Polymers interacting with mesoscopic particles

E Eisenriegler

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract.   We consider the depletion interaction between mesoscopic particles and non-adsorbing free polymer chains. For one and two spherical particles we investigate the depletion profiles of monomer and end densities of the embedding polymer solution. The profiles take a finite limit for large Flory radius and Edwards screening length. The influence of the excluded volume interaction between chain monomers is studied for the case of one particle. We demonstrate how the polymer-induced force between two particles emerges from the monomer density profile near the surface of one of the particles. The evaluation of the polymer densities follows from a new type of 'fusion procedure' in the equivalent field theory.

The depletion interaction between mesoscopic dissolved particles and non-adsorbing free polymer chains is one of the fundamental interactions in colloid physics. Recent experiments on *individual* colloidal particles [1, 2] and simulations [3] have lead to a renewed interest. Although this entropy-dominated interaction has been studied theoretically since the fifties, exact results [4–10] are still rare. Since solutions of long flexible polymers are a beautiful example of a 'critical system' [11], one may exploit the powerful methods of critical phenomena and field theory.

The properties of a single dissolved spherical particle depend on the ratios of its radius R and mesoscopic lengths such as the unperturbed Flory radius $\mathcal{R}$ or the screening length ξ [11] that characterize the polymer solution. The depletion effects for large particle size $R \gg \mathcal{R}, \xi$ closely resemble those for planar walls [4, 6]. Here we consider the other extreme—*small particle size* $R \ll \mathcal{R}, \xi$—and investigate the depletion of the densities $\mathcal{M}(\mathbf{r})$ of chain monomers and $\mathcal{E}(\mathbf{r})$ of chain ends near one and two particles in the solution. We normalize the densities so that they approach 1 in the bulk solution. At large distances from the particle(s) depletion effects have been studied before [9, 10]. Here we consider *arbitrary* ratios of the distance and the size, provided both are much smaller than $\mathcal{R}$ and ξ. The case of small particle size and long flexible chains is dominated by configurations where the chain coils around the particle(s), and approximations that treat the chains as non-deformable [4] fail completely.

First we study the influence of the *excluded volume interaction* (EVI) between chain monomers on the depletion of the monomer density $\mathcal{M}_s(r)$ around a single spherical particle. Here r is the distance from the centre of the sphere. The variation of $\mathcal{M}_s$ (or $\mathcal{E}_s$) with R, r in the domain $R, r \ll \mathcal{R}, \xi$ is independent of $\mathcal{R}, \xi$ and only depends on the ratio $\rho = r/R$†. Neglecting the EVI in the case of a dilute solution [9], i.e. considering a solution of 'ideal chains', or treating a semidilute solution of strongly interpenetrating chains in mean field fashion [8] leads to the same simple result $\mathcal{M}_{s,id} = (1 - \rho^{-(d-2)})^2$. Here d is the dimension

---

† In our case of finite obstacles such as one or two spheres, the normalized densities $\mathcal{E}$ and $\mathcal{M}$ remain *finite* in the limit $\mathcal{R}, \xi \to \infty$. In the case of an infinitely extended planar wall the densities *vanish* in this limit for all finite distances from the wall.

of space, and we assume $d > 2$. The small spherical particle significantly perturbs the bulk density within a distance of order R from its surface (while for a large particle or a planar wall the corresponding 'healing' distance is of order $\mathcal{R}$ or ξ) (see previous footnote). For a dilute solution of chains with EVI, $\mathcal{M}_s$ is *different* from above. In the limit $R \ll r$ in which r is far away from the sphere, one finds that $\mathcal{M}_s \to 1 - \alpha\rho^{-x}$. Here $x = d - 1/\nu$ with ν the Flory exponent [11], and the amplitude α is the product of the universal amplitudes A and σ introduced in [10]. Table 1 shows that x and α are larger and smaller, respectively, than the results $x_{id} = d - 2$ and $\alpha_{id} = 2$ for ideal chains. Thus the EVI leads to a *smaller* depletion effect. In the other limit $r - R \ll R$ in which r is close to the surface of the sphere, $\mathcal{M}_s \to \beta(\rho - 1)^{1/\nu}$. Here β is given by ABx/S_d with the universal amplitude B defined in [12] and with S_d the surface area of the d-dimensional sphere of radius unity. In this limit the EVI also leads to a decrease in the depletion effect, compare the values of $1/\nu$ and β in table 1 which are smaller and larger, respectively, than the values $1/\nu_{id} = 2$ and $\beta_{id} = (d - 2)^2$ for ideal chains.

