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Steric stabilization II

A generalization of Fischer's solvency theory

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With 6 figures and 2 tables

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Introduction

In the preceding paper (1) we showed that with the exception of *Fischer's* germinal solvency theory (2), the qualitative predictions of the theories of steric stabilization advanced to-date (3-5) appear to be at odds with the results of experiments. It seems reasonable to infer that the quantitative predictions of such theories may also disagree with experiment.

We also noted that *Fischer's* germinal solvency theory is not without its quantitative limitations; it calculates the repulsive potential energy primarily from the interpenetration process without much regard for compression; it uses a mean segment density step function rather than the more exact segment density distribution function; and it ignores all virial coefficients higher than the second. We now show, using a lattice approach, how *Fischer's* theory may be extended to allow for both compression and a more exact segment density distribution function.

This approach differs from those proposed previously (4, 5) in that it does not consider the compression of the polymer chain in terms of a random flight chain, composed of non-interacting segments. The latter model regards θ -solvents as being equivalent to athermal solvents. However, θ -solvents are not athermal but somewhat poor solvents; only at the experimentally inaccessible temperature $\theta = 0^\circ\text{K}$ may θ -solvents be taken as athermal (6).

The basic dissolution equation for attached polymer chains

We will develop a theory of steric stabilization through the basic dissolution equations for attached polymer chains. This is derived from the *Flory-Krigbaum* theory (7) for the mixing of randomly oriented polymer chains, whose centres of gravity are fixed in space, with pure solvent. This will show explicitly how conformational changes of the polymer are allowed for in this approach.

Consider a volume element δV located completely within a dissolved macromolecule. We will assume that this volume element resulted from the telescoping of two volume elements, each of size δV , that were separately situated in the pure solvent and in the pure, disoriented polymer respectively. The *Gibbs* free energy change for mixing in the volume element may be written:

$$\delta(\Delta G) = \delta(\Delta G_M^*) + \delta(\Delta G_{SP}) \quad [1]$$

where ΔG_M^* = free energy of mixing calculated solely from external considerations of mixing segments and solvent and ΔG_{SP} = free energy changes due to all other interactions, including specific interactions between near neighbours. The *Flory-Krigbaum* theory yields, on the respective evaluation of each term, that

$$\delta(\Delta G) = kT \{\ln(1 - v_2) + \chi_1 v_2\} \delta n_1 \quad [2]$$

where the subscripts 1 and 2 refer to the solvent and polymer respectively, v = volume fraction, χ_1 = interaction parameter ($\chi_1 =$

$1/2 + \chi_1 - \psi_1$) and n_1 = the number of solvent molecules in δV . But

$$\delta n_1 = \frac{(1 - \varrho_2 V_s)}{V_1} \delta V \quad [3]$$

where V_1 = volume of a solvent molecule, V_s = volume of a segment and ϱ_2 = number of polymer segments per unit volume. Substitution of relation [3] into eq. [2] yields on expansion of the logarithmic terms:

$$\begin{aligned} \delta(\Delta G) = kT \frac{V_s^2}{V_1} \left(\frac{1}{2} - \chi_1 \right) \varrho_2^2 \delta V - kT \frac{V_s}{V_1} \left(\frac{1}{2} - \chi_1 \right) \\ \times \varrho_2 \delta V - \frac{1}{2} kT \frac{V_s}{V_1} \varrho_2 \delta V \end{aligned} \quad [4]$$

where powers higher than the second are neglected.

Eq. [4] is the basic dissolution equation for polymer chains attached to particles. We now formulate a term-by-term interpretation of this relation.

First consider the dissolution of randomly oriented polymer segments into a θ -solvent in a volume element δV . The *Flory-Krigbaum* relationship yields

$$\delta(\Delta G_\theta) = kT \{ \ln(1 - v_2) + v_2 \chi_1^\theta \} \delta n_1.$$

Since $\chi_1^\theta = 1/2$, we have for small $v_2 (= \varrho_2 V_s)$

$$\delta(\Delta G_\theta) = - \frac{1}{2} kT \frac{V_s}{V_1} \varrho_2 \delta V. \quad [5]$$

This is the third term in the basic dissolution equation. We note that it is negative so that attached polymer molecules dissolve spontaneously in a θ -solvent.

