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Theory of Colloid Stabilization in Semidilute Polymer Solutions

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ABSTRACT: A universal asymptotically exact theoretical approach elucidating the origin of the depletion stabilization phenomenon is developed. The theory predicts that colloidal particles in a semidilute polymer solution may be kinetically stabilized by a long-range polymer-induced repulsion. It is shown that the repulsion is due to a depletion of chain ends in the middle of the slit between solid surfaces. A nonmonotonic concentration dependence of the stabilization effect is predicted. The theory is generalized to account for surface attraction of chain ends and for polydispersity of the chains. The stabilization is enhanced for more rigid and less polydisperse chains and for the case of reversible end-adsorption.

1. Introduction

Colloidal dispersions are indispensable for many technologically important applications.[1,2] The main problem however is that colloidal particles tend to aggregate due to unavoidable van-der-Waals attractive forces. Stabilization of colloidal systems is therefore an important goal recognized long ago. Colloid stability can be imparted in an efficient way by using polymers or copolymers.[2] Usually stabilization is achieved by attaching or adsorbing polymers to the surfaces of colloidal particles (the so-called steric stabilization[2,26,27]). However, increasing concentration of unanchored (free) polymer in the semidilute regime may also enhance colloidal stability.[3] Thus, *kinetic* stability can be induced by free polymers (this mechanism is often referred to as depletion stabilization[2]). This subtle effect is particularly important because of widespread presence of nonadsorbed polymer in colloidal systems including biological colloids such as liposomes, vesicles, and cells.[4,5]

Although depletion interactions were recognized since long ago,[6,7] the mechanism of depletion stabilization remains a subject of some debate.[3,8] It was analyzed theoretically either for models treating the polymers as hard or soft spheres,[9,10] or as rigid rods.[11] As for flexible polymers, their stabilizing effect was studied mostly using numerical approaches.[12,19,20,2]

In this paper we present a rather simple and general theoretical approach providing an asymptotically exact framework for studying depletion stabilization effects in semidilute solutions of flexible and semiflexible polymers. We first consider the polymer-induced (PI) interactions between inert solid walls (no specific polymer/solid forces); the theory is then generalized to allow for adsorption of end groups, and is further generalized for polydisperse chains. The results may aid to establish which physical and chemical conditions (polymer concentration, molecular weight, rigidity etc.) are optimal for polymeric stabilization of a particular colloidal system.

2. The Free Energy

Polymer chains in the bulk (outside colloidal particles) may be isolated (dilute polymer solution) or overlapping (semidilute solution). We focus on the latter regime. More specifically, we consider effective interaction between flat solid plates in a semidilute polymer solution at the distance $h \ll R$, where R is the coil size ($R^2 = 6a^2N$ is the mean-square end-to-end distance, $N \gg 1$ is the number of units per chain, $a_s = a\sqrt{6}$ is the polymer statistical segment). The interaction between spherical particles can be obtained from the flat-plate potentials by means of the Derjagin procedure. The classical theories, based on the ground-state dominance approximation,[13,14,2] predict attraction of plates for $h \sim \zeta$ and no (exponentially weak) interaction at $h \gg \zeta$, where ζ is the correlation length of concentration fluctuations in the bulk ($\zeta \ll R$ in the semidilute regime).

Generally, the interaction energy can be obtained by minimization of the effective free energy $F_{tot} = F_{tot}[c]$ as a functional of the concentration profile $c = c(x)$ (c is the concentration of monomer units). The classical models involve local $F_{tot}[c] = \int f_{tot}\, dx$; that is why these models do not yield any long-range interactions (for $h \gg \zeta$). Below we focus on the marginal solvent regime where $f_{tot} = f_{int} + f_{conf}$, $f_{int} \simeq (v/2)c^2 + (w/6)c^3$ is the free energy of excluded-volume interactions of units, v and w are virial coefficients, and

$$f_{conf} \simeq f_{grad} \equiv \frac{a^2}{4}\frac{(\nabla c)^2}{c} \tag{1}$$

accounts for conformational restrictions imposed by the concentration profile $c = c(x)$. (The thermal energy k_BT is the energy unit here and below.) Equation 1 is valid for the continuous Gaussian chain model[33] in the ground state dominance (GSD) approximation; it can be obtained by considering an ideal chain in an external field $U(x)$ giving rise to an extra energy term $F_{ext} = \int U(x)c(x)\, dx$.[15]

Below we derive a simple and asymptotically exact general expression incorporating the main correction to the free energy on the top of the GSD approximation for $h \ll R$ (it is this correction that produces the long-range interaction effects). It is useful to treat the conformational energy more generally as a function of 2 variables: the overall monomer distribution $c(x)$ and the distribution of chain ends $\rho(x)$: $F_{conf} = F_{conf}[c,\rho]$. Note that there are 2 ends per chain of N units, so

$$\int \rho \mathrm{d}x = (2/N) \int c \mathrm{d}x \tag{2}$$

Using the Edwards−Lifshitz approach,[15] it is easy to show that

$$F_{conf}[c,\rho_{ref}] = \int \left(f_{grad} + \frac{c}{N}\ln\frac{c}{Ne}\right)\mathrm{d}x \tag{3}$$

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for $\rho = \rho_{\mathrm{ref}}(x) \equiv (2/N)c(x)$; eq 3 is exact for continuous (Gaussian) chains: either the GSD approximation or the condition $h \ll R$ are not necessary for its validity. The above Hamiltonian is local, and hence no long-range force is generated for $\rho = \rho_{\mathrm{ref}}$. Conversely, the long-range interactions are generated if $\rho \neq \rho_{\mathrm{ref}}$ as shown below.

