Small mesoscopic particles in dilute and semidilute solutions of nonadsorbing polymers

E. Eisenriegler
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Polymer-induced interactions between two small mesoscopic particles of radius R and between a particle and a wall are investigated for dilute or semidilute embedding solutions of long flexible nonadsorbing polymer chains with radius of gyration $\mathcal{R}_g$. Asymptotically exact predictions are obtained using a ''small radius expansion,'' to express the interactions in terms of properties of the polymer solution *without* particles. The nonmonotonic dependence of the second virial coefficient B_2^{CC} of a dilute suspension of particles on the interchain overlap is discussed in detail. The magnitude of the minimum of B_2^{CC}/R^3 increases as a power law in $\mathcal{R}_g/R$. The exponent and amplitude are quite different from the earlier prediction of an integral-equation approach. For dilute polymers in two dimensions outside two circular disks in contact, exact results are given for the monomer-density depletion profile, the pressure variation along the perimeter of, and the polymer-induced force between the two disks. © *2000 American Institute of Physics.* [S0021-9606(00)50536-4]

I. INTRODUCTION

Colloidal particles embedded in a solution of nonadsorbing polymer chains experience a depletion interaction. For entropic reasons the chains avoid the space between two close particles, leading to an unbalanced pressure from outside which pushes the two particles towards each other. This mechanism is believed to be important for a variety of interesting colloids such as casein micelles,[1] red blood cells,[2] and globular proteins.[3]

Consider spherical particles of mesoscopic size dissolved in extreme dilution in a monodisperse solution of long flexible nonadsorbing polymer chains in a good solvent. On mesoscopic length scales and disregarding long range forces[4] the system is equivalent to a model containing only particles and chains in which the interactions both between a chain-monomer and a particle and between two chain-monomers (belonging to the same or to different chains) are of pure excluded volume type.[5,6] The polymer-induced depletion interaction between the particles has a rich structure which depends on the ratio of the particle and chain sizes[7] and on the degree of overlap between the chains, i.e., on whether the polymer solution is dilute or semidilute.[8]

For large particle size the depletion interaction closely resembles that for planar walls.[9,10] Here the focus is on *small* spherical particles whose radius R, though large on a microscopic scale, is much smaller than the radius of gyration $\mathcal{R}_g$ of an isolated chain in the dilute solution or the Edwards screening length (or ''blob'' size)[5,6] ξ in the semidilute solution. At a first glance the small particle case looks complicated, since it is dominated by configurations in which a chain coils *around* the particle and approximations treating the chains as nondeformable[9] fail completely. Probably this is one of the reasons why previous theoretical investigations concentrated more on the case of large particles. However,

for understanding, e.g., the role of polymers such as polyethylene glycol in the precipitation and crystallization of proteins,[11] the small particle case is also of interest.[3]

Asymptotically exact results can be given for particle radius R much smaller than the other relevant mesoscopic lengths, since the particle can be viewed as a weakly repulsive point-perturbation for chain monomers. With the center of the colloidal particle at $\mathbf{r}_C$ this leads[12,13] to a reduction factor

$$W_C = 1 - A_g R^{d-1/\nu} \mathcal{R}_g^{1/\nu} \theta(\mathbf{r}_C) \tag{1.1}$$

in the Boltzmann weight for chain configurations. Here A_g is a dimensionless amplitude discussed below, d is the spatial dimension,[14] ν is the Flory exponent,[5] $\mathcal{R}_g$ is the radius of gyration of a single chain in dilute solution as introduced above, and

$$\theta(\mathbf{r}) = \sum_P \frac{1}{N} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_{P,j}) \tag{1.2}$$

is the configuration-dependent number density of chains. The sum Σ_P runs over all polymer chains P in the solution, $\mathbf{r}_{P,j}$ is the position of monomer j in chain P, and N is the number of monomers per chain. Integrating θ over a volume element $d\mathbf{r}$, the contribution of each chain P equals the fraction of its monomers which, in a given configuration of the chains, are found inside $d\mathbf{r}$. Unlike N this fraction is independent of the precise definition of the monomer. The configurational average of θ in a solution without particles equals the usual number density n of chains in the solution. The dimensionless amplitude A_g in Eq. (1.1) is universal, i.e., independent of details of the long flexible polymer chains, in the same sense as the Flory exponent ν. For chains in good solvent in $d = 3$ spatial dimensions,[15]

$$A_g \approx 18.4; \quad d = 3, \quad \text{good solvent.} \tag{1.3}$$

Equation (1.1) describes the effective repulsion of the small particle *quantitatively*. For example, the free energy F_1 it costs to insert one particle in the bulk solution takes the form[12,13]

$$\frac{F_1}{k_B T} = A_g R^{d-1/\nu} n \mathcal{R}_g^{1/\nu}, \tag{1.4}$$

where n is the number density of chains in the pure bulk solution introduced above. This result, which follows from Eqs. (1.1) and (1.2), applies for arbitrary values of the overlap[6]

