Convective Depletion During The Fast Propagation Of A Nanosphere Through A Polymer Solution

Theo Odijk*, Complex Fluids Theory, Faculty of Applied Sciences, Delft University of Technology, Delft, and Colloids and Interfaces Group, Leiden Institute of Chemistry, Leiden (Dated: December 8, 2003)

Abstract

A theory of nonlinear convective depletion is set up as a nanosphere translates fast through a semidilute polymer solution. For nanospheres a self-consistent field theory in the Rouse approximation is often legitimate. A self-similar solution of the convective depletion equation is argued to be feasible at high velocities. The nature of the thin boundary layer in front of the propagating particle is analyzed. One example of convective depletion is when a charged protein moves through a semidilute polymer under the influence of a high electric field. The protein velocity is then proportional to the fifth power of the field. The theory could be useful in interpreting the separation of protein mixtures by microchip electrophoresis.

*Address for correspondence: T. Odijk, P.O. Box 11036, 2301 EA Leiden, The Netherlands. Fax 31-71-5145 346; E-mail: Odijktcf@wanadoo.nl
1 Introduction

The propagation of colloidal particles through polymer solutions presents us with mathematical problems of considerable complexity, both at low and high velocities. A major simplification results if we focus on a particle of nanometer dimensions for the following reasons:

1) If the size is much smaller than the correlation length of, say, a semidilute polymer solution, the equilibrium depletion theory simplifies considerably (1, 2).

2) If the solvent is intermediate rather than excellent as is often the case in practice (3), it suffices to use a self-consistent field description based on chain entropy alone (4, 5). The polymer may be viewed as quasi-ideal.

3) It can be argued that the motion may be split up into two types of dynamics: dynamic depletion as a result of the rearrangement of the local polymer density about the particle, and the translation of the dressed particle (i.e. the particle together with its depletion layer) through the strongly fluctuating polymeric suspension (5). This is valid because the two respective time scales are well separated.

4) The polymer stress is highest close to the moving nanoparticle (5) so it is reasonable to suppose the dynamics of a chain section nearby is Rouselike or freely draining (5, 6). In effect, the polymer density is low in the depletion layer, for the density must be zero at the particle surface.

5) In general, at very high velocities, the elasticity of the polymer must come into play which could lead to complex phenomena like shock waves (7). An important dimensionless variable is then the ratio of the particle velocity to that of the elastic waves. But it is probably safe to neglect these when the size of the nanoparticle is much smaller than the distance between entanglements in the polymer solution.

Besides being of intrinsic interest from a theoretical point of view, the fast translation of small particles through semidilute polymer does occur in practice, namely during capillary gel electrophoresis of biomacromolecules at high electric fields (8).

I focus on the fast propagation of a nanoparticle, a problem reminiscent of others in condensed matter physics (e.g. convective diffusion (9), runaway electrons in a plasma (10), the increase of dissociation of weak electrolytes (11) and the complex electrophoretics of charged colloidal spheres (12) under high electric fields). It turns out that the motion
of a nanoparticle through a semidilute polymer is quite similar, though not identical, to that of convective diffusion occurring near a particle translating through a solution of some molecular species, which is continuously absorbed at the surface of the particle. Hence, Levich’s analysis proves to be useful \cite{9}. The Peclet number $Pe = va/D$ is important in the theory of convective diffusion. A sphere of radius $a$ is surrounded by a zone of size $a$, partly depleted of absorbing, diffusing molecules. The time scale $a^2/D$ of diffusion where $D$ is the diffusion coefficient of the molecules, has to be balanced against the time scale $a/v$ of convection if the sphere has a speed $v$. At high Peclet numbers ($Pe \gg 1$), convection has a dramatic impact on the shape of the diffusional layer \cite{9}. In the polymer case, the analogous phenomenon may be termed convective depletion but it is determined by a different dimensionless number defined by}

\[ \Delta = \frac{va^3}{D_s A^2} \]  

In the case at hand \cite{5}, the depletion layer of size $a$ pertains to a section of polymer chain consisting of $a^2/A^2$ depleted segments of Kuhn Length $A$ and diffusion coefficient $D_s$. I thus introduce eq (1) in the Rouse approximation. Accordingly, one expects the depletion layer to be deformed strongly by convection at high $\Delta$.

