# Debye-Hückel interaction, or Yukawa potential, in different geometries

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**Abstract.** The Debye-Hückel interaction, or Yukawa potential, between point particles is used to evaluate the total interaction energy between spherical colloids. The charge of colloids is supposed to be uniformly distributed over their surfaces. The Helmholtz free energy corresponding to this interaction is evaluated as in van der Waals theory. The complete free energy shows phase separation. We evaluated the association isotherms and the phase diagram of the colloid system.

## 1 Interaction energies

The Debye-Hückel interaction, or Yukawa potential, among two particles, is given by,

$$u = \frac{\lambda e^{-\kappa r}}{r}, \tag{1}$$

where $\lambda$ is a constant with dimensions of energy $\times$ lenght. The parameter $\kappa$ is the inverse Debye screening lenght, since we study here mainly electrolyte solutions and colloids.

### 1- Particle-circle

We consider here a circle of radius $a$ with a uniform linear density of particles $\rho_l$, located in the $xy$ plane (fig. 1). We choose the origin at the center of the circle, and a particle at the position $P$, distant $z$ from the origin.

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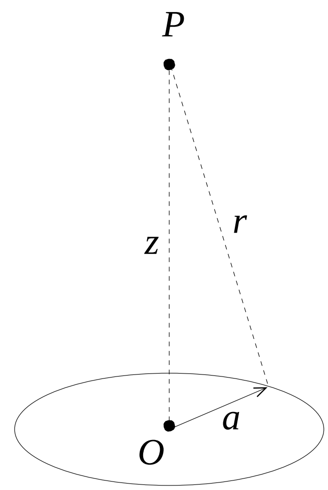


Fig. 1. A particle at $P$ interacting with a circle of radius $a$.

An infinitesimal element of arc $ds = ad\varphi$ at the circle contains $\rho_l ds$ particles, which interact with the particle at $P$ through the infinitesimal energy $du$,

$$du = \frac{\lambda e^{-\kappa r}}{r}\rho_l ds = \frac{\lambda e^{-\kappa r}}{r}\rho_l a d\varphi \,. \tag{2}$$

All arc elements are at the same distance $r$ from $P$. The total energy interaction is then an integral in $\varphi$, and we obtain,

$$u = \int du = \int_0^{2\pi} \frac{\lambda e^{-\kappa r}}{r}\rho_l a d\varphi = \frac{\lambda e^{-\kappa r}}{r}\rho_l a \int_0^{2\pi} d\varphi \,,$$

or,

$$u = 2\pi\lambda\rho_l a \frac{e^{-\kappa r}}{r} \,. \tag{3}$$

## 2- Particle-disc

In figure 2 we have a particle at $P$ interacting with a disc of radius $a$ and uniform surface density of particles $\rho_s$. Using the previous result with $\rho_l = \rho_s dx$, we can write interaction energy of the particle with the circle of radius $x$ and thickness $dx$,

$$du = 2\pi\lambda\rho_s dx\, x \frac{e^{-\kappa r}}{r} \,. \tag{4}$$

The interaction energy depends on an integral in $x$,

$$u = \int du = 2\pi\lambda\rho_s \int_0^a dx\, x \frac{e^{-\kappa r}}{r} \, .$$

The distance $z$ is constant, but not $x$ and $r$. We have then,

$$r^2 = x^2 + z^2 \, ,$$

hence,

$$2rdr = 2xdx \, ,$$

and,

$$u = 2\pi\lambda\rho_s \int_z^{\sqrt{z^2+a^2}} dre^{-\kappa r} \, .$$

The limits of integration are $r(x=0) = z$ and $r(x=a) = \sqrt{z^2+a^2}$.

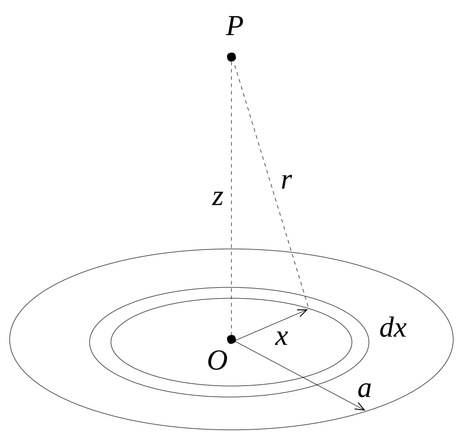


Fig. 2. A particle at $P$ intercat with a disc of radius $a$.

