Polymer depletion profiles around non-spherical colloidal particles

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Abstract

We study the effect of chain self-avoidance on the polymer density profiles that are induced by a single colloidal particle of non-spherical shape such as an ellipsoid, a dumbbell, or a lens in a solution of nonadsorbing polymers. For colloid sizes $\sigma$ much smaller than the size $R_x$ of the polymers, we observe a pronounced difference between ideal and self-avoiding chains. In the case of ideal polymers, the surfaces of constant density always have the same character as the surface of the particle, e.g. are oblate for an oblate ellipsoid. In the self-avoiding case, however, the character changes with increasing distance $r$ from the particle, and an oblate particle induces prolate surfaces of constant density if $\sigma \ll r \ll R_x$.

For $\sigma \ll r, R_x$, the isotropic and anisotropic contributions to the densities factor into a dependence on the particle size and shape and a dependence on $r, R_x$. The latter is determined by distance distributions within a chain in the absence of the particle. For self-avoiding polymers in two spatial dimensions, exact density profiles are derived for $\sigma, r \ll R_x$, which explicitly show the above-mentioned change of the contours of constant density.
I. INTRODUCTION

Nonadsorbing polymers induce an attractive depletion interaction between colloidal particles, which is of considerable practical and scientific interest. In a previous paper we analyzed the effective interaction between a non-spherical particle and a wall, which depends on both the particle-wall distance and the orientation of the particle. Ideal and self-repelling polymer chains were considered.

Here we study the simpler case of a single non-spherical particle, more amenable to a comparison with computer simulations. We find a remarkable difference between the anisotropic density depletion profiles that the particle induces in a dilute solution of ideal chains and self-repelling chains.

As in Ref. 3 we consider particles with an axis of rotational symmetry and with inversion symmetry about the center, such as ellipsoids, dumbbells, and lenses. An ellipsoid has diameters $D_\parallel$ and $D_\perp$ parallel and perpendicular to the axis and is prolate if $D_\parallel > D_\perp$ and oblate if $D_\parallel < D_\perp$. A dumbbell is formed by two spheres of equal size that intersect at an angle $\alpha$ along a circle with diameter $D$.

We concentrate on the case of “nano-particles” with a size $\sigma$ that is mesoscopic but much smaller than the size $R_x$ of the polymers. The latter is defined via the mean square end-to-end distance $R_x^2 \equiv dR_x^2$ of the polymer chain, where $d$ is the spatial dimension. We analyze the bulk-normalized densities $M(r)$ and $E(r)$ of chain-monomers and chain-ends that are induced by the particle with center at the origin. In Sec. II we consider the small particle limit where $\sigma \ll r, R_x$, and in Sec. III the long chain limit where $\sigma, r \ll R_x$.

II. SMALL PARTICLE LIMIT

The interaction of a small particle with polymers can be described by a multipole-type expansion. The leading isotropic and anisotropic behavior of the densities $E$ and $M$ induced by the particle in the dilute solution can be expressed in terms of particle amplitudes

$$I = \sigma^{2m} \bar{I}, \quad N = \sigma^d \bar{N}, \quad N' = \sigma^{2m+2} \bar{N}' ,$$

where $\bar{I}, \bar{N}, \bar{N}'$ are dimensionless and depend on the shape of the particle, and distributions

$$\eta(\rho), \quad \varphi(\rho), \quad \mu(\rho) ; \quad \bar{\rho} = \hat{r}/R_x$$

2
of the distance $\hat{r}$ between the two ends, between an end and any monomer, and between any two monomers of a single chain in free space, without the particle. Here we consider the scaling limit, i.e., a large number $M$ of monomers per chain, and assume the normalizations

$$\int d\hat{q} \eta(\hat{q}) = \int d\hat{q} \varphi(\hat{q}) = \int d\hat{q} \mu(\hat{q}) = 1.$$  \hspace{1cm} (2.3)

For ellipsoids, dumbbells, and lenses, explicit expressions$^7$ for the particle amplitudes (2.1) are given in Ref. 3.

We introduce polymer critical exponents $x_e, x_m$ that are related to the power law exponents$^4$ in the molecular weight dependence $M^\nu$ of $R_x$ and $M^{\gamma-1}$ of the partition function of a polymer with one end fixed in free space by

$$2x_e = d - \frac{\gamma}{\nu}, \quad x_m = d - \frac{1}{\nu}.$$ \hspace{1cm} (2.4)

