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Nanoparticles in a nanochannel: Van der Waals interaction and diffusion

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ABSTRACT

Kinetic processes occurring with participation of metal or oxide nanoparticles (NPs) in solution near or inside nanochannels fabricated in a membrane can be influenced by van der Waals interaction with a membrane. In addition, hydrodynamic slowdown of NP diffusion may be important under such conditions. In applications, NPs of this category can be covered by a thin protein layer referred to as protein corona, which may prevent direct contact of NPs with a membrane. In this context, an analytical expression is presented for van der Waals interaction of a spherical NP with a membrane when a NP is located near or inside a cylindrical nanochannel at the channel axis. The interaction is shown to be often appreciable (much higher than the thermal energy) and strongly dependent on the coordinate. Taking this factor and slowdown of diffusion into account, a general expression for the permeability of a channel is derived.

1. Introduction

Sub 100-nm-sized metal or oxide NPs are often suspended in solution. In biology-related situations, such NPs are frequently covered by a thin (∼1 nm) protein corona [1–3]. In the contexts of basic physics and applications, it is of interest how NPs of this category behave in nanochannels fabricated in a ∼100-nm-thick membrane. The corresponding phenomena are quite different compared to what happens in conventional nm-sized channels in a lipid membrane (the latter has been intensively studied a few decades; see, e.g., reviews [4–6], original (primarily theoretical) articles [7–17], and references therein). Although the experimental techniques allowing one to explore NPs in nanochannels are now available (see, e.g., recent studies [18–21] and references therein), the related empirical data are still rather limited. Theoretically, this subject has not been studied in detail either (to understand the state of the art here, one can, e.g., look through Refs. [22–24]).

This Letter is focused on two physical aspects of the behavior of a spherically shaped NP in a cylindrical nanochannel. First, we calculate the van der Waals interaction of a NP with a membrane in the situations when a NP is located (i) near the perfectly flat membrane and (ii) near or inside a channel fabricated in a membrane. Second, we briefly discuss the role of this interaction in diffusion of NPs via a membrane channel in the limit when the NP concentration in solution is low so that the so-called "single-file" effects are negligible. Our general analysis of the permeability of nanochannels by NPs takes hydrodynamic slowdown of diffusion near the interface into account. The latter effect has recently been scrutinized in the context of various diffusion-limited kinetic processes (Refs. [3] and [25–31]). Our work complement these studies. Retrospectively, our study is related to the earlier analytical treatment of some of the aspects of diffusion of NPs in a slab-shaped nanochannel [22] and also to Brownian dynamics simulations taking the NP-channel interaction into account [23]. Compared to [22, 23], our results outlined above are fully novel. On the other hand, we do not focus on the attachment of NPs to the channel internal surface as it was done in [22] and do not treat many-particle effects as it was performed in [23].

2. Van der Waals interaction

2.1. General equations

On the length scale above 1 nm, the interaction of a NP with the environment is often reasonably described phenomenologically by dividing it into the van der Waals, double-layer electrostatic, and hydration parts [32],

$$U = U_{\mathrm{vdW}} + U_{\mathrm{dl}} + U_{\mathrm{h}}. \tag{1}$$

The double-layer electrostatic and hydration forces operate on the length scale of 1–2 nm, while the range of the van der Waals forces

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may be appreciably larger. We are interested on the interaction on the length scale above 1–2 nm and accordingly focus on the van der Waals interaction of metal or oxide NPs with a membrane. In applications, as already noticed in the Introduction, such NPs can be surrounded by a ∼1-nm-thick protein corona (one of its functions is to prevent aggregation of NPs). Although we do not take explicitly this corona into account in our calculations below, our results can be used in the situations with a corona, because its contribution to the van der Waals interaction is minor and its role may be reduced to prevention of direct contacts and attachment of NPs with/to the membrane surface, i.e., to restriction of the space for NP diffusion.

In general, the van der Waals NP-membrane interaction can be calculated by integrating over the NP and membrane volumes (d^3r_1 and d^3r_2),

$$U_{\rm vdW} = -\frac{A}{\pi^2}\int \frac{d^3r_1\, d^3r_2}{|\mathbf{r}_1-\mathbf{r}_2|^6}, \qquad (2)$$

where A is the Hamaker NP-solution-membrane constant. In the literature (see, e.g., Refs. [32–34]), this integral was calculated for different geometries. For the geometries we are interested in, the analytical results are, however, lacking.

2.2. Interaction with a flat membrane

Omitting trivial details of the integration, we first present the expression for the van der Waals interaction of a NP with a perfectly flat membrane,

$$U_{\rm vdW} = -\frac{A}{6}\left[\frac{lR}{h(h+l)} + \frac{lR}{(h+2R)(h+l+2R)} - \ln\left(\frac{(h+l)(h+2R)}{h(h+l+2R)}\right)\right], \qquad (3)$$

where R is the NP radius, l is the membrane thickness, and h is the minimal NP-membrane distance (Fig. 1). For a thick membrane (at $l \to \infty$), expression (3) is reduced to

$$U_{\rm vdW} = -\frac{A}{6}\left[\frac{R}{h} + \frac{R}{h+2R} - \ln\left(\frac{h+2R}{h}\right)\right]. \qquad (4)$$

The latter expression is the same as that for two spheres in the limit when the radius of one of the spheres is large (see Eq. (1) in Ref. [33] at $R_2 \to \infty$).

