

INTERACTION OF SIMILARLY CHARGED SURFACES MEDIATED BY NANOPARTICLES

Klemen Bohinc^{a*} and Leo Lue^b

^a Faculty of Health Sciences, University of Ljubljana, SI-1000 Ljubljana, Slovenia

^b Department of Chemical and Process Engineering, University of Strathclyde, James Weir Building, 75 Montrose Street, Glasgow G1 1XJ, UK

Abstract We study the interaction between two like charged surfaces embedded in a solution of oppositely charged multivalent rod-like counterions. The counterions consist of two rigidly bonded point charges, each of valency Z . The strength of the electrostatic coupling increases with increasing surface charge density or valency of the charges. The system is analyzed by employing a self-consistent field theory, which treats the short and long range interactions of the counterions within different approximations. We find that in the weak coupling limit, the interactions are only repulsive. In the intermediate coupling regime, the multivalent rod-like counterions can mediate attractive interactions between the surfaces. For sufficiently long rods, bridging contributes to the attractive interaction. In the strong coupling limit, the charge correlations can contribute to the attractive interactions at short separations between the charged surfaces. Two minima can then appear in the force curve between surfaces.

Keywords: Electrostatics; Nanoparticle interactions; Theory.

INTRODUCTION

Electrostatic interactions between macromolecules in aqueous solutions are of fundamental importance in industry and biology^[1]. Usually the macromolecules appear as charged polymers (polyelectrolytes), membranes, proteins, viruses and even cells. The intervening solution always contains simple salts and often also multivalent ions. These multivalent ions in the solution can be multivalent metal ions, dendrimers, charged micelles, or polyamines.

Generally, multivalent ions are required to induce an attractive force between like-charged macroions^[2]. For example, divalent diamine ions induce the aggregation of rod-like M13 viruses^[3]. Multivalent ions mediate network formation in actin solutions^[4]. The condensation of DNA is induced by the presence of multivalent counterions^[5, 6]. Positively charged colloidal particles^[7, 8] complex with DNA. The cohesion of cement paste is controlled by divalent calcium counterions^[9].

Mean-field theories do not predict attraction between equally charged surfaces^[10]. Hence, the attraction must be caused by charge-charge correlations. Indeed, accounting for inter-ionic correlations between (multivalent) counterions and charged surfaces leads to the possibility of attractive forces^[11–13]. Monte-Carlo (MC) simulations of Guldbrand *et al.*^[14] first confirmed the existence of attraction between similarly charged surfaces immersed in a solution composed of divalent ions in the limit of high surface charge density. These and other^[15–17] MC simulations demonstrated that attractive interactions between similarly charged surfaces may

* Corresponding author: Klemen Bohinc, E-mail: klemen.bohinc@zf.uni-lj.si

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arise for sufficiently high surface charge densities, low temperatures, low relative permittivities, or polyvalent counterions.

The ions in solution which mediate interactions between macroions usually have an internal structure, with individually separated charges and possibly with additional internal degrees of freedom. Recently, Bohinc *et al.*^[18–21] demonstrated that intra-ionic correlations induced by the fixed distance within a particular rod-like ion are enough to change repulsive into attractive interactions between like charged surfaces. In this study, the rod-like ions carry a single elementary charge on each end. The minimum of the free energy occurs when the counterions are oriented perpendicularly to the like-charged surfaces, thus connecting them. Monte Carlo simulations confirmed the theoretical predictions^[19, 21, 22]. The analysis of the system was later extended to the intermediate and strong coupling regimes, where the interionic correlations alone can lead to an attraction between the surfaces^[23].

In this work, we examine the interaction between two like charged macromolecules or nanoparticles which are represented by charged planar surfaces. The only interactions between the rod-like counterions are the electrostatic interactions; excluded volume and other interactions are neglected. In the systems that we consider, the Bjerrum length is much larger than the cross section of the counterions (*e.g.*, spermidine molecules). Consequently, the electrostatic repulsion between the counterions does not allow them to get close enough for them interact through excluded volume forces. This justifies the neglect of the excluded volume interactions. We consider the conditions for attractive interactions mediated by multivalent rod-like ions. The influence of valency at the charged ends of the rods is considered. We examine the appearance of attractive interactions between like-charged surfaces due to the internal structure of multivalent ions, as well as to the correlations between different ions.