The leading isotropic contribution to the densities $\mathcal{E}$, $\mathcal{M}$ is given by

$$\{\mathcal{E}_{\text{iso}}(r), \mathcal{M}_{\text{iso}}(r)\} - 1 = -IR_x^{x_m} \left\{ \varphi \left( \frac{r}{R_x} \right), \mu \left( \frac{r}{R_x} \right) \right\},$$ \hspace{1cm} (2.5)

and the leading anisotropic contribution by the sum of

$$\{\mathcal{E}_{\text{aniso}}(r), \mathcal{M}_{\text{aniso}}(r)\} = -N R_x^{x_m} \frac{1}{r^2} \int_{r/R_x}^\infty \varphi \left( \frac{r}{R_x} \right), \mu \left( \frac{r}{R_x} \right) \right\},$$ \hspace{1cm} (2.6)

and

$$\{\mathcal{E}'_{\text{aniso}}(r), \mathcal{M}'_{\text{aniso}}(r)\} = -N'R_x^{x_m} \frac{\partial^2}{\partial r^2} \left\{ \varphi \left( \frac{r}{R_x} \right), \mu \left( \frac{r}{R_x} \right) \right\},$$ \hspace{1cm} (2.7)

as we show in Appendix A. In the long chain limit $R_x \rightarrow \infty$ the above expressions reduce to

$$\{\mathcal{E}_{\text{iso}}(r), \mathcal{M}_{\text{iso}}(r)\} - 1 \rightarrow -I \frac{1}{p x_m} \{c_e, c_m\},$$ \hspace{1cm} (2.8)
\[ \{ \mathcal{E}_{\text{aniso}}(\mathbf{r}), \mathcal{M}_{\text{aniso}}(\mathbf{r}) \} \rightarrow N \frac{r_\parallel^2}{r^2} \frac{1}{r^d} \frac{d}{d-1} \frac{\Gamma(d/2)}{2^d \pi^{d/2}} \{ x_e, x_m \}, \quad (2.9) \]

\[ \{ \mathcal{E}’_{\text{aniso}}(\mathbf{r}), \mathcal{M}’_{\text{aniso}}(\mathbf{r}) \} \rightarrow -N’ \frac{r_\parallel^2}{r^2} \frac{1}{r^{x_m+2}} x_m (x_m + 2) \{ c_e, c_m \}. \quad (2.10) \]

Here \( r_\parallel \) is the component of \( \mathbf{r} \) parallel to the particle axis, and \( c_e \) and \( c_m \) are positive amplitudes in the short-distance asymptotic forms \( \varphi(\varrho) \rightarrow c_e \varrho^{-x_e} \) and \( \mu(\varrho) \rightarrow c_m \varrho^{-x_m} \) for \( \varrho \ll 1 \). The leading long chain behavior \( (2.9) \) arises from the terms with integrals in \( (2.6) \) via the normalizations \( (2.3) \). An isotropic term has been discarded on deriving \( (2.10) \) from \( (2.7) \). The exponents \( x_e, x_m \), the amplitudes \( c_e, c_m \), and the functions \( \bar{I}, \bar{N}, \bar{N}’ \) and \( \eta, \varphi, \mu \) are “universal”, i.e. independent of the chemical microstructure of the chains, but different for ideal and self-repelling chains.

The two coefficients \( N \) and \( N’ \) describing the anisotropic behavior are both positive for prolate particle shapes such as dumbbells and prolate ellipsoids and both negative for oblate shapes. This applies to ideal\(^8\) as well as self-repelling\(^3\) polymer chains. Visualizing the anisotropy of the density profiles by means of contour surfaces of constant density, we find that the contribution \( (2.10) \) from \( N’ \) leads to an ellipsoidal contour with the same prolate/oblate character as the particle surface, while the contribution \( (2.9) \) from \( N \) has the opposite character\(^9\).

For self-repelling chains, \( \nu > 1/2 \), and thus \( (\sigma/r)^d \gg (\sigma/r)^{x_m+2} \) for small \( \sigma/r \), so that the \( N \)-term in \( (2.9) \) dominates, and the \( N’ \)-term in \( (2.10) \) can, in general, be neglected. This leads to the remarkable result that for \( \sigma \ll r \ll R \) the contour surfaces of an oblate particle are prolate and vice versa, if the chains are self-repelling.

However, for ideal chains, where \( x_m = d - 2 \), both anisotropic contributions \( (2.9) \) and \( (2.10) \) are of the same order, and their sum has the sign of the \( N’ \)-term in \( (2.10) \), so that the contour surfaces have the same character as the particle shape. This is discussed in more detail at the end of Appendix A, where we also present explicit expressions for the distance distributions \( \eta, \varphi, \mu \) and the amplitudes \( c_e, c_m \) of ideal chains.

**III. LONG CHAIN LIMIT**

On approaching the particle surface, \( \mathcal{E} \) and \( \mathcal{M} \) vanish in the scaling limit, i.e., the particle surface is a contour surface with density zero. In the case of self-repelling chains it is
interesting to explicitly see the changeover to the contour surfaces of opposite prolate/oblate character, mentioned above, as the distance from the particle increases. To this end consider the long chain limits\(^{10}\)

\[
\hat{\mathcal{E}}(\mathbf{r}) \equiv \lim_{R_x \to \infty} \mathcal{E}(\mathbf{r}) = \lim_{\tilde{r} \to \infty} \langle \Phi(\mathbf{r})\Phi(\tilde{\mathbf{r}}) \rangle_{\text{part}} / \langle \Phi(0)\Phi(\tilde{\mathbf{r}}) \rangle_{\text{bulk}}
\]