$$s = n \mathcal{R}_g^d \tag{1.5}$$

between chains. In the semidilute limit in which $s \to \infty$ with the monomer density $\propto n \mathcal{R}_g^{1/\nu}$ kept fixed at some small value, the screening length ξ remains finite, and A_g provides the numerical value of the amplitude a in the result of de Gennes[16] $F_1/k_B T = a(R/\xi)^{d-1/\nu}$, since a/A_g equals the well known amplitude $\mathcal{R}_g^{1/\nu} n \xi^{d-1/\nu}$ of a semidilute bulk solution.[5,6] For the case of a good solvent in three dimensions, the exponent $d - 1/\nu$ in Eq. (1.4) equals 1.3, and F_1 decreases more rapidly with decreasing R than the prediction $F_1 \propto R$ of mean field[17] or integral equation[8] approaches.

In this paper we derive asymptotically exact results for other interesting properties of small particles dissolved in a polymer solution with arbitrary overlap s between the chains. In Sec. II we consider the polymer-induced free energy of interaction (or potential of mean force) δF_2 between two particles. For two spheres in contact we discuss in Sec. III the depletion profile of the monomer density and the local pressure which varies along the surface of the spheres. Section IV presents results for the second virial coefficient B_2^{CC} of a dilute suspension of colloidal particles. The second virial coefficient, which can be measured by light scattering, is of particular interest, since in protein suspensions its value appears to be correlated with the success of protein crystallization.[18] We make contact with the results of Chatterjee and Schweizer,[8] based on an integral equation approach for arbitrary overlap and with the results of Sear[19] for the semidilute limit. Our quantitative results confirm the qualitative behavior of the dependence of B_2^{CC} on polymer concentration with a minimum at $n(4\pi/3)\mathcal{R}_g^3 \approx 1$, as pointed out in Ref. 8. However, the dependence of the minimum value of B_2^{CC} on $\mathcal{R}_g/R$ differs significantly from Ref. 8, as discussed in Secs. IV and VI.

In Sec. V the overlap-dependence of the polymer-induced interaction of a particle with a wall is considered. Section VI contains a summary and concluding remarks.

II. POTENTIAL OF MEAN FORCE BETWEEN TWO PARTICLES

If two particles A and B are immersed in the polymer solution with their centers at $\mathbf{r}_A$ and $\mathbf{r}_B$, the Boltzmann weight of each polymer configuration is reduced by $W_A W_B$. This factor is the product of reduction factors for single particles, each of which has the form (1.1) if the particles are small, i.e., if $R \ll r_{AB}, \mathcal{R}_g, \xi$ with the center-to-center distance $r_{AB} = |\mathbf{r}_A - \mathbf{r}_B|$. The free energy F_2 of immersion of the

two particles is the difference in polymer free energy in the presence and absence of the particles, i.e., $F_2 = -k_B T \ln\langle W_A W_B \rangle$, where the angular brackets denote an average over all chain configurations in the bulk solution without particles. The free energy of interaction or potential of mean force between the two particles

$$\delta F_2 = -k_B T \ln \frac{\langle W_A W_B \rangle}{\langle W_A \rangle \langle W_B \rangle} \tag{2.1}$$

is the difference between F_2 and the sum $2F_1$ of the free energies $-k_B T \ln\langle W_A \rangle$ and $-k_B T \ln\langle W_B \rangle$ for immersing A without B and B without A. Clearly δF_2 depends on r_{AB} and tends to zero for $r_{AB} \to \infty$. On expanding δF_2 in terms of $W_A - 1$ and $W_B - 1$ for small particles, the self-terms of first and second order drop out, and

$$\frac{\delta F_2}{k_B T} = -[\langle (W_A - 1)(W_B - 1) \rangle - \langle W_A - 1 \rangle \langle W_B - 1 \rangle]$$

$$= -\left(\frac{F_1}{k_B T n}\right)^2 K(r_{AB}), \quad R \ll r_{AB}, \mathcal{R}_g, \xi, \tag{2.2}$$

where

$$K(r_{AB}) = \langle \theta(\mathbf{r}_A) \theta(\mathbf{r}_B) \rangle - n^2 \tag{2.3}$$

is the normalized polymer density correlation function in the solution without particles. Here θ is defined in Eq. (1.2), and Eqs. (1.1) and (1.4) have been used in the second step of Eq. (2.2). Equations (2.2) and (2.3) generalize Eq. (8) of Sear,[19] valid for the semidilute limit, to *arbitrary overlap* and provide the missing prefactor in this relation.

If the distance r_{AB} between the two particles is much smaller than $\mathcal{R}_g$ and ξ, the quantity K in Eq. (2.2) is given by the density correlation deep inside a *single* polymer coil,[6] and[13]

$$K(r_{AB}) \to n \frac{\sigma_g}{\mathcal{R}_g^{1/\nu} r_{AB}^{d-1/\nu}}; \quad r_{AB} \ll \mathcal{R}_g, \xi \tag{2.4}$$

increases *linearly* with the chain density n throughout the whole dilute to semidilute concentration range. Here σ_g is a known universal amplitude with the value[15]

$$\sigma_g \approx 0.069; \quad d = 3, \quad \text{good solvent.} \tag{2.5}$$

In the limit of a dilute polymer solution $K(r_{AB})$ reduces to $nC_2(r_{AB})/\mathcal{R}_x^{2/\nu}$, with C_2 the n-independent monomer density pair correlation function introduced in Eq. (1.17) of Ref. 13.

