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Density distribution of polymer chain segments near a nonadsorbing wall

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Abstract. — The density distribution of polymer chain segments near a non-adsorbing wall has been obtained. It can be applied to short chains. The theoretical distribution is in good agreement with the experimental data by D. Ausserré, H. Hervet and F. Rondelez (Phys. Rev. Lett. 54 (1985) 148).

1. Introduction.

A polymer molecule becomes a statistical coil in a dilute solution. This coil keeps its shape near a non-adsorbing wall, it only touches the wall by its surface. This is due to the fact that the state of the coil flattened over the wall is of a small statistical weight and will be realized in very rare cases. The density of chain segments near the wall will consequently have the same distribution as the distribution of chain segment density with respect to the centre of the macromolecule mass. This concept may already be considered classical [1-4].

Recently, D. Ausserré, H. Hervet and F. Rondelez [5] have measured the density of segment distribution near a wall by the evanescent wave induced fluorescence method [6]. Experimental results showed that the density at a distance of the order of the chain radius of gyration is in good agreement with theory, but near the wall it does not tend to zero as theory predicts. In reference [7] D. Ausserré, H. Hervet and F. Rondelez obtained the density distribution, based on model physical considerations, which agrees with the experimental data.

In this paper a practically accurate density distribution of chain segments has been obtained within the framework of the existing theory owing to improving the calculation method. This distribution is valid for chains with a small number (N) of Kuhn segments. Near the wall the segment density is proportional to 1/N. In references [1-4] terms of the order of 1/N were omitted since N is usually very large. In reference [5] N = 18, so theory must be more accurate to interpret experiments with such short chains.

2. The distribution of segment density of an ideal chain.

As is known, any ideal chain can be compared with an equivalent freely jointed chain of the same length and with the same radius of gyration. This determines the magnitude of the Kuhn segment (a) in the freely jointed chain and the number (N) of Kuhn segments in the chain. The number N depends only on the chain length, and the magnitude of the Kuhn segment (a) can be regarded as a degree of flexibility of a real chain, A partition function of the freely jointed chain in the volume V can be written in the form

\[ Z = \int_V \cdots \int g(|x_0 - x_1|) \cdots g(|x_{N-1} - x_N|) \times \right dx_0 \cdots dx_N \]

(1)

where \( x_i \) is the radius vector of the end of the i-th segment of the chain, and

\[ g(|x - y|) = \delta (|x - y| - a) \]  

(2)

Since only the size of the Kuhn segment enters into the final expressions, other expressions for g are also possible. We will assume that

\[ \int g(|x|) dx = 1 \]

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The $i$-th segment density distribution will be

$$n_i(x) = \int_{V} \cdots \int_{V} G(x_0, x_i) G(x_i, x_N) \mathrm{d}x_0 \cdots \mathrm{d}x_N$$

(3)

where

$$G_{|i-j|}(x_i, x_j) = \int_{V} \cdots \int_{V} g(|x_i - x_{i+1}|) \cdots g(|x_{i-1} - x_i|) \times \mathrm{d}x_{i+1} \cdots \mathrm{d}x_{i-1}$$

(4)

and the density distribution is

$$n(x) = \sum_{i=0}^{N} n_i(x).$$

(5)

As is well known (e.g. see Ref. [14]) for the $|i-j|$ iterated kernel we have:

$$G_{|i-j|}(x_i, x_j) = \sum_{k} \lambda_k^{-|i-j|} \psi_k(x_i) \psi_k(x_j)$$

(6)

where $\lambda_k$ and $\psi_k$ are eigenvalues and eigenfunctions of the integral equation

$$\lambda \psi(x) = \int_{V} g(|x - y|) \psi(y) \mathrm{d}y.$$  

(7)

If $\psi$ slightly varies at distance of an order of the Kuhn segment $a$, solutions of integral equation (7) are close to the solution of the differential equation [9]:

$$\lambda \psi(x) = \psi(x) + \frac{a^2}{6} \Delta \psi(x).$$

(8)

Moreover, $a^2|\Delta \psi/\psi| \ll a^2 k^2 \ll 1$ where $k$ is constant, and consequently, $\lambda = 1 + E$ where $|E| \approx a^2 k^2$.

