for the oxidation of unsaturated hydrocarbons.[12] Trace amounts of some transition metal ions, which strongly catalyze hydroperoxide decompositions,[11] might also produce the observed result.

There appears to be an unexpected, and possibly spurious, effect of polymer concentration on the efficiency of chain cleavage. Oxidations at 1.08 and 2.5 M in polymer gave nearly identical chain cleavage efficiencies while doubling the polymer concentration again to 5.0 M (experiment 9) reduced the cleavage efficiency by one-third.

It should be kept in mind that the amount of cleavage reported in Table I is actually net cleavage; that is, the figure is total cleavage minus the amount of cross-linking effected by the oxidation. The lower scission efficiency at 5.0 M polymer concentration would be consistent with the proposal of enhanced cross-linking. However, there is no reason to suspect that a cross-linking reaction plays a major role under the reaction conditions used here. In oxidations of neat amorphous polypropylene at 22 °C, Decker and Mayo[3] assigned all of the cross-linking reaction to the geminate radical pairs reactions. In our relatively low viscosity system, we anticipate little cage reaction of this type. Also, the recent investigation by Niki, Shiono, Ido, and Kamiya[7] of amorphous polypropylene oxidation in solution under a variety of conditions indicates little likelihood of major cross-linking. They published the gel permeation chromatograms for the reactant polypropylene superimposed on the chromatograms of the oxidation products. In all cases there was no indication that any materials were being formed which had a higher molecular weight than the starting polymer.

Finally, the results here can be compared with those reported by Decker and Mayo.[3] In their analysis of the oxidation of neat, amorphous polypropylene at 22 °C, chain cleavage was equated to a linear dependence on total initiation while oxygen absorption was analyzed as a composite of first and half-order initiation processes. For their experiments where initiation was by Co-60 irradiation, the values of $G_{O_2}/G_{\text{scissions}}$, which are to be compared with the values in the last column of Table I, range from 29 to 16. The agreement between the two sets of data is remarkably good when the number of variables that have been changed is considered.

In conclusion, the reaction which leads to cleavage of polypropylene chains during oxidation is a relatively minor one and appears to accompany the propagation reaction. In the oxidation of a model compound, 2,4,6-trimethylheptane,[13] yields of hydroperoxides were lower than those in the oxidation of 2,4-dimethylpentane and substantial amounts of products corresponding to carbon–carbon chain cleavage were found. In so far as carbon–carbon bond breaking is concerned, the trend seems to have actually been reversed somewhat in the polymer case.

### References and Notes

(1) C. E. H. Bawn and S. A. Chaudhri, *Polymer*, **9**, 123 (1968).
(2) L. Reich and S. Stivala, *J. Appl. Polym. Sci.*, **13**, 23 (1969).
(3) C. Decker and F. R. Mayo, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2847 (1973).
(4) C. A. Glover, "Advances in Analytical Chemistry and Instrumentation", Vol. 5, C. N. Reilley and F. W. McLafferty, Ed., Interscience, New York, N.Y., 1966, p 1.
(5) D. E. Van Sickle, *J. Polym. Sci., Part A-1*, **10**, 275 (1972).
(6) D. E. Van Sickle, *J. Polym. Sci., Part A-1*, **10**, 355 (1972).
(7) E. Niki, T. Shiono, T. Ido, and Y. Kamiya, *J. Appl. Polym. Sci.*, **19**, 3341 (1975).
(8) J. A. Howard and J. H. B. Chenier, *Int. J. Chem. Kinet.*, **6**, 527 (1974).
(9) A. V. Tobolsky, P. M. Norling, N. H. Frick, and H. Yu, *J. Am. Chem. Soc.*, **86**, 3925 (1964).
(10) E. Niki, C. Decker, and F. R. Mayo, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2813 (1973).
(11) A. Auerbach, N. Indictor, and T. Jochsberger, *Macromolecules*, **8**, 632 (1975).
(12) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2480 (1958).
(13) D. E. Van Sickle, *J. Org. Chem.*, **37**, 755 (1972).

---

# Comments on the Theory of Steric Stabilization

**Paul R. Gerber and M. A. Moore***

*Institut für Theoretische Physik, Universität Basel, Basel, Switzerland, and the Department of Theoretical Physics, The University, Manchester, U.K.*

*Received September 14, 1976*

ABSTRACT: Steric stabilization of colloidal particles in theta and good solvents is examined theoretically. For near-theta solvents an analytic solution to the equations solved numerically by Dolan and Edwards is presented and the domain of validity of their approach delineated. In good solvents a scaling analysis is employed which makes use of the analogies between magnetic systems and polymers to give asymptotic expressions for the interaction potential between the colloidal particles. In both types of solvent it is found that metastable stabilization by a potential barrier can be produced for polymer coverages of the particles insufficient to cause stability right at the theta point.