Next at constant T , we increase the quality of the solvent from a θ -solvent to some value of $\chi_1 < 1/2$, whilst retaining the random coil θ -solvent conformation. Clearly for this process $\delta(\Delta G_M^*) = 0$ and from the *Flory-Krigbaum* theory we have

$$\delta(\Delta \Delta G_{\chi_1}) = kT \left\{ \chi_1 v_2 - \frac{1}{2} v_2 \right\} \delta n_1$$

which for small v_2 gives

$$\delta(\Delta \Delta G_{\chi_1}) = - kT \frac{V_s}{V_1} \left(\frac{1}{2} - \chi_1 \right) \varrho_2 \delta V. \quad [6]$$

This is the second term in the basic dissolution equation. Note that it too is negative as would be expected.

The remaining term

$$+ kT \frac{V_s^2}{V_1} \left(\frac{1}{2} - \chi_1 \right) \varrho_2^2 \delta V$$

is associated with the conformational change of the polymer that occurs in a solvent better than a θ -solvent. It includes both enthalpy

and entropy changes associated with this conformational change and allows for the presence of the solvent. The positive sign denotes that the loss of configurational entropy due to the adoption of a less random conformation outweighs the favourable, but here truncated, enthalpy changes that usually accompany this process. This term would be expected intuitively to vary as the square of the segment density because it corresponds to intramolecular interpenetration (or the reverse) [8]. Note that the sum of the first two terms in eq. [4] is negative as must be the case in going from a θ -solvent to a good solvent.

It is this first term in the basic dissolution equation that formally allows for changes in the conformation of the attached polymer chains such as those caused by compression. In this case the conformational change is induced by a solvency change but suitable thermodynamic cycles may easily be devised so that this term properly allows for *all* conformational changes, wherever their origin (e.g., attachment to an interface, compression, etc.).

We can therefore write the basic dissolution equations

$$\delta(\Delta G) = \delta(\Delta G_\theta) + \delta(\Delta G_{\chi_1}) + \delta(\Delta G_{\text{conf}}) \quad [7]$$

where $\delta(\Delta G_{\text{conf}})$ = free energy change due to conformational changes. It is this latter term that renders the volume restriction term used by *Meier* (4) superfluous.

Calculation of steric repulsion

Flat plates

The basic dissolution equation applies to polymer chains attached to colloidal particles because the centres of gravity of the macromolecules are incapable of independent motion. We will assume that there are ν monodisperse chains attached to unit area of the flat plates, each chain being composed of i segments. The chains are irreversibly attached to the plates; we need not include the free energy of attachment (ΔG_{att}) in the following discussion because the term cancels if it is assumed that ΔG_{att} is independent of the distance of separation of the plates. We assume a constant segment density parallel to the surface (i.e., high and complete surface coverages) and a continuous segment distribution normal to the interface.

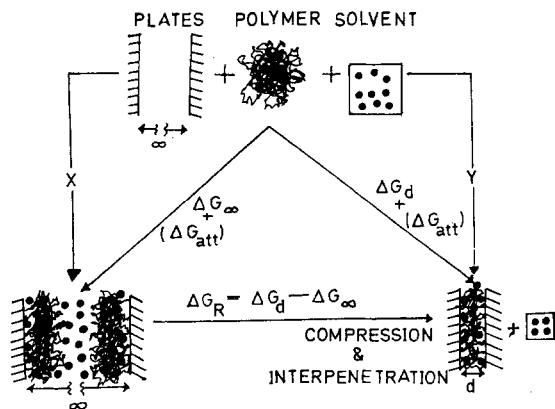


Fig. 1. Schematic representation of the close approach of two sterically stabilized plates