Table 1. Exponents and amplitudes in the power law behaviour for $r/R \to \infty$ and $r/R \to 1$ of the monomer density profile around a single spherical particle in spatial dimension d.

d	x	x_{id}	α	α_{id}	$1/\nu$	$1/\nu_{id}$	β	β_{id}
4	2	2	2	2	2	2	4	4
3	1.33	1	≈ 1.3	2	1.67	2	≈ 1.3	1
2	$\frac{2}{3}$	—	1.061	—	$\frac{4}{3}$	—	0.812	—

For dilute self-repelling chains in a *plane* ($d = 2$) the ρ-dependence of the depletion profile of the monomer density outside a circular disc can be obtained in closed form. For $\rho - 1 < \sqrt{2}$

$$\mathcal{M}_s = \frac{8\pi}{45\sqrt{3}}(\rho - \rho^{-1})^{4/3}\rho^{-2/3} \, {}_3F_2\left(\frac{1}{3}, \frac{2}{3}, \frac{7}{3}; \frac{11}{6}, 2; -\frac{1}{4}(\rho - \rho^{-1})^2\right) \quad (1)$$

where ${}_3F_2$ is a generalized hypergeometric function and the expression for $\rho - 1 > \sqrt{2}$ follows by analytic continuation. The result is shown in figure 1 and reduces to the above-mentioned limiting forms for $\rho \to \infty$ and $\rho \to 1$, which are also shown.

Situations with well separated length scales such as R, $r \ll \mathcal{R}$ can be handled most efficiently in terms of short distance expansions or fusions. On a large length scale the small object can be viewed in leading order as a point-like isotropic perturbation with an amplitude that depends on its internal structure. This has been used before to describe a small spherical particle in a critical system for $R \ll r, \mathcal{R}$ [9, 10, 13] or two particles a distance D apart for $R, D \ll r, \mathcal{R}$ [10]. To describe the case of one particle with $R, r \ll \mathcal{R}$ and to derive (1), we fuse the density operator at r with the spherical particle centred at the origin. In the standard field theory (FT) of an n-component field Φ equivalent to the statistics of a self-repelling chain in the limit $n \to 0$ [7, 11], this yields

$$\langle \ldots \cdot \Phi^2(r) \rangle_s \to \langle \ldots \cdot \Phi^2(0) \rangle_{bulk} \mathcal{A}(\rho). \quad (2)$$