THEORY

In order to examine the interaction between two nanoparticles, we consider two parallel surfaces, separated by a distance D , which carry a uniform negative surface charge density Σ . Between these surfaces is an aqueous solution containing a collection of N positively charged, multivalent, rod-like counterions. Each rod-like counterion carries two identical positive charges q of valency Z (*i.e.*, $q = Ze_0$, where e_0 is the fundamental unit of charge), separated by a fixed distance l . The point charges are restricted to lie between the surfaces. A schematic diagram of the system is provided in Fig. 1. We define our coordinate system such that the x -axis and y -axis are parallel to the surfaces, and the z -axis is perpendicular to the surfaces. The origin is located on the left surface.

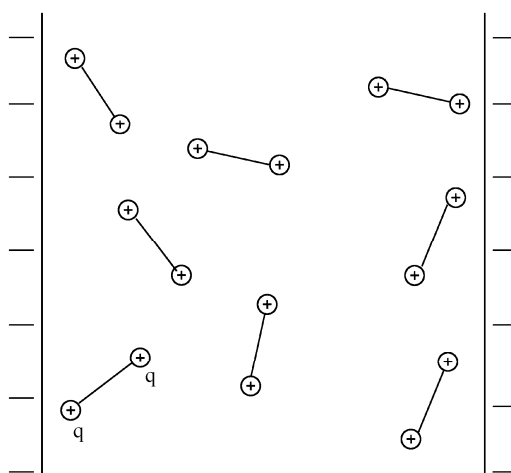


Fig. 1 Schematic illustration of the system

The surfaces are uniformly charged and immersed in solution of rod-like counterions composed of two point charges, each with valency Z .

In this work, we only consider electrostatic interactions between the rods. We neglect other types of interactions between the rods, such as excluded volume and dispersion interactions.

The total charge density Q of such a system is

$$Q(\mathbf{r}) = \Sigma \delta(z) + \Sigma \delta(z - D) + \rho(\mathbf{r}), \quad (1)$$

where the first term corresponds to the surface charge density on the first plane, and the second term corresponds to the charge on the second plate. The final term is the charge density of the mobile counterions, which is given by

$$\rho(\mathbf{r}) = \sum_{k=1}^N [q \delta^3(\mathbf{r} - \mathbf{R}_k) + q \delta^3(\mathbf{r} - \mathbf{R}_k - \mathbf{n}_k l)], \quad (2)$$

where in the sum the first term is due to a point charge located at a position $\mathbf{R}_k$ and the second term is due to a point charge located at a position $\mathbf{R}_k + \mathbf{n}_k l$; the unit vector $\mathbf{n}_k$ indicates the orientation of rod k . The energy of the electrostatic interactions is

$$E^{\text{elec}} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' Q(\mathbf{r}) G(\mathbf{r}, \mathbf{r}') Q(\mathbf{r}') - \sum_{k=1}^N e^{\text{se}}(\mathbf{R}_k, \mathbf{n}_k), \quad (3)$$

where $G(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$ is the Green's function of the Poisson equation, and e^{se}

$$e^{\text{se}}(\mathbf{R}, \mathbf{n}) = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' Q_s(\mathbf{r} - \mathbf{R}, \mathbf{n}) G(\mathbf{r}, \mathbf{r}') Q_s(\mathbf{r}' - \mathbf{R}, \mathbf{n}) \quad (4)$$

is the self energy of a rod (*i.e.*, the interaction of the rod with its own potential) and $Q(\mathbf{r} - \mathbf{R}, \mathbf{n}) = q \delta^3(\mathbf{r} - \mathbf{R}) - q \delta^3(\mathbf{r} - \mathbf{R} - \mathbf{n})$.

There are two key length scales for this system: the Bjerrum length $l_B = \beta q^2 / \epsilon$ (where $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, and T is the absolute temperature of the system), and the Gouy-Chapman length $\mu = (2\pi\beta q \|\Sigma\|/\epsilon)^{-1}$. The strength of the electrostatic interactions in the system is characterized by the coupling parameter $\Xi = l_B/\mu$, which is defined as the ratio of these two length scales. $\Xi \ll 1$ corresponds to weak coupling regime where the electrostatic interactions are relatively weak, and $\Xi \gg 1$ corresponds to the strong coupling regime.