In case the walls are non-adsorbing, the function $\psi$ must obey the boundary condition on the wall [9-12]

$$\psi(x_0) = 0.$$  

(9)

However, this boundary condition is inaccurate and it should be replaced by

$$\psi'_n(x_0)/\psi(x_0) = 1/b$$

(10)

where $\psi'_n(x_0)$ is the derivative normal to the surface; $b$ is of an order of the Kuhn segment $a$. One can see this if one tries to approximately satisfy integral equation (7) at a surface point. For this aim we expand $\psi(y)$ in (7) in a series and keep first- and second-order terms, then we have

$$\lambda \psi(x) = \frac{1}{2} \left[ \psi(x) + \psi'_n(x_0) \bar{x} + \frac{a^2}{6} \Delta \psi(x_0) \right]$$

(11)

where

$$\bar{x} = \int_{V} g(|x - x_0|)(x - x_0) \mathrm{d}x.$$  

For $\psi$ to satisfy equation (11) up to the first order of $ak$ it is necessary that

$$\psi'_n(x_0)/\psi(x_0) = 1/\bar{x}.$$  

(11')

The given « derivation » of relation (10) is aimed at showing the necessity of a boundary condition (10). Equation (10) is a boundary condition of the third kind for the second-order equation (8). A boundary condition of this kind has been used by de Gennes in papers [10], and also by Grossberg in paper [15] for investigating the pressure distribution over a nonspherical globule. The value of $b$ slightly depends on a specifics of kernel $g$. Since our consideration is related not to the actual chain but to the equivalent freely jointed one, a theoretical calculation of $b$ for kernel (2) makes no sense. Indeed, actual chains with the same Kuhn segment but with different flexibility mechanisms (persistent or rotationally isomeric one) behave differently near the wall. Therefore, it is reasonable to introduce a parameter $\beta$ via the relation

$$b = \beta a.$$  

(12)

This parameter will be defined by experiment. For a freely jointed chain $\bar{x} = 0.5 a$, one may assume that $\beta$ must always be close to 0.5.

Since, near a flat wall, the density distribution depends only on the normal coordinate, we shall further consider the one-dimensional equation (8) only. The normal coordinate is denoted by $x$.

Eigenfunctions and eigenvalues of equation (8) are known:

$$\psi_k \sim \sin (kx + \delta), \quad \lambda_k = 1 - \frac{(ka)^2}{6}.$$  

(13)

The boundary condition on the wall ($x = 0$) can be written as

$$tg \delta = kb.$$  

(14)

From (6) and (13) we have:

$$G_m(x, y) \sim \int_{0}^{\infty} dk \ e^{-m^2k^2} \frac{6}{\sin (kx + \delta) \sin (ky + \delta)}.$$  

(15)

if $m$ is large. For large $m$ an essential contribution to (15) comes from small $k$ ($ak \ll 1/\sqrt{m}$). Since $b \approx a$, the r.h.s. of (14) is small and a good approximation is given by

$$\delta = kb.$$  

(16)

In this approximation

$$G_m(x, y) \sim \frac{1}{R_m} \left( e^{-\frac{(x-y)^2}{4R_m^2}} - e^{-\frac{(x+y+2b)^2}{4R_m^2}} \right).$$  

(17)
The density distribution is expressed through quantities of the type

\[ n_m^e(x) = \int_0^{\infty} G_m(x, y) \, dy. \]  \hspace{1cm} (18)

Integrating (17) over \( y \), we obtain

\[ n_m^e(x) = \frac{1}{2} \left[ \phi \left( \frac{x}{2R_m} \right) + \phi \left( \frac{x + 2b}{2R_m} \right) \right], \]  \hspace{1cm} (19)

where

\[ \phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, dt \] (the error function)

is a normalized density distribution of the final segment in the chain of \( m \) Kuhn segments. Using (19), one can write the density distribution as

\[ n(x) = \frac{n_0}{N + 1} \sum_{m=0}^{N} n_m^e(x) n_{N-m}(x) \]  \hspace{1cm} (20)

where \( n_0 \) is the density far from the wall.