Here $\langle \cdot \rangle_s$ and $\langle \cdot \rangle_{bulk}$ denote cumulant averages over Φ-configurations in the presence and absence of the sphere [9, 10]. The quantity $\Phi^2(r)$ is the energy density in the FT, normalized so that $\langle \Phi^2(r) \rangle_{bulk}$ vanishes at the critical point $T = T_c$ of the FT. The ellipses denote fluctuating fields Φ or Φ^2 located at distances from the sphere much larger than R and r. The correlation length of the FT must also be much larger than R and r. Equation (2) is also expected to apply if the ellipses represent the square of integrals $(\int dr' \, \Phi(r'))^2$, in which case the two averages in (2) yield monomer densities around the sphere and in the bulk, respectively, on applying a
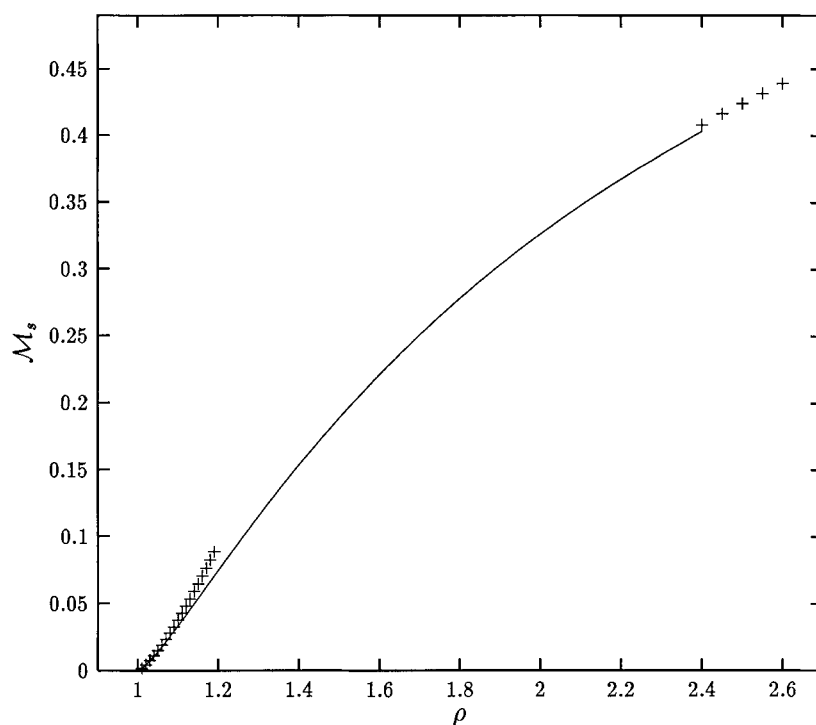
Figure 1. Monomer density $\mathcal{M}_s$ around a circular disc in a two-dimensional dilute solution of long flexible chains with excluded volume interaction between monomers as a function of the ratio $\rho = r/R$ of the distance r from the centre and the radius R of the disc. The full curve is the result given by equation (1). The limiting forms for $\rho \to 1$ and $\rho \to \infty$ given in the text with exponents and amplitudes for $d = 2$ in table 1 are shown as crosses.

Laplace transform with respect to the deviation $T - T_c$ from the critical point. The amplitude function $\mathcal{A}$ in (2) is independent of $T - T_c$, and therefore $\mathcal{A}(\rho)$ is to be identified with $\mathcal{M}_s(r)$. Since $\mathcal{A}$ is also independent of the type of field represented by the ellipses, (2) allows one to relate $\mathcal{M}_s$ to other quantities, such as the correlation function of energy densities of the FT at the critical point in the presence of the sphere. (Here one replaces the ellipses in (2) by $\Phi^2(r')$ and identifies $\mathcal{A}$ as the limit of the ratio of critical energy density correlation functions in the presence and absence of the sphere as $r' \to \infty$.) In $d = 2$ the latter quantity can be obtained via a conformal transformation from the known [14] result in the half plane, which leads to (1). In general dimension d the expression for the amplitude β given above (and used to obtain the β values in table 1) follows by the same reasoning from the critical energy density correlation function as r tends to the planar boundary of the half-space. The amplitude function $\mathcal{A}$ also appears in the leading singular $T - T_c$ dependence of the energy density profile in the presence of the sphere $\langle \Phi^2(r) \rangle_s$, which is given by the singular dependence of the bulk density $\langle \Phi^2(0) \rangle_{bulk}$ multiplied by $\mathcal{A}(\rho)$. This can easily be checked for the simple case of a Gaussian FT, equivalent to ideal chains, in which the amplitude function equals $\mathcal{M}_{s,id}(r)$.

For the end density one can use a fusion relation similar to (2) but with Φ^2 replaced by Φ. Its amplitude function equals $\mathcal{E}_s(r)$ and is identified as the limit of the ratio of critical order-parameter correlation functions as $r' \to \infty$. It can be determined once the order-parameter correlation function is known for the n-component theory in the half-space at criticality.