For step X envisaged in fig. 1 we may write on integration of eq. [4] that for one plate

$$\Delta G_{\infty} = kT \frac{V_s^2}{V_1} (1/2 - \chi_1) \int_{x=0}^{\infty} \varrho^2 dV - kT \times \frac{V_s}{V_1} (1/2 - \chi_1) \int_{x=0}^{\infty} \varrho_{\infty} dV - kT \frac{V_s}{2V_1} \int_{x=0}^{\infty} \varrho_{\infty} dV$$

where ϱ_{∞} = segment density distribution function at infinite separation of the plates. Since ϱ_{∞} is a function only of x ,

$$dV = A dx = dx$$

if we consider unit surface area. Denoting the normalized distribution function by $\hat{\varrho}_{\infty}$ we have

$$\int_{x=0}^{\infty} \hat{\varrho}_{\infty} dV = \int_{x=0}^{\infty} \hat{\varrho}_{\infty} dx = \nu i$$

where νi = total number of segments in the volume normal to unit surface area. Accordingly,

$$\Delta G_{\infty} = kT \frac{V_s^2}{V_1} \left(\frac{1}{2} - \chi_1 \right) \nu^2 i^2 \int_0^{\infty} \hat{\varrho}_{\infty}^2 dx - kT \times \frac{V_s}{V_1} \left(\frac{1}{2} - \chi_1 \right) \nu i - kT \frac{V_s}{2V_1} \nu i. \quad [8]$$

We can perform an analogous dissolution to describe step Y in fig. 1 and so find ΔG_d for the dissolution of polymer when the separation is d :

$$\Delta G_d = kT \frac{V_s^2}{V_1} \left(\frac{1}{2} - \chi_1 \right) \nu^2 i^2 \int_0^d \hat{\varrho}_d^2 dx - kT \times \frac{V_s}{V_1} \left(\frac{1}{2} - \chi_1 \right) \nu i - \frac{kT V_s}{2V_1} \nu i \quad [9]$$

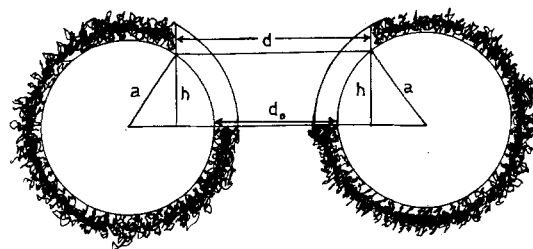


Fig. 2. The Deryagin method for calculating the repulsive potential for two equal spheres from that of flat plates (Not to scale)

where $\hat{\varrho}_d$ = normalized segment density distribution function when the separation is d such that $\int_0^d \hat{\varrho}_d dx = \nu i$.

The Gibbs free energy of compression per unit area (ΔG_C) for two plates is obtained by subtracting eq. [8] from eq. [9] and multiplying by two to allow for the interaction of two plates:

$$\Delta G_C = \Delta G_d - \Delta G_{\infty} = 2kT \frac{V_s^2}{V_1} \left(\frac{1}{2} - \chi_1 \right) \nu^2 i^2 \times \left[\int_0^d \hat{\varrho}_d^2 dx - \int_0^{\infty} \hat{\varrho}_{\infty}^2 dx \right] \quad [10]$$

This is the free energy change resulting from the compression of the stabilizing moieties.

Eq. [10] makes no allowance for the interpenetration of the polymer chains attached to the two surfaces that occurs when $d < 2L$. The form of the free energy of interpenetration per unit area (ΔG_I) must be similar to that derived by Flory and Krigbaum (7) for the interpenetration of two chains in free solution:

$$\Delta G_I = 2kT \frac{V_s^2}{V_1} \left(\frac{1}{2} - \chi_1 \right) \nu^2 i^2 \int_0^d \hat{\varrho}_d \hat{\varrho}'_d dx \quad [11]$$

where $\hat{\varrho}'_d$ is the mirror image of $\hat{\varrho}_d$ obtained by reflection and translation of the coordinate axis. The total free energy change per unit surface area on close approach is thus given by

$$\Delta G_R = \Delta G_C + \Delta G_I = 2kT \frac{V_s^2}{V_1} \left(\frac{1}{2} - \chi_1 \right) \nu^2 i^2 \times \left[\int_0^d \hat{\varrho}_d^2 dx + \int_0^d \hat{\varrho}_d \hat{\varrho}'_d dx - \int_0^{\infty} \hat{\varrho}_{\infty}^2 dx \right] \quad [12]$$

This relation has been given previously (9, 10) without proof. The right hand side of eq. [12] was in fact first calculated by *Meier* (4) but regarded by him as excluding conformational changes of the polymer. The foregoing discussion shows that conformational changes are included.

