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SHORT COMMUNICATION

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Brownian motion of a polymer-bound colloidal particle

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Abstract A simple model of Brownian motion of a colloidal particle attached to the flat surface by a polymer thread is presented. The model results are discussed in terms of the measurability of the elastic properties of a linear polymer chain in the dispersion medium by observation of the motion of a colloidal particle connected to a fixed point by the polymer.

Key words Polymer-bound particle – Brownian motion – Spring constant of polymeric connection

Introduction

Macromolecule-mediated binding of colloidal particles is a problem of practical importance in processes of flocculation, filtration, microbial adhesion and pigment binding to surfaces, to name just a few. The effectiveness of macromolecules used in these various applications depends, among other factors, on the properties of polymer bridges formed between particle/particle or particle/collector surfaces. Recently, van de Ven and coworkers [1–3] proposed a method for probing the properties of polymer bridges based on the observation of quasi-free Brownian motion of colloidal particles attached to the surface by polymer chains. By analysing the particle motion and modelling the connection as an elastic spring, van de Ven and coworkers [2, 3] determined the spring constant of the polymeric link, the value of which was then compared with that predicted by polymer theory.

In this paper, a statistical description of the movement of a colloidal particle attached to the surface by a polymer chain is reconsidered, taking into account the specific geometry of the experimental observation, a finite length of the polymer chain and experimental parameter values which are compared with theoretical predictions. The model is validated by testing its applicability in characterizing the elasticity of the polymeric connection on the basis of observations of the particle movement, employing the data published by van de Ven and coworkers [2, 3].

Model

Let us assume that a colloidal particle is linked to a glass transparent plate at a point O by a section of the polymer chain. The particle movement can cause stretching or compressing of the polymer in comparison to its equilibrium state, resulting in a decrease in entropy, which, in turn, gives rise to an elastic force. Thus, one can consider the polymer link as an elastic thread and the particle attached to the surface by polymer segments as an oscillator.

The elastic force can be calculated from the equation

$$F = G(\Delta r)\Delta r \ , \qquad (1)$$

where Δr is the change in the spring length caused by the force F, and G is given by the equation [4]

$$G(\Delta r) = \frac{kT}{L_k \Delta r} L^* \left(\frac{\Delta r}{nL_k} \right) = \frac{kT}{L_k \Delta r} \left(3 \frac{\Delta r}{nL_k} + \frac{9}{5} \left(\frac{\Delta r}{nL_k} \right)^3 + \cdots \right) , \tag{2}$$

where L^* is the reciprocal Langevin function, n is the number of segment units in the polymer chain section, L_k is the Kuhn segment length, k is the Boltzmann constant and T is the temperature.

If small Δr values $(\Delta r \langle \langle nL_k)$ are assumed, Eq. (2) can be simplified to [5]

$$G = \frac{3kT}{C_\infty n L_{\text{seg}}^2} , \tag{3}$$

where L_{seg} is the length of the polymer segment and C_∞ is the Kuhn ratio characteristic of the polymer [6]. The G value (defined as the spring constant) is independent of the chain length. Now, Eq. (1) becomes the simple Hooke's law and the polymer chain can be treated as a harmonic oscillator.

Let us assume, for the sake of simplicity, that any external forces in the system (gravitational field, London and electrostatic forces, etc.) can be neglected. For a particle linked to a plate by a polymer chain with the spring constant defined by Eq. (3), the single-body probability distribution p for the particle distance r from the point O is a Gaussian distribution with the expected value equal to the average end-to-end distance r_0 [7]:

$$p = Z \exp\left(-\frac{G(r - r_0)^2}{2kT} \right) , \tag{4}$$

where Z denotes the normalization constant.

For the Δr values comparable to the polymer contour length, the spring constant depends on Δr and the probability distribution function is much more complicated than shown in Eq. (4).

