \]

\[ D + d \leq a \]

and

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When two particles approach each other, two-spherical volumes of diameter \( D + d \) which enclose macromolecules begin to overlap at mutual distance \( a \) equal to \( D + d \). With further decrease of the volume of the overlapping region increases and therefore the attraction acts between particles. The quantity \( S \) in (3.1) is the area of the circular cross section of the overlapping region at the middle of \( a \), and \( \mu \) is the osmotic pressure of the solution of macromolecules. Since the interaction between macromolecules was neglected in deriving the above result, \( \mu \) was expressed by van't Hoff's formula.

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The potential energy \( U \) of this force \( P \) is given by

\[ U(a) = -\mu (\pi/12)[2(D + d)^{3} - 3(D + d)u + a^{3}] \]

\[ D \leq a \leq D + d \]

\[ 0 \]

\[ D + d \leq a \]

If \( D \gg d \), (4) can be approximated by

\[ U(a)/kT = -{(5/2)\pi a^{3} \delta \phi \beta} \]

\[ 0 \leq x \leq 1 \]

where \( x = (D + d - a)/D, \beta = D/d, \phi = (\pi/6)\delta \phi \pi V \); here \( \phi \) means the volume concentration of macromolecules. At \( x = 1 \) or \( a = D, U \) takes the minimum value \( -{(5/2)\pi a^{3} \delta \phi} \). For example, if \( \beta = 50 \) and \( \delta = 10^{-5} \), then \( U_{a}/kT = -0.75 \). The attractive potential between particles is of long range, but usually its absolute value is not very much larger than \( kT \) in dilute solutions of rigid spherical macromolecules.

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Assuming that the square of diameter \( d \) of chain macromolecules is proportional to their polymerization degree or molecular weight, we can prove from (5) that as the molecular weight of chain macromolecules is increased at a constant weight concentration, the range of force between suspended particles is increased and the value of \( U_{a} \) is kept nearly constant. Therefore, with increasing molecular weight we can expect an increasing number of aggregates.

Now, let us consider a solution of rigid ellipsoidal macromolecules of length \( A \) and diameter \( B \). By the same method as in the previous section, we can obtain the potential energy \( U \) between spherical particles suspended
in this solution if we take into account the limited freedom of orientation of ellipsoidal macromolecules near particles. When \( D \) is very much larger than \( A \) and \( B \), the result for \( A/B(\sim q) \geq 1 \) is given by

\[
-U\phi/kT = (3/2)\beta\psi[(1/3)q^3 + (2/3)]
\]

\[
-\left[ q^2(1 - 1)^{1/3}(1 - x) \ln(q^2 + (q^2 - 1))^{1/3} - (1 - x)x \right]
\]

for \( x = (D + A - a)/A \) between 1 and 1 - \( q^2 \); here \( \phi \) is the volume concentration of ellipsoidal macromolecules and \( \beta = 3D/A \). The formula for \( 0 < x < 1 - q^2 \) is not written here because it is too long. The result for \( A/B < 1 \) is obtained by replacing \( \ln(q^2 + (q^2 - 1))^{1/3} \) in (6) by \((q^2 + (q^2 - 1))^{1/3} - \sin^{-1}(q\sqrt{2}) \) and \( x \) in (6) by \( x + 2(x^2 - D + B - a)/B \). The value of \( U \) at \( a = D \), namely, when two particles are in contact with each other, is written

\[
-U_a/kT = \frac{3}{2}\beta\psi\left(1/3\right)q^3 + (2/3)
\]

\[
-\left(3/2\beta\psi\left(1/3\right)q^3 + (2/3)q^3 \right)
\]

over the whole range of \( q \); here \( \psi \) is the volume of the macromolecule. At a constant concentration and a constant volume, \( U_a \) takes a minimum value when \( q = 1 \). With increasing dielectricity of solution macromolecules, both the range of force and the absolute value of potential energy are increased. The ratio of \( -U_a \) in a solution of ellipsoidal macromolecules to \( -U_{m} = -U_{1/2} \) in a solution of spherical macromolecules of the same volume at the same concentration is given by \((1/3)\psi^2 + (2/3)\psi^3\).