## I. Introduction

A dispersion of colloidal particles may be stabilized against flocculation by the adsorption or attachment of flexible polymer molecules onto the particles of the suspension. In the absence of a macromolecular covering of the particles, flocculation will rapidly take place because of the attractive van der Waals forces between the particles which causes them to stick together. The presence of polymers between the surfaces of the particles gives rise to a repulsive force between the particles; when two such particles approach, the reduction in the number of configurations available to the flexible polymer chains gives rise to an "entropic" repulsive force between the particles. This may keep two colliding particles so far apart that the van der Waals interaction energy is insufficient for coherence. For a recent reappraisal of current theory and references to other relevant work, the reader is referred to the article by Osmond et al.[2a]

We shall distinguish between (i) theta solvents, (ii) worse than theta solvents, and (iii) better than theta solvents (good solvents). Most theoretical work to date has concentrated on theta solvents since, for such solvents, the statistics of the polymer chains will be of the simple random-flight type.[2b,3] The essential features are summarized in section II. For conditions corresponding to temperatures or solvent composition which make the solvent just better than a theta solvent, a perturbation type analysis is possible. It is shown in section II how this analysis can be accomplished without going into the heavy numerical work found in the paper of Dolan and Edwards.[4] These authors did not mention the possibility of obtaining an analytic solution to their equations in the region of most immediate physical interest. It is found that above the theta point a potential barrier between particles is produced which, if sufficiently high, can provide a metastable form of stability.

For solvents much worse than theta solvents a dimensional collapse of the polymer chains into globules will take place. The globules may adhere to the surface of the colloidal particles if there are sufficiently strong polymer–surface interactions. If not, connections between the globule and particle surface will only occur when protuberances of a few loops or tails of polymer from the globule happen to touch the particle. This is a complicated problem which we shall not discuss here, as it has little relevance to most experimental work on steric stabilization. However, it is obvious that when such a dimensional collapse has taken place, the polymer-induced repulsive force between the particles will only be appreciable at closer distances of approach than found at the theta point and will have less chance of preventing flocculation of the particles.

Flocculation in good solvents is theoretically a difficult topic, since for good solvents perturbation theory is no longer sufficient. In section III we offer a "scaling" analysis. Such scaling analyses have already been shown to give useful insights into the behavior of dilute and semidilute polymer solutions.[5] The inspiration for the various scaling assumptions derives from analogies with corresponding quantities in a magnetic system. The formal connection between a certain limiting form of a magnetic system and polymers was first clearly stated by de Gennes.[6] Results which are moderately well-established for such systems allow one to give an account of the role of excluded volume forces, so important in good solvents, and the results found show that stabilization in a good solvent is quantitatively, if not qualitatively, of a quite different form than in a solvent just above its theta temperature.

The model we shall adopt for the polymer-coated colloidal particles is the following. It will be supposed that the particles are sufficiently close together that the interaction between them can be approximated by that between two parallel flat plates of area $S$, separated by a distance $d$. The van der Waals energy of attraction $V_{\mathrm{A}}$ is then just

$$V_{\mathrm{A}} = -AS/12\pi d^2 \tag{1}$$

where $A$ is the Hamaker constant. The conditions under which this plate geometry is a good approximation to reality are discussed by Dolan and Edwards. [3]

Each plate is imagined to have $\frac{1}{2}N$ attached polymers of link length $l$ and overall length $L$ and therefore having $M = L/l$ segments. The number of polymers between the plates is just $N$. Each polymer is anchored at one end to a plate. In reality, the polymer may be attached at several points along the chain and adsorption and desorption of polymer at the surface may take place during a particle collision. This means that "loops" in which both ends of the polymer are attached to the same plate will have to be considered in a full theoretical treatment. Adsorption changes on collision will be ignored. An experiment due to Napper,[7] in which the chains were chemically anchored to the colloidal particles, suggests that there are situations in which this will be a satisfactory approximation.

The surface coverage by polymer is assumed to be large enough so that the local density of segments between the plates is just a function of its distance $z$ from one of the plates, i.e., a one-dimensional approximation can be used. The results of section II suggest that this is likely to be adequate for coverages high enough to prevent flocculation.

To account for the interaction between the polymer segments, the excluded volume parameter $v$ is needed. It is a measure of the potential energy of interaction, when multiplied by $kT$, between two segments in the presence of solvents and is related to the Flory parameter $\chi$ by

$$v = (\tfrac{1}{2} - \chi)V_{\mathrm{s}}^2/V_1$$

where $V_{\mathrm{s}}$ and $V_1$ are the volumes of a segment and solvent molecule, respectively. Its temperature dependence may be linearized near the theta point as

$$v = v_0(1 - \theta/T) \tag{2}$$

It will be assumed that the time of encounter of two colliding colloidal particles is sufficiently long that the polymers can adjust their configurations to the equilibrium appropriate at the (time varying) distance $d$; Hesselink suggests that this may be a not unreasonable approximation for typical solvent viscosities.[2b] If so, it allows the application of equilibrium statistical mechanics.

Finally, in section IV, we shall discuss the experimental situation, especially the mechanism of the flocculation observed in sterically stabilized dispersions when the solvent is changed from a good solvent to a theta or near-theta solvent.