As one can expect that the polymer chain is not highly stretched by the Brownian forces, Eq. (4) is usually used for the interpretation of experimental data [2, 3, 8]. Nevertheless, it seems interesting to compare the applicability of Eq. (4) and a more general probability distribution in modelling the quasi-free Brownian motion of a polymer-bound particle. A comparison of the Langevin, Gaussian and modified Gaussian distribution is shown in Fig. 1. When the chain extensions are not extremely high, the Langevin and cut-off Gaussian distributions are very similar. Let us assume that the particle position can be described by the Gaussian probability distribution truncated at the length of the bridging section of a macromolecule, $L_{\max}$:

$$p = \begin{cases} Z \exp\left(-\frac{G(r-r_0)^2}{2kT} \right) & \text{for} \quad |r| \le L_{\max} \\ 0 & \text{for} \quad |r| > L_{\max} \end{cases} . \tag{5}$$

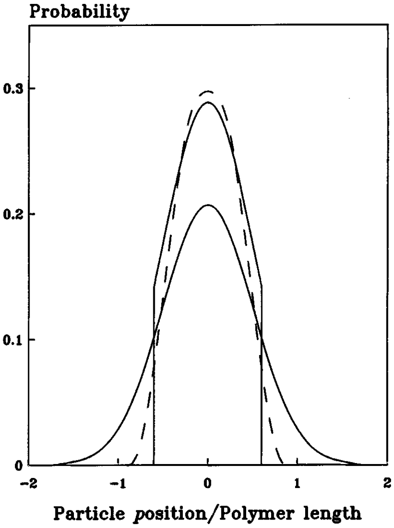

Fig. 1 A comparison of the Langevin (*dashed line*), Brownian and cut-off Brownian (*solid line*) distributions

As can be seen, the cut-off procedure, despite the very low probability of reaching $L_{\max}$ by the polymer-bound particle, results in the mutual dependence of particle movements in different directions.

In practice, instead of the distance of a polymer-attached particle from the point O, only the horizontal or vertical component of the particle movement is followed [2, 3, 8]. The horizontal component is obtained from the observation of changes in the projection of the particle position on the glass plate in the course of the experiment [2, 3]. The probability $p_=$ that a particle projection can be found at a distance l from the point of attachment is given by Eq. (6):

$$p_= = \begin{cases} Z\, l \sqrt{L_{\max}{}^2 - l^2} \exp\left(-\frac{Gl^2}{2kT} \right) & \text{for} \quad |l| \le L_{\max} \\ 0 & \text{for} \quad |l| > L_{\max} \end{cases} . \tag{6}$$

The mean value of the projection of the distance between the point O and the particle, r_0, is 0.

The vertical component of the particle motion is obtained on the basis of experimentally observed changes in the distance between the plate and the particle [8]. The distribution of the probability $p_\perp$ of encountering the particle at a distance x from the plate is given by Eq. (7):

$$p_\perp = \begin{cases} Z(L_{\max}{}^2 - x^2) \exp\left(-\frac{G(x-x_0)^2}{2kT} \right) & \text{for} \quad x \le L_{\max} \text{ and } x \ge 0 \\ 0 & \text{for} \quad x > L_{\max} \text{ and } x < 0 \end{cases} , \tag{7}$$

where x_0 is the mean distance between the plate and the particle.

Distributions (6) and (7) are determined by two parameters: $L_{\max}$ and G. The spring constant G can be evaluated theoretically from the length of the polymer chain (Eq. 3).

Introducing Eq. (3) into Eq. (6), we have

$$p_{=} = \begin{cases} Z\, l \sqrt{L_{\max}{}^2 - l^2} \exp\left(-\frac{3Nl^2}{2C_\infty n L_{\mathrm{seg}}^2}\right) & \text{for} \quad |l| \le L_{\max} \\ 0 & \text{for} \quad |l| > L_{\max} \end{cases} , \tag{8}$$

where N denotes the "apparent" number of polymer bridges which link the particle with the plate. If the length of the bridges is the same, N is simply the number of bridges. However, in the case when the bridges are formed by different numbers of polymer segments, the N value, according to Eq. (3), is given by

$$N = \min(L_i) \sum_i \frac{1}{L_i} , \tag{9}$$

where L_i denotes the length of the ith bridge.