For distances $r_{A,B}$ between the two particles in the regime (2.4), the ratio $F_2(r_{A,B})/F_2(\infty)$ deviates from 1 by an amount proportional to $-(R/r_{A,B})^{d-1/\nu}$, which is independent of $\mathcal{R}_g$ and ξ (and thus independent of the overlap) and suggests that the range of the interaction between two small spheres is of the order of their radius R. However, this power law is not integrable. Integrals such as the second virial coefficient given in Eq. (4.1) below are dominated by much larger distances $r_{A,B}$ of the order of $\mathcal{R}_g$ or ξ and have a nontrivial overlap-dependence.

Strictly speaking the expression in Eq. (2.2) only applies to distances r_{AB} between the two particles which are much

larger than their radius R and should be compared with the potential of mean force $(\delta F_2/k_B T)_{r_{AB}=2R}$ for the smallest possible distance $r_{AB}=2R$, i.e., for two spheres in *contact*. This has the form

$$\left(\frac{\delta F_2}{k_B T}\right)_{r_{AB}=2R} = -(2-m)\frac{F_1}{k_B T}, \tag{2.6}$$

where mF_1 is the free energy of immersion of a pair of spheres in contact.[20] The value of m for polymers in good solvent equals $(\pi/2)^{2/3}$ in $d=2$ while near the upper critical dimension[5] in $d=4-\epsilon$ it follows[20] from the ϵ-expansion of the energy density profile in a critical Ginzburg-Landau model between parallel plates[21] as

$$\frac{m}{m_{\text{id}}} = 1 + \frac{\epsilon}{4}\left(\ln\frac{\pi}{2} - \frac{1}{4}\right) = 1 + 0.0504\epsilon. \tag{2.7}$$

Here $m_{\text{id}} = 2(1-2^{3-d})\zeta(d-2)$ is the value of m for *ideal* polymers with ζ the Riemann zeta function. Enhancement of m due to monomer-monomer repulsion as implied by Eq. (2.7) is also found for the case $d\to 2$ ($\epsilon\to 2$) in which $m/m_{\text{id}}\to m = 1.35$.

Extrapolating expressions (2.2) and (2.4) to $r_{AB}=2R$ also leads to the form (2.6), with $2-m$ replaced by $A_g\sigma_g/2^{d-1/\nu}$. Comparison of the two amplitudes shows that for three dimensions and good solvent the extrapolation approximates the amplitude $2-m\approx 0.5$ in Eq. (2.6) rather well.

III. POLYMER DENSITY, PRESSURE, AND FORCE FOR TWO PARTICLES IN CONTACT

The depletion effect leads to a monomer density profile that decreases on approaching the surface of a particle with[10] the distance from the surface to the power $1/\nu$. The prefactor of this power law is proportional to the local pressure which the polymer solution exerts onto the surface element considered. For two spherical particles A,B the pressure p acting on a surface element dS_A of A is determined by[22]

$$B_g\frac{p}{k_B T} = \frac{\mathcal{R}_g^{1/\nu}\langle\theta(\mathbf{r})\rangle_{A,B}^{(\text{as})}}{(|\mathbf{r}-\mathbf{r}_A|-R)^{1/\nu}} \tag{3.1}$$

with the density θ from Eq. (1.2) and B_g a universal density-pressure amplitude.[15] Here $\langle\;\rangle_{A,B}$ denotes an average over chain configurations in the presence of the two particles and the superscript (as) means that $\mathbf{r}$ is—within the scaling regime—*as*ymptotically close to the surface. The pressure $p=p(\cos\vartheta)$ depends on the projection $\cos\vartheta$ of the inward pointing surface normal onto the center-to-center distance vector $\mathbf{r}_B-\mathbf{r}_A$. Since this is the direction of the total force $\mathbf{f}$ pushing particle A towards particle B the magnitude f of the force is

$$\partial F_2/\partial r_{AB} = f = \int dS_A\cos\vartheta\; p$$

$$= (2R)^{d-1}\Omega_{d-1}\int_0^\infty d\tau(1-\tau^2)$$

$$\times \tau^{d-2}(1+\tau^2)^{-d}p. \tag{3.2}$$

The explicit form of the integral over the surface S_A as given for general dimension d in the last expression of (3.2) involves

$$\tau = \tan(\vartheta/2) \tag{3.3}$$

and the surface $\Omega_{d-1} = 2\pi^{(d-1)/2}/\Gamma((d-1)/2)$ of the sphere with radius 1 in $d-1$ dimensions.