Evaluating the integral we have the interaction energy among the particle and the disc,

$$u = \frac{2\pi\lambda\rho_s}{\kappa} \left[ e^{-\kappa z} - e^{-\kappa\sqrt{z^2+a^2}} \right] \, . \tag{5}$$

## 3- Particle-sphere (as an assembly of discs)

The interaction energy among a particle and a sphere can be evaluated considering a sphere as an assembly of discs (fig. 3). If the sphere has constant volume particle density $\rho_v$, the particle surface density of a disc with thickness $dz'$ is $\rho_s = \rho_v dz'$.

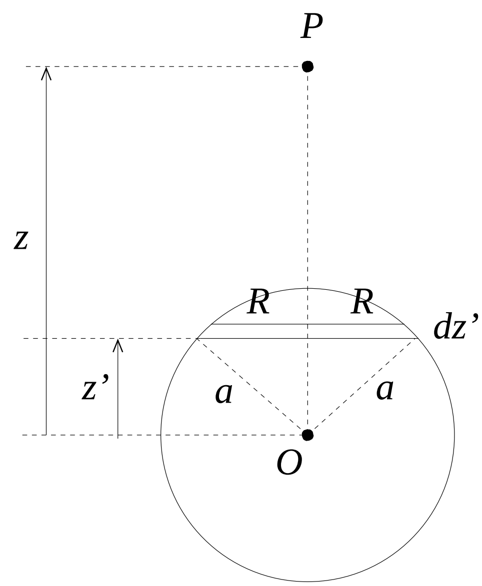


Fig. 3. A particle at $P$ interact with a sphere of radius $a$.

Using the previous result, the interaction energy among a disc of radius $R$ and a particle is,

$$du = \frac{2\pi\lambda\rho_v dz'}{\kappa}\left[e^{-\kappa(z-z')} - e^{-\kappa\sqrt{(z-z')^2+R^2}}\right]. \tag{6}$$

The distance between the disc and the center of the sphere is $z'$. Also,

$$R^2 + z'^2 = a^2 .$$

hence,

$$(z-z')^2 + R^2 = z^2 - 2zz' + a^2 .$$

The expression (6) is then,

$$du = -\frac{2\pi\lambda\rho_v dz'}{\kappa}\left[e^{-\kappa\sqrt{z^2-2zz'+a^2}} - e^{-\kappa(z-z')}\right], \tag{7}$$

and the interaction energy is,

$$u = \int du = -\frac{2\pi\lambda\rho_v}{\kappa}\int_{-a}^{+a} dz'\left[e^{-\kappa\sqrt{z^2-2zz'+a^2}} - e^{-\kappa(z-z')}\right]. \tag{8}$$

We define in the first integral,

$$x^2 = z^2 - 2zz' + a^2 ,$$

then,

$$dz' = -\frac{xdx}{z}\,.$$

The equation (8) becomes,

$$u = -\frac{2\pi\lambda\rho_v}{\kappa}\left[-\frac{1}{z}\int_{z+a}^{z-a} xdxe^{-\kappa x} - \int_{-a}^{+a} dz'e^{-\kappa(z-z')}\right]\,,$$

or,

$$u = -\frac{2\pi\lambda\rho_v}{\kappa}\left[\frac{1}{z}\int_{z-a}^{z+a} xdxe^{-\kappa x} - \int_{-a}^{+a} dz'e^{-\kappa(z-z')}\right]\,. \tag{9}$$

Evaluating the integrals we obtain,

$$u = \frac{2\pi\lambda\rho_v}{\kappa^3}\frac{e^{-\kappa z}}{z}\left\{e^{\kappa a}(\kappa a - 1) + e^{-\kappa a}(\kappa a + 1)\right\}\,. \tag{10}$$

Defining the function,

$$f(x) \equiv e^{x}(x-1) + e^{-x}(x+1)\,, \tag{11}$$

we have,

$$u = \frac{2\pi\lambda\rho_v}{\kappa^3} f(\kappa a)\frac{e^{-\kappa z}}{z}\,. \tag{12}$$

## 4- Particle-infinitesimal shell

We may consider an infinitesimal shell, that is, a spherical shell of infinitesimal thickness, as an assembly of circles and use (3) to write $du$, and then integrate over the shell. Figure 4 shows a spherical shell of radius $a$ interacting with a particle at $P$.

The element of area is,

$$dA = a^2 \mathrm{sen}\,\theta\, d\theta\, d\varphi\,,$$

or,

$$dA = 2\pi a^2 \mathrm{sen}\,\theta\, d\theta\,,$$

since we have symmetry in the angle $\varphi$.

