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Short Communication

Polymer adsorption near the surface of a polymer solution:
$\varepsilon$-expansion of a universal law

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Résumé. — Quand la surface libre d'une solution de longs polymères dans un bon solvant est fortement attractive, le profil de concentration est donné par une loi universelle. En particulier, dans le cas semi-dilué, la concentration kuhnienne est donnée par la loi d'échelle $C_k(x) = C_k/\Psi (C_k x^{d-1/\nu})$ où $d$ est la dimension d'espace et $\nu$ l'exposant de taille. On montre que pour de petites valeurs de $\varepsilon = 4 - d$, on a $\Psi (y) = \tanh^2 \left( y \varepsilon M^2 / 2 \right)^{1/2}$. Cette formule précise des résultats antérieurs trouvés par P.G. de Gennes et par E. Eisenriegler.

Abstract. — When the free surface of a solution of long polymers in a good solvent is strongly attractive, the concentration profile is given by a universal law. In particular, in the semi-dilute case, the kuhnian concentration is given by the scaling law $C_k(x) = C_k/\Psi (C_k x^{d-1/\nu})$ where $d$ is the space dimension and $\nu$ the size exponent. It is shown here that for small values of $\varepsilon = 4 - d$, we have $\Psi (y) = \tanh^2 \left( y \varepsilon M^2 / 2 \right)^{1/2}$. This formula generalizes previous results obtained by P.G. de Gennes and by E. Eisenriegler.

1. Introduction.

We consider here very long polymers in a good solvent. We assume that the polymers are attracted by a plane free surface, the attraction resulting from van der Waals forces, and we want to study the concentration profile near this surface.

In a preceding communication (denoted by I), we studied the marginal case, where the surface is just saturated with polymers and where the monomer concentration vanishes far from the strongly attractive surface (in the bulk). The polymers were supposed to be infinitely long. In such cases, to define the monomer concentration in a proper way (i.e. consistent with the model), we must use the kuhnian concentration $C_k$.

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We thus showed that, in the vicinity of the surface, the kuhnian concentration is given by a power law \[1, 3\] of the form

\[C_k (x) = \frac{A(d)}{x^{d-1/\nu}}\]  

(1)

where \(d\) is the space dimension, \(\nu\) the size exponent of an isolated polymer in good solvent, and \(A(d)\) a universal coefficient depending only on \(d\). In particular, we saw that \(A(1) = 1\) and that \(A(4-\varepsilon) = 2/\pi^2 \varepsilon (0 < \varepsilon \ll 1)\).

We want to extend this result to the case where the kuhnian concentration does not vanish at infinity.

2. A universal law.

Long polymers in good solvent are represented as kuhnian chains and the mean square end-to-end distance of an isolated polymer in the solvent is denoted by

\[R^2 = dX^2\]

Let us consider a solution. Its kuhnian concentration \(C_k\) can be considered as proportional to the number of monomers per unit volume and is defined by

\[C_k = CX^{1/\nu}\]

where \(C\) is the mean number of polymers per unit volume inside the solution.

We say that, at a distance \(x\) from the strongly attractive surface, the kuhnian concentration \(C_k (x)\) is given by a universal law of the form

\[C_k (x) = \frac{C_k}{\Psi \left(C_k x^{d-1/\nu}, C_k X^{d-1/\nu}\right)}\]  

(2)

with \(\Psi (\infty, z) = 1\)

Such scaling laws are not new and similar ones were written by Eisenriegler \[4\] several years ago. Still there is a small difference which is important for practical applications: here all the quantities which appear in the scaling laws are well-defined and measurable.

In particular, if the chains are very long (semi-dilute regime everywhere: \(C_k X^{d-1/\nu} \gg 1\)), we have

\[C_k (x) = \frac{C_k}{\Psi \left(C_k x^{d-1/\nu}\right)}\]  

(3)

where \(\Psi (y) \equiv \Psi (y, \infty)\)

Here, we shall study this case only and we note that

\[\Psi (\infty) = 1\]
\[\Psi (y) \simeq \frac{y}{A(d)} \quad (y \ll 1)\]

in agreement with equation (1).

3. A mean field method.

To derive the form of the universal law (3) corresponding to small values of \(\varepsilon = 4 - d\), we can generalize the mean field method used in (I). We represented the polymer by a brownian chain of
area $S$, in equilibrium in a self-consistent potential $V(x)$ produced by the other chains.

The following result has been previously obtained in a slightly different form by Lubensky and Rubin [5, 4] but indirectly by using a mean field approximation in field theory. Here, we deal directly with polymers. Therefore the approach is much simpler and, in particular, it is easier to get the exact numerical factors which we need; this is why we shall describe this method with some detail.

Let $C(x)$ be the brownian concentration (an area per unit volume). The potential is

$$V(x) = bC(x)$$

where $b$ is the usual interaction parameter [2]. We note that since here $C(\infty) = C = CS$ is finite, the potential does not vanish at infinity.