Let us consider

$$\tilde{F}[U,\rho] = \min_{c}\,[F_{\mathrm{conf}}[c,\rho] + \int Uc\,\mathrm{d}x] \tag{4}$$

$\tilde{F}$ is the Legendre transform of $F_{\mathrm{conf}}[c]$ with ρ being a parameter (for uniqueness, we demand in addition that $c = c_0$ and $U = 0$ in the bulk). Physically $\tilde{F}$ is the free energy of a system of noninteracting (ideal) chains with a given end-distribution ρ under external field $U = U(x)$. To find $\tilde{F}$ we note that the partition function $G(x_1,x_2)$ of a single chain with ends at x_1 and x_2 is factorized (G is also called the Green function). Neglecting a correction which is exponentially small for $h \ll R$:

$$G(x_1,x_2) = \mathrm{const}\;\psi(x_1)\psi(x_2) \tag{5}$$

where ψ is related to U via the Edwards equation

$$-a^2\nabla^2\psi + U\psi = 0 \tag{6}$$

with appropriate boundary conditions: $\psi = 0$ at the walls, $\psi = 1$ in the bulk. Therefore, the chain ends are distributed independently like ideal-gas particles, with *a priori* distribution density $\propto \psi(x)$. Hence

$$\tilde{F}[U,\rho] = \mathrm{const} + \int \rho \ln\frac{\rho}{\psi}\,\mathrm{d}x = \tilde{F}[U,\rho_{\mathrm{ref}}] + F^{(1)}$$

$$F^{(1)} = \int\left[\rho\ln\frac{\rho}{\psi} - \rho_{\mathrm{ref}}\ln\frac{\rho_{\mathrm{ref}}}{\psi}\right]\mathrm{d}x \tag{7}$$

where const depends on U but not on ρ. The minimum in eq 4 corresponds to $c = c_0\psi^2$ for $\rho = \rho_{\mathrm{ref}} \equiv (2/N)c$, otherwise a correction emerges: $c^{(\min)} = c_0\psi^2 + c^{(1)}$. Physically $c^{(1)}$ is due to tail chain sections of size $\sim h$. The number of units in a tail is $g \sim h^2/a^2$, therefore $|c^{(1)}/c| \sim g/N \sim h^2/R^2 \ll 1$. Using the well-known properties of Legendre transformations we find

$$F_{\mathrm{conf}}[c,\rho] = F_{\mathrm{conf}}[c,\rho_{\mathrm{ref}}] + F^{(1)} + F^{(2)}$$

where $F^{(1)}$ is defined in eq 7 with $\psi^2 = c/c_0$

$$F^{(2)} \simeq -\frac{1}{2}\int\frac{\delta F^{(1)}}{\delta c}\,c^{(1)}\,\mathrm{d}x$$

Therefore, $|F^{(2)}/F^{(1)}| \sim |c^{(1)}/c| \ll 1$, i.e. $F^{(2)}$ can be neglected. Thus, we get using eqs 3 and 7:

$$F_{\mathrm{conf}}[c,\rho] \simeq \int\left\{\frac{a^2}{4}\frac{(\nabla c)^2}{c} + \rho\ln\rho - \frac{\rho}{2}\ln\frac{4ec}{N}\right\}\mathrm{d}x \tag{8}$$

Equation 8 does produce a long-range force because of the nonlocal additional condition 2. In fact, let us turn to the PI interaction between flat solid plates located at $x = 0$ and $x = h$. We consider 1-dimensional profiles $c(x)$, $\rho(x)$, $0 < x < h$. The free energy is $F = F_{\mathrm{int}} + F_{\mathrm{conf}} + F_{\mathrm{s}}$, where $F_{\mathrm{int}} = \int f_{\mathrm{int}}\,\mathrm{d}x$, F_{conf} is defined above, and $F_{\mathrm{s}} = \int [U_{\mathrm{s}}(x)c(x) + \varphi(x)\rho(x)]\,\mathrm{d}x$ is the surface energy (accounting for local polymer/wall interactions); $\varphi(x)$ is the wall potential acting on end monomer units, $U_{\mathrm{s}}(x)$ is the wall potential for all other units.

By virtue of a variational approach[14] the force P per unit area is related to the concentrations $c = c_{\mathrm{m}}$ and $\rho = \rho_{\mathrm{m}}$ at $x = h/2$: $P = P_{\mathrm{gs}} + P_{\mathrm{e}}$, where $P_{\mathrm{gs}} = -f_{\mathrm{int}}(c_{\mathrm{m}}) + \mu_0 c_{\mathrm{m}} - \Pi_0$ and $P_{\mathrm{e}} \simeq \rho_{\mathrm{m}} - \rho_0 - \rho_0 \ln \rho_{\mathrm{m}}/\rho_0$ for $h \gg \zeta$. ($\mu_0 = \mu(c_0)$ is the bulk chemical potential, $\mu(c) = \partial f_{\mathrm{int}}/\partial c \simeq vc + wc^2/2$, Π_0 is the bulk osmotic pressure, $\rho_0 = 2c_0/N$ is the bulk concentration of ends.) Here P_{gs} is the classical force obtained in the GSD approximation; P_{gs} corresponds to depletion attraction:[14] $P_{\mathrm{gs}} < 0$ since $c_{\mathrm{m}} \neq c_0$. On the other hand, P_{e} is due to the ρ-dependent free energy terms; it represents the polymer-end induced *repulsion*: $P_{\mathrm{e}} > 0$ if $\rho_{\mathrm{m}} \neq \rho_0$. In the examples considered below, $\rho_{\mathrm{m}} < \rho_0$, so the repulsion is due to *depletion* of *end*-units in the middle of the gap between the walls.