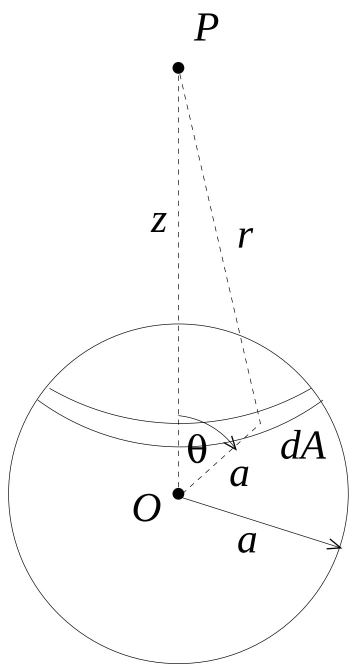


Fig. 4. A particle located at $P$ interact with a shell of radius $a$.

Using (1) we have,

$$du = \rho_s dA \lambda \frac{e^{-\kappa r}}{r}\,,$$

where $\rho_s$ is the uniform particle surface density on the shell. The number of particles in $dA$ is therefore $\rho_s dA$, and all are at the same distance $r$ from $P$. Substituting $dA$,

$$du = 2\pi a^2 \rho_s \lambda \mathrm{sen}\,\theta\, d\theta \frac{e^{-\kappa r}}{r}\,.$$

The variables $r$ and $\theta$ are related by,

$$r^2 = a^2 + z^2 - 2za\cos\theta\,,$$

hence,

$$2rdr = 2za\mathrm{sen}\,\theta\, d\theta\,,$$

and,

$$\mathrm{sen}\,\theta\, d\theta = \frac{rdr}{za}\,.$$

Substituting this in $du$ we obtain,

$$du = 2\pi\rho_s\lambda\frac{a}{z}dre^{-\kappa r}\,. \tag{13}$$

The interaction energy between the shell and the particle at $P$ is then,

$$u = \int du = 2\pi\rho_s\lambda\frac{a}{z}\int_{z-a}^{z+a} dre^{-\kappa r}\,,$$

or,

$$u = 2\pi a\rho_s\lambda\frac{e^{-\kappa z}}{\kappa z}(e^{\kappa a} - e^{-\kappa a})\,. \tag{14}$$

## 5- Particle-sphere (as an assembly of shells)

We may evaluate de interaction energy between a particle and a sphere considering the sphere as an assembly of shells (fig. 5). If the sphere has a volume particle density $\rho_v$, the surface particle density of a shell with radius $r$ and thickness $dr$ is $\rho_s = \rho_v dr$.

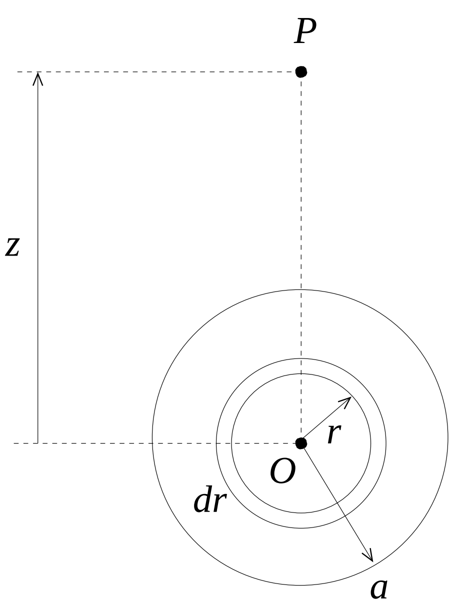


Fig. 5. A particle located at $P$ interact with a sphere of radius $a$. The solid sphere is considered as an assembly of spherical shells, each with radius $r$ and thickness $dr$.

Using (14) we have the interaction energy between a particle and a shell of radius $r$ as,

$$du = 2\pi\rho_v dr\lambda\frac{r}{\kappa z}e^{-\kappa z}(e^{\kappa r} - e^{-\kappa r})\,. \tag{15}$$

This expression must be integrated in $r$ to give the total energy $u$,

$$u = \int du = 2\pi\rho_v\lambda\frac{e^{-\kappa z}}{\kappa z}\int_0^a rdr(e^{\kappa r} - e^{-\kappa r})\,.$$

We obtain,

$$u = 2\pi\lambda\rho_v\frac{e^{-\kappa z}}{\kappa^3 z}\left[e^{\kappa a}(\kappa a - 1) + e^{-\kappa a}(\kappa a + 1)\right]\,,$$

or,

$$u = \frac{2\pi\lambda\rho_v}{\kappa^3}f(\kappa a)\frac{e^{-\kappa z}}{z}\,, \tag{16}$$

that is identical to (12), as it should be.