For example, the value of this ratio \( U_a/U_{m} \) becomes 3 at \( q = 5 \) and 18 at \( q = 20 \). With \( a = 10^{-4} \), \( \beta = 6 \), and \( q = 20 \), \( U_a/kT = 1.2 \). Thus, in a solution of dissymmetrical (for example, rodlike) macromolecules, a larger number of aggregates of suspended particles can be formed than in solutions of spherical macromolecules of the same volume.

IV. Interaction in Solutions of Charged Macromolecules

The osmotic pressure \( p \) of solutions of charged macromolecules is very much larger than the osmotic pressure \( p_o \) of solutions of uncharged macromolecules of the same concentration. The ratio \( p/p_o \) \((= f)\) is equal to the number of free counter ions per macromolecule when the solution contains no low molecular salts. When low molecular salts are added, \( f \) is decreased but is still somewhat larger than unity. If two parallel and infinitely large plates be immersed in such a solution of charged macromolecules, the attractive force \( F \) between the plates would be \( f \)-times as large as the force \( F_o \) in a solution of uncharged macromolecules of the same concentration. When two spherical particles are immersed, the ratio of the forces \( F/F_o \) \((= f)\) does not become \( f \) because some counter ions can enter the narrow region between two particles. Nevertheless, this ratio is larger than unity. It is difficult to obtain the exact expression of \( F \), but the approximate value of \( F \) can be estimated as follows.

Let us consider spherical particles of diameter \( D \) suspended in a solution of charged spherical macromolecules of diameter \( d \) which is very much smaller than \( D \). When two particles approach each other, there appears a region between particles into which the macromolecules are forbidden to enter. This region has a circular cross section area \( S \) with diameter \( D + d \) - \( a \) \((= \psi)^{1/3} \). Some counter ions entering by macromolecules near the boundary of the region and are drawn outward. Consequently, they are moving near the circumference of the region. Few counter ions are in the central part of the region. The thickness of the circumference layer wherein counter ions are moving is of the order of the Debye-Hückel ionic atmosphere radius \( D^2/2 \) which is determined by the molar concentration of free counter ions in the solution. With decreasing distance \( a \) between particles, \( D^2 \) becomes larger than \( D + d - a \) and the region containing few counter ions begins to appear. Then the force due to osmotic pressure of counter ions begins to net between the particles. When \( D^2 \) is sufficiently larger than \( D + d - a \), the force \( F \) can be estimated by the equation

\[
P = -p\phi(S[D^2 - (D + d - a)/2]D^2/2)
\]

where \( p\phi \) is the osmotic pressure of the solution of charged macromolecules of concentration \( c \). By integrating this force, if \( D \gg d \), we have

\[
U_a/kT = \frac{3}{2}\beta\psi[(1/3)q^3 + (2/3)]
\]

\[
-\left[ q^2(1 - 1)^{1/3}(1 - x) \ln(q^2 + (q^2 - 1))^{1/3} - (1 - x)x \right]
\]

where \( U_a/kT = -p\phi/\beta\psi(S[D^2 - (D + d - a)/2]D^2/2) \), and \( U_a \) is the potential energy of particles at \( x = (D + d - a)/D \). We put \( D = 5000A_c \) and \( a = 100A_c \). When two particles are in contact with each other, \( D^2 = 1000A_c \), and when the distance between the surfaces of two particles is \( 50A_c, D^2 = 750A_c \). We assume that each macromolecule has 200 ionized groups and that there is no added low molecular salts. Most of the counter ions are bound by macromolecules and, in ordinary solutions of charged macromolecules without added salts, the osmotic coefficient is of the order of \( 0.1 \). Therefore, in the above numerical example we can put \( f = 20 \). When the molar concentration of ionized groups in the solution is between \( 10^{-4} \) and \( 10^{-3} \), the molar concentration of free counter ions is between \( 10^{-4} \) and \( 10^{-3} \). Then the thickness \( D^2/2 \) of the layer of counter ions entering the region between two approaching particles is between \( 40A_c \) and \( 400A_c \). We can expect that \( D^2/2 \) is a little less than the ionic atmosphere radius determined by the molar concentration of free counter ions estimated from the osmotic coefficient of the activity coefficient of counter ions.) Hence, we can see that \( D^2 \) is larger than \( D^2 + d \) unless \( a \) is too small. From (9) it is found that in the above example, \( U/kT \) at \( x = 1, U_a/kT \), is of the order of \( 10U_{1/2}/kT \), to \( 3U_{1/2}/kT \). Thus the force between suspended particles is intensified by giving changes to macromolecules. The magnitude of the force is changed by changes in the charge of macromolecules and in concentrations of macromolecules.
in this solution if we take into account the limited freedom of orientation of ellipsoidal macromolecules near particles. When \( D \) is very much larger than \( A \) and \( B \), the result for \( A/(B+\varepsilon) \geq 1 \) is given by