## II. Theta and Near-Theta Solvents

Dolan and Edwards[3] have shown, using random-flight statistics, that the repulsive energy $V_{\mathrm{R}}$ right at the theta point is well-approximated by

$$V_{\mathrm{R}} = NkT\left\{\frac{\pi^2 lL}{6d^2} + \ln d\left(\frac{3}{8\pi lL}\right)^{1/2}\right\}, \quad d^2/lL \le 3 \tag{3}$$

$$V_{\mathrm{R}} = NkT2\exp(-3d^2/2lL), \quad d^2/lL > 3 \tag{4}$$

The mean-square end-to-end distance $R_{\mathrm{M}}$ in bulk solution equals $Ll$ ($M = L/l$ is the number of segments in the polymer). When $d < R_{\mathrm{M}}/3^{1/2}$, eq 3 is a good approximation to $V_{\mathrm{R}}$. In this limit the number density of polymer segments across the plates varies as (see eq 13)

$$2(NL/ld)\sin^2(\pi z/d) \tag{5}$$

In the opposite limit, $d > R_{\mathrm{M}}/3^{1/2}$, the density falls off from each plate as a function of distance $\delta$ as $\exp(-(\delta/R_{\mathrm{M}})^2)$ (ignoring numerical factors). Equations 3 and 4 arise from the volume restrictions which a second surface places on the density distribution of polymers about the first surface.

The total interaction between the particles is just the sum $V = V_{\mathrm{A}} + V_{\mathrm{R}}$ and its form is sketched in Figure 1 for the case in which the repulsive force dominates near the origin. The van der Waals force always dominates the repulsive force at large distances but clearly fails to dominate at the origin if

$$\frac{NlL}{S} > \frac{1}{2\pi^3}\frac{A}{kT} \tag{6}$$

Should this inequality not be satisfied, "strong" flocculation would take place in which the particles adhere closely. Even if the inequality is satisfied, "weak" flocculation will take place if the depth of the minimum $V_{\min}$ is greater than around $1kT$, when $\exp(-V_{\min}/kT) > 1$. This looser form of association of the colloidal particles takes place if

$$\frac{lL}{S} < \frac{1}{8\pi}\frac{A}{kT\ln 2N} \tag{7}$$

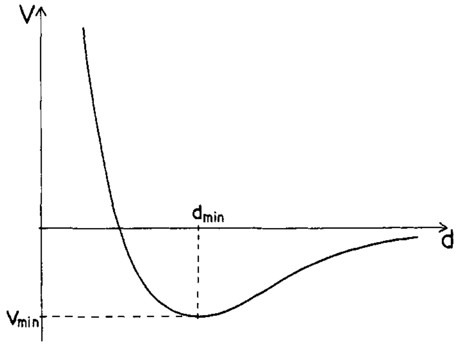

**Figure 1.** The form of the total interaction energy $V = V_R + V_A$, when the system is stabilized by the polymers right at the theta temperature.

and the average separation between them will be of order $d_{\min}$.

The right-hand side of eq 6 is typically of order 0.4, which implies that for stability there must be overlap between the various attached polymers which allows the use of a one-dimensional approximation.

Above the theta point, Dolan and Edwards[4] provided an extension of the Edwards self-consistent-field approximation to the problem of steric stabilization. Their results can be expressed in the following form: for $d^2 < 3Ll$,

$$V_R = NkT\frac{\pi^2 lL}{6d^2}\phi\left(\frac{N\upsilon Ld}{Sl^3}\right) \tag{8}$$

where for small $x$, $\phi(x) = 1 + (9/2\pi^2)x + 0(x^2)$ and for large $x$,

$$V_R \rightarrow \frac{kT}{2}\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\rho(\mathbf{r}_1)\upsilon(\mathbf{r}_1-\mathbf{r}_2)\rho(\mathbf{r}_2)$$
$$= \tfrac{1}{2}kT\upsilon\left(\frac{NL}{lSd}\right)^2 Sd, \quad [\upsilon(\mathbf{r}_1-\mathbf{r}_2) = \upsilon\delta(\mathbf{r}_1-\mathbf{r}_2)] \tag{9}$$

In the large $x$ limit, the density of segments becomes uniform across the width of the slab at the value $\rho = NL/lSd$, and $V_R$ is just the interaction energy of $NL/l$ segments confined in a volume $Sd$ when effects due to chain connectivity are negligible (in reality, the density will fall to zero at the walls over a length of order of the Edwards "screening" length[8] ca. $l/(\rho\upsilon)^{1/2}$).

Dolan and Edwards' results were achieved by a numerical solution of a very complicated integro-differential equation. It may be useful to point out that in the limit $d^2 < 3Ll$, an approximate analytic solution to their equations is possible, by finding the $\psi(z)$ which minimizes the integral

$$\frac{V_R}{kT} = N\int_0^d dz\left[\frac{l^2}{6}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 + \tfrac{1}{2}\sigma\upsilon\psi^4\right] \tag{10}$$

subject to the constraint

$$\int_0^d \psi^2(z)\,\mathrm{d}z = L/l \tag{11}$$

$\sigma = N/S$ is the number of polymers per unit area of slab. $\rho(z) = N\psi^2(z)/S$ is the local density of polymer segments. The first term in (10), the gradient term, arises from the chain connectivity of the segments while the second term arises from the potential energy of interaction between the segments.