## 6- Two spherical shells

We consider now two spherical shells of radius $a$ e $b$, and particle surface densities $\rho_s'$, $\rho_s$ (fig. 6). We write $du$ as the interaction energy bwtween one of the shells and an element of area $dA$ at the other sphere. Using (14) we have,

$$du = 2\pi\rho_s'(\rho_s dA)\lambda\frac{a}{\kappa r}e^{-\kappa r}[e^{\kappa a} - e^{-\kappa a}]\,.$$

Substituting $dA = 2\pi b^2 \operatorname{sen}\theta\, d\,\theta$,

$$du = 4\pi^2 b^2\rho_s'\rho_s\,\lambda\frac{a}{\kappa}\operatorname{sen}\theta\, d\,\theta\frac{e^{-\kappa r}}{r}[e^{\kappa a} - e^{-\kappa a}]\,. \tag{17}$$

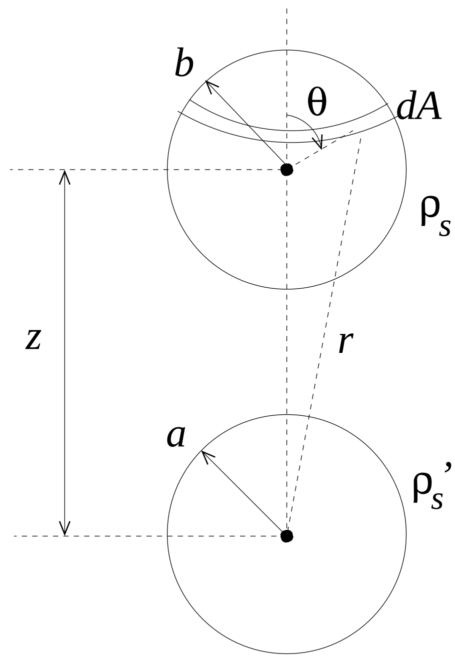


Fig. 6. Two spherical shells at distance $z$.

The relation between variables $r$, $\theta$ is,

$$r^2 = b^2 + z^2 + 2zb\cos\theta\,,$$

therefore,

$$rdr = -zb\,\mathrm{sen}\,\theta\, d\,\theta\,.$$

The interaction energy is then,

$$u = \int du = -4\pi^2 ab\rho_s'\rho_s\,\lambda\frac{1}{\kappa z}[e^{\kappa a} - e^{-\kappa a}]\int_{z+b}^{z-b} dre^{-\kappa r}\,,$$

or,

$$u = 4\pi^2 ab\rho_s'\rho_s\,\frac{\lambda}{\kappa^2}(e^{\kappa a} - e^{-\kappa a})(e^{\kappa b} - e^{-\kappa b})\frac{e^{-\kappa z}}{z}\,. \tag{18}$$

## 7- Sphere (as an assembly of shells)- spherical shell

A sphere may be considered formed by spherical shells. Using this representation we may evaluate the interaction energy between a sphere and a spherical shell (fig. 7). If the particle volume density of the sphere is $\rho_v$, the particle surface density of a spherical shell with thickness $dr$ is $\rho_s' = \rho_v dr$. Using the expression (18) we write $du$ as,

$$du = 4\pi^2 b\rho_v\rho_s \frac{\lambda}{\kappa^2}(e^{\kappa b} - e^{-\kappa b})\frac{e^{-\kappa z}}{z}(e^{\kappa r} - e^{-\kappa r})rdr\,, \tag{19}$$

and the interaction energy is,

$$u = \int du = 4\pi^2 b\rho_v\rho_s \frac{\lambda}{\kappa^2}(e^{\kappa b} - e^{-\kappa b})\frac{e^{-\kappa z}}{z}\int_0^a (e^{\kappa r} - e^{-\kappa r})rdr\,.$$

Evaluating the integral we obtain,

$$u = 4\pi^2 b\rho_v\rho_s \frac{\lambda}{\kappa^4}(e^{\kappa b} - e^{-\kappa b})\left\{e^{\kappa a}(\kappa a - 1) + e^{-\kappa a}(\kappa a + 1)\right\}\frac{e^{-\kappa z}}{z}\,,$$

or,

$$u = 4\pi^2 b\rho_v\rho_s \frac{\lambda}{\kappa^4}(e^{\kappa b} - e^{-\kappa b})f(\kappa a)\frac{e^{-\kappa z}}{z}\,. \tag{20}$$