### 2 Convective depletion at high velocities

The dynamics of a nanosphere in a semidilute solution of flexible polymer of concentration $c_0$ has been discussed previously \cite{5}. The free energy of depletion $F$ is solely of entropic origin and is a functional of $c(\vec{r}, t)$, the density of polymer segments at position $\vec{r}$ and time $t$

\[ F[c(\vec{r}, t)] = \frac{1}{6} A^2 k_B T \int d\vec{r} \left( \nabla \cdot c \right)^2 \]  

Here, $k_B$ is Boltzmann’s constant and $T$ is the temperature. For convenience, the sphere is held fixed and its centre is the origin of our Cartesian coordinate system. At great distances from the sphere, the polymer solution flows uniformly with velocity $-v_0$ in the $z$ direction. The flow is perturbed by two effects: the solvent is assumed to stick to the sphere, and the polymer segments cannot penetrate its surface; the stick boundary condition seems reasonable since the polymer density tends to zero at the surface (i.e. we have depletion) and we may argue that the segments within the depletion layer are essentially Rouselike,
exerting little backflow on the solvent itself ([5],[6]). The radius \(a\) of the sphere is much smaller than both the polymer correlation and hydrodynamic screening lengths. Hence, the velocity \(\vec{u}(\vec{r},t)\) of a test segment is given by a balance of forces

\[
\vec{u} = \vec{v} + m \vec{f}
\]  

(3)

where \(\vec{v}(\vec{r},t)\) is the background velocity of the incompressible solvent, \(\vec{f}\) is the force on the test segment by virtue of its connection to some chain section and \(m\) is the mobility of the segment.

The gradient of the chemical potential \(\vec{\nabla} \mu = -\vec{f}\) now drives the reorganization of the segment distribution via the equation of continuity and eqs (2) and (3); the chemical potential of a segment is \(\mu(\vec{r},t) = \delta F/\delta c(\vec{r},t)\).

\[
\frac{\partial \varphi^2}{\partial t} + \vec{v} \cdot \vec{\nabla} (\varphi^2) = -B \vec{\nabla} \cdot \left( \varphi^2 \vec{\nabla} (\varphi^{-1} \Delta \varphi) \right)
\]  

(4)

I have here introduced \(B \equiv \frac{1}{8} m A^2 k_B T\) and a dimensionless “wavefunction” \(\varphi(\vec{r},t) \equiv (c(\vec{r},t)/c_0)^{\frac{1}{4}}\). This equation has been solved for a sphere translating slowly under stationary conditions in the absence of convection ([5]). Here, I wish to investigate convective depletion for fast uniform propagation of the sphere in the steady state. It turns out to be expedient to let the Stokes stream function \(\psi\) become the independent variable in problems involving convection ([4]).

\[
\psi = -\frac{1}{2} v_0 \sin^2 \theta \left( r^2 - \frac{3}{2}ar + \frac{1}{2} a^3 \right)
\]  

(5)

\[
v_r = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta} = -v_0 \cos \theta \left( 1 - \frac{3a}{2r} + \frac{a^3}{2r^3} \right)
\]  

(6)

\[
v_\theta = \frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} = \frac{1}{2} v_0 \sin \theta \left( 2 - \frac{3a}{2r} - \frac{a^3}{2r^3} \right)
\]  

(7)

The Stokes stream function and velocity of the solvent, here given in terms of spherical coordinates \((r, \theta, \varphi_s)\) ([13]), are assumed to be unperturbed by the polymer within the zone of depletion. I next switch from the variables \((r, \theta)\) to the new independent variables \((\theta, \psi)\) assuming axisymmetry. It is readily shown that the convective term in eq (4) reduces to

\[
\vec{v} \cdot \frac{\partial \varphi^2}{\partial \vec{r}^2} = \frac{v_\theta}{r} \frac{\partial \varphi^2}{\partial \psi} \bigg|_\psi
\]  

(8)

with the help of eqs (6) and (7).
At this juncture, I introduce an approximation at high $\Delta$. Levich has treated the convective diffusion of a fast moving sphere at high Peclet number ([9]) and it is expedient to follow closely the spirit of his analysis of the thin boundary layer in front of such a particle. There is a stagnation point at $\theta = 0$ and $r = 0$, so at high velocities one may picture the region of polymer depletion as in fig. 1. It is compressed by convection into a layer thinner than the radius of the sphere. Hence, I introduce the coordinate $y = r - a$ with $y \ll a$ in the regime of interest and approximate eqs (5-7) to the leading order as follows

$$\psi \simeq -\frac{3}{4}wy^2 \sin^2 \theta$$  \hspace{1cm} (9)

$$v_r \simeq \frac{1}{a^2 \sin \theta} \frac{\partial \psi}{\partial \theta} \simeq -\frac{3}{2}w \left( \frac{y}{a} \right)^2 \cos \theta$$  \hspace{1cm} (10)

$$v_\theta \simeq -\frac{1}{a \sin \theta} \frac{\partial \psi}{\partial y} \simeq \frac{3}{2}w \left( \frac{y}{a} \right) \sin \theta$$  \hspace{1cm} (11)