Minimization of F with respect to ρ (with the additional condition 2) yields

$$\rho(x) = \mathrm{const}\,\sqrt{c(x)}\,\mathrm{e}^{-\varphi(x)}$$

The profile $c(x)$ is just weakly affected by the end effects (since $c^{(1)} \ll c_0$, where $c^{(1)}$ is defined just below eq 7), so $c(x)$ involved in the above equation can be obtained using the ground-state dominance approximation: $c(x) \simeq c_0\psi(x)^2$ (here ψ (x) is defined by eq 6 with $U = U_s + U_{\mathrm{int}}$, where $U_{\mathrm{int}} = \delta F_{\mathrm{int}}/\delta c(x)) = \mu(c) - \mu_0$; this equation can be obtained by minimization of F, neglecting the end-correction terms in F_{conf}). Hence

$$\rho(x) \simeq \mathrm{const}\;\psi(x)\mathrm{e}^{-\varphi(x)} \simeq \rho_{\mathrm{m}}\psi(x)\mathrm{e}^{-\varphi(x)}$$

Thus, both $c(x)$ and $\rho(x)$ must be nearly constant in the region outside the ζ layers near the walls (we always assume that $h \gg \zeta$ and that the range of polymer/wall interactions is $r_{\mathrm{e}} \lesssim \zeta$); this "flat" region takes the lion's share of the gap between the walls. More precisely, $c(x) \simeq c_{\mathrm{m}} \simeq c_0$ and $\rho(x) \simeq \rho_{\mathrm{m}}$ for $x \gg \zeta$ and $h - x \gg \zeta$ ($c_{\mathrm{m}} \simeq c_0$ since $\mu(c_{\mathrm{m}}) \simeq \mu_0$ due to the equilibrium between the chains in the gap and in the reservoir outside it, where concentration is $c = c_0$).

Consider the integral $J = \int_0^h [\rho(x)/\rho_{\mathrm{m}} - c(x)/c_0]\,\mathrm{d}x$. It can be represented as a sum of three terms $J = J_1 + J_2 + J_3$ corresponding to the regions $(0,\Lambda)$, $(\Lambda,h - \Lambda)$ and $(h - \Lambda,h)$, respectively. (The length Λ is such that $\zeta \ll \Lambda \ll h$.) The middle term $J_2 \simeq 0$ since $\rho \to \rho_{\mathrm{m}}$ and $c \to c_0$ in the middle region. The other two terms, J_1 and J_3, must be equal: $J_1 = J_3 \simeq \Delta_{\mathrm{e}}$, where

$$\Delta_{\mathrm{e}} = \int_0^{\Lambda}(\psi\mathrm{e}^{-\varphi} - \psi^2)\,\mathrm{d}x \tag{9}$$

On the other hand, on using eq 2 the integral J reduces to

$$J = (\rho_0/\rho_{\mathrm{m}} - 1)\int_0^h\frac{c(x)}{c_0}\,\mathrm{d}x \simeq (\rho_0/\rho_{\mathrm{m}} - 1)h$$

Therefore, $(\rho_0/\rho_{\mathrm{m}} - 1)h \simeq 2\Delta_{\mathrm{e}}$, and

$$\rho_{\mathrm{m}} \simeq \rho_0\frac{h}{h + 2\Delta_{\mathrm{e}}} \tag{10}$$

for $h \gg \zeta$. Note that Δ_{e}, eq 9, defines the effective *single-wall excess* of end points for the case of the semiinfinite system ($0 < x < \infty$) with single wall at $x = 0$: this case formally corresponds to $h \to \infty$, so $\rho_{\mathrm{m}} \to \rho_0$ and $\Delta_{\mathrm{e}} \simeq \int_0^{\Lambda}(\rho(x)/\rho_0 - c(x)/c_0)\,\mathrm{d}x$; here, for consistency, we must demand $\zeta \ll \Lambda \ll R$.

The repulsion energy per unit area of the plates for $\zeta \ll h \ll R$ is

$$W_e = \int_h^\infty P_e \, dx = \frac{2c_0}{N}\left[2\Delta_e - h \ln\left(1 + \frac{2\Delta_e}{h}\right)\right] \qquad (11)$$

This result can be generalized to lift the condition $h \ll R$.

Note that the interaction energy W_e depends on the surface/monomer interactions via the parameter Δ_e defined in eq 9. This feature holds true also in the general case, for large separations, $h \gtrsim R$. To see this consider the system of non-interacting chains in the presence of external fields: $U = U(x)$ acting on each monomer and $\varphi = \varphi(x)$ acting on end monomers only. More precisely, we consider $\mathcal{N}$ polymer chains in the gap between solid walls at $x = 0$ and $x = h$, $h \gg \zeta$; the presence of the walls is accounted for by the field U. The free energy of the system is

$$\mathscr{F}[U,\varphi] = \min_{c,\rho}\,[F_{\text{conf}}\ [c,\rho] + \int Uc\,dx + \varphi\rho\, dx]$$

(Thus, $\mathscr{F}$ is essentially the Legendre transform of $\tilde{F}$ with respect to ρ.) If $\varphi(x) = \varphi_{\text{ref}}(x) \equiv -\ln \psi(x)$, where $\psi(x)$ is defined in eq 6, then $c = c_0\psi^2$, $\rho = 2/N\, c$, and F_{conf} is given by eq 3. In this case the single chain partition function is $Z = Z_{\text{ref}} \equiv \int \psi^2(x)\, dx = N\mathcal{N}/c_0$, and $\mathscr{F} = -\ln Z^{\mathcal{N}}/\mathcal{N}!)$ is just proportional to the number of chains $\mathcal{N} \propto \int c dx$:

$$\mathscr{F}[U,\varphi_{\text{ref}}] = \frac{1}{N} \ln \frac{c_0}{Ne} \int c dx \qquad (12)$$

In the general case $\varphi \neq \varphi_{\text{ref}}$, the free energy $\mathscr{F}$ is

$$\mathscr{F}[U,\varphi] = \mathscr{F}[U,\varphi_{\text{ref}}] - \mathcal{N} \ln(Z/Z_{\text{ref}}) \qquad (13)$$