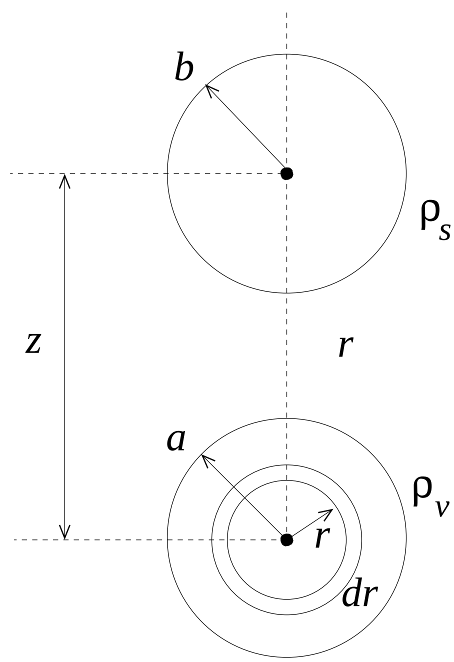


Fig. 7. A sphere as an assembly of spherical shells interacts with a spherical shell at distance $z$.

## 8- Sphere (as an assembly of shells)-sphere

We can now evaluate the energy of interaction between two spheres considering one of them as an assembly of spherical shells (fig. 8). Using the equation (20),

$$du = 4\pi^2 \rho_v \rho_v' \, \frac{\lambda}{\kappa^4} \left\{ e^{\kappa a}(\kappa a - 1) + e^{-\kappa a}(\kappa a + 1) \right\} \frac{e^{-\kappa z}}{z} r dr (e^{\kappa r} - e^{-\kappa r}) \, . \qquad (21)$$

The energy of interaction is then,

$$\begin{aligned} u &= \int du = 4\pi^2 \rho_v \rho_v' \, \frac{\lambda}{\kappa^4} \left\{ e^{\kappa a}(\kappa a - 1) + e^{-\kappa a}(\kappa a + 1) \right\} \frac{e^{-\kappa z}}{z} \times \\ &\quad \times \int_0^b r dr (e^{\kappa r} - e^{-\kappa r}) \, . \end{aligned}$$

Evaluating the integral we have,

$$\begin{aligned} u &= 4\pi^2 \rho_v \rho_v' \, \frac{\lambda}{\kappa^6} \left\{ e^{\kappa a}(\kappa a - 1) + e^{-\kappa a}(\kappa a + 1) \right\} \times \\ &\quad \times \left\{ e^{\kappa b}(\kappa b - 1) + e^{-\kappa b}(\kappa b + 1) \right\} \frac{e^{-\kappa z}}{z} \, , \end{aligned}$$

or,

$$u = 4\pi^2 \rho_v \rho_v' \, \frac{\lambda}{\kappa^6} f(\kappa a) f(\kappa b) \frac{e^{-\kappa z}}{z} \, . \qquad (22)$$

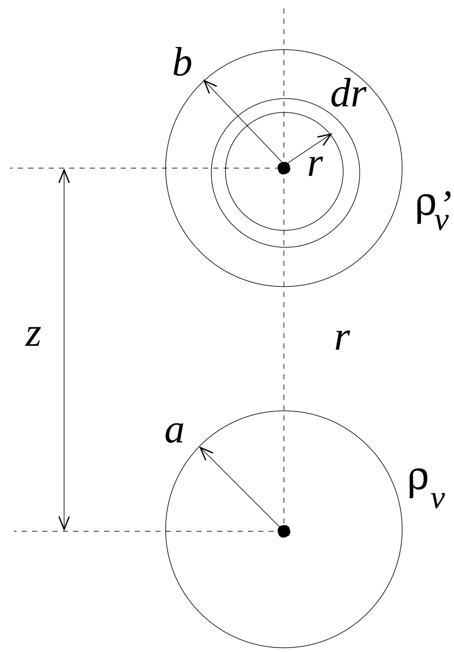


Fig. 8. Two spheres interacting at distance $z$. One of them can be considered as an assembly of spherical shells.