\[
-U(\varepsilon)/kT = (3/2) \phi k(1/3)\varepsilon + (2/3) - q(\varepsilon - 1)^{-1}(1-x) \ln (q + (\varepsilon - 1)^{-1}(1-x)) \tag{6}
\]

for \( x = (D + A - \varepsilon)/A \); between 1 and 1 - \( q^{-1} \), here \( q \) is the volume concentration of ellipsoidal macromolecules and \( \beta = D/A \). The formula for \( 0 < x < 1 - q^{-1} \) is not written here because it is too long. The result for \( A/B < 1 \) is obtained by replacing \( \ln (q + (\varepsilon - 1)^{-1}(1-x)) \) in (6) by \( (\varepsilon - 2) - \sin^{-1} q \) and \( x \) in (6) by \( x' = (D + B - \varepsilon)/B \). The value of \( U/kT = D \), namely, when two particles are in contact with each other, is written

\[
-U(\varepsilon)/kT = (3/2) \phi k(1/3)\varepsilon + (2/3) - (3/2) k(4/3)^{-1/3} x(1/3) - (2/3)x^{1/3} \tag{7}
\]

over the whole range of \( q \); here \( x \) is the volume of the macromolecule at a constant concentration and a constant volume \( s = -U(\varepsilon)/kT \) takes a minimum value when \( q = 1 \). With increasing disymmetry of solute macromolecules, both the range of force and the absolute value of potential energy are increased. The ratio of \( -U(\varepsilon)/kT \) to \( -U(\varepsilon)/kT \) in a solution of spherical macromolecules of the same volume at the same concentration is given by \( (3/2)\varepsilon + (2/3)\varepsilon^{1/3} \). For example, the value of this ratio \( U(\varepsilon)/kT \) becomes \( 3 \) at \( q = 5 \) and \( 18 \) at \( q = 20 \). When \( \varepsilon = 10^{-4}, \beta = 6, \) and \( q = 20, -U(\varepsilon)/kT = 1.2 \). Thus, in a solution of disymmetrical (for example, rodlike) macromolecules, a larger number of aggregates of suspended particles can be formed than in solutions of spherical macromolecules of the same volume.

### IV. Interaction in Solutions of Charged Macromolecules

The osmotic pressure \( \rho \) of solutions of charged macromolecules is very much larger than the osmotic pressure \( \rho_0 \) of solutions of noncharged macromolecules of the same concentration. The ratio \( \rho/\rho_0 (= \gamma) \) is equal to the number of free counter ions per macromolecule when the solution contains no low molecular salts. When low molecular salts are added, \( \gamma \) is decreased but is still somewhat larger than unity. If two parallel and infinitely large plates be immersed in such a solution of charged macromolecules, the attractive force \( P \) between the plates would be \( f \) times as large as the force \( P_0 \) in a solution of noncharged macromolecules of the same concentration. When two spherical particles are immersed, the ratio of the forces \( P/P_0 (= \gamma) \) does not become \( f \) because some counter ions can enter the narrow region between two particles. Nevertheless, this ratio is larger than unity. It is difficult to obtain the exact expression of \( P \), but the approximate value of \( P \) can be estimated as follows.

Let us consider spherical particles of diameter \( D \) suspended in a solution of charged spherical macromolecules of diameter \( d \) which is very much smaller than \( D \). When two particles approach each other, there appears a region between particles into which the macromolecules are forbidden to enter. This region has a circular cross section area \( S \) with diameter \( D + d \).

\[
-(D + d)^3 - a^3 \tag{8}
\]