where $Z = \int G(x,x')\, dx\, dx'$, $G(x,x')$ is the Green function in the presence of $\varphi(x)$, and $Z_{\text{ref}} = \int G_{\text{ref}}(x,x')\, dx\, dx' = N\mathcal{N}/c_0$ with $G_{\text{ref}}(x,x')$, the Green function for the reference end-potential $\varphi_{\text{ref}}(x)$. Obviously $G(x,x') = K(x)K(x')G_{\text{ref}}(x,x')$, where $K(x) = e^{-\varphi(x)+\varphi_{\text{ref}}(x)} = e^{-\varphi(x)}/\psi(x)$. Hence $\Delta Z \equiv Z - Z_{\text{ref}}$ can be represented as $\Delta Z = \Delta Z_1 + \Delta Z_2$, where $\Delta Z_1 = 2 \int k(x)G_{\text{ref}}(x,x')\, dx\, dx'$, $\Delta Z_2 = \int k(x)k(x')G_{\text{ref}}(x,x')\, dx\, dx'$, $k(x) = K(x) - 1$. Recall that $\psi \simeq 1$ away from the surfaces, and that both fields φ and U vanish there (at monomer/surface distances exceeding Λ, $\zeta \ll \Lambda \ll h$). Therefore, $k(x)$ is localized in these Λ layers. Hence ΔZ is dominated by the first term ΔZ_1 which is proportional to the probability that one chain end is in a Λ layer (while ΔZ_2 is proportional to the probability that *both* chain ends are in Λ layers). Taking into account that $\int G_{\text{ref}}(x,x')\, dx' = e^{-2\varphi_{\text{ref}}(x)} = \psi(x)^2$

$$\Delta Z \simeq \Delta Z_1 = 2 \int (\psi e^{-\varphi} - \psi^2)\, dx \simeq 2(2\Delta_e)$$

where Δ_e is defined in eq 9 (the additional factor 2 accounts for two Λ layers near the two surfaces).

Thus, the first-order correction ΔZ_1 is proportional to Δ_e. In a similar manner one can show that the second-order correction, ΔZ_2, is proportional to Δ_e^2. Therefore, for $h \gg \zeta$ the effect of surface potentials $\varphi(x)$, $U(x)$ on the free energy is absorbed in the integral quantity Δ_e. In other words, the PI interaction between the surfaces (note that this interaction is generated by the second term in eq 13: the first term defined in eq 12 is essentially local) is the same for different surface potentials provided Δ_e is the same. This means that the PI interaction for $\Delta_e \ll R$ and $h \sim R$ can be obtained in the following way: (1) keeping Δ_e constant change the surface potentials in such a way that ρ/ρ_0 and c/c_0 are close to 1 everywhere (by making the surface potentials weaker but somewhat more long-range; the resultant potentials are still localized if $\Delta_e \ll h$); (2) apply the perturbation approach (RPA) to calculate the free energy (see ref 16). The result is

$$W_e \simeq \frac{4c_0{\Delta_e}^2}{Nh} H(h/R), \quad h \gg \Delta_e \qquad (14)$$

where $H(z) = \tilde{\sum}_{n=-\infty}^{\infty} f(2\pi^2n^2/3z^2)$, $f(u) \equiv (1 - e^{-u}(1 + u))/(u - 1 + e^{-u})$ and $\tilde{\sum}$ is a regularized sum.[25] Exactly the same result can be obtained by a slight generalization of the rigorous (but more lengthy) approach proposed in ref.[17] Combining eq 11 valid for $h \ll R$ and eq 14 valid for $h \gg \Delta_e$ (and taking into account that $H(z) \simeq 1$ for $z \ll 1$) we get the long-range interaction energy for any $h \gg \zeta$ (if $\Delta_e \ll R$):

$$W_e \simeq \frac{2c_0}{N}\left[2\Delta_e - h \ln\left(1 + \frac{2\Delta_e}{h}\right)\right] H(h/R) \qquad (15)$$

Note that the range of $W_e(h)$ is $\sim R$; this long-range effect was originally predicted in ref 17 and was recently qualitatively confirmed by simulations.[18]

3. Results and Discussion

Let us consider a few characteristic examples.

Case 1. Nonadsorbing (Repulsive) Walls in Semidilute Solution. In this case $F_s = 0$ and the wall effect is accounted for by the boundary conditions $c(0) = c(h) = 0$. Δ_e is defined in eq 9 with $c/c_0 = \psi^2$, $\rho/\rho_0 = \psi$, where $\psi = \psi(x)$ is defined by the Edwards eq 6 with $U = \mu(c) - \mu_0$. (In the mean-field approximation the formal external field U is replaced by the total potential of a monomer unit including both the surface potential $U_s(x)$ and the mean molecular potential $U_{\text{int}}(x)$ due to interactions with surrounding monomer units. In the present case $U_s = 0$ for $x > 0$ and $U_{\text{int}} = \mu(c) - \mu_0$.) Thus, we get

$$\Delta_e = \frac{\sqrt{6}a}{\sqrt{wc_0}} I\left(2 + \frac{3v}{wc_0}\right) \qquad (16)$$

$I(\alpha) \equiv (1 - 1/(\sqrt{1+\alpha}))\ln(1 + \sqrt{1+\alpha})/\sqrt{\alpha} - \ln 2/(\sqrt{1+\alpha}) + 2/(\sqrt{1+\alpha})\ln(\sqrt{1+\alpha} + 1 - \sqrt{\alpha})$. Noting that $\Delta_e \sim \zeta \ll h$, where

$$\xi \simeq a/\sqrt{2c_0(v + wc_0)} \qquad (17)$$

we simplify eq 11 to yield $W_e \simeq 4c_0\Delta_e^2/(Nh)$, $\zeta \ll h \ll R$, in agreement with the theory[17] based on a different approach.

The ground-state attraction energy is[14] $W_{gs} = \int_h^\infty P_{gs}\, dx \sim -c_0^2 v\zeta e^{-h/\xi}$. The total interaction $W = W_{gs} + W_e$ is attractive for $h < h^*$ and is repulsive for $h > h^*$, showing a maximum $W^* = W(h^*)$.