In order to obtain an approximate theory that is applicable in both the weak and strong, as well as in intermediate, regimes, we divide the Green's function of the electrostatic interactions into a short range G_s and a long range G_l contribution:

$$G = G_s + G_l. \quad (5)$$

We make this division using the operator P , such that $G_l = PG$, and $G_s = (1-P)G$. This operator “filters” out the short wavelength components of a function. Its form is relatively arbitrary, and different choices can be made. In this work, we select $P = [1 - \sigma^2 \nabla^2 + \sigma^4 \nabla^4]^{-1}$, where the parameter σ is the length scale which distinguishes between short wave length and long wavelength phenomena; it is used as a variational parameter within our theory.

We then use the Hubbard-Stratonovitch transformation to represent the grand partition function of the system as a functional integral over two fields: a slowly varying (in space) field ψ_l associated with G_l , and a quickly varying field ψ_s associated with G_s . The functional integration with respect to ψ_s is approximated with a first order cumulant expansion, and the functional integration with respect to ψ_l is performed using the mean-field approximation. This leads directly to an approximate expression for the Helmholtz free energy of the system. This method has been found to work well for the one-component plasma model^[24], point charges confined between charged surfaces^[25, 26] as well as for rods confined between surfaces^[23]. Details of this procedure for the case of dimer rods can be found in Ref. [23].

For the system in the planar geometry we consider in this work, this approximate theory leads to the following expression for the distribution $\rho(z, s)$ of the counterions

$$\rho(z, s) = v_0 \Theta(z) \Theta(z+s) \Theta(D-z) \Theta(D-z-s) e^{-\beta u(z, s) - q i \bar{\psi}_1(z) - q i \bar{\psi}_1(z+s)}, \quad (6)$$

where $s = l \mathbf{n} \cdot \mathbf{e}_z$ is the projection of the dimer length with respect to the z -axis, Θ is the Heaviside step function, v_0 is a constant with units of density, $i \bar{\psi}_1 = P\beta\phi(\mathbf{r})$ is the long wavelength component of the electric potential ϕ of the system, and u is a one-body potential that represents the short range contribution of the electrostatic interaction of each rod counterion with the fixed charge distribution located on the surfaces, which is given by^[23]

$$\begin{aligned} \beta u(z, s) = & -\frac{2\sigma}{\sqrt{3}\mu} \left[e^{\frac{\sqrt{3}z}{2\sigma}} \cos\left(\frac{z}{2\sigma}\right) + e^{\frac{\sqrt{3}}{2\sigma}(z+s)} \cos\left(\frac{z+s}{2\sigma}\right) \right. \\ & \left. + e^{\frac{\sqrt{3}}{2\sigma}(D-z)} \cos\left(\frac{D-z}{2\sigma}\right) + e^{\frac{\sqrt{3}}{2\sigma}(D-z-s)} \cos\left(\frac{D-z-s}{2\sigma}\right) \right] \\ & - \frac{l_B}{\sigma\sqrt{3}} - \frac{l_B}{l} \left[1 - e^{\frac{\sqrt{3}l}{2\sigma}} \left(\cos\left(\frac{l}{2\sigma}\right) + \frac{1}{\sqrt{3}} \sin\left(\frac{l}{2\sigma}\right) \right) \right]. \end{aligned} \quad (7)$$

To get a better understanding of the physical content of the approximate theory we use in this work, the expression for the counterion distribution given in Eq. (6) should be compared with that from mean-field theory (such as the Poisson-Boltzmann theory). In this case the density distribution of dimers becomes^[20]

$$\rho(z, s) = v_0 \Theta(z) \Theta(z+s) \Theta(D-z) \Theta(D-z-s) e^{-\beta q \phi(z) - \beta q \phi(z+s)}. \quad (8)$$

Within this theory, each counterion rod interacts directly with the average electric potential ϕ generated by the surface charges and the other counterions in the system. However, in general this is not a good approximation, as the repulsive electrostatic interactions between the counterions causes each counterion to interact not with a mean electric potential, but with a potential that is altered by the counterion-counterion correlations. Replacing the mean electric potential $\beta\phi$ with $i \bar{\psi}_1$ accounts for this effect. The presence of the one-body potential accounts for the residual short-ranged electrostatic interactions of the counterions with the surface charges.

The approximate expression given in Eq. (8) becomes accurate when $\Xi \ll 1$ and the electrostatic interactions between the dimers are weak. For these conditions, the value of the splitting parameter becomes small (*i.e.*, $\sigma \rightarrow 0$) and $i \bar{\psi}_1 \approx \beta\phi$ and $\beta u \approx 0$. In this limit, Eq. (6) reduces to Eq. (8).