Hesselink, *Vrij* and *Overbeek* (5) have tabulated the sum of the integral terms in eq. [12] for loops and tails as a dimensionless function that we denote by R [their $M(\bar{i}, d)$]:

$$R = \langle r^2 \rangle^{1/2} \left[\int_0^d \hat{q} a^2 dx + \int_0^d \hat{q} a \hat{q} a' dx - \int_0^d \hat{q}^2_{\infty} dx \right]$$

where $\langle r^2 \rangle^{1/2} =$ r. m. s. end-to-end length of the chains in *free* solution. We may therefore write

$$\Delta G_R = \frac{2kTV_s^2}{\langle r^2 \rangle^{1/2} V_1} \left(\frac{1}{2} - \chi_1 \right) \nu^2 i^2 R. \quad [13]$$

Eq. [13] is the fundamental relationship for evaluating the repulsive *Gibbs* free energy in the steric stabilization of flat plates. Because it contains the lattice parameters V_s and V_1 , eq. [13] is not the most convenient form for calculating ΔG_R . We can, e.g., substitute into eq. [13] the approximate *Flory* relationship for the expansion factor α

$$\alpha^5 - \alpha^3 = 2C_M \psi_1 (1 - \theta/T) M^{1/2}$$

where $\psi_1 =$ entropy of dilution parameter and $\theta = (\kappa_1/\psi_1)T$, where $\kappa_1 =$ enthalpy of dilution parameter. This yields the more tractable form:

$$\Delta G_R \sim \frac{2(2\pi)^{3/2}}{27} \langle r^2 \rangle \nu^2 (\alpha^2 - 1) R kT. \quad [14]$$

The value of ν is best determined experimentally from adsorption studies. Alternatively a crude estimate of ν may be obtained in the following way. It has been shown theoretically (11) that the mean extension of tails or loops from an impenetrable interface is ca. double their extension in the absence of that interface. *Tanford* (12) has suggested that in a good solvent the thermodynamic volume of a hard-core sphere equivalent to a free polymer is $0.18 \langle r^2 \rangle^{3/2}$. If we assume that this equivalent volume remains unchanged on attachment to the interface, the effective area per molecule becomes $0.25 \langle r^2 \rangle$. Therefore $\nu \sim 4/\langle r^2 \rangle$. Substitution of this value into eq. [14] leads on simplification to:

$$\Delta G_R \sim \frac{32(2\pi)^{3/2}}{27} \frac{(\alpha^2 - 1)}{\langle r^2 \rangle} R kT. \quad [15]$$

The total interaction free energy (V_T) for two flat plates is obtained by summing the steric repulsion and the *London-van der Waals* attraction (13).

$$V_T = \frac{2kTV_s^2}{\langle r^2 \rangle^{1/2} V_1} (1/2 - \chi_1) \nu^2 i^2 R - \frac{A^*}{12\pi \langle r^2 \rangle \delta^2} \quad [16]$$

where $A^* =$ net *Hamaker* constant and $\delta = d/\langle r^2 \rangle^{1/2}$.