The predicted $W(h)$ can be quantitatively compared with the numerical results of Scheutjens and Fleer (SF)[19,20] for an athermal system with $N = 100$, $w = v^2$, $\phi = c_0v = 0.1$ and purely repulsive walls. In this case

$$W_{gs} \approx -32v\xi {c_0}^2 e^{-h/\xi} \qquad (18)$$

and W_e is defined in eq 14 where $\Delta_e \approx \sqrt{2}\,(1 - \ln 2)a/\sqrt{\phi}$ follows from eq 16 for $wc_0/v \ll 1$. The ground-state energy W_{gs} sensitively depends on the correlation length ζ. The calculations in refs 19 and 20 were performed on a hexagonal lattice (with lattice parameter = 1). Equation 17 is valid for the continuous model considered in the present paper; it yields $\zeta \approx 0.9$, i.e. ζ is smaller than the lattice parameter. In this case we expect a significant effect of the lattice on the correlation

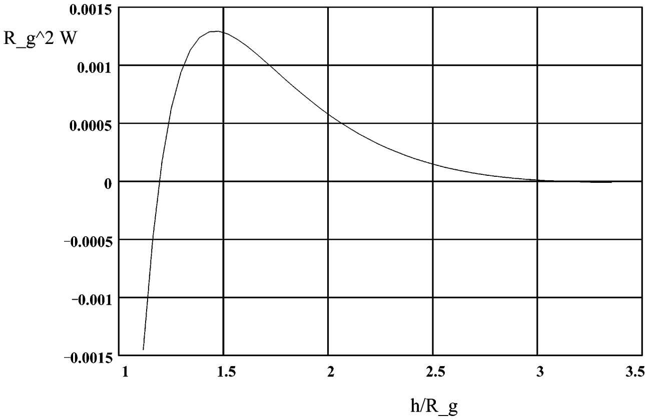

Figure 1. Dependence of the reduced interaction energy WR_g^2 vs reduced wall separation h/R_g for athermal system with $N = 100$, $\phi = 0.1$.

length ζ (an analysis shows that ζ must be smaller in the lattice case). Therefore, we treat ζ as a fitting parameter. Demanding that the maximum W^* equals to the value $W^* \approx 0.0013/R_g^2$ obtained in refs[19,20] (see the curve marked '0.1' in Figure 7b of ref 20; R_g is polymer chain gyration radius; note that $W \approx (2/\sqrt{3})\Delta f_p/(k_BT)$ where Δf_p is the free energy of interaction per surface site as calculated in refs 19 and 20), we get $\zeta = 0.70$ in a reasonable agreement with the "continuous" eq 17. The dependence of the reduced energy $WR_g^2 = (W_{gs} + W_e)R_g^2$ on h/R_g for $\zeta = 0.70$ is shown in Figure 1. The shape of the interaction curve is similar to the dependence shown in Figure 7b of ref 20. A good agreement is also found for the position of the maximum h^*: $h^*/R_g \approx 1.47$ (the present theory) and $h^*/R_g \approx 1.58$.[20] Concerning the latter result, note that $h = \sqrt{2/3}\,M$, where M is the number of lattice layers between the walls.

The maximum W^* defines the potential barrier that may prevent coagulation of solid particles (imparting their kinetic stabilization). Asymptotically (for $R \gg \zeta$)

$$h^* \simeq \xi \ln \frac{Na^2}{\xi^2},\ W^* \simeq \frac{24\sqrt{2}a}{N\sqrt{w}} \sqrt{1 + \frac{v}{wc_0} \frac{I^2(2 + 3v/wc_0)}{\ln(Na^2/\xi^2)}} \tag{19}$$

The barrier W^* is increasing with concentration for low c_0, reaches a maximum

$$W^* \simeq \frac{1.31a}{N\sqrt{w}\ln(Nv^2/w)},\ h^* \simeq \frac{8\sqrt{wa}}{3\sqrt{2}v}$$

at an optimum concentration $c_0 = c^* \simeq (3/8)(v/w)\ln(Nv^2/w)$ and decreases at high c_0. Thus, as c_0 increases, a colloidal dispersion may change from instability to stability, and then possibly to instability again. Such effect of added free polymer to naked colloidal particles was indeed observed.[2,21]

Thus, we distinguish two contributions in the PI interactions between colloidal particles: a short-range depletion attraction (accounted for by W_{gs}) and long-range depletion repulsion (W_e). The concentration dependence of W_{gs} is mainly defined by the exponential factor (see eq 18): the magnitude of W_{gs} decreases with c_0 following a decrease of the correlation length ζ. Conversely, the depletion repulsion becomes stronger with c_0 in a certain concentration range. As a result a colloid system may gain stability on increasing concentration. A similar restabilization effect[2] was predicted in the case of sterically stabilized colloids.[26,27] The important difference is that in the latter case the steric repulsion *decreases* with polymer concentration, so the restabilization is solely due to (a faster) weakening of depletion attraction.

A similar stabilization effect was found also in many simulation studies.[28−32] Unfortunately a quantitative comparison of the present theory with the simulation results is not possible as the simulated regimes do not match the theoretical conditions (small colloidal particles whose diameter is smaller than the chain size were considered in ref 28; other studies deal with concentrated solution, $\phi 0.5$,[29,30] and/or with short chains, $N \sim 20$[31,32]).

It is convenient to characterize the repulsion by the reduced non-dimensional barrier $\tilde{W} = Wh^2$. Note that the stabilization is possible if the repulsion is stronger than the van-der-Waals attraction, i.e., if $\tilde{W}A_H/12\pi$, where A_H is the relevant Hamaker constant (in k_BT units). The reduced barrier at $c_0 = c^*$, $h = h^*$ is

$$\tilde{W} \simeq \frac{4.66}{\ln(Nv^2/w)} \frac{a^3\sqrt{w}}{v^2N} \tag{20}$$

Therefore, the effective depletion interaction is stronger for more rigid chains (with longer a). This conclusion is in agreement with a series of experimental and theoretical results.[7,2,22] The theory can be *qualitatively* applied to a solution of rigid rods (of length L, diameter d, $L \gg d$) corresponding to $N = 1$, $a \sim L$, $v \sim L^2d$. Equation 19 with these parameters yields $W^* \sim 1/Ld$ for $c_0 \sim 1/v$. The scaling behavior of W^* agrees with the predictions[11] for the depletion potential in a solution of rigid rods at this c_0.