Taking into account the fact that the shortest bridge determines the maximum possible separation between the tethered particle and the point of its attachment, one can write

$$\min(L_i) = L_{\max} . \tag{10}$$

Substituting $L_{\max} = nL_{\mathrm{seg}}$, Eq. (8) can be rewritten in the form

$$p_{=} = \begin{cases} Z\, l \sqrt{L_{\max}{}^2 - l^2} \exp\left(-\frac{3l^2}{2C_\infty L_{\mathrm{seg}} L_{\mathrm{app}}}\right) & \text{for} \quad |l| \le L_{\max} \\ 0 & \text{for} \quad |l| > L_{\max} \end{cases} , \tag{11}$$

where L_{app} is defined by Eq. (12):

$$\frac{1}{L_{\mathrm{app}}} = \sum_i \frac{1}{L_i} . \tag{12}$$

Taking into account Eqs. (10) and (12) one can notice that

$$L_{\mathrm{seg}} \le L_{\mathrm{app}} \le L_{\max} \le L_{\mathrm{contour}} , \tag{13}$$

where L_{contour} is the length of the fully extended chain. One can also notice that when there is only one bridge linking the particle with the surface $L_{\mathrm{app}} = L_{\max}$. Thus, the distribution function (Eq. 11) is determined, for a given polymer-solvent system, by only two parameters, L_{app} and $L_{\max}$, where the requirement $L_{\mathrm{app}} \le L_{\max}$ is the only correlation between these two parameters.

In order to compare the theoretical probability distribution with experimental data taken from the literature [2, 3] we transformed Eq. (11) into the form:

$$p_{*} = \begin{cases} Z\left(L_{\max}{}^2 - y^2\right) \exp\left(-\frac{3y^2}{2C_\infty L_{\mathrm{seg}} L_{\mathrm{app}}}\right) & \text{for} \quad |l| \le L_{\max} \\ 0 & \text{for} \quad |l| > L_{\max} \end{cases} , \tag{14}$$

where y is the distance between the projection of the particle position on the plate and the straight line in the plate and passing through point O.

Results and discussion

Figure 2 presents the probability distributions (Eqs. 6, 7) of the distance l of the projection of the particle position on the surface from point O and the distance x of the particle from the plate, respectively.

The properties of the probability distribution (Eq. 14) of the projection of the particle position on the flat surface around point O of the polymer attachment are illustrated in Figs. 3 and 4. The effect of the length of the shortest polymer bridge on the shape of the probability function is shown in Fig. 3. It can be seen that the longer the bridge the more the curve shape resembles the shape of a simple normal distribution. The dependence of the distribution shape on the Kuhn ratio is shown in Fig. 4. For flexible chains, i.e. small values of the Kuhn ratio, a Gaussian-like distribution is obtained. When the rigidity of the polymer increases the distribution becomes broader and the effect of the limits (i.e. finite length of the polymer bridge, $L_{\max}$) becomes more distinct.

The experimental points taken from the literature [2, 3] representing the frequency of the projection of the particle position with respect to time together with the theoretical curves obtained by fitting the parameters of

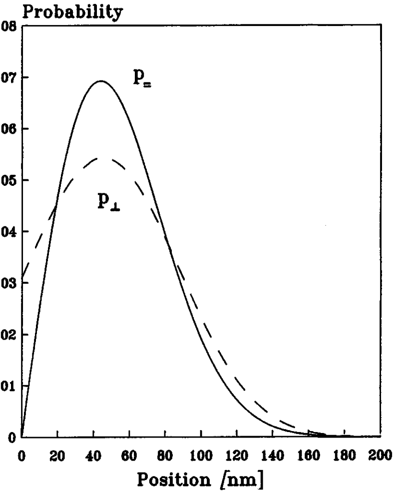

Fig. 2 The frequency histogram of the particle position at the coordinate vertical to the plate ($p_{\perp}$) and the projection of the particle position on the plate ($p_{=}$)