Some counter ions entering by macromolecules near the boundary of the region and are drawn outward. Consequently, they are moving near the circumference of the region. Few counter ions are in the central part of the region. The thickness of the circumference layer wherein counter ions are moving is of the order of the Debye-Hückel ionic atmosphere radius \( D^0/2 \) which is determined by the molar concentration of free counter ions in the solution. With decreasing distance between particles, \( D^0 \) becomes larger than \( D + d \) and the region containing few counter ions begins to appear. Then the force due to osmotic pressure of counter ions begins to net between the particles. When \( D^0 \) is sufficiently larger than \( D + d \), the force \( P \) can be estimated by the equation

\[
P = -\rho_0(3(D^0 - D - d))/D^0 \tag{9}
\]

where \( \rho_0(0) \) is the osmotic pressure of the solution of charged macromolecules of concentration \( c \). By integrating this force, if \( D > d \), we have

\[
U(kT) = -\rho_0(3(D^0 - D - d))/D^0 \tag{10}
\]

where \( U(kT) = -\rho_0(3(D^0 - D - d))/D^0 \). We put \( D = 500 \) and \( d = 100 \). When two particles are in contact with each other, \( D^0 = 1000 \), and when the distance between the surfaces of two particles is \( 50 \), \( D^0 = 700 \). We assume that each macromolecule has 200 ionized groups and that there is no added low molecular salts. Most of the counter ions are bound by macromolecules and, in ordinary solutions of charged macromolecules without added salts, the osmotic coefficient is of the order of 0.1. Therefore, in the above numerical example we can put \( f = 20 \). When the molar concentration of ionized groups in the solution is between \( 10^{-1} \) and \( 10^{-3} \), the molar concentration of free counter ions is between \( 10^{-1} \) and \( 10^{-3} \). Then the thickness \( D^0/2 \) of the layer of counter ions entering the region between two approaching particles is between 40 and 400. (We can expect that \( D^0/2 \) is a little less than the ionic atmosphere radius determined by the molar concentration of free counter ions estimated from the osmotic coefficient or the activity coefficient of counter ions.) Hence, we can see that \( D^0 \) is larger than \( D + d \) unless \( d \) is too small. From (9) it is found that in the above example, \( U(kT) = 0 \), \( U(kT) = 0 \), or the order of \( 10^9 \), \( 10^9 \) to \( 3(10^9) \) depends on the force between suspended particles is intensified by giving charges to macromolecules. The magnitude of the force is changed by charges in the change of macromolecules and in concentrations of macromolecules.

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and salts. By addition of low molecular salts, \( D^* \) is slowly decreased and \( f \) is more rapidly decreased; consequently, \(-U/kT\) is decreased.

V. Aggregation of Suspended Particles

When a large number of particles are suspended in the solution of macromolecules, they are attracted to each other through the negative potential \( U \), and some of them form aggregates. In ordinary solutions of noncharged rigid spherical macromolecules, however, the number of these aggregates is not very large. From (5), the ratio of the number of pairs of two particles \( M_2 \) to the number of dispersed particles \( M_1 \) is calculated by

\[
M_2/M_1 = 12kT/\beta \tag{10.1}
\]

\[
K = \int \left( \frac{1}{N_0} \right) \exp \left[ -U/a_0 \right] \, dt \tag{10.2}
\]

where \( G = -U/kT \) and \( \phi = (\alpha/a_0) \). The volume concentration of dispersed particles. Two particles at a distance less than \( a = D + d \) are regarded as a pair. In the numerical example of Section II where \( U/a_0 = -0.72 \), \( M_2/M_1 \) becomes \((1/4)\). This ratio \( M_2/M_1 \) increases rapidly with increasing \(-U/kT\). Therefore, the numerical estimation in Sections III and IV suggests that in solutions of chains or disymmetrical macromolecules and especially in solutions of charged macromolecules, a large number of aggregates can be formed and even a macroscopic aggregation can occur.

We calculate the critical (volume) concentration \( \Phi^* \) of suspended particles where the macroscopic aggregation takes place. It is assumed that in the macroscopic phase of aggregation each particle has 12 neighboring particles and that the interaction energy between two neighboring particles can be given by \((5), (6), \) or (9). When \( D \gg a_0 \), the interactions between particles in the macroscopic aggregate are large enough for macromolecules to enter and, as will be shown later, the average distance \( a_{av}(x) \) between neighboring particles in the aggregate satisfies the condition \( 1 \gg 1 - x_a > 0 \). Accordingly, we can use the above assumption for the interaction energy between particles in the aggregate.