The variational equation leads to an Euler–Lagrange differential equation for $\psi(z)$. The boundary conditions for impermeable walls which do not adsorb the polymer are $\psi = 0$ at $z = 0$ and $z = d$. The Euler–Lagrange equation is

$$-\frac{l^2}{6}\frac{\mathrm{d}^2\psi}{\mathrm{d}z^2} + \sigma\upsilon\psi^3 = \lambda\psi(z) \tag{12}$$

where $\lambda$ is a Lagrangian multiplier introduced to handle the constraint condition eq 11.

For $\upsilon = 0$ the solution is trivial,

$$\psi_n(z) = \left(\frac{2L}{ld}\right)^{1/2}\sin\frac{n\pi z}{d}, \quad n = 1, 2, 3, \ldots \tag{13}$$

are all possible solutions to the differential equation which satisfy the constraint. The corresponding eigenvalues are

$$\lambda_n = \tfrac{1}{6}\,l^2\pi^2 n^2/d^2$$

The lowest eigenvalue gives the smallest free energy, when the repulsive interaction $V_R$ between the plates is just

$$V_R = NkT\pi^2 lL/6d^2 \tag{14}$$

The use of the formalism based on eq 10 and 11 is valid when $V_R$ is dominated by a single eigenvalue, which leads in turn to the condition $d^2 < 3lL$. When one eigenvalue dominates, it is a trivial matter to derive (10) from the Dolan–Edwards equations.

For $\upsilon > 0$, the solution to eq 12 can be expressed in terms of the Jacobian elliptic functions:[9]

$$\psi(z) = \psi_1 sn((6\lambda - 3\sigma\upsilon\psi_1^{\,2})^{1/2}z/l\,|\,m) \tag{15}$$

where $(6\lambda - 3\sigma\upsilon\psi_1^{\,2})^{1/2}d = 2lK(m)$ and

$$(6\lambda - 3\sigma\upsilon\psi_1^{\,2})^{1/2}(K(m) - E(m)) = 3\sigma\upsilon L/2l^2 \tag{16}$$

with $m = \sigma\upsilon\psi_1^{\,2}/(2\lambda - \sigma\upsilon\psi_1^{\,2})$. The unknowns $\psi_1$ $(=\psi(z = d/2))$ and $\lambda$ can be obtained by solving eq 15 and 16. This is only easy in limiting cases, i.e., $x$ small or $x$ large, where $x = N\upsilon Ld/Sl^3$ and the results have been given above. The full solution shows the healing of the density at the walls on the scale of the Edwards screening length (provided one assumes that the coverage $\sigma \sim 0(1/lL)$, i.e., the spacing between the attached polymers is of the order of their theta point radii of gyration). It also provides expressions for the function $\phi(x)$ of eq 8.

We turn now to determining the domain of validity of the Dolan–Edwards approach. Despite being set up as a self-consistent calculation, it is strictly only valid within perturbation theory and, as such, is satisfactory if[10]

$$\upsilon/\{l/L + 2\upsilon\rho\}^{1/2} \ll l^3 \tag{17}$$

When $2\upsilon\rho \ll l/L$, this reduces to the condition $\upsilon L^{1/2} \ll l^{7/2}$, the usual requirement for a Fixman-type perturbation expansion[11] to be valid. For $2\upsilon\rho \gg l/L$, we require $\upsilon \ll \rho l^6$, which, writing $\sigma = N/S = \omega/Ll$ where $\omega$ is a numerical constant whose size indicates the surface coverage of the slab by polymer molecules, implies that

$$\upsilon \ll \omega l^4/d \tag{18}$$

for the validity of the calculation. Notice that for large $x$ we must have

$$\upsilon \gg l^4/\omega d \tag{19}$$

so that only for large surface coverage $\omega$ can one pass from a situation in which at the theta point the density is described by a $\sin^2$ variation to a uniform density variation above the theta point and still use the Dolan– Edwards approach.

There is a more illuminating way of determining the domain of validity of the calculation. In the large $x$ limit the density is essentially uniform between the plates and $V_R$ just corresponds to the work done against the osmotic pressure $\Pi$ (produced by the higher concentration of polymer between the plates than outside) when the plates are brought together from infinity to a separation $d$, viz.,

$$V_R = -S\int_\infty^d \Pi\,dz \tag{20}$$

If for $\Pi$, the expression

$$\Pi = \frac{kT}{2} v\rho^2 \tag{21}$$

where $\rho = NL/lSz$ is substituted, then one obtains eq 14 for $V_R$ (the van't Hoff term $kT\rho/M$ is absent because the polymers here are anchored to the surface and so there can be no contribution to $\Pi$ from the overall translational motion). The validity of eq 21 is limited to that region in the bulk system in which the osmotic pressure is adequately represented by

$$\Pi = kT\rho/M + \frac{kT}{2} v\rho^2 \tag{22}$$

However, this is the region of intermediate density discussed by Edwards.[8] In it one requires $v \ll \rho l^6$, which is equivalent to (17) when $2v\rho \gg l/L$.[10]

One advantage of having obtained an analytic solution is that one can more easily sketch the curve $V(d)$ as a function of $d$. Above the theta point it is possible for it to have the form indicated in Figure 2.