These equations describe the unperturbed flow of the incompressible solvent in the boundary layer. Eq (4) is now rewritten as

$$v_\theta \frac{\partial \varphi^2}{a \frac{\partial \theta}{\partial y}} \bigg|_\psi = -B \frac{\partial}{\partial \psi} \left[ \varphi^2 \left( \frac{\partial \varphi^{-1} \varphi_{yy}}{\partial \psi} \right) \right] \bigg|_\theta$$  \hspace{1cm} (12)

with the help of eqs (8-11). Hence, we attain an expression for the convective depletion within the boundary layer at the front of the sphere as a function of two new independent variables: the Stokes stream function $\psi$ by first eliminating $y$ using eqs (9) and (11), and the variable $s$ for convenience.

$$\frac{\partial \varphi^2}{\partial s} = -\frac{\partial}{\partial \psi} \left[ \varphi^2 \sqrt{-\psi} \left( \frac{\partial \varphi^{-1} \sqrt{-\psi} \frac{\partial \varphi}{\partial \psi}}{\partial \psi} \right) \right]$$  \hspace{1cm} (13)

$$s \equiv Ba^2 (3w)^{3/2} I(\theta) + c_1$$  \hspace{1cm} (14)

$$I(\theta) \equiv \int_0^\theta d\theta \sin^4 \theta$$  \hspace{1cm} (15)

Here, $c_1$ is a constant.
It is now useful to introduce the boundary conditions.

\[
\varphi = 0 \text{ at } \psi = 0 \quad (16)
\]

\[
\varphi = 1 \text{ as } \psi \rightarrow -\infty \quad (17)
\]

\[
\varphi = 1 \text{ at } \theta = 0, \psi = 0 \quad (18)
\]

\[
\varphi \frac{\partial^3 \varphi}{\partial y^3} \bigg|_\theta - \varphi \frac{\partial^2 \varphi}{\partial y^2} \bigg|_\theta \frac{\partial \varphi}{\partial y} \bigg|_\theta = 0 \text{ at } y = 0 \quad (19)
\]

The first equation expresses the usual depletion of the polymer at the surface which I suppose to be independent of the velocity of the particle. Far away from it, the polymer density must tend to the bulk value (eq (17)). However, eq (16) does not hold at \( \theta = 0 \) for there is a point of stagnation at \( \theta = 0, \psi = 0 \) so we require the boundary condition given by eq (18).

Finally, polymer segments cannot penetrate the sphere so the radial flux of polymer to the surface must be zero. This leads to the condition given by eq (19) upon temporarily reverting to the variable \( y \). In view of the boundary conditions and the form of eq (13), it is now possible to posit a similarity solution \( \varphi(\eta) \) in terms of the variable \( \eta \equiv -\psi/s^{2/5} \). The resulting equation is then further simplified with the help of the new independent variable \( p = \sqrt{\eta} \).

\[
\frac{32}{5} p^2 \varphi \frac{d \varphi}{dp} = \varphi \frac{d^4 \varphi}{dp^4} - \left( \frac{d^2 \varphi}{dp^2} \right)^2 \quad (20)
\]

This nonlinear equation looks rather awkward but a local analysis turns out to be useful.