It is also interesting that the reduced barrier $\tilde{W}$ increases as the solvent quality (characterized by v) is decreased, i.e., as Θ-conditions for polymer chains are approached. This is in a *qualitative* agreement with numerical results[19,20] for concentration $\phi = 0.2$.

Case 2. Chains with Reversibly Adsorbing Ends. We consider the same system as before, but now end groups are attracted to solid surfaces. This interaction is described by the local potential $\varphi(x)$, x is the end/surface distance; $\varphi(x) < 0$ for $0 < x < r_e$, where $r_e \ll \zeta$ is the attraction range. Thus, the surface energy $F_s = \int \varphi(x)\rho(x)\,dx$; hence, $\rho/\rho_0 = \psi e^{-\varphi}$ and $\Delta_e = \Delta_{e0} + \Delta_{e1}$, where Δ_{e0} is defined in eq 16 and

$$\Delta_{e1} = \int_0^{r_e} (e^{-\varphi} - 1)\psi dx \simeq Q\psi'(0),$$

$$Q \equiv \int_0^{r_e} (e^{-\varphi} - 1)x\,dx \tag{21}$$

The effect of end-attraction is significant if $Q \gg \zeta^2$. In this case $\Delta_{e1} \gg \Delta_{e0}$, i.e. $\Delta_e \simeq Q\psi'(0)$. The function $\psi(x)$ is the same as in the previous case, $\psi'(0) \sim 1/\zeta$, more precisely

$$\psi'(0) \simeq \frac{1}{a}\sqrt{vc_0/2 + wc_0^{\,2}/3}$$

The energy of long-range repulsion W_e is defined in eq 15. The repulsion force is

$$P_e = -\frac{\partial W_e}{\partial h} = \frac{2c_0}{N}\left[\ln\left(1 + \frac{2\Delta_e}{h}\right) - \frac{2\Delta_e}{h + 2\Delta_e}\right] \tag{22}$$

For $h \ll \Delta_e$ (this condition was implied, although not stated explicitly, in ref 23), this gives

$$P_e \simeq \frac{2c_0}{N}\ln\left(\frac{2}{e}\frac{\Delta_e}{h}\right) \tag{23}$$

The force between surfaces induced by weakly end-adsorbed polymers was calculated in ref 23. The analytical result was as follows:[23] $P_e \approx c_0\,\epsilon/N$, where ϵ is the end-adsorption energy. On the other hand, eq 23 yields (in the logarithmic approximation and for $r_e \sim \zeta$):

$$P_e \simeq \frac{2c_0}{N}\left(\epsilon + \ln\frac{r_e}{h}\right) \tag{24}$$

(note that $\varphi(x) = -\epsilon$ for $x < r_e$; hence, $\Delta_e \simeq e^{\epsilon} r_e^2/\zeta$ since $\Delta_e \simeq Q\psi'(0)$, $\psi'(0) \sim 1/\zeta$ and $Q \sim e^{\epsilon} r_e^2$; see the second eq 21). Thus, the c_0, N, and ϵ dependencies of P_e obtained in ref 23 are in agreement with eq 24. The prefactor of 2 in eq 24 accounts for the difference between the models considered here (2 adsorbing ends per chain) and in ref 23 (just one adsorbing end). The important difference however is due to the log-term in eq 24: the force depends on h as $\ln(1/h)$. The distance-dependent log-term was missing in ref 23 due to approximations involved. Thus, the force P_e *increases* at smaller separations, in qualitative agreement with numerical results shown in Figure 3 of ref 23.

The physical meaning of eq 24 is simple. The total number of chain ends in the gap is $2c_0h/N$; nearly all of them are adsorbed (for $h \ll \Delta_e$); the adsorption energy $-2\epsilon c_0h/N$ is decreasing with h giving rise to the repulsive force $2\epsilon c_0/N$ (the first term in eq 24). Next, we recall that the adsorption implies that the chain ends are localized near the walls. The entropy loss due to the localization is $\sim\ln(r_e/h)$ per chain end; it gives rise to the second contribution in eq 24.

A similar physical interpretation of the repulsion energy W_e holds true also in the general case: W_e is largely due to the entropy of *redistribution* of chain ends in the gap between the walls. At large separations, the end excess at one wall is proportional to $\Delta_e\rho_0$. At separations $h \sim \Delta_e$, the total number of chain ends is comparable with $\Delta_e\rho_0$, so the concentration of ends must be considerably reduced in the midzone between the surfaces (outside the r_e regions where monomer units directly interact with the walls). The entropy cost of the resultant considerably nonuniform end-distribution provides a positive contribution to W_e, thus generating the repulsive interaction.

As $\Delta_e \gg \zeta$, the maximum of the total energy $W = W_{gs} + W_e$ is attained at $h \ll \Delta_e$. The height of the repulsion barrier is

$$W^* \simeq \frac{4c_0\Delta_e}{N} \simeq \frac{4c_0}{N}\frac{Q}{a}\sqrt{vc_0/2 + wc_0^2/3} \tag{25}$$

Obviously, W^* increases with concentration c_0 and with solvent quality v. Equation 25 is valid if $\Delta_e \ll R = \sqrt{6}\,aN^{1/2}$ corresponding to the regime of weakly deformed coils as opposed to the polymer brush regime of strongly stretched chains. For $\Delta_e \sim h \sim aN^{1/2}$ the reduced barrier $\tilde{W} = Wh^2 \sim 4c_0a^3N^{1/2}$. In particular, for semirigid chains of diameter d with Kuhn segment l and contour length $L = Nl$ at $c_0 \sim 4/l^2d$: $\tilde{W} \sim l/d\ N^{1/2}$. The repulsion dominates over the van der Waals attraction if $\tilde{W} \gtrsim A_H/12\pi$. This condition can be easily satisfied for $l \gg d$ (high stiffness) and moderate N. For example, the Hamaker constant $A_H \sim 1$ (in k_BT units) for latex particles (see ref 2, p 6), so $A_H/(12\pi) \sim 0.03$. On the other hand, typically $l/d = 5$ even for flexible polymers, so with $N \sim 100$ we get $\tilde{W} \sim l/d\ N^{1/2} \sim 50$. Therefore, $\tilde{W} \gg A_H/(12\pi)$ in this case: the van der Waals attraction is indeed dominated by the repulsion.