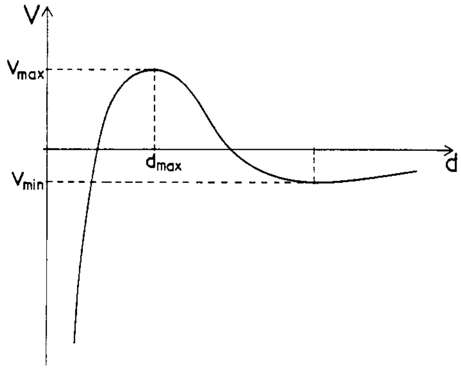

**Figure 2.** The form of the total interaction energy $V = V_R + V_A$, when the coverage is insufficient to provide stability right at the theta temperature.

The situation depicted in Figure 2 corresponds to a surface coverage insufficient to prevent "strong" flocculation at the theta point. The extra repulsive force causing the maximum $V_{\max}$ is, of course, due to the polymer–segment excluded volume interaction $v$, which opposes any attempt to overlap polymers attached to different plates and also by increasing the size of each polymer causes them to stick out further from each plate and so produce a repulsive force at larger separations. Provided the barrier height $V_{\max} > skT$, $s \approx 20$, a metastable form of equilibrium may ensue. This is because the number of collisions which result in very close approach and so adherence of the particles is reduced by the Boltzmann factor $\exp(-V_{\max}/kT)$. Hence, for $s \approx 20$, this is a very small number, and strong flocculation will be prevented on any reasonable time scale. "Weak" flocculation at the minimum may still occur if it is of a depth of around $1kT$. If the surface coverage is sufficiently high so that at the theta point strong flocculation is not possible, then the potential curve above the theta point is qualitatively similar to that of Figure 1.

It is easy to work out the height of the potential barrier $V_{\max}$ if it lies at values of $d$ for which eq 9 holds. Then

$$d_{\max} = \frac{A}{3\pi kT}\left(\frac{lS}{LN}\right)^2 \frac{1}{v} \tag{23}$$

and

$$V_{\max} = \frac{3\pi kT}{4A} SkTv^2 \left(\frac{NL}{lS}\right)^4 \tag{24}$$

The minimum $V_{\min}$ probably lies in the region $d > R_M$ and to estimate its depth one would need to solve the full Dolan–Edwards set of equations.

## III. Scaling and Universality Arguments for Good Solvents

In order to be able to make connection to well studied magnetic cases we restrict ourselves for the moment to determining the free energy of a single polymer chain attached with one end to one of the plates. The corresponding magnetic case appears to be reasonably well understood in terms of scaling laws.[12,13] In order to make the connection it is customary to consider the generating function for attached chains,

$$G(y,d) = 1 + \sum_{M=1}^{\infty} Q_M(d) y^M \tag{25}$$

where $Q_M$ is the partition function for $M$-step chains on a lattice starting at the origin and avoiding the half spaces $z < 0$ and $z > d$. In spin systems $G(y,d)$ corresponds to the susceptibility $\chi_1(t,d)$ which describes the response of the surface magnetisation (at $z = 0$) to application of a uniform magnetic field. $t = (T - T_{c,\infty})/T_{c,\infty}$ denotes the deviation of the temperature $T$ from the critical temperature $T_{c,\infty}$ for $d = \infty$. In the analogy to polymer $t$ corresponds to $1 - (y/y_\infty)$ where $y_\infty$ is the critical value of the parameter $y$ for the case $d \to \infty$.

Let us now simply state a few properties of the function $\chi_1(t,d)$ which follow from general crossover scaling arguments and have been checked rather extensively.[12,13] For $d$ large compared with the range of interactions and small $t$ the behavior of $\chi_1(t,d)$ is asymptotically described by a crossover scaling form

$$\chi_1(t,d) = A(Bd^{1/\nu})^{\gamma_1} f(tBd^{1/\nu}) \tag{26}$$

where the exponents $\gamma_1$ and $\nu$ and the function $f(x)$ are universal while $A$ and $B$ are dependent on particular features like lattice structure, specific form of the short-range interaction, etc. It is, however, possible to normalize $f(x)$ (by choosing an appropriate scale for $x$) such that $Bt = \xi^{-1/\nu}$ where $\xi$ is the correlation length of the system which governs the exponential decay of the two-point correlation function at large distances. The function $f(x)$ satisfies conditions which account for the proper critical behavior of $\chi_1$, namely: (1) $f(x) \simeq x^{-\gamma_1}$, $x \to \infty$, giving $\chi_1(t,\infty) \simeq At^{-\gamma_1}$; (2) $f(x) \simeq f_0(x_0 + x)^{-\bar{\gamma}}$, $x \to -x_0$. This gives the correct critical behavior for a system of finite width $d$. First it determines the asymptotic behavior of the critical temperature

$$t_c(d) \simeq -x_0/Bd^{1/\nu} \tag{27}$$

Second it accounts for the expected singularity

$$\chi_1(t,d) \simeq Af_0(Bd^{1/\nu})^{\gamma_1-\bar{\gamma}}[t - t_c(d)]^{-\bar{\gamma}} \tag{28}$$

where $t$ approaches the critical temperature $t_c(d)$ for a system of finite $d$.