Spheres

Model dispersions of sterically stabilized colloidal particles are usually composed of monodisperse spheres. It has not yet proved possible in general to solve the case of two sterically stabilized spheres of equal radius, a . We can, however, exploit the *Deryagin* approximation (14) to calculate the repulsive potential for spheres from that developed for flat plates, provided only that the thickness of the stabilizing layer is considerably less than the radius of the particles. This situation is commonly encountered in practice. The *Deryagin* method calculates the repulsive potential for spheres by summing the contributions of infinitesimally thick planar rings parallel to each other at a distance d (fig. 2). The repulsive potential per pair of spheres (ΔG_R^S) is given by

$$\Delta G_R^S = \int_0^{\infty} 2\pi h (\Delta G_R^{FP}) dh \quad [17]$$

where $\Delta G_R^{FP} =$ *Gibbs* free energy of repulsion per unit area for flat plates and $h =$ radius of the ring.

(i) Equal spheres

Simple geometric considerations of fig. 2 give that

$$(d - d_0)/2 = a - (a^2 - h^2)^{1/2}$$

where $d_0 =$ minimum distance of surface separation for the two spheres of equal radii. Therefore

$$2hdh = a(1 - (h^2/a^2))^{1/2} dd \sim add$$

since $h \ll a$ in the *Deryagin* approximation. Accordingly

$$\begin{aligned} \Delta G_{R(a,a)}^S &= \pi a \int_{d_0}^{\infty} (\Delta G_R^{FP}) dd \\ &= 2\pi a \frac{V_s^2}{V_1} (1/2 - \chi_1) \nu^2 i^2 S kT \quad [18] \end{aligned}$$

where $S = \int_{d_0}^{\infty} R d\delta$ and $\delta_0 = d_0/\langle r^2 \rangle^{1/2}$. Alter-

natively using eq. [15] we may write

$$\Delta G_R^S(a, a) = \frac{(2\pi)^{5/2}}{27} \langle r^2 \rangle^{3/2} \nu^2 (\alpha^2 - 1) a S k T \quad [19]$$

and if, as discussed above, we set $\nu = 4/\langle r^2 \rangle$ the repulsive free energy becomes

$$\Delta G_R^S(a, a) \sim \frac{16(2\pi)^{5/2}}{27} \frac{(\alpha^2 - 1)}{\langle r^2 \rangle^{1/2}} a S k T \quad [20]$$

The total free energy of interaction per pair of particles (V_T) is obtained by summing the steric repulsion and the London-van der Waals attraction [previously calculated by Hamaker (13)]:

$$V_T = \frac{(2\pi)^{5/2}}{27} \langle r^2 \rangle^{3/2} \nu^2 (\alpha^2 - 1) a S k T - \frac{A^* a}{12 \langle r^2 \rangle^{1/2} \delta_0} \quad [21]$$

Table 1. Values of the parameter S for tails (T) and loops (L) at different separations (δ_0) of the spheres

δ_0	S_T	δ_0	S_L
0.4	2.666	0.6	0.720
0.6	1.680	0.7	0.500
0.8	1.070	0.8	0.338
1.0	0.678	0.9	0.219
1.2	0.416	1.0	0.135
1.4	0.249	1.1	0.080
1.6	0.141	1.2	0.044
1.8	0.075	1.3	0.022
2.0	0.038	1.4	0.011
2.2	0.018	1.5	0.005
2.4	0.007	1.6	0.002

Values of S estimated graphically for various values of the distance parameter δ_0 are shown in table 1 for tails (T) and loops (L). The prerequisite functions for flat plates were taken from Hesselink, Vrij and Overbeek (5) and were interpolated before integration.

(ii) Unequal spheres

Consider two spheres of unequal radii a and b (fig. 3). The repulsion potential is again given by eq. [20]. We have from fig. 3

$$d - d_0 = (a + b) - (b^2 - h^2)^{1/2} - (a^2 - h^2)^{1/2}$$

so that

$$h dh = \frac{ab dd}{a \left(1 - \frac{h^2}{b^2}\right)^{-1/2} + b \left(1 - \frac{h^2}{a^2}\right)^{-1/2}} \sim \frac{ab}{a + b} dd$$

since $h \ll a, b$. Therefore the repulsion potential per pair of particles is

$$\Delta G_R(a, b) = \frac{2\pi ab}{(a + b)} \int_{d_0}^{\infty} (\Delta G_R^{FP}) dd = \frac{2b}{a + b} \Delta G_R^S(a, a)$$

where $\Delta G_R^S(a, a)$ = steric repulsion per pair of monodisperse spheres of radius a calculated using eq. [18] or [19].