## 9- Finite shell-particle

With the previous results we can evaluate the energy between a spherical shell of finite thickness and a particle. Using (16),

$$u = \frac{2\pi\lambda\rho_v}{\kappa^3}[f(\kappa b) - f(\kappa a)]\frac{e^{-\kappa z}}{z}\,, \tag{23}$$

in which we consider a shell of finite thickness, of internal radius $a$ and external radius $b$. The energy of interaction with a particle may be written then as the energy with a sphere of radius $b$ minus the energy with a sphere of radius $a$.

It is interesting to study the limit of an infinitesimal thickness. We make $b = a + \delta$ and take the limit $\delta \to 0$. We have,

$$f(\kappa b) - f(\kappa a) \cong (e^{\kappa a} - e^{-\kappa a})\kappa^2\, a\, \delta + O(\kappa\delta)^2\,, \tag{24}$$

hence,

$$u \cong 2\pi a\lambda\rho_v\delta(e^{\kappa a} - e^{-\kappa a})\,\frac{e^{-\kappa z}}{\kappa z}\,.$$

In the limit $\delta \to 0$ the product $\rho_v \delta$ becomes the surface density $\rho_s$, and the above expression becomes identical to (14), for the interaction between a particle and an infinitesimal shell.

## 10- Finite shell-Infinitesimal shell

We consider now a shell of finite thickness, with internal radius $a$ and external radius $b$, interacting with a shell of infinitesimal thickness with radius $c$. We write the energy of interaction as the energy between the shell and a sphere of radius $b$, minus the energy of the shell with a sphere of radius $a$. Using the relation (20),

$$u = 4\pi^2 c \rho_v \rho_s \frac{\lambda}{\kappa^4} (e^{\kappa c} - e^{-\kappa c})[f(\kappa b) - f(\kappa a)] \frac{e^{-\kappa z}}{z} \, . \tag{25}$$

We may obtain the energy of interaction between two shells of infinitesimal thickness doing $b = a + \delta$ in the above expression and taking the limit $\delta \to 0$, as before.

## 11- Finite shell-sphere

The energy of interaction between a finite shell with internal radius $a$ external radius $b$, with a sphere of radius $c$, can be written as the energy between two spheres of radius $b$ and $c$, minus the energy between two spheres of radius $a$ and $c$. Using the equation (22),

$$u = 4\pi^2 \rho_v \rho_v' \frac{\lambda}{\kappa^6} f(\kappa c)[f(\kappa b) - f(\kappa a)] \frac{e^{-\kappa z}}{z} \, . \tag{26}$$

In the limit $\delta \to 0$, with $b = a + \delta$, we obtain (20), for the energy between a sphere and a shell of infinitesimal thickness.

## 12- Finite shell-finite shell

We consider a shell of finite thickness with internal radius $a$ and external radius $b$, interacting with a finite shell with internal radius $c$ and external radius $d$. With the expression for the energy between two spheres, eq.(22), we have,

$$\begin{aligned} u &= (u_{bd} - u_{ad}) - (u_{bc} - u_{ac}) \, , \\ u &= 4\pi^2 \rho_v \rho_v' \frac{\lambda}{\kappa^6} \frac{e^{-\kappa z}}{z} \left[ f(\kappa b) f(\kappa d) - f(\kappa a) f(\kappa d) \right. \\ &\quad \left. - f(\kappa b) f(\kappa c) + f(\kappa a) f(\kappa c) \right] \, , \end{aligned}$$

or,

$$u = 4\pi^2 \rho_v \rho'_v \frac{\lambda}{\kappa^6} \frac{e^{-\kappa z}}{z} [f(\kappa d) - f(\kappa c)][f(\kappa b) - f(\kappa a)] \,. \tag{27}$$

We consider the limit of infinitesimal shells. Doing first $c = d + \varepsilon$ and then $\varepsilon \to 0$, and using (24),

$$u = 4\pi^2 \rho_v \rho'_v \frac{\lambda}{\kappa^6} \frac{e^{-\kappa z}}{z} [(e^{\kappa c} - e^{-\kappa c})\kappa^2 c\, \varepsilon][f(\kappa b) - f(\kappa a)] \,.$$

Substituting $\rho'_v \varepsilon$ by $\rho'_s$, we obtain the energy of interaction between a finite shell and an infinitesimal shell,

$$u = 4\pi^2 c \rho_v \rho_s \frac{\lambda}{\kappa^4} \frac{e^{-\kappa z}}{z} (e^{\kappa c} - e^{-\kappa c})[f(\kappa b) - f(\kappa a)] \,.$$

Using again the expression (24), now doing $b = a + \delta$, we obtain the expression for the interaction between two shells of infinitesimal thickness, in the limit $\delta \to 0$,

$$u = 4\pi^2 a c \rho_s \rho'_s \frac{\lambda}{\kappa^2} \frac{e^{-\kappa z}}{z} (e^{\kappa c} - e^{-\kappa c})(e^{\kappa a} - e^{-\kappa a}) \,,$$

in which we replace $\rho_v \delta$ by $\rho_s$.