With this list of properties we can now return to the function $G(y,d)$. One then has to take for the universal quantities $\nu$, $\gamma_1$, $\bar{\gamma}$, and $f_0$ the ones appropriate for the polymer system, rather than the magnetic system. The Flory value for $\nu$ is $3/5$.

For $d = \infty$ we hence obtain

$$G(y,\infty) \simeq A\left(1 - \frac{y}{y_\infty}\right)^{-\gamma_1} = \mathrm{A}\sum_{\mathrm{M}} \binom{-\gamma_1}{M} y_\infty{}^{-M}(-y)^M$$
$$= A\sum_M \binom{M+\gamma_1-1}{M}\left(\frac{y}{y_\infty}\right)^M$$

giving

$$Q_M(\infty) \simeq Ay_\infty{}^{-M}M^{\gamma_1-1} \tag{29}$$

For finite $d$ we have analogously

$$G(y,d) \simeq Af_0(Bd^{1/\nu})^{\gamma_1-\bar{\gamma}}\left(1+\frac{x_0}{Bd^{1/\nu}}\right)^{-\bar{\gamma}} \times \left\{1-\frac{y}{y_\infty[1+x_0(Bd^{1/\nu})^{-1}]}\right\}^{-\bar{\gamma}} \quad (30)$$

giving

$$Q_M(d) \simeq Af_0(Bd^{1/\nu})^{\gamma_1-\bar{\gamma}}\left(1+\frac{x_0}{Bd^{1/\nu}}\right)^{-\bar{\gamma}-M} y_\infty{}^{-M}M^{\bar{\gamma}-1} \quad (31)$$

whence

$$\frac{Q_M(d)}{Q_M(\infty)} \simeq f_0\left(\frac{Bd^{1/\nu}}{M}\right)^{\gamma_1-\bar{\gamma}}\left(1+\frac{x_0}{Bd^{1/\nu}}\right)^{-\bar{\gamma}-M} \quad (32)$$

The free energy change produced upon bringing up the second surface from infinity to a distance $d$ is then simply given by $\Delta F(d) = kT \ln [Q_M(d)/Q_M(\infty)]$. Keeping in mind that we are interested in the range $M \rightarrow \infty$, $Bd^{1/\nu}/M$ small but finite, we may introduce the quantity (see ref 14 and 15)

$$R_{\mathrm{M}} \simeq B^{-\nu}\nu^{-\nu}(1-\nu)^{-(1-\nu)}M^{\nu} \quad (33)$$

which, for an isolated polymer in the absence of walls, governs the asymptotic behavior of the end-to-end distribution function for large distances which behaves as $\exp\{-(r/R_{\mathrm{M}})^{1/(1-\nu)}\}$. This then leads to the following universal asymptotic behavior

$$\frac{\Delta F}{kT}(d) \simeq x_0\nu(1-\nu)^{(1-\nu)/\nu}\left(\frac{R_{\mathrm{M}}}{d}\right)^{1/\nu} + \frac{\overline{\gamma}-\gamma_1}{\gamma}\ln\frac{d}{R_{\mathrm{M}}} \quad (34)$$

$$d < R_{\mathrm{M}}$$

The leading scaling result given by the first term $\Delta F \sim d^{-1/\nu}$ has been used by Daoud and de Gennes[16] in their scaling description of finite size effects in polymer systems. Equation 34 makes in addition use of the universality principle to give a universal curve provided $d$ is measured in terms of the quantity $R_M$. Numerical values for the case of polymers are presently only known for the exponents $\nu$ and $\overline{\gamma}$. However, in order to obtain an order of magnitude estimate for the two coefficients in (34) we may use the corresponding values for the Ising model, where detailed numerical calculations and checks have been performed.[12,18] They give $x_0 \simeq 5.0$[12,17] and $\overline{\gamma} - \gamma_1 \simeq 0.9$.[18,19] The critical exponents $\nu$, $\overline{\gamma}$, etc., are known to vary only in the 10% range in going from the Ising model to the self-avoiding walk system. Assuming that the same is true for the unknown $\gamma_1$ and $x_0$ we may make the rough estimate

$$\frac{\Delta F(d)}{kT} \simeq 1.6\left(\frac{R_{\mathrm{M}}}{d}\right)^{5/3} + 1.5\ln\frac{d}{R_{\mathrm{M}}} \quad (35)$$

In view of the fact that experiments which would test the form of (35) quantitatively seem not feasible at present we have made no effort to determine the coefficients in separate numerical work.

For large distances $d > R_{\mathrm{M}}$ we may mention that a simple argument can be applied to give a qualitative form for the behavior of $\Delta F(d)$. This can be derived from the asymptotic behavior of the end-to-end distribution probability $p_M(\mathbf{r})$, which is known to be of the form[14,15]

$$p_M(\mathbf{r}) \sim R_{\mathrm{M}}{}^{-3}f\left(\frac{\mathbf{r}}{R_{\mathrm{M}}}\right)\exp\left[-\left(\frac{r}{R_{\mathrm{M}}}\right)^{1/(1-\nu)}\right] \quad (36)$$