At constant values of the average distance \( a \) between neighboring particles, we can obtain the partition function \( z \) per particle composing the aggregate by using a method similar to the free volume method in the theory of liquid, namely, where \( z \) is given by

\[
z(a) = \int_{a=a_0}^{z_{av}} \exp \left[ -U(a)/kT \right] \, da \tag{11}
\]

Energy \( U(a) \) is the average potential energy of a particle surrounded by 12 neighboring particles when the position of the surrounded particle deviates from the center of the free volume by distance \( a \). When the concentration of macromolecules and other conditions of the medium are given, the average value of \( a_0, a_{av} \) in the macroscopic aggregate is determined by the maximum condition of \( z(a) \) as a function of \( a \). The value of \( z \) at this maximum, \( z_{av} \), gives the activity of a particle in the macroscopic aggregate. The volume concentration \( \Phi^* \) of dispersed particles in equilibrium with this macroscopic aggregate is given by

\[
\Phi^* = \left( \frac{D}{D^*} \right) = \frac{M_2}{V} = x_a^{-1} \tag{12}
\]

Some examples of the results of numerical calculation are shown in Table I.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>Critical Volume Concentration of Suspended Particles at Macroscopic Aggregate at Various Values of Interaction Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D/a )</td>
<td>( U/a_0 )</td>
</tr>
<tr>
<td>50</td>
<td>2.10</td>
</tr>
<tr>
<td>50</td>
<td>2.91</td>
</tr>
<tr>
<td>50</td>
<td>4.31</td>
</tr>
</tbody>
</table>

In a solution containing suspended particles of volume concentration \( 10^{-2} \), when the value of \( U/a_0 \) is changed from \(-2.2 \to -3.2\), the state of particles is changed from complete dispersion to complete aggregation. When the volume concentration of macromolecules is \( 10^{-3} \), this change of \( U/a_0 \) corresponds to the increase of \( U/a_0 \), from about 3 to about 4.

In real solutions of charged macromolecules, such an increase of \( U/a_0 \) is easily brought about by increasing the activity coefficient of counter ions or by increasing the charge of macromolecules. Conversely, a decrease of charge, a decrease of activity coefficient of counter ions, or an increase of concentration of added salts can bring about the dispersion of aggregated particles.

From Table I and the results obtained in Section III, it is found that in solutions of macromolecules having a great asymmetry the macroscopic aggregation of suspended particles can actually take place and the state of particles is strongly affected by the charge of the shape of solute macromolecules. Chain macromolecules can change their shape with the change of composition of solvents. When they have charge, extended linear macromolecules in a solution without salts are contracted to a solid spherical shape by the addition of a small amount of salts.

With decreasing radius of suspended particles, the critical volume concentration of these particles at macroscopic aggregation is rapidly decreased.

The number of \( M_i \) of aggregates composed of \( i \) particles is calculated by

\[
M_i/M_i = 36a^4/kT/\beta^2 \tag{13.1}
\]

\[
M_i/S_i - 6H^4/(i - 1)/(i - 2) \quad 4 \leq i < 10 \tag{13.2}
\]

\[
H = (6a^4/\pi)^2 kT/\beta^2 \tag{13.3}
\]

where \( K \) is given in (10.2) and the interaction energy between two neighboring particles is assumed to be written in the form of (5). When the macroscopic aggregation occurs, \( H \) becomes larger than unity. When the volume concentration of suspended particles is \( 10^{-2} \), the value of \( K/\beta \)
and salts. By addition of low molecular salts, \( D^* \) is slowly decreased and \( f \) is more rapidly decreased; consequently, \( -U/kT \) is decreased.

V. Aggregation of Suspended Particles

When a large number of particles are suspended in the solution of macromolecules, they are attracted to each other through the negative potential \( U \) and some of them form aggregates. In ordinary solutions of non-charged rigid spherical macromolecules, however, the number of these aggregates is not very large. From (5), the ratio of the number of pairs of two particles \( M_2 \) to the number of dispersed particles \( M_1 \) is calculated by

\[
M_1/M_2 = 12\Phi(K/\beta) \tag{10.1}
\]

and

\[
K = \text{exp} \left\{ -\frac{a}{\Phi} \right\} \tag{10.2}
\]

where \( \Phi = -U/kT \) and \( \Phi = -(\Phi/kT) \) is the volume concentration of dispersed particles. Two particles at a distance less than \( a = D + \delta \) are regarded as a pair. In the numerical example of Section II, where \( U/kT = -0.25 \), \( M_1/M_2 \) becomes \((1/4)\Phi\). This ratio \( M_1/M_2 \) increases rapidly with increasing \( -U/kT \). Therefore, the numerical estimation in Sections III and IV suggests that in solutions of chain or disymmetrical macromolecules and especially in solutions of charged macromolecules, a large number of aggregates can be formed and even a macroscopic aggregation can occur.