The value of the constant v_0 is determined from the overall neutrality of the system:

$$\int_0^D dz \rho(z) = -2 \Sigma \quad (9)$$

That is, the sum of the total charge of the counterions and the total charge of the surfaces should equal zero. The charge density corresponding to the density distribution given in Eq. (6) for the counterions is

$$\rho(z) = q \frac{v_0}{l} \int_{-\min[l, z]}^{\min[l, D-z]} ds e^{-\beta u(z, s) - q i \bar{\psi}_1(z) - q i \bar{\psi}_1(z+s)}. \quad (10)$$

The Helmholtz free energy F of the system is given by

$$\begin{aligned}
\frac{1}{A} \beta F[\rho, \Sigma] \approx & \frac{1}{2l} \int_0^D dz \int_{-\min[l, z]}^{\min[l, D-z]} ds \rho(z, s) [\ln \rho(z, s) A^3 - 1 + \beta u(z, s)] \\
& - \frac{1}{8\pi} \int_0^D dz \phi'(z) i \bar{\psi}_1'(z) + \int_0^D dz \rho(z) i \bar{\psi}_1(z) + \Sigma [i \bar{\psi}_1(0) + i \bar{\psi}_1(D)] \\
& + \frac{N}{A} \frac{2\sigma}{\sqrt{3}\mu} \left[1 + e^{-\frac{\sqrt{3}D}{2\sigma}} \cos\left(\frac{D}{2\sigma}\right) \right],
\end{aligned} \tag{11}$$

where A is the cross-sectional area of the system.

The value of the electric potential ϕ can be found by minimizing the Helmholtz free energy with respect to ψ_1 . This leads to a Poisson equation for the system:

$$\begin{aligned}
-\frac{\varepsilon}{4\pi} \phi''(z) &= \rho(z) \\
&= q \frac{v_0}{l} \int_{-\min[l, z]}^{\min[l, D-z]} ds e^{-\beta u(z, s) - q i \bar{\psi}_1(z) - q i \bar{\psi}_1(z+s)},
\end{aligned} \tag{12}$$

with the boundary conditions

$$\phi'(0) = -\frac{4\pi\Sigma}{\varepsilon} \quad \text{and} \quad \phi'(D) = +\frac{4\pi\Sigma}{\varepsilon}. \tag{13}$$

By solving this integral-differential equation, we can obtain the electric potential ϕ , and consequently $i \bar{\psi}_1$. The value of the parameter σ in the operator P is determined by the condition

$$\frac{\partial \beta F[\rho, \Sigma]}{\partial \sigma} = 0. \tag{14}$$

Equations (12) and (14), along with the electroneutrality condition Eq. (9), form a complete set of equations for the system.

The pressure can be obtained by taking the derivative of the free energy with respect to the plate spacing:

$$\beta p = -\frac{1}{A} \frac{\partial \beta F[\rho, \Sigma]}{\partial D}. \tag{15}$$

Using the approximation for the Helmholtz free energy given in Eq. (11), the expression for the pressure then becomes to:

$$\beta p = \frac{v_0}{l} \int_0^{\min[l, D]} ds e^{-\beta u(D-s) - q i \bar{\psi}_1(D) - q i \bar{\psi}_1(D-s)} - 2\pi\beta\Sigma^2. \tag{16}$$

RESULTS AND DISCUSSION

Here we examine the properties of multivalent rod-like counterions confined between two like charged surfaces separated by a distance D . Our results can be related to some natural, charged macroions, like DNA with surface charge density of 0.15 C m^{-2} , actin molecules with 0.03 C m^{-2} , M13 viruses with 0.05 C m^{-2} , and cell membranes with 0.04 C m^{-2} . The attractive interactions between such similarly charged surfaces can be induced by the multivalent rod-like ions, such as three-valent or four-valent spermidines.

Figure 2 shows the volume charge density as a function of the distance from the left charged surface for two surface charge densities and two lengths of the rod-like counterions. We observe a kink in the volume

charge density at $z = l$ and $z = D - l$ which is the result of the orientational restriction of the rods close to the plate. If we decrease the distance between the charged plates, then the noncontinuous derivative of volume charge density disappears. Further, with increasing surface charge density, the concentration of the counterions close to the plate increases. For a surface charge density of 0.1 C m^{-2} , the relative volume charge density is approximately equal to 1 nm^{-3} , whereas for 0.01 C m^{-2} , the relative volume charge density drops to 10^{-2} nm^{-3} . The reason for this is the strong attraction between the counterions and the charged plates.