where $f(\mathbf{r})$ varies slowly compared to the exponential function. Remembering the geometry of our situation it is straightforward to see that the fraction of chains ending at a distance $d > R_{\mathrm{M}}$ is proportional to $\exp[-(d/R_{\mathrm{M}})^{1/(1-\nu)}]$. The same is certainly true for the number of chains exceeding the distance $d$ with any of its segments. The fraction $q(d)$ of configurations allowed in the presence of an impenetrable wall at distance $d$ is hence of the form

$$q(d) = 1 - g\left(\frac{d}{R_{\mathrm{M}}}\right)e^{-(d/R_{\mathrm{M}})^{1/(1-\omega)}} \quad (37)$$

$$d \gg R_{\mathrm{M}}$$

where $g(x)$ is slowly varying compared with the exponential, e.g., like a simple power in $x$. This gives for the change in free energy

$$\frac{\Delta F(d)}{kT} = -\ln q(d) \simeq g\left(\frac{d}{R_{\mathrm{M}}}\right)e^{-(d/R_{\mathrm{M}})^{1/(1-\nu)}} \quad (38)$$

$$d > R_{\mathrm{M}}$$

The main feature of this form is that $\Delta F(d)$ is vanishingly small for large $d$ and is appreciable when $d$ becomes of the order of $R_{\mathrm{M}}$. The exact form of $\Delta F(d)$ in the intermediate region ($d \sim R_{\mathrm{M}}$) until (34) applies is however unknown. But (34) is sufficient to make the basic statements about stability of colloids. A few comments are in order on how (34) is to be modified to deal with loops of $M$ links. First, the leading term of the form $(R_{\mathrm{M}}/d)^{1/\nu}$ remains unchanged, whereas in the less important logarithmic correction the exponents $\overline{\gamma}$ and $\gamma_1$ are altered.[20] But since we will eventually only retain the leading term we neglect these changes.

A second comment concerns the fact that in a real situation the loops and tails may be of various lengths. With $R_{\mathrm{M}}$ behaving as

$$R_{\mathrm{M}} = R_0M^{\nu} \quad (39)$$

where $R_0$ is a nonuniversal scale factor one simply obtains for the average limiting law

$$\frac{\Delta F}{kT} \simeq x_0\nu(1-\nu)^{(1-\nu)/\nu}\left(\frac{R_0}{d}\right)^{1/\nu}\langle M\rangle \quad (40)$$

$$d \rightarrow 0$$

which shows that only the average segment number $\langle M\rangle$ is relevant, always provided that for all chains $R_{\mathrm{M}} \gg d$.

A third and more difficult question concerns the changes one might expect when neighboring chains are attached so closely to each other that they begin to overlap considerably. The conjecture has been advanced[16] that the limiting behavior of $\Delta F$ for $d \rightarrow 0$ remains of the general form of (40). This may be justified by saying that $d$ is eventually the shortest characteristic distance of the system so that the probability of encountering another chain within this distance is small and that one might hence expect to be left with the single chain like term. It is however not clear why entanglement effects might not change this form.

The repulsive interaction potential $V$ due to the chain is given by (see 40)

$$V_{\mathrm{R}}(d) = N\Delta F(d) = 1.6NkT(R_0/d)^{5/3}\langle M\rangle \quad (41)$$

$$d \lesssim R_{\mathrm{M}}$$

Now $N\langle M\rangle$ is just the number of segments of monomers between the plates. An interesting feature of (41) is that the polymer length, $Ml = L$, has disappeared and only the surface coverage in terms of number of segments enters. A similar result was obtained in the region $d < R_{\mathrm{M}}$ for the theta point solvent (eq 14). The only other quantity related to the stabilizing species (and its behavior in the solvent) is $R_0$.

Straightforward calculation now gives the following results. The total potential $V = V_{\mathrm{R}} + V_{\mathrm{A}}$ will look like that of Figure 2. There is a maximum at

$$d_{\max} = \left(\frac{AS}{16\pi kT}\right)^3\frac{1}{N^3\langle M\rangle^3R_0{}^5} \quad (42)$$

This leads to a first trivial but important condition for stabilization. Since $d_{\max}$ has to be small compared with $R_M$ in order for the limiting law to apply, we require

$$\frac{N}{S} R_M{}^2 > \frac{A}{16\pi kT} \text{ (cf. eq 6)} \qquad (43)$$

which generalizes the random-flight condition, eq 6, and also indicates the minimal number of polymers that have to be attached to obtain a maximum in $V$ in the region where (41) holds. We doubt whether a maximum can exist outside this region. The value of the right-hand side of (43) is usually less than 0.5. Once (43) is fulfilled, one obtains a second criterion for stability against strong flocculation by requiring that $V_{\max}$ is bigger than say $skT$ with $s$ of order 20. This gives the condition

$$\frac{S}{d_{\max}{}^2} \gg \frac{16\pi kT}{A}$$

or

$$V_{\max} = \frac{4N}{15}\left(\frac{16\pi kT}{A}\frac{N}{S} R_{\mathrm{M}}{}^2\right)^5 kT > skT \qquad (44)$$

It seems likely that as $R_{\mathrm{M}}{}^2 \ll S$ in order that the particles can be considered as parallel plates, the condition (44) will be automatically fulfilled if this view of the geometry of the particles is valid and (43) is satisfied. Smaller particles may be expected to show consistently different behavior due to geometrical factors. Keeping this in mind, (43) remains the main conditions for stabilization against strong flocculation and we expect the particle size to be a minor factor in determining the stability of not too small colloidal particles.