To further demonstrate that the depletion stabilization effect can be significant, let us consider interaction of two colloidal particles of diameter D. Using the Derjagin approximation and eq 15 we get the height of the depletion repulsion energy barrier U_s^*:

$$U_s^*/k_BT \simeq 2\pi D(c_0/N)\Delta_e^2(\ln(R/\Delta_e) - 1.43)$$

On setting, for example, $\Delta_e = 0.1R$, this equation simplifies as $U_s^*/k_BT \sim 0.05\phi D a_s^2/v_0$, where $\phi = c_0v_0$ is polymer volume fraction, $a_s = \sqrt{6}a$, the statistical segment, v_0, monomer volume. For $\phi = 0.2$ and for the typical values $a_s \sim 1$ nm, $v_0 \sim 0.1$ nm^3, and $D \sim 200$ nm, the barrier amounts to $U_s^* \sim 20k_BT$; i.e. it is high enough.

Case 3. Polydisperse Chains. We now take up the assumption of monodispersity. The number fraction of chains of length n (n chains) in the bulk is $p(n)$, $\sum_{n=1}^{\infty} p(n) = 1$, $N = \sum np(n)$ is the *number-average* polymerization degree. In the polydisperse case, shorter chains tend to preferentially accumulate in the slit in order to increase concentration of chain ends there as the ends benefit from interactions with the walls.

We first consider the reference system with surface potential $\varphi(x) = \varphi_{ref}(x) = -\ln\psi(x)$. In this case the ends of all chains are distributed in the same way: the partial concentration of ends of n-chains is $\rho_n(x) = (2/N)c(x)p(n)$. The number of chains in the slit between the plates (per unit area) is

$$\mathcal{N}_n = \frac{c_0}{N}h_{eff}p(n) = z_nh_{eff} \tag{26}$$

Here $z_n = (c_0/N)p(n)$ is concentration of n chains in the bulk reservoir outside the gap, and h_{eff} is the effective distance between the plates:

$$h_{eff} = \frac{1}{c_0}\int c(x)\,dx$$

where the integral is taken over the gap between the plates. The "eff" subscript is omitted in what follows. Note the obvious normalization condition:

$$\sum_n nz_n = c_0 \tag{27}$$

Alternatively, $\mathcal{N}_n$ can be formally obtained by minimization of the thermodynamic potential

$$\Omega = F\{\mathcal{N}_n\} - \sum_n \mathcal{N}_n \ln z_n \tag{28}$$

where $F\{\mathcal{N}_n\}$ is the free energy of the chains in the gap as a function of the chain numbers there, $\{\mathcal{N}_n\} = \{\mathcal{N}_1, \mathcal{N}_2, ...\}$; the bulk concentrations of n -chains define their activities z_n. The minimization of Ω must be performed keeping the total number of monomers in the slit constant:

$$\sum_n n\mathcal{N}_n = hc_0 = \text{const} \tag{29}$$

Next we allow for an *arbitrary* surface potential $\varphi(x)$ localized in the r_e regions near the walls ($r_e \lesssim \zeta$). A variation $\delta\varphi(x)$ of the potential results in the free energy increment $\delta F = \int \rho(x)\delta\varphi(x)\,dx$, where $\rho(x) = \sum_n \rho_n$ is the total concentration of chain ends. $\rho(x)$ is affected by the field $\varphi(x)$: $\rho(x) \simeq \rho_m\psi(x)e^{-\varphi(x)}$ where $\rho_m \simeq 2\mathcal{N}/(h + 2\Delta_e)$ is the concentration of ends far from the walls (see equation on the line just above eq 9) and $\mathcal{N} = \sum_n \mathcal{N}_n$ is the total number of chains in the gap. Using eq 9 we find: $\int \psi e^{-\varphi}\delta\varphi\,dx = -2\delta\Delta_e$, where $\delta\Delta_e$ is the variation of Δ_e. Therefore

$$\delta F \simeq -2\,\frac{2\mathcal{N}}{h+2\Delta_{\mathrm{e}}}\,\delta\Delta_{\mathrm{e}}$$

Integrating we find

$$F = F_{\mathrm{ref}} - 2\mathcal{N}\ln\left(1+\frac{2\Delta_{\mathrm{e}}}{h}\right) \tag{30}$$

Minimization of Ω, eq 28, with F, eq 30, under the condition, eq 29, is *equivalent* to minimization of $\Omega_{\mathrm{ref}} = F_{\mathrm{ref}}\{\mathcal{N}_n\} - \sum_n \mathcal{N}_n \ln z_n$ with *renormalized* z_n:

$$z_n = \frac{c_0}{N}\,p(n)\mathrm{e}^{A}\mathrm{e}^{-\mu n},\ A \equiv 2\ln\left(1+\frac{2\Delta_{\mathrm{e}}}{h}\right) \tag{31}$$

Here μ is an arbitrary constant which accounts for the condition 29; μ is chosen in order to satisfy the normalization condition 27:

$$\frac{1}{N}\,\mathrm{e}^{A}\sum_n np(n)\mathrm{e}^{-\mu n} = 1 \tag{32}$$

This Ω_{ref} formally corresponds to the reference system with number concentrations of n-chains in the bulk reservoir equal to z_n, eq 31. Hence the result of minimization of Ω must be defined by eq 26 with this z_n:

$$\mathcal{N}_n = hz_n \tag{33}$$

Using eqs 33 and 31, we get the total number of chains in the gap

$$\mathcal{N} = \sum_n \mathcal{N}_{\mathrm{n}} = \frac{hc_0}{N}\,\mathrm{e}^{A}\Phi(\mu) = hc_0\,\frac{\Phi(\mu)}{\Phi_1(\mu)} \tag{34}$$

where $\Phi(\mu) = \sum_n p(n)\mathrm{e}^{-\mu n}$, $\Phi_1(\mu) = -\mathrm{d}\Phi/\mathrm{d}\mu$, and μ is defined by the normalization condition 32 which can be rewritten as

$$\Phi_1(\mu) = N\mathrm{e}^{-A} = N\left(1+\frac{2\Delta_{\mathrm{e}}}{h}\right)^{-2} \tag{35}$$

The number-average chain length in the slit is

$$\tilde{N} = \frac{1}{\mathcal{N}}\sum_n n\mathcal{N}_{\mathrm{n}} = \frac{\Phi_1(\mu)}{\Phi(\mu)}$$

$\tilde{N}$ is different from (smaller than) the analogous number in the surrounding bulk reservoir: $\tilde{N} < N$ since $\mu > 0$ (for clarity, it is assumed that $\varphi(x)$ corresponds to attraction of chain ends to the walls, $\Delta_{\mathrm{e}} > 0$).