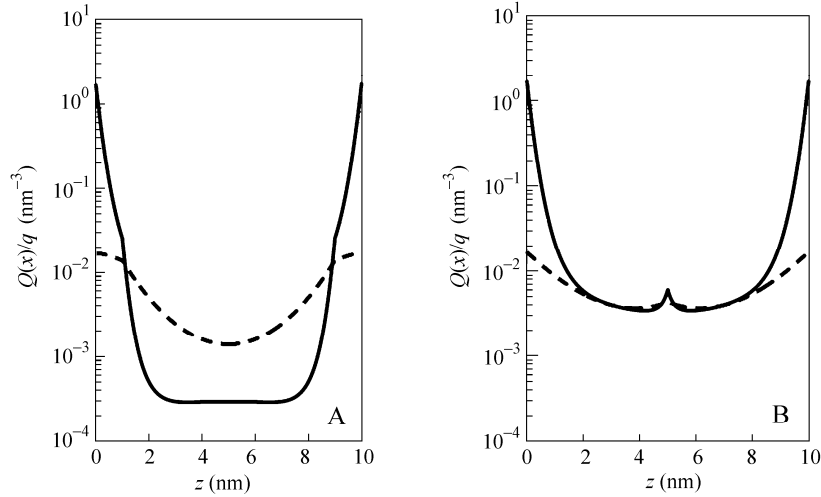


Fig. 2 Volume charge density as a function of the distance from the left charged surface for rods of length $l = 1 \text{ nm}$ (A) and $l = 5 \text{ nm}$ (B)

The surface charge densities are $\Sigma = 0.01 \text{ C m}^{-2}$ (dashed lines) and $\Sigma = 0.1 \text{ C m}^{-2}$ (full lines); The distance between the plates is $D = 10 \text{ nm}$ and the valency $Z = 2$.

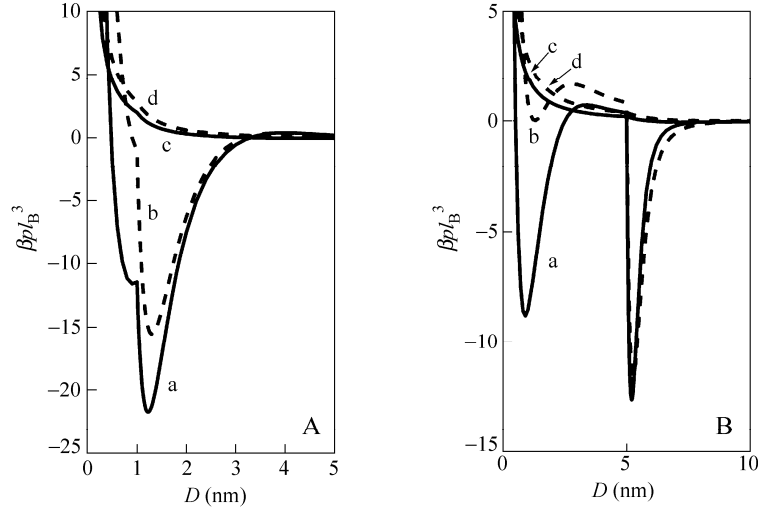


Fig. 3 Pressure as a function of the separation between the charged surfaces for rods of length $l = 1 \text{ nm}$ (A) and $l = 5 \text{ nm}$ (B)

The surface charge density is $\Sigma = 0.01 \text{ C m}^{-2}$ (c, d) and $\Sigma = 0.1 \text{ C m}^{-2}$ (a, b); The dashed lines correspond to valency $Z = 1.5$, and the full lines correspond to valency $Z = 2$.

Figure 3 shows the pressure as a function of the plate separation. For a surface charge density $\Sigma = 0.01 \text{ C m}^{-2}$, the force between the plates is entirely repulsive, but for $\Sigma = 0.1 \text{ C m}^{-2}$, an attractive force between the plates is observed. The pressure results show that for short rods and small surface charge densities, only repulsive forces between like charged plates are observed. If the surface charge density or the valency is

increased, then an attractive force between the plates is seen. The increased valency decreases the equilibrium distance between the surfaces.