Now let us consider the chains whose origin is at a distance $x_0$ from the free surface and whose end point is at a distance $x$ from it. By arguing as in (I), we can see that the partition function $^0Z(x_0, x, S)$ corresponding to these chains can be written in the form

$$^0Z(x_0, x; S) = e^{-E_0S}\varphi_0(x_0)\varphi_0(x) + e^{bCS}\int_0^\infty dk \ e^{-k^2S}\varphi(x_0, k)\varphi(x, k)$$

(with $E_0 < bC$)

where $\varphi_0(x)$ and $\varphi(x, k)$ are solutions of the equation

$$\left(\frac{1}{2} \frac{\partial^2}{\partial x^2} + E - V(x)\right) = 0$$

Thus, for very long chains (see(I)), we have

$$C(x) \propto [\varphi_0(x)]^2$$

where $\varphi_0(x)$ corresponds to the ground state and is a solution of the self-consistent equation

$$\left(\frac{1}{2} \frac{\partial^2}{\partial x^2} + E_0 - bC(x)\right)\varphi_0(x) = 0$$

Here, $E_0$ is an eigenvalue which has to be determined by boundary conditions.

Let us set

$$C(x) = y^2(x)$$

$$C = C(\infty) = y_\infty^2$$

We see that we have to solve the equation

$$y'' + 2E_0y - 2by^3 = 0$$

(with $y(\infty) = y_\infty$).

Let us multiply this equation by $2y'$ and let us integrate; as $y'(\infty) = 0$, we obtain

$$y'^2 = \left(y^2 - y_\infty^2\right)\left(by^2 + by_\infty^2 - 2E_0\right)$$

We now remark that $y'$ must always be negative. Therefore, we now have

$$\frac{y'}{(y^2 - y_\infty^2)^{1/2}(y^2 + y_\infty^2 - 2E_0/b)^{1/2}} = -b^{1/2}$$
Before proceeding further, let us make two remarks.

1) As the equation must remain meaningful for all values of \( y (y > y_\infty) \), we must have

\[
2E_0/b \leq 2y_\infty^2
\]

and we see from (4) that this condition also implies that \( E_0 \) can be the eigenvalue of a bound state.

2) If \( y \to y_\infty \), then \( x \to \infty \).

Consequently the integral

\[
\int_y^{\infty} \frac{dt}{(t^2 - y_\infty^2)^{1/2} ((t^2 + y_\infty^2 - 2E_0/b)^{1/2}}
\]

must diverge when \( y \to y_\infty \).

Therefore, we must have

\[
E_0 = by_\infty^2
\]

and this equality tells us that, in this case as in (I), the bound state is marginal. The value of \( E_0 \) is now determined and we check that, when \( C(\infty) = C = 0 \), then \( E_0 = 0 \); this was the case treated in (I).

Now equation (6) simplifies and gives

\[
\int_y^{\infty} \frac{dt}{t^2 - y_\infty^2} = b^{1/2} x
\]

Finally, we obtain

\[
y = \frac{y_\infty}{\text{th} (y_\infty b^{1/2} x)}
\]

and therefore according to equation (5)

\[
C(x) = \frac{C}{\text{th}^2 (C^{1/2} b^{1/2} x)}
\]

This is the mean field result.

4. The universal law for semi-dilute solutions and small values of \( \varepsilon = 4 - d \).

To obtain the universal law for small values of \( \varepsilon = 4 - d \), we must transform the mean field result by renormalization.

Firstly, we note that

\[
C_k(x)/C_k = C(x)/C
\]

Now let us consider the product \( Cb \) which appears in (7). The relation between the brownian concentration \( C \) and the kuhnian concentration \( C_k \) is

\[
C S^{-1} = C_k X^{-1/2} = C
\]

where \( C \) is the number of polymer per unit volume. The interaction \( b \) can be expressed in terms of the dimensionless parameter \( z \)

\[
z = b S^{2-d/2} (2\pi)^{-d/2}
\]

Moreover, to first order in \( \varepsilon, z \approx g \) where \( g \) is the osmotic parameter which represents the interaction of two chains [1], in a more precise manner than \( z \).
With the help of all these equalities, we can write

$$C^{1/2}b^{1/2} x \simeq \left( C_k x^{d-1/\nu} \right)^{1/2} \left( X^2 / S \right)^{\frac{1}{2} - \frac{d}{4}} \left( \frac{x}{X} \right)^{1 - \frac{d}{2} + \frac{1}{2\nu}} \left( g (2\pi)^{d/2} \right)^{1/2}$$

In the mean field approximation, the swelling of the chains is neglected. Therefore, in the second factor in the right hand side, we may take $X^2 / S \simeq 1$. For $d = 4 - \epsilon$, the exponent $1 - \frac{d}{2} + \frac{1}{2\nu}$ is of order $\epsilon$; thus the third factor can also be replaced by unity. Finally, in the fourth factor, we can take the asymptotic limit $g \rightarrow g^* \simeq \epsilon / 8$ and we may put $d = 4$. We obtain

$$C^{1/2}b^{1/2} x \simeq \left( C_k x^{d-1/\nu} \epsilon \pi^2 / 2 \right)^{1/2}$$

This equation and the mean field approximation (7) lead us to the final formula

$$C_k (x) = \frac{C_k}{\text{th}^2 \left[ (C_k x^{d-1/\nu} \epsilon \pi^2 / 2)^{1/2} \right]}$$

(8)

This result is in agreement with equations (3) and (1); it is expected to be valid in the semi-dilute domain for small values of $\epsilon$.

References


[2] DES CLOIZEAUX J. and JANNINK G., Les Polymères en Solution: leur Modélisation et leur Structure (Les Editions de Physique) 1987 (see chapter XII);

The reader may also look at the following article DES CLOIZEAUX J., J. Phys. France 42 (1981) 635.

[3] An incomplete version of this law was previously given by P. G. de Gennes;