One can also calculate \( n_m^e(x) \), accurately taking account of boundary condition (14). With this boundary condition in (15) we get

\[ G_m(x, y) = \int_0^{\infty} dk \, e^{-\frac{k^2 y^2}{2}} \left[ \cos k(x - y) - \frac{(1 - (kb)^2)}{1 + (kb)^2} \right]. \]  \hspace{1cm} (21)

The integrals in (21) can be expressed by

\[ \int_0^{\infty} e^{-a_1 x} \cos a_2 x \, dx = \frac{\pi}{4a_3} \times \left( e^{-a_3 x} \left[ 1 - \phi \left( a, a_3 - \frac{a_2}{a_1} \right) \right] - e^{-a_3 x} \left[ 1 - \phi \left( a_3 + \frac{a_2}{a_1} \right) \right] \right) \]  \hspace{1cm} (22)

(see e.g. [16]). Upon calculating \( G_m(x, y) \) and integrating over \( y \) (see (18)), we have

\[ n_m^e(x) = \phi \left( \frac{x}{2R_m} \right) + e^{(R_m/b)^2 + \frac{x}{b}} \left[ 1 - \phi \left( \frac{R_m}{b} + \frac{x}{2R_m} \right) \right]. \]  \hspace{1cm} (23)

The resulting expression is slightly more complicated than (19). The expression for density (20) with \( n_m^e(x) \) from (23) is also valid for chains of a small number of Kuhn segments. It was obtained with the following approximations: eigenvalues for the Gaussian kernel \( g \), used in calculating (6), and eigenfunctions slightly inaccurate at a distance of the order of the Kuhn segment from the wall.

3. Comparison of the theory with experimental data from reference [5].

The density distribution of xanthan segments was measured in the diluted solution (96 ppm). The xanthan chain has persistent flexibility under experimental conditions. The chain length is 1.8 \( \mu m \); the Kuhn segment is 0.1 \( \mu m \) long. D. Ausserré, H. Hervet and F. Rondelez found, as mentioned in the Introduction, that the density distribution

\[ n_\phi = n_0 \tan^2 \left( \frac{x + a}{R_y \sqrt{2}} \right) \]  \hspace{1cm} (24)

where \( R_y = 0.18 \mu m \), \( a = 0.1 \mu m \) is in good agreement with the experimental data. Therefore, density distribution (20) obtained in this paper should be compared with distribution (24).

Figure 1 shows curves of \( n(x) \) and \( n_{18}(x) \) for \( \beta = 0.44 \) and \( \beta = 0.86 \) (the latter is too large to be possible).

![Normalized density distributions of chain segments and the density distribution of end segments near the wall \( x = 0 \). The chain consists of 18 Kuhn segments (a denotes the Kuhn segment). The distribution \( n_\phi \) from reference [7] is shown by a solid hold-face line. A light-face solid line and line (-----) show \( n(x) \) for \( \beta = 0.44 \) and \( \beta = 0.86 \), respectively. There is also \( n_{18}(x) \) for these values: crosses denote \( n_{18}(x) \) for \( \beta = 0.44 \), the dashed line is for \( \beta = 0.86 \).](image)

According to references [8, 13] the xanthan sample under investigation had the polydispersity index \( M_w/M_n = 1.35 \). To compare theory with experiment, the chain length averaging was performed. Since there were no data on the molecular weight distribution, it was assumed that it has a normal form

\[ P_N = \exp \left[ \left( N - \overline{N} \right)^2 / 2(k - 1) \overline{N}^2 \right] \]  \hspace{1cm} (25)

where \( \overline{N} \) was taken to be 18, \( k = 1.35 \).
In figure 2 one can see curves of $n(x)$ for $\beta = 0.5$ with averaging ($k = 1.35$) and without averaging ($k = 1$). In the experimentally accessible region ($x/a > 0.7$) $n(x)$ differs from $n_0(x)$ by not more than 3%. The maximum difference is on the wall where $n_0 = 0.14$ and $n(0) = 0.085$. Therefore, a direct measurement of the xanthan concentration on the wall, as proposed in reference [7], is of current importance.

4. Conclusion.

The density distribution of polymer segments near the wall has been obtained in this paper for short chains. This distribution is in good agreement with the experimental data measured by D. Ausserré, H. Hervet and J. Rondelez [5] and with the density distribution, proposed by them [7]. The density distribution is proportional to $\left(\frac{a}{R_g}\right)^2$ on the wall and it should be used when quantities of that order can be measured. The theoretical density distribution near the wall in the semi-dilute regime should also be corrected. In this case concentration near the wall will be proportional to $(a/\xi)^2$ where $\xi$ is the correlation length (see Ref. [9]).

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