The density-pressure relation (3.1) applies to situations with arbitrary ratios of mesoscopic lengths $R/\mathcal{R}_g, r_{AB}/\mathcal{R}_g$, and arbitrary overlap s. We now consider the limit $\mathcal{R}_g\to\infty$ with R, r_{AB}, and s fixed in which the normalized monomer density $\mathcal{M}_{A,B}(\mathbf{r})\equiv\langle\theta(\mathbf{r})\rangle_{A,B}/n$ and thus $p/(n\mathcal{R}_g^{1/\nu})$ and $f/(n\mathcal{R}_g^{1/\nu})$ become *independent* of $\mathcal{R}_g$ and s. This is consistent with the corresponding behavior (2.2)–(2.4) of δF_2. In this limit $\mathcal{M}_{A,B}$ can be obtained from the energy-density correlation function at the critical point of the corresponding field theory and by conformally mapping the outer space of the two particles onto simpler geometries.[22] For two spherical particles in *contact* the outer space can be mapped onto the space between two parallel walls. For chains in two dimensions $d=2$ outside two circular disks and with monomer–monomer repulsion we now exactly calculate $\mathcal{M}_{A,B}$ from the known[23] energy-density correlation function with the result

$$\mathcal{M}_{A,B}(\mathbf{r}) = \left(\frac{\pi^2}{4\rho^2\cos(\pi\rho_\parallel/\rho^2)}\right)^{2/3}\frac{8\pi}{45\sqrt{3}}\frac{1}{\kappa}$$

$$\times {}_3F_2\left(\frac{1}{3},\frac{2}{3},\frac{7}{3};\frac{11}{6},2;-\frac{1}{4\kappa}\right). \tag{3.4}$$

Here the contact point of the two disks with radius R is the origin of the $\mathbf{r}$ coordinate system and $\rho_\parallel R$ and $\rho_\perp R$ are, respectively, the components of $\mathbf{r}$ parallel and perpendicular to the line connecting the contact point with the centers of the disks (so that the centers are located at $\rho_\perp=0$ with $\rho_\parallel=\pm 1$), $\rho^2=\rho_\parallel^2+\rho_\perp^2$, and

$$4\kappa = \frac{\text{Cosh}^2(\pi\rho_\perp/\rho^2)}{\cos^2(\pi\rho_\parallel/\rho^2)} - 1. \tag{3.5}$$

The hypergeometric function ${}_3F_2$ has a convergent series representation for $4\kappa>1$ and is defined for $4\kappa<1$ by analytic continuation.[24]

Far from the two disks the density tends to its bulk value and the $\kappa\to 0$ behavior[24] in Eq. (3.4) implies a leading correction

$$1 - \mathcal{M}_{A,B}\to(\pi/2)^{2/3}A_g\sigma_g(R/r)^{2/3} \tag{3.6}$$

which is isotropic and is by a factor $m(d=2)=(\pi/2)^{2/3}$ larger than for a *single* disk. The quantity m is the same as in Eq. (2.6).

The upper and lower curves in Fig. 1 show the behavior of $\mathcal{M}_{A,B}$ in Eq. (3.4) along the lines $\rho_\parallel=0$ and $\rho_\perp=0$, respectively. On approaching the perimeter of disk A, $\cos(\pi\rho_\parallel/\rho^2)$ in Eqs. (3.4) and (3.5) approaches zero, κ approaches infinity, and one finds from Eq. (3.1) with $\nu(d=2)=3/4$ and from Eq. (3.3) the explicit expression
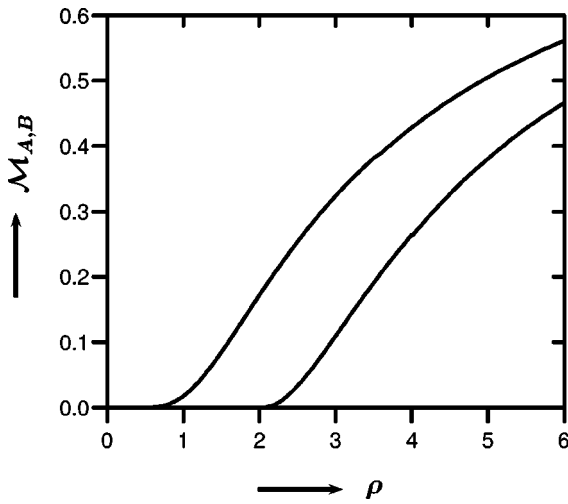
FIG. 1. Normalized monomer density $\mathcal{M}_{A,B}(\mathbf{r})$ for polymers in two dimensions outside two small circular disks in contact. The variation of $\mathcal{M}_{A,B}$ with distance ρR from the contact point is shown along the common tangent line of the two disks (upper curve) and along the line passing through the centers of the disks (lower curve). $\mathcal{M}_{A,B}$ approaches 1 for large ρ.