We calculate the critical (volume) concentration \( \Phi^* \) of suspended particles where the macroscopic aggregation takes place. It is assumed that in the macroscopic phase of aggregation each particle has 12 neighboring particles and that the interaction energy between two neighboring particles can be given by (5), (6), or (9). When \( D = \delta \), the distances between particles in the macroscopic aggregate are large enough for macromolecules to enter and, as will be shown later, the average distance \( a_0(x_{a0}) \) between neighboring particles in the aggregate satisfies the condition \( 1 > 1 - x_{a0} > 0 \). Accordingly, we can use the above assumption for the interaction energy between particles in the aggregate.

At constant values of the average distance \( a \) between neighboring particles, we can obtain the partition function \( z \) per particle composing the aggregate by using a method similar to the free volume method in the theory of liquid-\( i \)\( a \)\( 4 \), namely, where \( z \) is given by

\[
z(a) = \int_{-\infty}^{\infty} \exp \left\{ -U(a)/kT \right\} 4\pi a^2 da \tag{11}
\]

Energy \( U(a) \) is the average potential energy of a particle surrounded by 12 neighboring particles when the position of the surrounding particle deviates from the center of the free volume by distance \( a \). When the concentration of macromolecules and other conditions of the medium are given, the average value of \( a_0 \), \( a_{00} \), in the macroscopic aggregate is determined by the maximum condition of \( z(a) \) as a function of \( a \). The value of \( z \) at this maximum, \( z_{\text{max}} \), gives the activity of a particle in the macroscopic aggregate. The volume concentration \( \Phi^* \) of dispersed particles in equilibrium with this macroscopic aggregate is given by

\[
\Phi^*/(k/kT) = M_1/M_2 = \frac{\Phi}{1 - x_{a0}} \tag{12}
\]

Some examples of the results of numerical calculation are shown in Table I.

<table>
<thead>
<tr>
<th>( M_1/M_2 )</th>
<th>( \Phi^*/(k/kT) )</th>
<th>( \Phi_{\text{calc}}/(k/kT) )</th>
<th>( \Phi_{\text{calc}}/(k/kT) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.10</td>
<td>2.9 \times 10^{-2}</td>
<td>0.004</td>
</tr>
<tr>
<td>50</td>
<td>2.01</td>
<td>3.9 \times 10^{-2}</td>
<td>0.010</td>
</tr>
<tr>
<td>50</td>
<td>4.21</td>
<td>4.8 \times 10^{-2}</td>
<td>0.044</td>
</tr>
</tbody>
</table>

In a solution containing suspended particles of volume concentration \( 10^{-2} \), when the value of \( U/kT \) is changed from \(-2.2\) to \(-3.2\), the state of particles is changed from complete dispersion to complete aggregation. When the volume concentration of macromolecules is \( 10^{-2} \), this change of \( U/kT \) corresponds to the increase of \( U/kT \) from \( 3 \) to \( 4 \). In real solutions of charged macromolecules, such an increase of \( U/kT \) is easily brought about by increasing the activity coefficient of counter ions by increasing the charge of macromolecules. Inversely, a decrease of charge, a decrease of activity coefficient of counter ions, or an increase of concentration of added salts can bring about the dispersion of aggregated particles.

From Table 1 and the result obtained in Section III, it is found that in solutions of macromolecules having a great disymmetry the macroscopic aggregation of suspended particles can actually take place and the state of particles is strongly affected by the change of shape of solute macromolecules. Chain macromolecules can change their shape with the change of composition of solvents. When they have charge, extended linear macromolecules in a solution without salts are contracted to an obdial spherical shape by the addition of a small amount of salts.

With decreasing radius of suspended particles, the critical volume concentration of these particles at macroscopic aggregation is rapidly decreased.