### 3 Analysis of eq (20)

Usually one would substitute \( \varphi = \exp b \) and \( j = db/dp \) into eq (20) to decrease the order of the equation by one but this does not appear to be useful here. I have not attempted to derive a uniformly valid approximation to eq (20) because the term \( (d^2 \varphi/dp^2)^2 \) appears to play a significant role at \( p = O(1) \). Nevertheless, a local analysis within three regimes is fruitful for this term happens to be negligible close to and far away from the sphere.
3.1 Inner region

At the surface of the sphere, the polymer density vanishes (eq (16)) so that a series expansion of the form

\[ \varphi = c_2 \left( p^\alpha + c_3 p^{\alpha + \beta} + c_4 p^{\alpha + 2\beta} + \ldots \right) \]  

(21)

may be assumed with \( \alpha > 0 \) and \( \beta > 0 \) and where \( c_2, c_3 \) and \( c_4 \) are constants. Upon substituting this into eq (20), one discerns that there are only two viable solutions, if \( \alpha = 1 \) and \( \alpha = 3/2 \). Next if the radial polymer flux to the sphere is required to vanish (eq (19)), \( \alpha \) must either be equal to unity or be greater than 3/2. Hence, the only feasible solution for \( \varphi \) is if \( \alpha = 1 \). Again inserting eq (21) into eq (20) establishes the value of \( \beta = 5 \) and the constants \( c_3 \) and \( c_4 \)

\[ \varphi = c_2 \left( p + \frac{4}{225} p^6 + \frac{68}{556875} p^{11} + \ldots \right) \]  

(22)

The term in eq (20) containing the second derivative contributes only at order \( p^{11} \) in eq (22). Next, the boundary condition at the point of stagnation (eq 18) determines the value of the constant \( c_1 = 0 \); at \( \theta = 0, p \) must be nonzero for \( y > 0 \).

3.2 Outer region

Next, I attempt a WKB approximation in the region far away from the sphere by writing \( \varphi = 1 + h \) with \( |h| \ll 1 \). The term containing the second derivative is then subdominant and the order of the resulting linear equation is reduced by unity with the aid of the substitution \( g = dh/dp \)

\[ \frac{32}{5} p^2 g = \frac{d^3 g}{dp^3} \]  

(23)

There seems to be a turning point at \( p = 0 \) but I focus on the outer region \( p \gg 1 \) only, since there is at least one intermediate regime centered around \( p = O(1) \) where \( (d^2 \varphi/dp^2)^2 \) competes with \( \varphi d^4 \varphi/dp^4 \). There are three WKB solutions to eq (23) (14)

\[ g \sim \left( \frac{32p^2}{5} \right)^{-\frac{1}{4}} \exp S_0 \]  

(24)

\[ S_0 = w \int dp \left( \frac{32p^2}{5} \right)^{\frac{1}{4}} \]  

(25)
where \(1, -\frac{1}{2} + \frac{1}{2}\sqrt{3}i\) and \(-\frac{1}{2} - \frac{1}{2}\sqrt{3}i\) are the three roots of the equation \(w^3 = 1\). The outer solution obeying eq (17) is then

\[
\varphi = 1 + c_5 \int_0^\infty dp \, p^{-\frac{1}{3}} e^{-\frac{1}{2} H p^{5/3}} \sin \left( \frac{1}{2} \sqrt{3} H p^{5/3} + c_6 \right)
\]

\[H = \frac{3}{5} \left( \frac{32}{5} \right)^{1/3}\]

### 3.3 Intermediate region

According to eqs (22) and (26), the (square root of) the polymer density exhibits the oscillatory profile depicted in fig (2) with an as yet unknown intermediate regime at around \(p = O(1)\) with at least one maximum, the first, centered at \(p_1\) say. We Taylor expand \(\varphi(p)\) around \(p_1\)

\[
\varphi(p) = \varphi(p_1) - \frac{1}{2} c_7 (p - p_1)^2 + \frac{1}{6} c_8 (p - p_1)^3 + \frac{1}{24} c_9 (p - p_1)^4
\]

Upon substituting this in eq (20), we see that the coefficient \(c_9\) is positive as it should be. One expects \(p_1 = O(1)\) and \(\varphi(p_1) = O(1)\) so that \(c_7\) and \(c_9\) are also \(O(1)\) for consistency.

It is difficult to ascertain the stability of the solution determined by eq (20) with regard to eq (4) under general circumstances in view of the inhomogeneity of the fluid velocity coupled to the nonlinear depletion (even though it is quasilinear). Nevertheless, it can be shown that the solution is Hadamard stable.