(3.1)

and

\[
\hat{\mathcal{M}}(\mathbf{r}) \equiv \lim_{R_x \to \infty} \mathcal{M}(\mathbf{r}) = \lim_{\tilde{r} \to \infty} \langle \Psi(\mathbf{r})\Psi(\tilde{\mathbf{r}}) \rangle_{\text{part}} / \langle \Psi(0)\Psi(\tilde{\mathbf{r}}) \rangle_{\text{bulk}}
\]

(3.2)

of \(\mathcal{E}\) and \(\mathcal{M}\) for \(R_x \to \infty\), which using the polymer-magnet equivalence\(^4\) can be obtained from correlation functions \(\langle \rangle_{\text{part}}\) and \(\langle \rangle_{\text{bulk}}\) at the critical point of the zero component vector field theory, in the presence and absence of the particle. Here \(\Phi\) is the order-parameter density, and \(\Psi\) is proportional\(^3\) to the energy density in the field theory.

For \(r \gg \sigma\) the three leading contributions to the right hand sides of (3.1) and (3.2) are given by the right hand sides of (2.8)-(2.10), as expected and shown in Appendix B.

Results for arbitrary \(r\) are obtained for the monomer density \(\hat{\mathcal{M}}\) of self-repelling chains in \(d = 2\) spatial dimensions outside an ellipse, a dumbbell of two intersecting circles, and a lens with two circular surface lines, using the corresponding correlation functions \(\langle \Psi\Psi \rangle_{\text{part}}\) given\(^{11}\) in Appendix A of Ref. 3.

### A. Ellipsoids

For the ellipse in \(d = 2\) with diameters \(D_{\parallel} < D_{\perp}\),

\[
\hat{\mathcal{M}}_{\text{ell}} = \left[ \frac{\tilde{E}^2}{4(E^2 + H^2)} \right]^{1/3} \frac{q_{\text{ell}}^{2/3}}{} \mathcal{G}(q_{\text{ell}}).
\]

(3.3)

Here

\[
\tilde{E} = E + \sqrt{1 + E^2},
\]

(3.4)

\(E\) and \(H\) are elliptic coordinates given by

\[
2f\sqrt{1 + E^2} = \sqrt{r_{\parallel}^2 + (|r_{\perp}| + f)^2} + \sqrt{r_{\parallel}^2 + (|r_{\perp}| - f)^2},
\]

\[
2f\sqrt{1 - H^2} = \sqrt{r_{\parallel}^2 + (|r_{\perp}| + f)^2} - \sqrt{r_{\parallel}^2 + (|r_{\perp}| - f)^2},
\]

(3.5)
with the interfocal distance

\[ 2f = \sqrt{D_\perp^2 - D_\parallel^2}, \quad (3.6) \]

and

\[ q_{\text{ell}} = \frac{1}{g E^2 - 1}, \quad g = \frac{D_\perp - D_\parallel}{D_\perp + D_\parallel}. \quad (3.7) \]

The quantity \( q \) tends to \(+\infty\) and 0 if the distance of \( r \) from the particle surface tends, respectively, to zero and infinity. For moderate distances,

\[ G(q) = \frac{8\pi}{45\sqrt{3}} \xi^3 F_2 \left( \frac{1}{3}, \frac{2}{3}, \frac{7}{6}, 2; -\frac{1}{4\xi} \right), \quad \xi = q(1 + q), \quad (3.8) \]

where \( 3F_2 \) is a generalized hypergeometric function\(^\text{12} \). For larger distances, \( G \) follows from analytic continuation. In particular for \( q \to 0 \),

\[ G(q) \to \xi^{-2/3} [1 - \xi^{1/3}|B_2| + 2\xi/3 + \mathcal{O}(\xi^{4/3})] , \quad (3.9) \]

where \(|B_2| = 1.05 \), see footnote 24 in Ref. 13. The leading anisotropic behavior

\[ \hat{\mathcal{M}}_{\text{ell}, \text{aniso}} = -\frac{1}{3} f^2 \frac{r_\parallel^2}{r^4} \quad (3.10) \]

of \( \hat{\mathcal{M}}_{\text{ell}} \) at large distances comes from the first factor on the right hand side of (3.3), which tends to \( 1 - H^2/(3E^2) \), while \( q^{2/3} G \) tends to 1. Eq. (3.10) is consistent with (2.9), since the particle amplitude \( N \) is negative and given by \( N = -(\pi/2)g[(D_\perp + D_\parallel)/2]^2 \), see Eq. (3.6) in Ref. 3. Unlike the particle surface, the contour surface \( \hat{\mathcal{M}}_{\text{ell}} = \text{const} \), with \text{const} slightly below 1, extends farther in the \( \parallel \) than in the \( \perp \) direction. For an ellipse with \( D_\parallel/D_\perp = 1/3 \) and a “needle” with \( D_\parallel = 0 \) in \( d = 2 \), this is shown in Fig. 1. As a consequence, the two graphs \( \hat{\mathcal{M}}(r_\perp = r, r_\parallel = 0) \) and \( \hat{\mathcal{M}}(r_\perp = 0, r_\parallel = r) \) must \text{cross} at a certain \( r = r_c \). For the needle this is shown in Fig. 2.