For comparison, we recall that the contribution of the hydration forces to the interaction of a NP with a flat surface is described as [35]

$$U_{\rm h} = 2\pi\alpha^{-1} B R \exp(-\alpha h), \qquad (5)$$

where $B \simeq 0.03$ J/m^2 and $\alpha = 3.8$ nm^{-1} are the empirical parameters. According to (5), the hydration energy rapidly drops with increasing h. The double-layer electrostatic energy rapidly drops as well (to not obscure the main line of the presentation, we do not present the corresponding equations). For this reason, these interactions are significant only at short distances, below a few nm.

For metals (e.g., Au, Ag, Cu) in water, the Hamaker constant is in the range from 10 to 40×10^{-20} J [32]. For oxides, it may be lower. With these values of the Hamaker constant, the van der Waals NP-membrane interaction is appreciable, $\gg k_{\rm B}T$ (Fig. 1), and NPs not covered by the protein corona can be trapped near a membrane.

2.3. Interaction near and in a channel

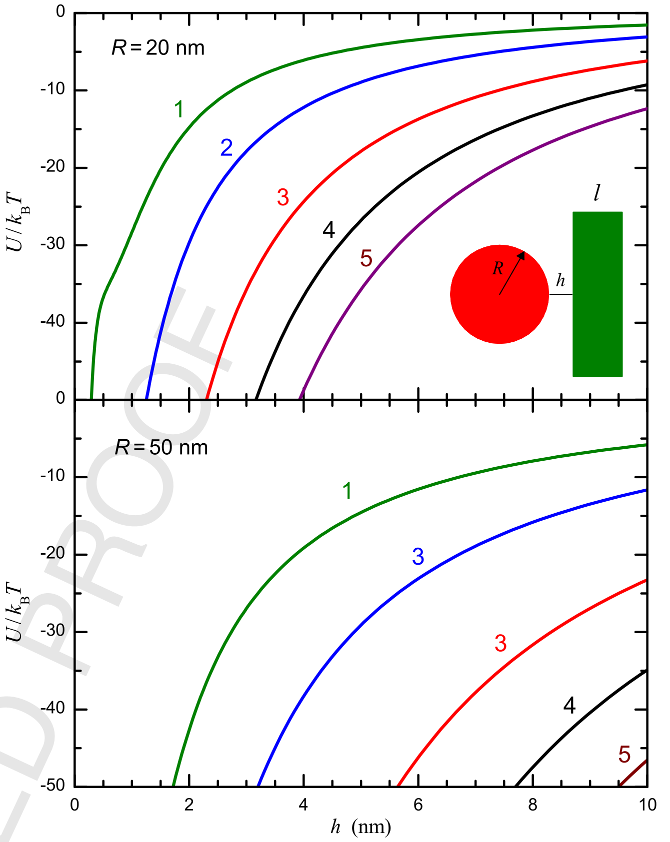

Fig. 1. Energy of the van der Waals and hydration interaction, $U = U_{\rm vdW} + U_{\rm h}$ (normalized to $k_{\rm B}T$ with $T = 300$ K), of a NP with a perfectly flat membrane as a function of the minimal distance between them. The NP radius is 20 (upper panel) and 50 nm (lower panel), while the membrane thickness is 50 nm. Curves 1–5 are for $A = 5$, 10, 20, 30, and 40×10^{-20} J, respectively. The parameters for the hydration interaction are $B = 0.03$ J/m^2 and $\alpha = 3.8$ nm^{-1}.

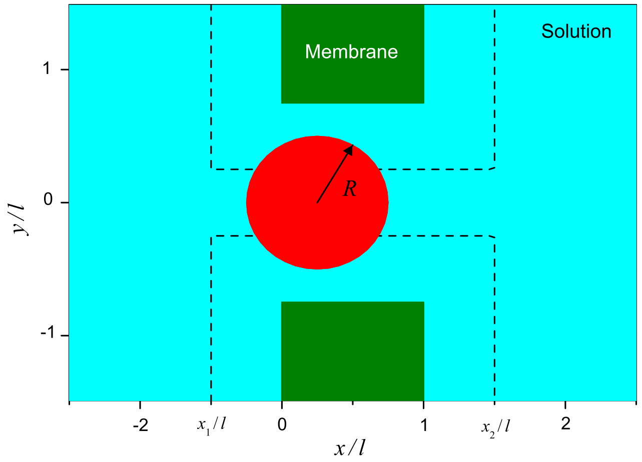

Fig. 2. Schematic arrangement of a NP in a nanochannel. The dashed lines indicate the near-membrane region which cannot be reached by the center of a NP.

If a NP is located near or inside a cylindrical channel fabricated in a membrane (Fig. 2), its van der Waals interaction with the membrane can be calculated analytically. For an arbitrary NP location, the results are, however, too cumbersome. One of the features of this interaction is clear without calculations. By analogy with a perfect membrane (Fig. 1), the interaction is often large ($\gg k_{\rm B}T$) if a NP not covered by the protein corona is located near (within 1–2 nm) the channel wall, and such particles can be trapped in a channel. The protein corona can prevent close contact with the channel wall, and NPs possessing the corona can penetrate a channel. To illustrate the scale of the van der Waals interaction in this

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