Next we consider *two* spherical particles of radius R with closest surface-to-surface distance D. As above the monomer and end densities can be inferred from field theoretical correlation functions at criticality in the space outside the two particles. These functions can be obtained by a conformal transformation from the highly symmetric space between two *concentric* spheres. The polymer densities can be predicted for ideal chains in $d > 2$ since the correlation functions are explicitly known [13] for the equivalent Gaussian FT†. Placing the centres of the two particles on the z-axis of the coordinate system at $\pm(R + D/2)$, and denoting the particles by $+$ and $-$, one finds that the end density at point r depends on its z-component z and its distance r from the origin according to

$$\mathcal{E}_{ss,id} = 1 - (2z_0)^{2\delta}(Q_+Q_-)^{-\delta/2} \sum_{l=0}^{\infty} C_l^{(\delta)}(\eta) \frac{(Q_+/Q_-)^{\lambda/2} + (Q_-/Q_+)^{\lambda/2}}{\theta^{-\lambda} + 1}. \quad (3)$$

Here l are integers, $\lambda = l + \delta$, $\delta = (d-2)/2$, $Q_\pm = r^2 + z_0^2 \pm 2zz_0$, $\eta = (r^2 - z_0^2)/\sqrt{Q_+Q_-}$ and C_l are Gegenbauer polynomials and z_0 and θ are defined via

$$z_0 = \sqrt{(2R + D/2)D/2} = (\theta^{-1/2} - \theta^{1/2})R/2 \qquad 0 \leqslant \theta \leqslant 1. \quad (4)$$

As a consequence $\theta^{-1/4} - \theta^{1/4}$ is equal to $(D/R)^{1/2}$. Two known limiting cases are contained in the general result (3). (i) For fixed radius R and fixed distance r_+ of r from the centre of particle $+$, (3) reduces to the single-sphere result $\mathcal{E}_{s,id} = 1 - (R/r_+)^{d-2}$ as $D \to \infty$. (ii) For $r \to \infty$ with D, R fixed, $Q_\pm \to r^2$, $\eta \to 1$, and $\mathcal{E}_{ss,id}$ in (3) tends to $1 - (R/r)^{d-2}m$ with

$$m = 2(\theta^{-1/2} - \theta^{1/2})^{d-2} \sum_{l=0}^{\infty} \binom{l+d-3}{l} /(\theta^{-\lambda} + 1)$$

depending on D/R. The amplitude m is the amount by which two spheres perturb the polymer system at large length scales more strongly than a single sphere with radius R, and was introduced before in [10].

As a new application of (3) we calculate the monomer density near the surface S_+ of particle $+$. This is interesting since it is related by the density–force relation [12]

$$n_b \mathcal{R}^{1/\nu} \int dS_+ [\mathcal{M}_{ss}^{(as)}/(r_+ - R)^{1/\nu}] \cos \vartheta = Bf/k_B T \quad (5)$$

to the local pressure, which the polymers exert onto the surface element dS_+. Here f is the magnitude of the total force pushing particle $+$ towards particle $-$, n_b is the density of chains in the bulk, $\mathcal{M}_{ss}^{(as)}$ is the normalized monomer density asymptotically close [12] to S_+, and $\cos \vartheta$ is the projection of the inward pointing surface normal onto the direction of the total force. The universal amplitude B depends on the precise definition of $\mathcal{R}$. We define $d\mathcal{R}^2$ as the unperturbed mean square end to end distance of a single chain (i.e. $\mathcal{R}$ equals the quantity $\mathcal{R}_x$ of [10, 12]). For our long ideal chains $1/\nu = 2$ and $\mathcal{M}_{ss,id}^{(as)}/(r_+ - R)^2 = (\partial_\perp \mathcal{E}_{ss,id})^2$ with $\partial_\perp$ denoting a normal derivative at the surface S_+. From (3) one finds

$$\partial_\perp \mathcal{E}_{ss,id} = \frac{1}{R} \frac{(\theta^{-1/2} - 2\eta + \theta^{1/2})^{d/2}}{\theta^{-1/2} - \theta^{1/2}} \sum_{l=0}^{\infty} C_l^{(\delta)}(\eta) \frac{2\lambda}{\theta^{-\lambda/2} + \theta^{\lambda/2}} \quad (6)$$