It is difficult to estimate the depth of the minimum, i.e., $V_{\min}$ as it is likely to lie at $d \gtrsim R_{\mathrm{M}}$, just in the very region where it is not permissable to use either of the asymptotic formulas for $\Delta F(d)$ eq 35 and 38.

## IV. Experimental Section

Comparison with experiment has to be on a crude and qualitative level, because the complexity of the experimental situation hardly allows one to produce the simple conditions envisaged in the theoretical description. We consider the experiments by Napper[7] as the most suitable ones for comparison, because by using a technique of anchoring the stabilizing chains chemically he avoided the additional complications which can arise due to change of adsorption of polymer on the surface of the particles as they approach each other. Napper varied the composition of the solvent and the temperature to achieve flocculation. It is not clear whether at the point of flocculation in his experiment the solvents were sufficiently poor so that one can apply conditions for just above the theta point flocculation or were still sufficiently good for the good solvent conditions for flocculation to apply. Qualitatively, there is little difference between them, as both involve a potential energy of interaction as depicted in Figure 2.

It is important to note that both for theta and good solvents the conditions for stability are very sensitive to temperature. Thus, eq 44 shows that $V_{\max}$ varies as $T^6$ and also has extra temperature dependence through the variation of $R_0$ with temperature. In the good solvent region, $R_0$ varies with $v$ as[21]

$$R_0 \sim l(v/l^3)^{1/10}$$

and

$$v \sim v_0(1 - \theta/T)$$

cf. eq 2.

We think the following experimental observations are consistent with the calculations presented here.

(1) Slow flocculation could be observed, confirming the presence of an energy barrier $V_{\max}$ and only metastable equilibrium.

(2) Onset of flocculation on varying the composition took place in a very narrow interval. It was also difficult to find slow flocculation. We would interpret these observations by point out the strong dependence of $V_{\max}$ on $R_0$ in eq 44.

(3) Relatively large changes in particle size could be compensated for by rather small changes in solvent composition. This might be interpreted as either due to the dependence of $V_{\max}$ in, say, (44) on $R_0{}^{10}$ compared to the linear dependence on $N$ (or $S$), or possibly as due to the size independence of (43). Equation 43 is essentially the condition that a potential barrier exists.

(4) On varying the surface coverage a critical coverage appears below which stabilization was no longer observed. This is in accord with (43) or (6).

## V. Conclusion

In conclusion, we believe that the theory of Dolan and Edwards for theta point solvents and the scaling analysis for good solvents provide a satisfactory account of the metastable steric stabilization of colloids.

**Acknowledgment.** Research supported in part by the Science Research Council under Grant B/RG/5935-6. Most of the calculations in this paper were done while the authors were at the University of Sussex, Brighton, U.K.

## References and Notes

(1) (a) Universität Basel; (b) The University.
(2) (a) D. W. Osmond, B. Vincent, and F. A. Waite, *Colloid Polym. Sci.*, **253,** 676 (1975); (b) F. Th. Hesselink, *J. Phys. Chem.*, **75,** 65 (1971).
(3) A. K. Dolan and S. F. Edwards, *Proc. R. Soc. London, Ser. A*, **337,** 509 (1974).
(4) A. K. Dolan and S. F. Edwards, *Proc. R. Soc. London, Ser. A*, **343,** 427 (1975).
(5) M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, and P. G. de Gennes, *Macromolecules*, **8,** 804 (1975).
(6) P. G. de Gennes, *Phys. Lett. A*, **38,** 339 (1972).
(7) D. H. Napper, *Trans. Faraday Soc.*, **64,** 1701 (1968).
(8) S. F. Edwards, *Proc. Phys. Soc., London*, **88,** 265 (1966).
(9) M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Functions", National Bureau of Standards, 1964, Chapter 16.
(10) M. A. Moore, to be published.
(11) M. Fixman, *J. Chem. Phys.*, **23,** 1656 (1955).
(12) M. E. Fisher, "Proceedings of the Enrico Fermi Summer School", Vol. 51, Academic Press, New York, N.Y., 1971, p 1.
(13) M. E. Fisher, *J. Vac. Sci. Technol.*, **10,** 665 (1973).
(14) M. E. Fisher, *J. Chem. Phys.*, **44,** 616 (1966).
(15) D. S. McKenzie and M. A. Moore, *J. Phys. A: Gen. Phys.*, **4,** L82 (1971).
(16) M. Daoud and P. G. de Gennes, preprint.
(17) M. E. Fisher and R. J. Burford, *Phys. Rev.*, **156,** 583 (1967).
(18) K. Binder and P. C. Hohenberg, *Phys. Rev. B:*, **6,** 3461 (1972).
(19) M. E. Fisher, *Rep. Progr. Phys.*, **30,** 615 (1967).
(20) K. M. Middlemiss and S. G. Whittington, *J. Chem. Phys.*, **64,** 4684 (1976).
(21) D. J. Burch and M. A. Moore, *J. Phys. A:*, **9,** 435 (1976).