## 13- Particle-infinite line

We consider now the interaction between a particle and an infinite line (fig. 9). One example of this system is a solution of linear polyelectrolytes [27].

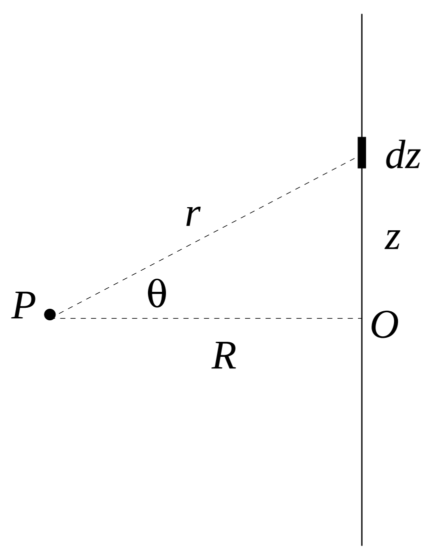


Fig. 9. A particle at $P$ interact with an infinite line at the $z$ axis.

The infinitesimal energy between the particle and an element $dz$ of the line is,

$$du = \lambda \frac{e^{-\kappa r}}{r} \rho_l dz \,.$$

We see from the figure that $r^2 = z^2 + R^2$, hence,

$$u = \lambda \rho_l \int_{-\infty}^{+\infty} \frac{e^{-\kappa\sqrt{R^2+z^2}}}{\sqrt{R^2+z^2}} dz = 2\lambda \rho_l \int_{0}^{+\infty} \frac{e^{-\kappa\sqrt{R^2+z^2}}}{\sqrt{R^2+z^2}} dz \,.$$

Doing the change of variables $R^2 t^2 = R^2 + z^2$,

$$u = 2\lambda \rho_l \int_{1}^{+\infty} \frac{e^{-\kappa R t} dt}{\sqrt{t^2 - 1}} \,.$$

The above integral is the integral representation of the modified Bessel function of the second kind, of order zero, $K_0$. Therefore,

$$u = 2\lambda \rho_l K_0(\kappa R) \,. \tag{28}$$

| System | $u$ |
|---|---|
| Particle<br>-circle of radius $a$ | $2\pi\lambda\rho_l a\frac{e^{-\kappa r}}{r}$ |
| Particle<br>-disc of radius $a$ | $-\frac{2\pi\lambda\rho_s}{\kappa}\left[e^{-\kappa\sqrt{z^2+a^2}}-e^{-\kappa z}\right]$ |
| Particle<br>-sphere of radius $a$ | $\frac{2\pi\lambda\rho_v}{\kappa^3}f(\kappa a)\frac{e^{-\kappa z}}{z}$ |
| Particle<br>-spherical shell of radius $a$ | $2\pi a\rho_s\lambda\frac{e^{-\kappa z}}{\kappa z}(e^{\kappa a}-e^{-\kappa a})$ |
| Two spherical shells<br>of radius $a$ e $b$ | $4\pi^2 ab\rho_a\rho_b\frac{\lambda}{\kappa^2}(e^{\kappa a}-e^{-\kappa a})(e^{\kappa b}-e^{-\kappa b})\frac{e^{-\kappa z}}{z}$ |
| Sphere of radius $a$<br>and spherical shell of radius $b$ | $4\pi^2 b\rho_v\rho_s\frac{\lambda}{\kappa^4}(e^{\kappa b}-e^{-\kappa b})f(\kappa a)\frac{-\kappa z}{z}$ |
| Sphere-sphere | $4\pi^2 b\rho_a\rho_b\frac{\lambda}{\kappa^6}f(\kappa a)f(\kappa b)\frac{-\kappa z}{z}$ |
| Finite shell -<br>particle | $\frac{2\pi\lambda\rho_v}{\kappa^3}[f(\kappa b)-f(\kappa a)]\frac{e^{-\kappa z}}{z}$ |

Table 1. Interaction energies for some systems (see text).