where $\eta = [2 + (\theta^{-1/2} + \theta^{1/2})\cos\vartheta]/[2\cos\vartheta + \theta^{-1/2} + \theta^{1/2}]$. The monomer density and local pressure is larger near the surface point $\mathcal{L}$ of particle $+$ with the largest distance from particle $-$ (the point on the z-axis at $2R + D/2$ with $\eta = \cos \vartheta = 1$) than near the surface point $\mathcal{S}$ with the smallest distance from particle $-$ (the point at $D/2$ with $\eta = \cos \vartheta = -1$), see figure 2.

† In the case of ideal chains our representation of $\mathcal{E}$ as the ratio of the critical order parameter correlation functions with $r' \to \infty$ reduces to the *harmonic* function $\mathcal{E}_{ss,id}$ in (3), which vanishes on the surface of the spheres and approaches 1 far away from the spheres.
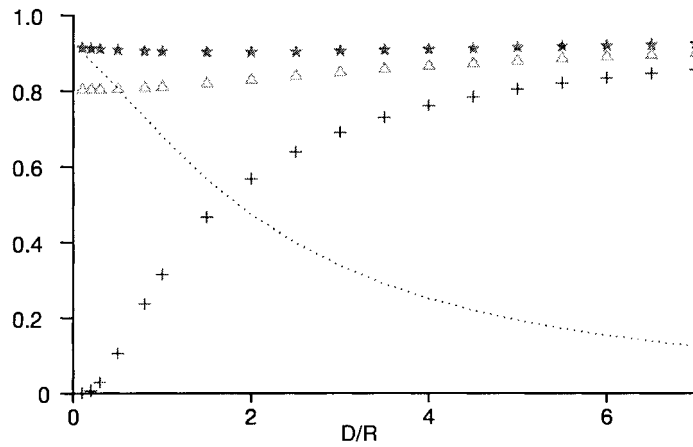
Figure 2. Density–force relation for two spherical particles $+$ and $-$ in a solution of ideal chains in three dimensions (see equation (5)). The monomer density near the surface S_+ of particle $+$ is determined by the normal derivative at the surface $\partial_\perp \mathcal{E}_{ss,id}$ of the bulk-normalized end density. Results from (6) for $R\partial_\perp \mathcal{E}_{ss,id}$ at the surface points with $\cos\vartheta = 1$ (point $\mathcal{L}$), $\cos\vartheta = 0$ and $\cos\vartheta = -1$ (point $\mathcal{S}$) are denoted, respectively, by asterisks, triangles, and crosses. The magnitude of the reduced force $f_{id,d=3}/(k_B T n_b \mathcal{R}^2)$ acting on particle $+$ is given by the broken curve. Note the minimum at $D \approx 1.6R$ in the results for point $\mathcal{L}$ with a value 0.904 which is only slightly smaller than the value 0.916 (Catalan's constant) at $D = 0$.

For distant spheres the leading contribution to $R\partial_\perp \mathcal{E}_{ss,id}$ is the isotropic contribution $d-2$ of a single sphere, while the leading anisotropic contribution is given by $\cos\vartheta\,(R/D)^{d-1}(d-2)d$. Using expression (6), we have checked the density force relation (5) for arbitrary D/R by analytically evaluating the surface integral. With the value $B = B_{id} = 2$ for ideal chains this leads to the expression $n_b \mathcal{R}^2 A_{id}(\partial m/\partial D)R^{d-2}$ for $f_{id}/k_B T$, which is consistent with equation (3.13) in [10] for the potential of mean force. Here the quantity m is given above, and $A_{id} = 2\pi^{d/2}/\Gamma((d/2)-1)$.

It is interesting to compare the depletion attraction between two small spheres (with $R \ll \mathcal{R}, \xi$) with the attraction between one small sphere and a planar wall [15]. In both cases the total free energy gain on changing the distance between the two objects from ∞ to zero is of order $R^{d-1/\nu}$ times the monomer density in the bulk of the polymer solution. However, the range of the polymer induced interaction is of order R in the case of the two spheres and of order $\mathcal{R}$ or ξ in the case of the sphere near a planar wall.