The total potential energy is thus (13)

$$V_T = \frac{2b}{a + b} \Delta G_R^S(a, a) - \frac{A^* ab}{6(a + b) \langle r^2 \rangle^{1/2} \delta_0} \quad [23]$$

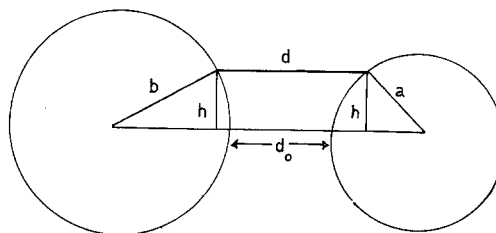


Fig. 3. The Deryagin method applied to unequal spheres

(iii) Flat plates and spheres

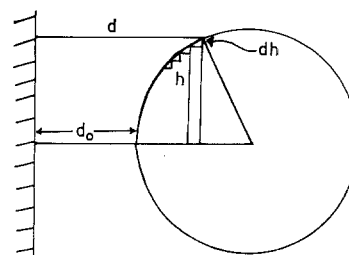


Fig. 4. The Deryagin method applied to sphere/plate interaction

For the case of a sphere interacting with a flat plate, which is another commonly encountered geometry in colloid studies, we have from fig. 4

$$d - d_0 = a - (a^2 - h^2)^{1/2}.$$

Thus

$$h dh = (1 - h^2/a^2)^{1/2} add \sim add.$$

Therefore the repulsive potential for a single sphere interacting with a flat plate is given by

$$\Delta G_R^{SP} = 2\pi a \int_{d_0}^{\infty} (\Delta G_R^{FP}) dd = 2\Delta G_R^S(a, a). \quad [24]$$

Relation [24] can also be derived from eq. [22] by letting b tend to infinity:

$$\Delta G_R^{SP} = \Delta G_R^S(a, \infty) = \lim_{b \rightarrow \infty} (2/(1 + a/b)) [\Delta G_R^S(a, a)] = 2\Delta G_R^S(a, a).$$

The total potential energy in this case is thus [13]

$$V_T = 2\Delta G_R^S(a, a) - \frac{A^*a}{6\pi\langle r^2 \rangle^{1/2}\delta_0} \quad [25]$$

Table 2 summarizes the results for the steric repulsive potential energy for the three geometrical situations frequently encountered in colloid studies.

Table 2. The relationship between the repulsive potentials for different geometries in the *Deryagin* approximation

System	Repulsion energy
Equal spheres (radii a)	$\Delta G_R^S(a, a)$
Unequal spheres (radii a, b)	$(2b/[a + b])\Delta G_R^S(a, a)$
Flat plate/sphere (radius a)	$2\Delta G_R^S(a, a)$

Comparison of the theory for spheres with experiment

Eq. [21] can be used to calculate the total potential energy curves for two sterically stabilized spherical particles. These are displayed in fig. 5 for two equal poly(vinyl acetate) particles in an aqueous latex sterically stabilized by PEO loops of $M = 96,000$ [corresponding (10) to Polyox WSRN80]. For convenience we have in fact used eq. [20] to calculate the repulsive potential. The effective *Hamaker* constant was taken as $A^* = 3 \times 10^{-21} J$ but as shown later, the exact value of A^* chosen has little influence in general on the curves if $\alpha > 1.000$. The radius of each particle was taken as 10^3 \AA .

We will assume that flocculation is observed if the net attractive potential exceeds $2.5 kT$. Precisely what value is chosen here for the potential energy of attraction will not influence the following discussion provided it is somewhat greater than thermal energy.