The density profile (3.3) for self-repelling polymers, which depends on both coordinates \( E \) and \( H \), should be compared with the corresponding profile for ideal chains around ellipsoidal particles. In this case the surfaces of constant monomer density are ellipsoids confocal with the particle surface, since the profile only depends on \( E \). For example, for an oblate ellipsoid\(^\text{1,8} \) in \( d = 3 \),

\[ \hat{\mathcal{M}}_{\text{ell}}^{(\text{ideal})} = \left[ 1 - \frac{\arctan(1/E)}{\arctan \sqrt{(D_\perp/D_\parallel)^2 - 1}} \right]^2. \quad (3.11) \]
Here $|r_\perp|$ in (3.5) is the modulus of the two-dimensional component of $r$ perpendicular to the rotation axis. The contour surfaces $\hat{N}_{\text{ell}}^{(\text{ideal})} = \text{const}$ for an ellipsoid with $D_\parallel/D_\perp = 1/3$ and a circular disk with $D_\parallel = 0$ in $d = 3$ are shown in Fig. 3.

### B. Dumbbells and Lenses

For the dumbbell with $0 \leq \alpha \leq \pi$ and the lens with $\pi \leq \alpha \leq 2\pi$ shown in Figs. 1 and 2 of Ref. 3,

$$\hat{N}_{\text{db}}^{(\text{l})}(r) = \left(\frac{\pi}{\alpha}\right)^{4/3} \left\{ |W^2 - 1| |\text{Re} \left[ \left( \frac{\theta_+ \bar{\theta}_-}{\theta_+ \bar{\theta}_-} \right)^{\pi/(2\alpha)} \right] | \right\}^{-2/3} G(q_{\text{db/l}}), \quad (3.12)$$

where

$$W = \frac{r_\perp + ir_\parallel}{D/2}, \quad \bar{W} = \frac{r_\perp - ir_\parallel}{D/2}, \quad (3.13)$$

and where $D$ is the distance between the intersection points of the two circular surface lines,

$$\theta_\pm = 1 \pm \frac{1}{W}, \quad \bar{\theta}_\pm = 1 \pm \frac{1}{\bar{W}},$$

$$q_{\text{db/l}} = \left| \frac{(\theta_+)^{\pi/\alpha} - (\theta_-)^{\pi/\alpha}}{4 \text{Re}[(\theta_+ \bar{\theta}_-)^{\pi/\alpha}]} \right|, \quad (3.14)$$

and $G$ is the function in Eq. (3.8). The intersection points are located at $r_\perp = \pm D/2$, $r_\parallel = 0$, and $R = D/(2\sin(\alpha/2))$ is the radius of the circular surface lines.

For the special case $\alpha = 0$ of a dumbbell of two touching circles of radius $R$, Eqs. (3.12)-(3.14) lead to the result given in Eqs. (3.4) and (3.5) of Ref. 13 and to the density contour lines given in Fig. 4 of the present paper. The lower curve in the numerical plot in Fig. 1 of Ref. 13 is erroneous and is corrected in Fig. 5 of the present paper. The crossing of $\hat{N}(r_\perp = \rho R, 0)$ and $\hat{N}(0, r_\parallel = \rho R)$, that appears in Fig. 5 slightly below $\rho = 5$, implies contours $\hat{N}$ that are more extended along the $r_\parallel$ axis and the $r_\perp$ axis for const $\ll 1$ and const $\to 1$, respectively. This agrees with Fig. 4 and is consistent with (2.9), since the particle amplitude $N = -D^2(\pi/6)[1 - (\pi/\alpha)^2]$ for the dumbbell or lens is positive, $N = R^2\pi^3/6$, for $\alpha = 0$.

The special cases of a needle of length $l$ and a circle of radius $R$ in $d = 2$ correspond to $D_\perp = l, D_\parallel = 0$ and to $D_\perp = D_\parallel = 2R$ in Eq. (3.3) and to $D_\perp = D_\parallel = 2R, \alpha = 2\pi$ and $D = 2R, \alpha = \pi$ in Eq. (3.12). The result for the circle is given in Eq. (1) of the second paper in Ref. 10.
For small distances from the particle surface, $M_{\text{ell}}$ and $M_{\text{dhl}}$ are proportional to the distance raised to the power $1/\nu$, with $1/\nu = 4/3$ in $d = 2$.

IV. SUMMARY AND CONCLUDING REMARKS

We have shown that chain self-avoidance has a pronounced effect on the anisotropic density profiles that are induced by a non-spherical colloidal particle in a polymer solution. In particular, we considered the densities $M$ of chain monomers and $E$ of chain ends induced by mesoscopic particles with the shapes of ellipsoids, dumbbells, and lenses and with sizes $\sigma$ much smaller than the polymer size $R_x$.