The number of \( M_1 \) of aggregates composed of \( i \) particles is calculated by

\[
M_1/M_0 = 36\Phi(K/\beta)^2 \tag{13.1}
\]

\[
M_1/M_0 = 6(i-1)(i-2) \tag{13.2}
\]

\[
H = (6\Phi^2/\Phi)\Phi(K/\beta)^2 \tag{13.3}
\]

where \( K \) is given in (10.2) and the interaction energy between two neighboring particles is assumed to be written in the form of (5). When the macroscopic aggregation occurs, \( H \) becomes larger than unity. When the volume concentration of suspended particles is \( 10^{-4} \), the value of \( (K/\beta) \)
at $H = 1$ is about 15. In this case, $M_1/M_2 = 0.02$ and $M_1/M_1 = 0.07$. This means that at macroscopic aggregation, the number of aggregates composed of $i$ particles takes a minimum at $i = 3$ as a function of $i$. Such a minimum is found in most cases of the condensation phenomena.

VI. Discussion

We have assumed that there is no direct interaction between particles and solute macromolecules, and that the particles themselves have no electric charge. In reality, we have no such ideal example, but we have examples in which suspended particles are aggregated by addition of macromolecules. Chain macromolecules are more effective than rigid macromolecules. Aggregation of red blood cells can be brought about non-specifically by adding to the suspension chain macromolecules or highly disymmetrical macromolecules. According to experimental results, many electrolytic and non-electrolytic macromolecules have the ability to make aggregates of blood cells. The high molecular weight and the disymmetrical shape of molecules were found to be most important factors. As the degree of polymerization of chain macromolecules increases, the aggregation effect becomes stronger. Monomer or polymer of a low polymerization degree cannot bring about the aggregation. Most of the rigid spherical macromolecules, for instance, globular protein molecules, have no ability to make aggregates of the cells. Even when they have the ability to aggregate, a very high concentration of macromolecules is necessary for the occurrence of aggregation. As another example, it is well known that aggregates of rubber latex particles can be formed by adding various chain macromolecules, including fibrous proteins and linear polyethylene molecules. Soil particles can also be aggregated by chain macromolecules. Rigid spherical macromolecules cannot form aggregates of these particles. In most of these non-specific aggregation phenomena, there are found only few macromolecules adsorbed on particles and therefore, in current opinion, the aggregation has been considered to be caused by the adsorbed particles by hydrophilic macromolecules. Such explanation, however, cannot satisfy us because the dehydrated effect is ambiguous. We want to emphasize that the qualitative features of these phenomena can be reasonably explained by our theory. The osmotic force derived in this paper probably takes an important role in these phenomena.

Of course, the interaction between suspended particles and solute macromolecules cannot always be disregarded. In some cases, macromolecules are remarkably adsorbed on particles and form bridges between them. As a result, a gel-like aggregation can occur. We can easily develop a general theory based on eq. (1) of the force between particles mediated by solute molecules and investigate the effect of energetic interaction between particles and solute molecules. Discussions on this kind of force were made by Tenak and others. We describe here some results of our calculation. When the interaction energy $u$ between particles and solute molecules is positive, namely when the interaction is repulsive, the interaction energy $U$ between particles is always negative and an attraction appears.

References

(3) B. Tenak, Divalent Ions, Soc. Pol., 25, 60 (1950).
(4) B. Tenak et al., ibid., 194.

Synopsis

An attractive force appears between particles suspended in solutions of macromolecules when there is neither direct interaction between particles nor energetic interaction between particles and solute macromolecules. The magnitude of this force is of
INTERACTION BETWEEN PARTICLES

at $H = 1$ is about 15. In this case, $M_1/M_2 = 0.02$ and $M_4/M_3 = 0.07$. This means that at macroscopic aggregation, the number of aggregates composed of 3 particles takes a minimum at $i = 3$ as a function of $t$. Such a minimum is found in most cases of the condensation phenomena.