It becomes apparent from consideration of eq. [21] and fig. 5 that the steric repulsion usually increases faster than does the *van der Waals* attraction at all distances of separation. The upshot of this is that the potential energy curves for sterically stabilized particles do not usually exhibit the maximum that is so characteristic of electrostatically stabilized dispersions. We have carried out many different calculations apart from those presented and always found this to be true. The absence of this maximum explains why flocculated sterically stabilized dispersions, or stable lattices that have been compacted by centrifugation, redisperse spontaneously

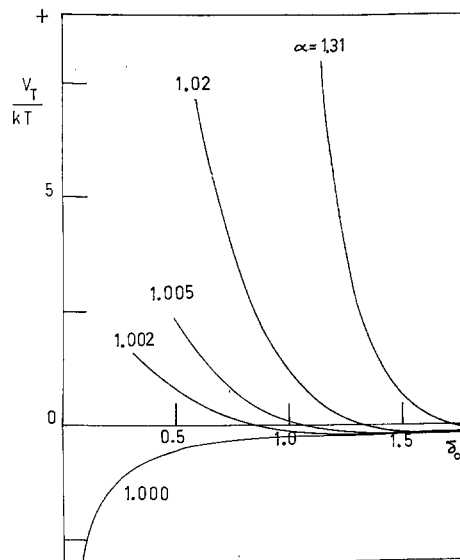


Fig. 5. The total potential energy curves for two spherical poly(vinyl acetate) particles stabilized by poly(ethylene oxide) loops of molecular weight 9.6×10^4 . The radii of the particles is 10^3 \AA , the effective *Hamaker* constant is $3 \times 10^{-21} J$ and $T = 303 \text{ }^\circ K$.

under suitable solvency conditions (9, 10). There is in all instances where $\alpha > 1.000$ a very shallow minimum at the larger distances of separation. This is analogous to the secondary minimum in electrostatic stabilization but it is too shallow for flocculation to be observed in it in the large number of different cases for which we have made calculations.

The curves also show that stable dispersions would be expected if $\alpha = 1.002$ but that instability would be evident if $\alpha = 1.000$. A sharp transition from stability to instability is thus predicted, as is observed experimentally (9, 10). These two values of α correspond, according to the *Flory* equation for α , to a temperature difference of less than $1 \text{ }^\circ K$. Thus as $\alpha = 1.000$ corresponds to the θ -point, we see that the theory predicts the presence of a sharp transition from stability to instability very close to the θ -point. The strong correlation between the θ -point and the c.f.p. observed experimentally has already been described. Obviously the theory also predicts the observed insensitivity of the c.f.p. to the molecular weight of stabilizing moieties, since the θ -point is independent of molecular weight. Finally inspection of eq. [21] shows that as both the attraction and the repulsion increase linearly with a , the above conclusions will be almost independent of the particle radius a , since the

point at which $V_T \sim 0$ is independent of the radius; again experiments support this conclusion. All of the parameters for which we have chosen specific values in the above discussion can be varied over wide ranges without altering the general conclusions presented herein.

We conclude that the theory of steric stabilization outlined above is in agreement with all the qualitative features of steric stabilization that have been observed to date. It is essentially an extension of *Fischer's* solvency theory; it treats compression as an intramolecular interpenetration process characterized by the same enthalpy and entropy of dilution parameters as intermolecular interpenetration (8). This explains why the predictions of *Fischer's* germinal theory are in qualitative accord with experiments.

An alternative explanation of flocculation

An alternative way of viewing sterically stabilized latex particles is to regard them as polymer molecules of (almost) infinite molecular weight. Attachment of the soluble stabilizing chains to the particles removes their ability to move separately in the solvent and hence removes their ideal contributions to the thermodynamic properties of the solution. Their non-ideal contributions, however, remain intact. The ideal contributions of the particles may be safely neglected. It is as if the sterically stabilized particles were graft homopolymers with a backbone polymer of almost infinite molecular weight but with soluble lower molecular weight side chains.

The θ -point has long been recognized as the critical miscibility limit of homopolymers of infinite molecular weight. Thus sterically stabilized particles would be expected to phase separate (i.e., flocculate) at the θ -point. This is, of course, what is observed experimentally (9, 10). It raises the question of the solubility of attached stabilizing moieties at or near the θ -point. We will explore this question elsewhere. However, we have shown above that attached polymer chains are soluble in θ -solvents.