Returning to the free energy, we note that a variation of the surface potential $\varphi(x)$ induces a variation δA of the parameter A defined in eq 31; the corresponding free energy variation is $\delta F = -\mathcal{N}\delta A$ (see eq 30). According to the theorem on small variations $\delta\Omega = \delta F$. Using eq 34, 35 we thus obtain

$$\delta\Omega = -\mathcal{N}\delta A = hc_0\,\frac{\Phi}{\Phi_1^{\,2}}\,\delta\Phi_1$$

Integrating the last expression, we find

$$\Omega = \mathrm{const} - hc_0\left(\frac{\Phi(\mu)}{\Phi_1(\mu)} + \mu - \frac{1}{N}\right)$$

where μ is related to Δ_{e} via eq 35, and const $= \Omega_{\mathrm{ref}}$ does not depend either on μ or on h. The end-induced long-range (repulsion) energy is therefore

$$W_{\mathrm{e}} = \Omega_{|h} - \Omega_{|h=\infty} = \frac{4c_0\Delta_{\mathrm{e}}}{N} - hc_0\left(\frac{\Phi(\mu)}{\Phi_1(\mu)} + \mu - \frac{1}{N}\right) \tag{36}$$

The above equation is valid for $\zeta \ll h \ll R$ and $\Delta_{\mathrm{e}} \ll R$. For the monodisperse case ($p(n) = \delta(n - N)$) the above equation is equivalent to eq 11. For the Schultz−Zimm distribution $p(n) = \mathrm{const}\ n^{1/\delta-1}\mathrm{e}^{-n/(N\delta)}$, where $\delta = N_{\mathrm{w}}/N - 1$ is the polydispersity degree, we get

$$W_{\mathrm{e}} \simeq \frac{4c_0}{N}\,\Delta_{\mathrm{e}}g\left(\frac{h}{2\Delta_{\mathrm{e}}},\delta\right),$$

$$g(y,\delta) = 1 - \frac{1+\delta}{2\delta}\,y\left[\left(1+\frac{1}{y}\right)^{2\delta/(1+\delta)} - 1\right]$$

For $\delta < 1$ the function $g(y, \delta)$ monotonically decreases with both δ and y (from $g = 1$ at $y = 0$ to $g = 0$ at $y = \infty$). The repulsion force between spherical particles is proportional to W_{e} which decreases with δ, hence the potential barrier preventing their coagulation reduces for higher polydispersity. A similar effect was predicted earlier for solutions of polydisperse beads.[24] Note that the stabilization barrier disappears completely for $\delta \geq 1$. In particular, there is no long-range force ($W_{\mathrm{e}} \equiv 0$) for the Flory distribution $p(n) = \mathrm{const}\ \mathrm{e}^{-n/N}$ corresponding to $\delta = 1$.

The predicted end-induced repulsion W_{e} can be compared with the fluctuation interaction $W_{\mathrm{fl}} \simeq 1/16\pi h^2$.[25] The ratio $W_{\mathrm{e}}/W_{\mathrm{fl}} = 16\pi\tilde{W}$. Using eq 20 we get for $w \sim a^6$, $v \sim a^3/\sqrt{N}$ (i.e., for Θ-conditions): $W_{\mathrm{e}}/W_{\mathrm{fl}} \sim 100$, so the fluctuation effect is numerically small.

4. Conclusions

In summary, we develop a quantitative theory of colloid stabilization by semidilute polymers. In is shown that the interaction between two solid surfaces (colloidal particles) in a semidilute solution (the polymer coil size R is larger than the bulk correlation length ζ, $R \gg \zeta$) is a sum of two basic contributions (apart from very weak oscillations at $h > R$): a *short-range* depletion attraction (for separations $h \sim \zeta$) and a *long-range* depletion repulsion (for $\zeta \ll h \lesssim R$). The long-range interaction between solid walls is predicted to be rather universal for $\zeta \ll h \ll R$. The repulsion is related to the entropic cost of a redistribution of chain ends that tend to somewhat accumulate near the solid surfaces (even in the absence of any direct end/surface attraction). Both interactions (short-range attraction and long-range repulsion) are associated with depletion. Importantly, two distinct depletion effects are actually involved: short-range attraction is due to depletion of monomer units in the gap between the walls, while long-range repulsion is due to depletion of chain ends in the mid-region between the walls.

We analyze the effects of monomer concentration, chain stiffness, solvent quality, attraction of end groups to the solid surface and polydispersity on the end-induced repulsion. The predicted trends are in agreement with a number of experimental, simulation and analytical results.[2,3,11,17,19−24] The theory thus links together and explains the results of quite a few studies on depletion stabilization advancing the theoretical understanding of this important phenomenon. It is shown that the depletion stabilization in the semidilute regime is due to a depletion of chain *ends* in the middle of the gap between the particles. The range of the repulsion is comparable to the coil size R. The repulsion energy barrier is higher for more stiff and more monodisperse chains, and for polymers whose ends are attracted to the surface.

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(33) Real chains can be approximated by Gaussian chains at length-scales larger than monomer unit size. In the present case the relevant length-scale is ξ, it is indeed much larger than the monomer size in the semidilute regime, so the Gaussian approximation is valid.

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