$$B_g \frac{p}{k_B T} = n \left(\frac{\mathcal{R}_g}{R} \right)^{4/3} \left[\frac{1+\tau^2}{\mathrm{Cosh}(\tau\pi/2)} \right]^2 \frac{\pi^{11/3}}{45\sqrt{3}2^{1/3}} \qquad (3.7)$$

for the ϑ-dependence of the local pressure. Near the perimeter point $\rho_\perp = 0$, $\rho_\parallel = 2$, where $\vartheta = 0$ and the pressure is maximal, p is proportional to $1 - 0.117\vartheta^2$, while p becomes exponentially small near the contact point where $\vartheta = \pi$. An integration over the perimeter S_A as in Eq. (3.2) yields[15]

$$\frac{f}{k_B T} \Big/ \left[nR \left(\frac{\mathcal{R}_g}{R} \right)^{4/3} \right] = \frac{1}{B_g} \frac{16\pi^{8/3}}{135\sqrt{3}2^{1/3}} \approx 1.34 \qquad (3.8)$$

for the magnitude f of the total force on disk A. Approximating the force at contact by extrapolating Eqs. (2.2), (2.4) down to $r_{A,B} = 2R$ would lead in $d=2$ to an approximate value $A_g^2 \sigma_g / (2^{2/3}3) = 1.98$ for the left-hand side of Eq. (3.8) which overestimates the correct value by about 50%.

The results (3.7) and (3.8) for the polymer-induced pressure and force for two disks in contact should be compared with corresponding results for two spheres in four dimensions in which case one finds (apart from logarithmic corrections) the ideal chain behavior[5] with[22]

$$B_g \frac{p}{k_B T} = n \left(\frac{\mathcal{R}_g}{R} \right)^2 \frac{\pi^4}{2^6} \frac{(1+\tau^2)^4}{\tau^2} \frac{\mathrm{Sinh}^2(\tau\pi/2)}{\mathrm{Cosh}^4(\tau\pi/2)} \qquad (3.9)$$

and[15]

$$\frac{f}{k_B T} \Big/ [nR\mathcal{R}_g^2] = \pi^2 \left(\frac{\pi^2}{6} - 1 \right) = 6.36. \qquad (3.10)$$

Here p is proportional to $1 - 0.028\vartheta^2$ near $\vartheta = 0$. Note the different dimensions of n in Eqs. (3.8) and (3.10).

In the case of ideal chains the amplitude of the force between small spheres vanishes as $d \to 2$. For two touching spheres in three dimensions we thus expect that the universal amplitude $f/(k_B TnR^{d-1-1/\nu}\mathcal{R}_g^{1/\nu})$ for polymers in good solvent is *larger* than the value[13] $(\ln 2 - \frac{1}{4})(4\pi/3) = 1.86$ of the corresponding amplitude $f/(k_B Tn\mathcal{R}_g^2)$ for ideal $(\Theta-)$ poly-

mers in $d=3$. A more quantitative estimate would follow from a $4-d$ expansion of the energy-density correlation function between parallel walls.

IV. SECOND VIRIAL COEFFICIENT

Consider the contribution

$$b_2^{CC} = \frac{1}{2} \int_{(r_{AB}>2R)} d\mathbf{r}_{AB} \left[1 - \exp\left(-\frac{\delta F_2(r_{AB})}{k_B T} \right) \right] \qquad (4.1)$$

to the second virial coefficient $B_2^{CC} = B_2^{(HS)} + b_2^{CC}$ of a dilute suspension of colloidal particles which arises from the polymer-induced potential of mean force δF_2. The hard-sphere contribution $B_2^{(HS)}$ equals $16\pi R^3/3$ in three dimensions. For small particles we may expand the exponential in (4.1) and disregard the contribution from interparticle distances r_{AB} of order R. From Eq. (2.2) we obtain

$$2b_2^{CC} \to -\left(\frac{F_1}{k_B Tn} \right)^2 \int d\mathbf{r}_{AB} K(r_{AB}). \qquad (4.2)$$

On using the compressibility sum rule[6] for the density correlation function

$$\int d\mathbf{r}\, K(r) = n \Big/ \left(\frac{\partial}{\partial n} \frac{\Pi}{k_B T} \right) \qquad (4.3)$$

and the scaling form

$$\frac{\Pi}{k_B T} = n[1 + \mathcal{P}(s)], \qquad (4.4)$$

where $\mathcal{P}$ is a universal scaling function for the osmotic pressure Π of the monodisperse polymer solution without particles, one finds

$$\frac{2b_2^{CC}\mathcal{R}_g^d}{(F_1/(k_B Tn))^2} = -\frac{s}{1 + d[s\mathcal{P}(s)]/ds} \equiv \mathcal{B}(s). \qquad (4.5)$$