For $\sigma \ll r, R_x$ the profiles in dilute solution are determined by three universal amplitudes which characterize the size and shape of the particle and three distance distributions for a single chain without the particle present. This is shown in Eqs. (2.5)-(2.7) of Sec. II. For self-avoiding polymers in two spatial dimensions, we analyzed $M$ in the regime $\sigma, r \ll R_x$, which encompasses both $r$ close to the particle surface and $r$ much larger than the particle size.

The densities are depleted near the particle, where the polymer fluctuations are impeded. The anisotropic shape of the obstacle has two opposing effects on the densities. Consider, e.g., an oblate particle with the shape of a pancake or circular disk of diameter $l$ and compare a point $r_p = (r_\perp, 0)$, where $r_\perp = r > l/2$, in the plane of the disk with a point $r_a = (0, r)$ on its axis. Both points have the same distance $r$ from the particle center. (i) The closest distance to the obstacle in case of $r_a$ is $r$ and is larger than the closest distance $r - l/2$ in case of $r_p$. Therefore, one might expect that the densities at $r_a$ are larger than at $r_p$. (ii) However, the obstacle appears wider from $r_a$ than from $r_p$ suggesting a trend in the opposite direction. Actually, we find for $\sigma \ll r \ll R_x$ that the trends (i) and (ii) prevail in the absence and presence, respectively, of chain self-avoidance. This applies to general oblate particle shapes and also to prolate shapes, where the roles of $r_p$ and $r_a$ are interchanged. See Eqs. (2.9), (2.10), the two last paragraphs in Sec. II, and the comparison of self-avoiding and ideal chain results in (3.3) and (3.11).

Figs. 1, 3, and 4 illustrate this effect in terms of contour surfaces of constant density. The anisotropy of contour surfaces with $\sigma \ll r \ll R_x$ is opposite to that of the particle surface if the chains are self-avoiding. The $r$-dependence of the densities of self-avoiding
chains along $r_p$ and $r_a$ cross at a certain $r = r_c$, as shown in Figs. 2 and 5. The value of the bulk-normalized monomer density $M$ at the crossing is very close to $1/2$ for all our particle shapes in two dimensions.

It would be interesting to check our predictions for polymer density profiles about anisotropic particles in simulations. In the case of the needle in $d = 2$ considered in Fig. 1b, one could consider self-avoiding walks on a quadratic lattice with the lattice sites along a finite straight line excluded.

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**APPENDIX A: SMALL PARTICLE EXPANSION FOR DENSITY PROFILES**

Using the polymer-magnet equivalence, the polymer densities around the particle can be expressed as

$$
\mathcal{E}(r) = \mathcal{L} \langle \Phi(r) \phi \rangle_{\text{part}} / \Xi_{\text{bulk}},
$$

$$
\mathcal{M}(r) = \mathcal{L} \langle \Psi(r) \phi^2 \rangle_{\text{part}} / \mathcal{L} \langle \Psi(r) \phi^2 \rangle_{\text{bulk}},
$$

(A1)

and the distance distributions of a free chain as

$$
\eta(r/R_x) = R_x^d \mathcal{L} \langle \Phi(r) \Phi(0) \rangle_{\text{bulk}} / \Xi_{\text{bulk}},
$$

$$
\varphi(r/R_x) = R_x^{d-1/\nu} \mathcal{L} \langle \Psi(r) \Phi(0) \phi \rangle_{\text{bulk}} / \Xi_{\text{bulk}},
$$

$$
\mu(r/R_x) = R_x^{d-2/\nu} \mathcal{L} \langle \Psi(r) \Psi(0) \phi^2 \rangle_{\text{bulk}} / \Xi_{\text{bulk}}
$$

(A2)

in terms of correlation functions of the $n$-vector model in the limit $n \to 0$. The Laplace transform $\mathcal{L}$ relates the temperature deviation from the critical point of the $n$-vector model to the chain length and is defined in Eq. (2.5) of Ref. 3, the energy-density like quantity $\Psi$ is defined in Eqs. (2.4) and (2.8) of Ref. 3, and

$$
\phi = \int dr' \Phi(r'), \quad \Xi_{\text{bulk}} = \mathcal{L} \langle \Phi(r) \phi \rangle_{\text{bulk}}.
$$

(A3)

The normalization (2.3) of $\varphi$ and $\mu$ follows from Eq. (C2) in Ref. 3.

9
Eqs. (A2) imply the relations

\[ c_e = C_{\Phi \Psi \Phi} / B_{\Phi}, \quad c_m = C_{\Psi \Phi \Phi} / B_{\Psi} \]  

between the polymer short distance amplitudes \( c_e \) and \( c_m \) defined below Eq. (2.10) and the amplitudes\(^{14} \) in the operator product expansions \( \Psi(\mathbf{r})\Phi(\mathbf{0}) \to (C_{\Phi \Psi \Phi} / B_{\Phi})r^{-x_m} \Phi(\mathbf{0}) \) and \( \Psi(\mathbf{r})\Psi(\mathbf{0}) \to (C_{\Psi \Phi \Phi} / B_{\Psi})r^{-x_m} \Psi(\mathbf{0}) \) of the \( n \)-vector field theory.