Figure 3(B) shows the pressure for the longer rods (*i.e.*, $l = 5$ nm). Again for small surface charge densities, only a repulsive force is observed (see Fig. 3B, curves c, d). Also for the larger rod length, the increased surface charge density induces an attractive force (see Fig. 3B, curves a and b). The zeroes in the pressure correspond to the extrema (minima or maxima) in the interaction free energy between the plates. The zero pressure at the separations between the plates approximately equal to the length of rods is associated with the bridging of the rod like particles across the plates. The zero in the pressure located at shorter separations is associated with the attraction between plates in the intermediate and strong coupling regime. The increased valency can switch the bridging to the attractive interactions at short distances between the plates (see Fig. 3B, curves b to a).

CONCLUSIONS

In summary, we study the influence of counterion valency, surface charge density and the length of counterions on the interaction between like charged surfaces. We show that the increased valency or increased surface charge density is able to switch the bridging interaction into an attractive region at small surface separations. This attraction is the result of charge correlations which become important for high surface charge densities and large ion valencies.

REFERENCES

- 1 Evans, D.F. and Wennerström, H., "The colloidal domain, where physics, chemistry, biology and technology meet", VCH Publishers, New York, 1994
- 2 Hribar, B. and Vlachy, V., J. Phys. Chem. B, 1997, 101: 3457
- 3 Butler, J.C., Angelini, T., Tang, J.X. and Wong, G.C.L., Phys. Rev. Lett., 2003, 91: 028301
- 4 Angelini, T.E., Liang, H., Wriggers, W. and Wong, G.C.L., Proc. Natl. Acad. Sci. USA, 2003, 100: 8634
- 5 Bloomfield, V.A., Curr. Opin. Struct. Biol., 1996, 6: 334
- 6 Teif, V., Biophys. J., 2005, 89(4): 2574
- 7 Rädler, J.O., Koltover, I., Salditt, T. and Safinya, C.R., Science, 1997, 275: 810
- 8 Gelbart, W.M., Bruinsma, R., Pincus, P.A. and Parsegian, V.A., Physics Today, 2000, 53: 38
- 9 Jönsson, B., Nonat, B., Labbez, A., Cabane, C. and Wennerström, H., Langmuir, 2005, 21: 9211.
- 10 Safran, S.A., "Statistical thermodynamics of surfaces, interfaces, and membranes", Westview Press, Colorado, 2003
- 11 Carnie, S. and McLaughlin, S., Biophys. J., 1983, 44: 325
- 12 Kirkwood, J.G. and Shumaker, J.B., Proc. Natl. Acad. Sci. USA, 1952, 38: 863
- 13 Oosawa, F., Biopolymers, 1968, 6: 1633
- 14 Guldbrand, L., Jönsson, B., Wennerström, H. and Linse, P., J. Chem. Phys., 1984, 80: 2221
- 15 Svensson, B. and Jönsson, B., Chem. Phys. Lett., 1984, 108: 580
- 16 Moreira, A.G. and Netz, R.R., Phys. Rev. Lett., 2001, 87: 078301
- 17 Reščič, J. and Linse, P., J. Phys. Chem. B, 2000, 104: 7852
- 18 Bohinc, K., Iglič, A. and May, S., Europhys. Lett., 2004, 68(4): 494
- 19 May, S., Iglič, A., Reščič, J., Maset, S. and Bohinc, K., J. Chem. Phys. B, 2008, 112: 1685
- 20 Maset, S. and Bohinc, K., J. Phys. A: Math. Theor., 2007, 40: 11815
- 21 Maset, S., Reščič, J., May, S., Pavlič, I.J. and Bohinc, K., J. Phys. A: Math. Theor., 2009, 42: 105401
- 22 Kim, Y.W., Yi, J. and Pincus, P.A., Phys. Rev. Lett., 2008, 101(20): 208305
- 23 Hatlo, M.M., Bohinc, K. and Lue, L., J. Chem. Phys., 2010, 132(11): 114102
- 24 Hatlo, M.M., Karatrantos, A. and Lue, L., Phys. Rev. E., 2009, 80(6): 061107
- 25 Hatlo, M.W. and Lue, L., Europhys. Lett., 2010, 89(2): 25002
- 26 Hatlo, M.M. and Lue, L., Soft Matter, 2009, 5(1): 125