Note that the n-dependence of the left-hand side of Eq. (4.5) comes exclusively from b_2^{CC}. Equation (4.5) expresses b_2^{CC} in terms of the particle radius R, the amplitude A_g in Eq. (1.1), and properties of the polymer solution without particles. An accurate expression for $\mathcal{B}$ in $d=3$ is available, see $\mathcal{P}(s) = \mathcal{P}^*(\hat{s},[m])$ and $d[s\mathcal{P}(s)]/ds = J_c^{*-1}(\hat{s},[m]) - 1$ in Eqs. (17.52) and (17.53) of Ref. 6 with $\hat{s} = 3.584\,s$. Figure 2 shows $\mathcal{B}(s)$ for three dimensions as a function of $n(4\pi/3)\mathcal{R}_g^3 = (4\pi/3)\,s$, see Eq. (1.5). $\mathcal{B}(s)$ approaches $-s$ for small s, is proportional to $-s/s^{1/(d\nu-1)} = -s^{-0.31}$ for large s, and displays a minimum at $(4\pi/3)\,s \approx 1$, where the chains "begin to overlap," and ξ is of the order of $\mathcal{R}_g$. This implies a nonmonotonic n-dependence of b_2^{CC}, qualitatively explained[8] by Chatterjee and Schweizer as follows: On increasing the chain density n within the dilute regime ($s \ll 1$), the coefficient b_2^{CC} drops, since the attractive potential of mean force δF_2 is proportional to n, see Eq. (2.2) with $K \propto n$ as mentioned below (2.5). After the chains begin to overlap, the range of K is determined by ξ and decreases on further increasing n so that b_2^{CC} rises.

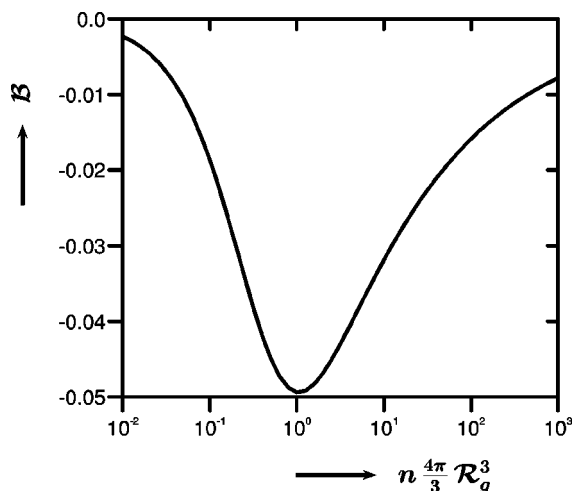The value of the minimum of $\mathcal{B}$ is -0.049 and implies the relation

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FIG. 2. Nonmonotonic overlap-dependence of the second virial coefficient b_2^{CC}. Shown is the universal combination $\mathcal{B}$ in Eq. (4.5) for three dimensions as a function of $n(4\pi/3)\mathcal{R}_g^3$.

$$(b_2^{CC})_{\min}/B_2^{(HS)} = -0.50(\mathcal{R}_g/R)^{0.401} \qquad (4.6)$$

for the coefficient b_2^{CC} at the polymer concentration where it is minimal. The exponent 0.401 is the value of $(2/\nu)-d$ in three dimensions. This should be compared with the result $-0.066(\mathcal{R}_g/R)^1$ for the left-hand side of Eq. (4.6) which follows from Eq. (43) of Ref. 8 and is based on an integral equation approach. The exponents differ by more than a factor of 2 and the amplitudes by a factor of roughly 1/10. Thus the asymptotically exact result (4.6) for the minimum of b_2^{CC} of small colloidal particles ($R \ll \xi, \mathcal{R}_g$) in a good solvent solution of long flexible chains close to their overlap concentration crosses the integral-equation based result at a value ≈ 29 of $\mathcal{R}_g/R$ and leads to a minimum which is less deep (deeper) for $\mathcal{R}_g/R$ larger (smaller) than this value.

V. INTERACTION BETWEEN A PARTICLE AND A WALL

Experiments measuring the polymer-induced force on *individual* colloidal particles have been performed both for a single pair of interacting particles[25] and for a single particle interacting with a wall.[26,27] The free energy $F_{1,\text{hs}}$ of immersion of a small particle in a polymer solution in a half space (hs) bounded by a planar wall can also be obtained by using Eq. (1.1). As in Sec. II, the free energy of a particle with its center at a distance z_C from the wall

$$F_{1,\text{hs}} = F_1 \mathcal{M}(z_C), \qquad R \ll z_C, \mathcal{R}_g, \xi \qquad (5.1)$$

is determined by the bulk-normalized monomer density profile

$$\mathcal{M}(z) = \langle \theta(\mathbf{r}) \rangle_{\text{hs}}/n \qquad (5.2)$$

in the solution in the half-space without the particle. Here $\langle \, \rangle_{\text{hs}}$ denotes an average over all chain configurations in the half space. The quantity $\mathcal{M}(z)$ is independent of the component $\mathbf{r}_\parallel$ parallel to the wall of the position vector $\mathbf{r} = (\mathbf{r}_\parallel, z)$ in Eq. (1.2) and approaches 1 for $z \to \infty$.