The operator expansion\(^3,7\)
\[
\exp(-\mathcal{H}_{\text{part}}) \propto 1 - I \Psi(\mathbf{r}_P) - NT_{\parallel \parallel}^{\Phi}(\mathbf{r}_P) - N'\partial_\parallel^2 \Psi(\mathbf{r}_P) + \ldots
\]  
for the Boltzmann factor of a small particle embedded at \( \mathbf{r}_P \) in the \( n \to 0 \) model allows us to relate the leading isotropic and anisotropic contributions in \( \mathcal{E} \) and \( \mathcal{M} \) to \( \eta, \varphi \), and \( \mu \) as given in Eqs. (2.5)-(2.7). Here \( \partial_\parallel \) and \( T_{\parallel \parallel} \) denote the directional derivative and the diagonal component of the stress tensor along the direction of the particle axis.

Consider first the leading isotropic contributions. Replacing \( \exp(-\mathcal{H}_{\text{part}}) \) in the statistical weight of (A1) by the first two terms on the right hand side of the expansion (A5) and using (A2) and (2.4) leads to the relation (2.5). In the case of \( \mathcal{M}_{\text{iso}} \) one also uses that \( L \langle \Phi \phi^2 \rangle_{\text{bulk}} = R_1 / \nu \Xi_{\text{bulk}} \), as follows from translational invariance of bulk averages and Eq. (C2) in Ref. 3. The relation (2.7) follows similarly.

To derive the relation for \( \mathcal{E}_{\text{aniso}} \) in (2.6), we consider
\[
R_{x}^d \frac{\mathcal{L}(T_{kl}(\mathbf{r}_P)\Phi(\mathbf{r})\phi^2)_{\text{bulk}}}{\Xi_{\text{bulk}}} = \frac{skst}{s^2} \tau_e(\varphi) + \delta_{kl}\tilde{\tau}_e(\varphi),
\]  
where \( s = \mathbf{r}_P - \mathbf{r} \) and \( \varphi = s / R_x \). The right hand side of (A6) follows from translational and rotational symmetry of bulk averages. The universal functions \( \tau_e, \tilde{\tau}_e \) are determined by the trace and continuity equations of the stress tensor \( T_{kl} \) given in Eqs. (C8) and (C9) of Ref. 3, which yield
\[
\tau_e + d\tilde{\tau}_e = -x_e \eta + \left( 2x_e + \varphi \frac{d}{d\varphi} \right) \varphi
\]  
and
\[
(d - 1)\tau_e + \varphi \frac{d}{d\varphi} (\tau_e + \tilde{\tau}_e) = -\varphi \frac{d}{d\varphi} \eta,
\]  
respectively. To derive (A7), we have used Eq. (C3) in Ref. 3 and
\[
\frac{d \ln[\Xi_{\text{bulk}}(R_x)^{-x_m}]}{d \ln R_x} = -2x_e.
\]
The sum of Eqs. (A7) and (A8) is a linear differential equation for $\tau_e + \tilde{\tau}_e$, with solution

$$
\tau_e(q) + \tilde{\tau}_e(q) = q^{-d} \int_0^\infty \tilde{d} q q^{d-1} \left[ (x_e + \tilde{q} \frac{d}{d\tilde{q}}) \eta(\tilde{q}) - (2x_e + \tilde{q} \frac{d}{d\tilde{q}}) \varphi(\tilde{q}) \right].
$$

(A10)

Eqs. (A10) and (A8) lead to an explicit expression for the anisotropy-coefficient $\tau_e$, which via (A6) implies the result for $\mathcal{E}_\text{aniso}$ in (2.6).

The result for $\mathcal{M}_\text{aniso}$ follows in a similar fashion by considering

$$
\mathcal{R}_x^d \frac{\mathcal{L} (T_{kl}(r_P) \Psi(r) \phi^2)_{\text{bulk}}}{\mathcal{L} (\Psi(r) \phi^2)_{\text{bulk}}} = \frac{s_k s_l}{s^2} \tau_m(q) + \delta_{kl} \tilde{\tau}_m(q).
$$

(A11)

Here

$$
\tau_m + d\tilde{\tau}_m = -2x_e \varphi + \left( 2x_e - \frac{1}{\nu} + \tilde{q} \frac{d}{d\tilde{q}} \right) \mu,
$$

(A12)

and

$$
(d - 1)\tau_m + \tilde{q} \frac{d}{d\tilde{q}} (\tau_m + \tilde{\tau}_m) = - 2 \tilde{q} \frac{d}{d\tilde{q}} \varphi.
$$

(A13)