VI. Discussion

We have assumed that there is no direct interaction between particles and solute molecules, and that the particles themselves have no electric charge. In reality, we have no such ideal example, but we have examples in which suspended particles are aggregated by addition of macromolecules. Chain macromolecules are more effective than rigid macromolecules. Aggregation of red blood cells can be brought about nonspecifically by adding to the suspension chain macromolecules or highly disymmetrical macromolecules.\(^\text{10-11}\) According to experimental results,\(^\text{12}\) many electrolytic and nonelectrolytic macromolecules have the ability to make aggregates of blood cells. The high molecular weight and the disymmetrical shape of molecules were found to be most important factors.\(^\text{13}\) As the degree of polymerization of chain macromolecules increases, the aggregation effect becomes stronger. Monomer or polymer of a low polymerization degree cannot bring about the aggregation. Most of the rigid spherical macromolecules, for instance, globular protein molecules, have no ability to make aggregates of the cells. Even when they have the ability to aggregate, a very high concentration of macromolecules is necessary for the occurrence of aggregation. As another example, it is well known that aggregates of rubber latex particles can be formed by adding various chain macromolecules, including fibrous proteins and linear polyacrylamide molecules.\(^\text{14-15}\) Soil particles can also be aggregated by chain macromolecules.\(^\text{16}\) Rigid spherical macromolecules cannot form aggregates of these particles. In most of these nonspecific aggregation phenomena, there are found only few macromolecules adsorbed on particles and therefore, in current, the aggregation has been considered to be caused by the dehydration of particles by hydrophilic macromolecules. Such explanation, however, cannot satisfy us because the dehydration is an ambiguous concept. We want to emphasize that the qualitative features of these phenomena can be reasonably explained by our theory. The osmotic force derived in this paper probably takes an important role in these phenomena.

Of course, the interaction between suspended particles and solute macromolecules cannot always be disregarded.\(^\text{16-17}\) In some cases, macromolecules are markedly adsorbed on particles and form bridges between them. As a result, a gel-like aggregation can occur. We can easily develop a general theory based on eq. (1), of the force between particles mediated by solute molecules and investigate the effect of energetic interaction between particles and solute molecules. Discussions on this kind of force were made by Tenak and others.\(^\text{4}\) We describe here some results of our calculation. When the interaction energy $Q$ between particles and solute molecules is positive, namely when the interaction is repulsive, the interaction energy $U$ between particles is always negative and an attraction appears. When $U$ is negative, $U$ as a function of distance $a$ depends on the magnitude and range of $u$ in a complex way. When two particles approach each other very closely, adsorbed molecules must be detached from the surface of particles and therefore, a repulsion usually appears between particles. If, however, molecules sandwiched between two approaching particles can interact with both particles and, for example, have negative energy $2u$, then an attraction can appear between particles and $U$ is negative when $a$ is not too small for molecules to enter the narrow region between particles. This attraction which is caused by bridging molecules becomes stronger with increasing concentration of solute molecules and takes a maximum value at the concentration where the surface of independent particles is not yet saturated by dissolved molecules and the region between two approaching particles is saturated by them. At higher concentrations, where the surface of independent particles is also saturated, this attraction is weakened. Under suitable conditions in the medium, $U$ as a function of $a$ can have two minimum points. One is caused by the bridging effect of solute molecules and the other taken at $a = D$ is caused by the osmotic effect. Between these two minimum there is a maximum caused by the detachment of adsorbed molecules. The details of this calculation will be reported elsewhere.

References

(2) Despagni and Landolt, Acta Physiochimica, 14, 633 (1941).
(4) B. Tenak et al., ibid., 194.

Synopsis

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A Study of Graft Copolymers. II. Viscosity and Light-Scattering Measurements

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INTRODUCTION

In the first paper of this series, the preparation and dilute solution viscosity properties of some graft polymers are described. These polymers were prepared by the redox polymerization of styrene in the presence of oxidized polystyrene or of oxidized copolymers of styrene and 4-vinylcyclohexene-1. Evidence that branching had occurred was obtained from measurements of monomer disappearance, of the decrease in hydroperoxide content of the backbone polymer during reaction, and of the infrared absorption by the polymer before and after the grafting procedure. It was then concluded that branched molecules consisting of several long linear branches attached at intervals along a backbone chain had been prepared.

Although the backbone polymer contained an average of up to 12 hydroperoxide groups, each being a potential site for the growth of a branch, values of Huggins' k' for the graft polymers were no higher than for linear polymers. Since there is considerable evidence that Huggins' k' is sensitive to small degrees of nonlinearity (in polymers branched by crosslinking or by chain transfer), it seemed desirable to obtain, from viscosity and light-scattering measurements, more direct and more quantitative information about the branching believed to be present in the graft polymers. An investigation of this nature seemed even more desirable because of the scarcity of viscosity and light-scattering information about well-characterized branched polymers. A few such studies of crosslinked or randomly branched polymers have been reported, but there has been no complete study of the effect of simple linear branches on viscosity and light-scattering properties. Although Jones and others have published light-scattering data for some graft polymers prepared by another method, they have not correlated these data with intrinsic viscosities.

In this paper, measurements of intrinsic viscosity and molecular weight, of molecular size, and of the second virial coefficient are reported which