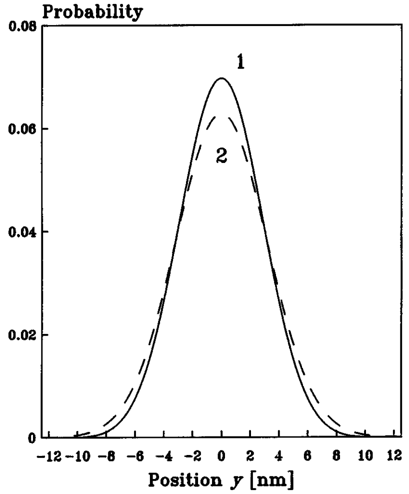

Fig. 3 The frequency histogram of the projection of the particle position at the plate y at different L_{max} parameters [$C_\infty = 300$, $L_{app} = 10$ nm, $L_{max} = 10$ (1) and 1000 (2) nm]

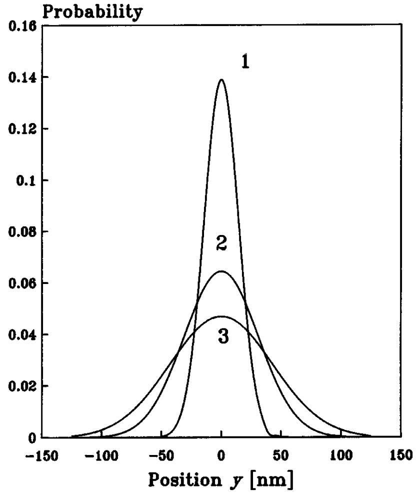

Fig. 4 The frequency histogram at different Kuhn parameter C_∞ values [$L_{app} = L_{max} = 200$ nm, $C_\infty = 10$ (1), 50 (2) and 100 (3)]

Eq. (14) to the experimental data sets are shown in Fig. 5. The parameters of the fit are given in Table 1. The values of the L_{app} parameter, as a result of its strong influence on the distribution shape, were determined with high accuracy; however, values of the L_{max} parameter could only be roughly estimated, since this parameter affects the distribution shape mainly in the region outside the peak. Any value of the L_{max} parameter greater than those given in Table 1 does not change the fitting variance. This means that in the system analysed the quasi-free Brownian motion of a polymer-bound particle is well approximated by a Gaussian distribution function and therefore the distribution of the projections of the particle position may be simplified to the equation

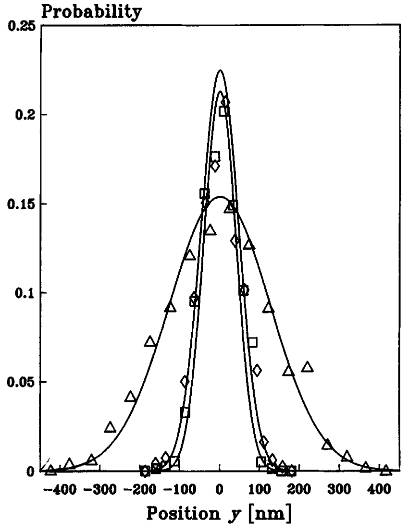

Fig. 5 The results of fitting the parameters of Eq. (14) to the experimental data [□-red blood cell (3 μm) + modified polyacrylamide [2], ◇-latex particle (2 μm) + modified polyacrylamide [2], △-latex particle (5.1 μm) + intraparticle polystyrene chain [3], nonlinear least-squares method]

$$p_* = Z \exp\left(-\frac{3y^2}{2C_\infty L_{seg} L_{app}}\right) . \tag{15}$$

Van de Ven and coworkers [2, 3] compared the value of the spring constant of polymeric connection obtained from experiment, G^{exp}, with that evaluated on the basis of polymer theory, G^{theor}. The value of G^{exp} was found to be a parameter of the normal distribution by the fitting procedure, whereas G^{theor} was calculated from Eq. (3), where the longest distance between point O and the projection of the particle position observed during the experiment, L_{max}^{exp}, was taken as the link length. The G^{theor} obtained was roughly twice as large as G^{exp}. One of the possible reasons for this discrepancy may be, in our opinion, the assumption of inadequate bridge length. The frequency of particle observation decreases with the

Table 1 The apparent and maximum lengths obtained by fitting parameters of Eq. (14) to the experimental data