### 4 Force on the sphere

Let us first rewrite the similarity variable \(p\) in terms of the original coordinates \(\theta\) and \(y\) pertaining to the boundary layer

\[
p = \frac{1}{2} \left( \frac{3v}{Ba^2} \right)^{1/5} \frac{y \sin \theta}{I^{1/5}(\theta)}
\]

Accordingly, I introduce an angular-dependent thickness of the layer defined by

\[
\delta(\theta) \equiv \left( \frac{D_s A^2 a^2}{v} \right)^{1/5} \frac{5 I^{1/5}(\theta)}{\sin \theta}
\]

Both \(p\) and \(\delta(\theta)\) are well behaved as \(\theta\) tends to zero and valid right up to \(\theta = \pi/2\), to a good approximation. I note that they are independent of the bulk density \(c_0\) because eq (4) is quasilinear.
Next, the force on the sphere is defined by
\[
\left| \vec{f} \right| = \int d\vec{r} c(\vec{r}) \nabla \mu = \frac{1}{6} A^2 c_0 k_B T \int d\vec{r} \varphi^2 \left| \nabla \left( \varphi^{-1} \Delta \varphi \right) \right| \tag{30}
\]
The integration applies only to the region definable as the boundary layer. Since \( \delta_0 \ll a \), I introduce a Derjaguin approximation where the distance of a point with coordinates \((R, y)\) to the surface of the sphere is given by \( y - a + \sqrt{(a^2 + R^2)} \approx y + (R^2/2a) \). The radial coordinate \( R \) is perpendicular to the \( z \) axis. The integral in eq (30) is thus rewritten as
\[
J \approx \int_0^a dR \int_0^a dy G \left( y + \left( R^2/2a \right) \right) \tag{31}
\]
where
\[
G(y) \equiv \varphi \frac{\partial^3 \varphi}{\partial y^3} - \frac{\partial \varphi}{\partial y} \frac{\partial^2 \varphi}{\partial y^2} (\theta \to 0)
\]
To the leading order, \( J \) may be simplified after several integrations by parts and the substitution \( q = R^2/2a \)
\[
J \approx 2\pi a \int_0^a dq \int_0^\infty dy \left( q + y \right) = 4\pi a \int_0^\infty dy \left[ \frac{\partial \varphi}{\partial y} \bigg|_{\theta=0} \right]^2 \approx \frac{a}{\delta(0)} \tag{32}
\]
We conclude that the force on the sphere is inversely proportional to the thickness of the boundary layer \( \delta(0) \).
\[
\left| \vec{f} \right| \approx A^2 a c_0 k_B T/\delta(0) \tag{33}
\]
This is consistent with the force of depletion \( \left| \vec{f} \right| \approx a^3 c_0 v/m = A^2 c_0 \Delta k_B T \) at low velocities derived previously (34); the crossover is at \( \Delta = O(1) \) and \( \delta(0) \approx a \).

5 Concluding remarks

The force on a sphere arising from convective depletion is illustrated for a globular protein propagating fast through a semidilute polymer under the influence of a constant uniform electric field \( \vec{E} \). If the protein bears \( Z \) positive elementary charges of charge \( q \), the force \( Zq \vec{E} \) on the protein ultimately causes it to translate uniformly with a velocity \( \vec{v} \) given by eqs (29) and (33),
\[
v \approx \frac{D_s A^2}{a^3} \left( \frac{ZqE}{A^2 c_0 k_B T} \right)^5 = \frac{D_s A^2}{a^3} \left( \frac{Z \Omega}{A^2 Q c_0} \right)^5 \tag{34}
\]
Here it is convenient to introduce \( \Omega \equiv qEQ/k_B T \), a dimensionless electric field scaled by the Bjerrum length \( Q(Q = 0.71 \text{ nm for water at room temperature; } \Omega = 2.76 \times 10^{-6} E \) if
$E$ is given in units of $V/cm$. Eq (34) is only valid at high enough fields: $E > E_*$ with $\Omega_* \simeq A^2 Q c_0 / Z$ because the crossover must occur when the dimensionless quantity given by eq (1) is of order unity; $E_*$ is about 1 kV/cm for a protein bearing 10 positive charges translating through a polymer solution of volume fraction 0.1. The electrophoretic velocity is thus a sensitive function of the protein charge and its dimensions. Electrophoresis in polymer gels at high electric fields could well be a useful technique for the separation of a mixture of proteins. Very high fields are currently employed in microchip electrophoresis because Joule heating may be kept to a minimum [15].

**Figure Captions**

Fig. 1 Fixed sphere in a fluid moving uniformly with velocity $-v_0$ in the $z$ direction at infinity. The dashed curve demarcates approximately the onset of the depletion layer.

Fig. 2 Square onset of the scaled polymer density as a function of the similarity variable $p$.

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