For later reference we note results for ideal chains which are also contained in the above expressions. For ideal chains the $n$ components of the $n$-vector model decouple, and (A1), (A2), (A5) can be used within a one-component field theory with Hamiltonian $H = \int dr'' [((\nabla \Phi)^2 + t\Phi^2)/2$ and Dirichlet boundary condition $\Phi = 0$ on the surface of the embedded particle. Here $t$ is the Laplace conjugate to the “chain length” $\mathcal{R}_x^2/2$, $\Psi = \Phi^2$, and $I, N, N'$ are the $n$-independent amplitudes of the $n$-component theory in the absence of anharmonicities. For ideal chains the scaling dimensions of $T_{||}$ and $\partial^2_{||} \Phi^2$ are degenerate and equal to $d$. It is convenient to introduce operators $O_{VI} = (\partial_{||} \Phi)^2/2$ and $O_{VII} = \Phi (\partial^2_{||} \Phi)/2$ so that $NT_{||} + N' \partial^2_{||} \Phi^2 = \beta_{VI} O_{VI} + \beta_{VII} O_{VII} + \text{iso}$, with “iso” denoting isotropic operators, and

$$
\beta_{VI} = 4N' + Nd/(d-1) \quad \text{and} \quad \beta_{VII} = 4N' - N(d-2)/(d-1).
$$

(A15)

The reason is that $O_{VI}$ does not contribute to $\mathcal{E}$ and $\mathcal{M}$, and

$$
\{\mathcal{E}_\text{aniso} + \mathcal{E}'_\text{aniso}, \mathcal{M}_\text{aniso} + \mathcal{M}'_\text{aniso} \} = -\{1, 2\} \beta_{VII} d(d-2) (\tilde{S}/2) \frac{1}{r^d} \frac{r^2}{r^2}
$$

(A16)
with $\tilde{S}_d = \Gamma((d/2) - 1)/(4\pi^{d/2})$. This is consistent with (2.9), (2.10), since $x_m = d - 2$, $x_e = x_m/2$, and

$$\{c_e, c_m\} = 2\tilde{S}_d \{1, 2\}$$

(A17)

follows from (A4) in the present Gaussian model. We also note that in $d = 3$

$$\eta(q) = \frac{1}{(2\pi)^{3/2}} e^{-q^2/2}, \quad \varphi(q) = \frac{1}{2\pi q} \text{erfc}\left(\frac{q}{\sqrt{2}}\right), \quad \mu(q) = \frac{4}{\pi q} i^2 \text{erfc}\left(\frac{q}{\sqrt{2}}\right).$$

Due to Eq. (A16) the height contours for $\sigma \ll r \ll R_x$ have the same prolate/oblate character as the particle, if the chains are ideal. The reason is that $\beta_{VII}$ has the sign of $N'$, i.e., is positive/negative for prolate/oblate particles. For ellipsoids and dumbbell/lenses this follows from the results of the first and second paper, respectively, in Ref. 8. For an oblate ellipsoid see also Eq. (3.11).

The amplitudes $c_e$ and $c_m$ also determine the leading isotropic variation for $\sigma \ll r \ll R_x$, see Eq. (2.8). For example, consider $M$ for self-repelling chains in $d = 2$, where

$$M_{iso} - 1 = -\frac{1}{r^{x_m}} I 2^{-x_m}|B_2|,$$

(A19)

with

$$2^{-x_m}|B_2| = \left(\frac{C_{\varepsilon\varepsilon\varepsilon}}{B^3/2 A_\varepsilon}\right)_{n=0}.$$

(A20)

Here we have used the expression for $c_m$ in (A4), the expression for $B_2$ in Eq. (A24) of Ref. 3, and have related $I$ and $\Psi$, respectively, to the coefficient $I$ and the energy density $\varepsilon$ with half space amplitude $A_\varepsilon$ as given in Ref. 3. The universal number $|B_2|$ is the one in Eq. (3.9). Substituting in (A19) the explicit forms of $I$ for an ellipse and a dumbbell or lens, as given in Eqs. (3.5) and (3.8) of Ref. 3, yields expressions consistent with our profiles (3.3) and (3.12).

**APPENDIX B: LARGE DISTANCE BEHAVIOR OF LONG CHAIN LIMIT**

Here we show that the expressions on the right hand sides of (2.8)-(2.10) not only follow from the small particle expressions (2.5)-(2.7) in the limit $r \ll R_x$ but also from the long chain expressions (3.1), (3.2) in the limit $\sigma \ll r$. In the latter case we insert the operator expansion (A5) into the long chain expressions. This leads to three-point functions in the bulk and at the critical point which can be taken, e.g., from Appendix A of Ref. 14.

12
This implies, for example, that the leading isotropic behavior of the monomer density (3.2) determined by the \( I \)-term is given by \(-I r^{-2m} C_{\Psi \Psi} / B_{\Psi}\), and thus by the second expression in (2.8), since the three and two point amplitudes \( C_{\Psi \Psi} \) and \( B_{\Psi} \) also determine the short distance amplitude \( c_m \), see (A4).