The dependence of $\mathcal{M}$ on z, $\mathcal{R}_g$, ξ in the scaling regime is quite complex, in general, and we only consider special cases. Particularly transparent is the case of small z, in which[10,20]

$$k_B T n \mathcal{R}_g^{1/\nu} \mathcal{M}(z) \to B_g \Pi z^{1/\nu}, \qquad z \ll \mathcal{R}_g, \xi \qquad (5.3)$$

with the bulk osmotic pressure Π introduced in Eq. (4.4) and the universal density-pressure amplitude B_g has the value[15]

$$B_g \approx 1.07, \qquad d=3, \quad \text{good solvent}. \qquad (5.4)$$

In the free energy formula (5.1) the relation (5.3) may only be used for the regime $R \ll z_C \ll \mathcal{R}_g, \xi$, while for a spherical particle *touching* the wall, i.e., for the smallest possible distance $z_C = R$,

$$(F_{1\text{hs}})_{z_C = R} = A_{\text{ts}} \Pi R^d \qquad (5.5)$$

with a universal amplitude A_{ts} introduced in Ref. 20. The value of A_{ts} for polymers in good solvent equals $\frac{1}{3}\pi^3 = 10.3$ in $d=2$ while in $d = 4 - \epsilon$ one finds

$$\frac{A_{\text{ts}}}{(A_{\text{ts}})_{\text{id}}} = \frac{d-2}{d-1/\nu}\left(1 + \frac{\epsilon}{48}\right) \qquad (5.6)$$

to first order in ϵ with $(A_{\text{ts}})_{\text{id}} = 2\pi^{d/2}(d-1)\zeta(d)/\Gamma(d/2)$ the value of A_{ts} for ideal chains. Equation (5.6) follows from the known[28,29] ϵ-expansions of the quantities Δ and C_T in Eq. (6.12) of Ref. 20 and suggests that $A_{\text{ts}} \approx 23.7$ in $d=3$. Extrapolating Eqs. (5.1) and (5.3) down to $z_C = R$ leads to Eq.(5.5), with A_{ts} replaced by the product $A_g B_g$. In $d=3$ this underestimates the amplitude in Eq. (5.5) by about 20%.

The free energy (5.5) it costs to immerse the small particle close to the wall, i.e., in a region which is already depleted from polymers, is smaller by a factor $\propto (R/\mathcal{R}_g)^{1/\nu}\Pi/(k_B T n)$ than the free energy (1.4) of immersion in the bulk of the polymer solution. The factor is proportional to $(R/\mathcal{R}_g)^{1/\nu}$ and $(R/\xi)^{1/\nu}$ for dilute and semidilute polymer solutions, respectively. This can be understood in terms of the effective pressure which the polymers exert on the surface of the particle. The pressure is proportional to the monomer density near the particle surface,[10,22] compare Eq. (3.1), and determines the derivative of the free energy of immersion with respect to R. For the small particle in the bulk solution the pressure is[22] proportional to $k_B T n (\mathcal{R}_g/R)^{1/\nu}$ and is much larger than the pressure $\propto \Pi$ acting on a wall or a small particle close to a wall.

The variation of $F_{1,\text{hs}}$ with particle wall distance z_C has a point of inflection, since the upward curvature $\propto z_C^{1/\nu} = z_C^{1.70}$ at small distances is followed by a downward curvature at large z_C so that $F_{1,\text{hs}}$ approaches the z_C-independent bulk free energy F_1 for $z_C \to \infty$. Thus the magnitude $\partial F_{1,\text{hs}}/\partial z_C$ of the polymer mediated mean force between wall and particle has a *maximum* at a distance of order $\mathcal{R}_g$ or ξ in a dilute or semidilute polymer solution.

VI. SUMMARY AND CONCLUDING REMARKS

We have discussed the polymer-induced depletion interactions between two particles and between a particle and a wall for dilute and semidilute solutions of long flexible polymer chains in a good solvent and mesoscopic spherical par-

ticles with a small radius R. In particular we consider the attractive free energy of interaction (potential of mean force) δF_2 between two particles, the resulting contribution b_2^{CC} to the second virial coefficient of a dilute suspension of particles, and the free energy $F_{1,hs}$ it costs to immerse a particle at a distance z_C from a planar boundary wall of a polymer solution in the half-space. For two spherical particles in contact the depletion of the monomer density and the variation of the local pressure along the particle surfaces have also been investigated. Results for these universal quantities are presented which contain no free parameters or unknown prefactors and apply for arbitrary interchain overlap ranging from zero (dilute solution) to infinity (semidilute limit).

Using small radius expansions (which are similar to "short distance expansions" in field theories) we have shown that the overlap dependence of both b_2^{CC} and $F_{1,hs}$ for a particle close to a wall can be expressed in terms of the overlap dependence of the osmotic pressure Π of the polymer solution without particles and walls. The dependence of b_2^{CC} is determined by the compressibility of the polymer solution, see Eq. (4.5) and Fig. 2. The minimum value of the reduced virial coefficient b_2^{CC}/R^3 at the polymer overlap-concentration depends on $\mathcal{R}_g/R$, with $\mathcal{R}_g$ the radius of gyration of one chain in dilute solution, as a power law, with an exponent and amplitude quite different from the predictions of an integral-equation approach,[8] see Eq. (4.6). For $\mathcal{R}_g/R$ larger (smaller) than ≈ 29 the minimum is less deep (deeper) than the minimum in the integral-equation approach.