For one and two spherical particles immersed in a low-density solution of long flexible non-adsorbing polymer chains, we have derived exact results for the depletion profiles of the densities of chain monomers and chain ends. We allow for arbitrary ratios of the particle size, the distance between the particles, and the distance of r from the particle surfaces, but assume that these lengths are much smaller than the unperturbed chain size and screening length. Density interference effects and the force between two particles are studied for ideal chains (see equations (3)–(6) and figure 2). For a single particle the influence of the excluded volume interaction between chain monomers is investigated in detail (see table 1, equation (1) and figure 1). Since interpenetration effects of different chains do not show up on the length scale we considered, the above results for chains with excluded volume interaction between monomers apply both to dilute and semidilute solutions†. Similarly, the above results for ideal

---

† This is similar to the well known behaviour of the monomer density correlation function in a polymer solution in free space, which at short distances becomes independent of the degree of overlap between the chains and is determined by single-chain properties.

chains will also appear in a mean field treatment of semidilute solutions with large screening length. Table 1 shows the importance of the (single-chain) excluded volume effects for the depletion profile near a small particle. Beyond their contribution to the physical understanding of polymer depletion, these exact results also provide a check for more versatile but approximate methods.

Acknowledgments

Note added in proof. The pressure on the surface of a single spherical particle is given by $(\beta/B)k_B T n_b (\mathcal{R}/R)^{1/\nu}$, compare table 1 and equation (5). The product of the pressure and the surface area of the particle equals the derivative with respect to R of the free energy to immerse the particle in the polymer solution [5, 9, 10, 15]. This relation between the free energy and the amplitude β in the monomer density profile near the particle surface applies to particles of *arbitrary* size. While β is a constant for small particles (see table 1), it depends on length ratios for arbitrary particle size. For example, for a solution of ideal chains in three dimensions $\beta = 1 + 4\sqrt{2/\pi}\,R/\mathcal{R} + 2(R/\mathcal{R})^2$.

References

[1] Rudhardt D, Bechinger C and Leider P 1998 *Phys. Rev. Lett.* **81** 1330
[2] Verma R, Crocker J C, Lubensky T C and Yodh A G 1998 *Phys. Rev. Lett.* **81** 4004
[3] Meijer E J and Frenkel D 1994 *J. Chem. Phys.* **100** 6873
[4] Asakura S and Oosawa F 1954 *J. Chem. Phys.* **22** 155
    Asakura S and Oosawa F 1958 *J. Polym. Sci.* **33** 183
[5] de Gennes P G 1979 *C. R. Acad. Sci., Paris* B **288** 359
[6] Joanny J F, Leibler L and de Gennes P G 1979 *J. Polym. Sci., Polym. Phys.* **17** 1073
[7] Eisenriegler E 1993 *Polymers Near Surfaces* (Singapore: World Scientific)
[8] Odijk T 1996 *Macromolecules* **29** 1842
    Odijk T 1996 *J. Chem. Phys.* **106** 3402
[9] Eisenriegler E, Hanke A and Dietrich S 1996 *Phys. Rev.* E **54** 1134
[10] Hanke A, Eisenriegler E and Dietrich S 1999 *Phys. Rev.* E **59** 6853
[11] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca: Cornell University Press)
[12] Eisenriegler E 1997 *Phys. Rev.* E **55** 3116
[13] Burkhardt T and Eisenriegler E 1995 *Phys. Rev. Lett.* **74** 3189
    Eisenriegler E and Ritschel U 1995 *Phys. Rev.* B **51** 13 717
[14] Burkhardt T, Eisenriegler E and Guim I 1989 *Nucl. Phys.* B **316** 559
    Burkhardt T and Eisenriegler E 1994 *Nucl. Phys.* B **424** 487
[15] Bringer A, Eisenriegler E, Schlesener F and Hanke A 1999 *Eur. Phys. J.* B **11** 101