The two anisotropic contributions (2.9), (2.10) follow in a similar way. In case of the \( N \)-contribution one uses that

\[
- \frac{C_{\Omega \Omega}}{B_{\Omega}} = \frac{d}{d - 1} \frac{1}{\Omega_d} x_{\Omega} ,
\]

where \( \Omega \) equals \( \Phi \) or \( \Psi \), \( x_{\Phi} \equiv x_e \), \( x_{\Psi} \equiv x_m \), and \( 1/\Omega_d = \Gamma(d/2)/(2\pi^{d/2}) \). Eq. (B1) follows, e.g., from the “shift identity”

\[
\int dx \langle T_{zz}(x,0) O(0,z_1) O(0,z_2) \rangle_{\text{bulk}} = \partial_{z_1} \langle O(0,z_1) O(0,z_2) \rangle_{\text{bulk}} \quad \text{(B2)}
\]

on inserting the form\(^{14}\) of the bulk correlations at the critical point. Here \( z_1 > 0, z_2 < 0 \), and \( x \) is the \( d-1 \) dimensional component of \( r = (x,z) \) perpendicular to the \( z \)-axis.

\[\text{References}\]

6. Our polymers are flexible, with a persistence length that is much smaller than \( \sigma \) and \( R_x \). The “nano-particle case” (or “protein-limit”) with \( \sigma \ll R_x \) has been investigated theoretically to a lesser extent than the “colloid-limit” with \( \sigma \gg R_x \). This refers to both analytical and simulation approaches.
7. In terms of the amplitudes \( I, N, N' \) and \( A \) in Ref. 3, our amplitudes \( I, N, N' \) in Eq. (2.1) read \( I = T 2^{-x_m} A, N = N', N' = N' 2^{-x_m} A \), so that \( I \psi = I \Psi, N T_{kl} = N' T_{kl} \), and \( N' \partial_k \partial_l \psi = N' \partial_k \partial_l \Psi \) in the Boltzmann factor of the small particle, see Eqs. (2.2), (2.3), and (2.8) in Ref. 3. For self-avoiding chains in \( d = 2 \), besides \( N' \) in (2.1), there is another next to leading amplitude of anisotropy, \( N'' \), with the same scaling dimension. See Eqs. (3.1) and (3.2) in Ref. 3.
The competition between $N$ and $N'$ in the polymer density profiles around a single anisotropic particle is not found in the polymer-induced orientational interaction with a close wall, where $N$ and $N'$ act in the same direction.\(^3\)

In accordance with Eq. (3.2), the quantities $q = q(r)$ and $\xi = \xi(r)$ in Secs IIIA and IIIB follow from $q = q(r_1, r_2)$ and $\xi = \xi(r_1, r_2)$ in Appendix A2 of Ref. 3 on replacing $r_1$ by $r$ and taking the limit $r_2 \to \infty$.


FIG. 1: (a) Density contour lines for $\hat{N}=0, 0.1, 0.2, 0.3, 0.4, 0.49; 0.51, 0.6, 0.7$ of long self-avoiding chains in $d = 2$ outside a non-adsorbing elliptical particle with aspect ratio $D_{\parallel}/D_{\perp} = 1/3$. Note that the contour $\hat{N}=0.7$ extends farther in the $\parallel$ than in the $\perp$ direction, i.e., has an anisotropy opposite to that of the particle surface where $\hat{N}=0$. (b) Same for a needle of length $D_{\perp}$ and with $D_{\parallel} = 0$ in $d = 2$. 
FIG. 2: (a) $\hat{M}(r_\perp = r, r_\parallel = 0)$ and $\hat{M}(r_\perp = 0, r_\parallel = r)$ shown by asterisks and crosses, respectively, for the needle of Fig. 1b. (b) The “crossing” region of Fig. 2a.
FIG. 3: (a) Density contours for $\hat{M}=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$ of long ideal chains in $d = 3$ outside a non-adsorbing oblate ellipsoidal particle with aspect ratio $D_∥/D_⊥ = 1/3$. Shown are contour lines in a plane $(r_⊥, r_∥)$ that contains the particle axis at $r_⊥ = 0$. (b) Same for a circular plate in $d = 3$ with $D_∥ = 0$. All the contours extend farther in the $⊥$ than in the $∥$ direction and have the same type of anisotropy as the particle surface.
FIG. 4: Density contour lines for $\hat{M}=0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.49, 0.51, 0.55, 0.6, 0.65$ about a dumbbell-particle of two touching circles of radius $R$ in $d=2$. The contour $\hat{M}=0.65$ extends farther in the $\perp$ than $\parallel$ direction, i.e., has an anisotropy opposite to the particle surface where $\hat{M}=0$. 

FIG. 5: (a) $\hat{M}(r_\perp = \rho R, r_\parallel = 0)$ and $\hat{M}(r_\perp = 0, r_\parallel = \rho R)$ shown by crosses and asterisks, respectively, for the dumbbell of Fig. 4. (b) The “crossing” region of Fig. 5a. Note that the value of $\hat{M}$ at crossing is very close to 1/2, both in Fig. 2 and Fig. 5.