We have also calculated the free energy of interaction and the force for two particles (and for a particle and a wall) in *contact*. In the case of three dimensions $d=3$ we estimate the free energy amplitudes from ϵ-expansions, compare Eqs. (2.7) and (5.6), and conjecture an inequality for the force between two particles, compare the last paragraph in Sec. III. In the case of two dimensions $d=2$ and for two particles (disks) we derive exact results for the monomer-density depletion profile, the surface pressure, and the force between the particles; compare Eqs. (3.4)–(3.8) and Fig. 1. These results for contact-situations cannot be inferred from small-radius expressions such as Eqs. (2.2), (2.4) or (5.1), (5.3) which are obtained via Eq. (1.1) and are valid for particle-center to particle-center distance $r_{A,B}$ (or particle-center to wall distance z_C) much smaller than $\mathcal{R}_g, \xi$, but much larger than the particle radius R. Extrapolating these expressions down to $r_{A,B}=2R$ (or to $z_C=R$) in general overestimates the magnitude of the free energy of interaction and the force of two particles in contact. It also underestimates both the free energy to insert a particle in contact with a wall and the force on this particle. Compare the force between two disks in contact which is overestimated by about 50% as discussed below Eq. (3.8) and the free energy $F_{1,hs}$ it costs to insert a sphere in contact with a wall in three dimensions which is underestimated by about 20% as discussed below Eq. (5.6).

Equations such as (2.2), (4.2), and (5.1), which relate properties of small particles in the polymer solution to properties of the solution without particles, are expected to apply even beyond the asymptotic good solvent scaling region (excluded-volume limit). In a simplified description of the crossover from theta to excluded volume behavior in which

chains at the theta point in $d=3$ are modeled as ideal, random walk chains, the relative reduction $1-W_C$ of the Boltzmann weight of chain configurations due to the presence of the particle in Eq. (1.1) can again be written as a product of the configuration-dependent chain number density θ in Eq. (1.2) and a configuration-*independent* factor depending on the particle radius R. This factor now also depends on the strength of the excluded volume interaction between chain monomers,[30] and for weak interaction, corresponding to a solution close to the theta point with a large crossover length λ, crosses over from ideal chain behavior $A_g^{(id)} R^{d-2} \mathcal{R}_{g,id}^2$ for $R \ll \lambda$ to the excluded volume behavior $A_g R^{d-1/\nu} \mathcal{R}_g^{1/\nu}$ of Eq. (1.1) for $R \gg \lambda$. This complicated factor drops out of the ratios $\delta F_2/F_1^2$, b_2^{CC}/F_1^2, and $F_{1,hs}/F_1$, which for arbitrary R/λ are completely determined by crossover-properties of the polymer solution without particles according to Eqs. (2.2), (4.2), and (5.1).

It would be interesting to compare these new predictions with computer simulations[31] in the appropriate region of mesoscopic length ratios and with real experiments.[3,4,25–27]

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[15] The amplitudes $A_g = (\mathcal{R}_x/\mathcal{R}_g)^{1/\nu} A_{D,D}$, $\sigma_g = (\mathcal{R}_g/\mathcal{R}_x)^{1/\nu}\sigma$, and $B_g = (\mathcal{R}_g/\mathcal{R}_x)^{1/\nu} B$ are related to the amplitudes $A_{D,D}$, σ, and B considered in Table I of Ref. 13 and in the paragraph containing Eq. (5.12) in Ref. 20 via the ratio $\mathcal{R}_x^2/\mathcal{R}_g^2 = (\mathcal{R}_{ee}^2/d)/\mathcal{R}_g^2$, where $\mathcal{R}_{ee}$ is the mean square end-to-end distance. For good solvent conditions in three dimensions the amplitudes in Eqs. (1.3), (2.5), and (3.4) follow from $A_{3,3} \approx 9.82$, $\sigma \approx 0.13$, $B \approx 2$, and (Ref. 6) $\mathcal{R}_x^2/\mathcal{R}_g^2 \approx 2.09$, $\nu \approx 0.588$ implying $(\mathcal{R}_x/\mathcal{R}_g)^{1/\nu} \approx 1.87$. In two dimensions $(\mathcal{R}_x/\mathcal{R}_g)^{1/\nu} \approx 2.34$ [see J. Cardy and A. Guttmann, J. Phys. (London) A **26**, 2485 (1993)] and the amplitudes follow from $A_{2,2}=3.810$, $\sigma \approx 0.278$, and $B \approx 2.01$. In four dimensions $(\mathcal{R}_x/\mathcal{R}_g)^{1/\nu}=3/2$, $A_{4,4}=19.74$, and $B=2$.

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