Flory (15) has suggested that the experimental results obtained with sterically stabilized dispersions may well imply that the *London-van der Waals* attraction between the core particles is relatively unimportant in determining flocculation of latices. Fig. 6 presents some typical potential energy curves

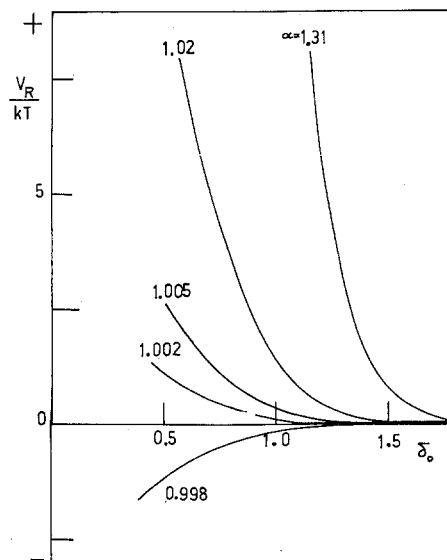


Fig. 6. The potential energy curves for two sterically stabilized particles if the *London-van der Waals* attraction is neglected. All parameters are as for fig. 6

for sterically stabilized dispersions if the *London-van der Waals* attraction between the core particles is ignored completely. Other conditions are as shown for fig. 5 and a comparison of the curves in figs. 5 and 6 shows that if $\alpha > 1.000$, neglect of the attraction between the core particles scarcely changes the overall repulsive potential. Moreover if $\alpha < 1.000$, the attraction between the sheaths must become relatively large as δ_0 tends to zero. It is obvious that flocculation would be observed if, e.g., $\alpha = 0.998$, i.e., within 1 °K of the θ -point. Hence flocculation would still be observed near to the θ -point even if we ignore the *van der Waals* attraction between the core particles. Flocculation would also be independent of the particle radius since the θ -point is independent of the partial radius. Currently the accuracy of the experiments fails to distinguish between flocculation induced by *van der Waals* attraction between the core particles and that induced by attraction between the stabilizing sheaths. We would expect that sheaths of very high molecular weight polymer (e.g., $M \sim 1 \times 10^6$) would prevent the core particles from exhibiting significant attraction except at extremely high compressions. (This effect is apparent even in fig. 5.) Yet latices stabilized by PEO of $M = 1 \times 10^6$ flocculate very close to the θ -point (14). We therefore strongly favour *Flory's* notion that flocculation of latices is induced as a result of the

attraction between the stabilizing sheaths, which in turn derives from the solvency of the dispersion medium being made marginally worse than a θ -solvent. Whether this conclusion will hold for metal sols, e.g., where the core attraction may be an order of magnitude larger, remains to be established experimentally.

We note also that *Doroszkowski* and *Lambourne* (16) have arrived at a similar conclusion from their studies of steric stabilization. There exists at least the theoretical possibility of preparing stable lattices in θ -solvents because the fourth and higher virial coefficients fail to vanish in θ -solvents. Only the second and third coefficients are effectively zero. Interpenetration and compression of the polymer chains to high segment densities will permit these higher virial coefficient repulsions to become operative. This is not allowed for in the above theories or any theories developed to-date. All models probably break down under these conditions. In addition the *Born* repulsion between the segments is not included yet it too becomes operative at high segment densities. Note also that the traditional estimate of the *van der Waals* attraction may have to be adjusted in light of the more exact theories being developed by *Ninham* and *Parsegian* (17, 18). Finally the values for ψ_1 and κ_1 to be used in the above theory are those derived from experiment.

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Summary

A theory of steric stabilization is developed that is essentially an extension of *Fischer's* solvency theory.

It treats both interpenetration and compression using a lattice approach. This permits the introduction of segment density distribution functions. One virtue of the new theory is that it is in good qualitative agreement with the results of experiment. Some limitations of the theory are also noted.

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