System	L_{app} [m]	L_{max} [m]
Red blood cell (3 μm) + modified polyacrylamide [2]	1.07×10^{-6}	$>2 \times 10^{-6}$
Latex particle (2 μm) + modified polyacrylamide [2]	1.47×10^{-6}	$>2 \times 10^{-6}$
Latex particle (5.1 μm) + intraparticle polystyrene chains [3]	1.0×10^{-5}	$>2 \times 10^{-5}$

distance from the line passing through point O, and the probabilities of particle detection at distances longer than $L_{\max}^{\exp}$ as we estimated on the basis of Eq. (14) are 10^{-6} and 10^{-4} for the systems described in Refs. [2] and [3], respectively. Thus, it is very likely that during a relatively short period of the observation, the particle did not occur at the most distant possible positions.

The analysis of the Brownian motion of a polymer-bound particle presented, which also assumes the applicability of Eq. (3) for the calculation the spring constant of the bridge, results in the distribution function (Eq. 14) of the probability of the particle position determined by the length of the polymeric links: L_{app} and $L_{\max}$. Thus, this is the fitting procedure that yields the bridge length. The values of L_{app} and $L_{\max}$ obtained by fitting the distribution given by Eq. (14) to experimental data taken from papers by van de Ven and coworkers [2, 3] exceed the reported maximum separation, $L_{\max}^{\exp}$. Thus, because of the uncertainty in the bridge length estimation, it is difficult to reach a conclusion about the correctness of the theory on the basis of a comparison between $G^{\exp}$ and G^{theor}, as was done in Ref. [2]. On the other hand, a good fit of Eq. (15) to the experimental data indicates that Eq. (3) approximates sufficiently the properties of a polymeric link. Moreover, despite the fact that only an inaccurate estimation of the $L_{\max}$ parameter could be made, comparison of the L_{app} and $L_{\max}$ lengths ($L_{\max} \approx 2L_{\mathrm{app}}$) indicates that there are probably two polymer threads connecting the particle and the surface.

Very recently, studies of the motion of a polymer-bound particle by means of a micro-mechanical technique have been reported [8]. The method employed, based on the monitoring of changes in the separation between the particle and the plate, yields information about the vertical component of the particle motion. The spring constant of the polymeric connection evaluated on the basis of the experimental observations was, in this case, about 50 times greater than the value found theoretically. Such a high value of $G^{\exp}$ was ascribed to the entanglement of the polymer.

However, as results from our analysis, the discrepancy between the theoretical and experimental values of the spring constant might be caused, at least in part, by disregard of the plate parallel component of the particle motion. In the experiment described in Ref. [8], not only the vertical but also the horizontal coordinate of the particle position could change. Thus, the distances x measured between the particle and the plate were, in most cases, smaller than the actual separations between the particle and its attachment point to the plate. Since $G^{\exp}$ was found to be a parameter of the Gaussian distribution of the particle distance from the plate instead of its distance from the attachment point, one may expect a divergence between the values obtained and the actual values. Indeed, the summation of all possible separations between the particle and point O leads to the distribution (Eq. 7) of the particle distance from the plate, the standard deviation of which is lower than that of the normal Gaussian distribution. Thus, the application of a Gaussian distribution instead of the probability distribution given by Eq. (7) for finding the polymer-attached particle, as done in Ref. [8], should lead to a value greater than the actual $G^{\exp}$ value.

Summary

The paper presents a statistical model describing the quasi-free Brownian motion of a colloidal particle bound at a fixed point to a flat surface with the aid of a linear polymer chain, that takes into account all possible directions of the particle motion and the limited scope of the motion resulting from a finite length of a polymer chain. The probability distributions of finding the particle at a distance x from the surface and of encountering the projection of the particle position on the surface at a distance l from the point of particle attachment are found. A comparison of the model predictions with experimental data taken from the literature is made and a critical analysis of published results is presented. A good fit of the distribution (Eqs. 14 or 15) to the data obtained by van de Ven and coworkers [2, 3] may support the applicability of Eq. (3), resulting from polymer theory, for the evaluation of the spring constant of a polymeric connection.

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