| System | $u$ |
|---|---|
| Finite shell-infinitesimal shell | $4\pi^2 c\rho_v\rho_s\,\dfrac{\lambda}{\kappa^4}(e^{\kappa c}-e^{-\kappa c})[f(\kappa b)-f(\kappa a)]\dfrac{e^{-\kappa z}}{z}$ |
| Finite shell-sphere | $4\pi^2\rho_v\rho_v'\,\dfrac{\lambda}{\kappa^6}f(\kappa c)[f(\kappa b)-f(\kappa a)]\dfrac{e^{-\kappa z}}{z}$ |
| Finite shell-finite shell | $4\pi^2\rho_v\rho_v'\,\dfrac{\lambda}{\kappa^6}\dfrac{e^{-\kappa z}}{z}[f(\kappa d)-f(\kappa c)][f(\kappa b)-f(\kappa a)]$ |
| Particle-infinite line | $2\lambda\rho_l K_0(\kappa R)$ |

Table 1 (cont.). Interaction energies for some systems (see text).

# 2 The free energy for spherical colloids

In this section we write de Helmholtz free energy for a colloidal solution with $N_p$ polyions, which are spheres of radius $a$ and charge $-Zq$, and positive counterions of charge $+q$ each, the proton charge. We can also have monovalent salt, or other valent salts, in the system. The free energy is a sum of the main contributions [24],

$$F = F_{id} + F_{ent} + F_{ion} + F_{dh} + F_{pp}\,, \tag{29}$$

where $F_{id}$ is the ideal gas term,

$$\beta F_{id} = \sum_s N_s[\ln\rho_s^* - 1]\,, \tag{30}$$

and the sum is over all species, polyions and free ions. The dimensionless density is $\rho^* = \rho\, a^3$, $\beta = 1/kT$, and $k$ is Boltzmann constant.

The entropic term describes all possible configurations of $n$ condensed ions at $Z$ sites [24, 39],

$$\beta F_{ent} = ZN_p[m\ln m + (1-m)\ln(1-m)]\,, \tag{31}$$

with $m = n/Z$ being the association fraction. The term describingeach with charge $-(1-m)q$, is [24, 39]

$$\beta F_{ion} = \frac{N_p(Z-n)^2}{2T^*}\,, \tag{32}$$

with $T^* = 4\pi\varepsilon akT/q^2$, and $\varepsilon$ is the absolute permitivity of water.

## 2.1 The interaction of the colloid and the ionic solution

The ionic solution contains spherical molecules of diameter and charge very larger than the ions in solution. We obtain an approximated Helmholtz free energy througy Debye-Hückel theory [3]. We consider a spherical molecule with radius $a$ and charge $Q$, in a ionic solution characterized by the parameter $\kappa$, the inverse Debye screening length. The ions in solution are considered as punctiform particle. We consider three cases: the charge at the center of the sphere, the charge uniformly distributed over the volume of the sphere, and the charge uniformly distributed over the surface of the sphere.

(a) Charge at the center of the sphere.

In this case, according Debye-Hückel theory, the electrostatic potential around the colloid is,

$$\begin{aligned} \phi_i &= \frac{Q}{4\pi\epsilon_i r} + A\,, \qquad r \le a\,, \\ \phi_e &= \frac{B\mathrm{e}^{-\kappa r}}{r}\,, \qquad r \ge a\,, \end{aligned}$$

where $\epsilon_i$ is the permittivity in $r \le a$ and $\epsilon$ is the permittivity in the ionic solution, in $r \ge a$. The derivatives with respect to $r$ are,

$$\begin{aligned} \frac{d\phi_i}{dr} &= -\frac{Q}{4\pi\epsilon_i r^2}\,, \qquad r \le a\,, \\ \frac{d\phi_e}{dr} &= -\frac{\kappa B\mathrm{e}^{-\kappa r}}{r} - \frac{B\mathrm{e}^{-\kappa r}}{r^2}\,, \qquad r \ge a\,. \end{aligned}$$

Using the boundary conditions,

$$\phi_i(a) = \phi_e(a)\,, \qquad \epsilon_i \frac{d\phi_i}{dr}(a) = \epsilon \frac{d\phi_e}{dr}(a)\,,$$

we obtain,

$$
\begin{aligned}
A &= \frac{Q}{4\pi\epsilon a}\left[\frac{1}{1+\kappa a} - \frac{\epsilon}{\epsilon_i}\right] , \\
B &= \frac{Q\mathrm{e}^{\kappa a}}{4\pi\epsilon(1+\kappa a)} .
\end{aligned}
$$

If $\epsilon_i = \epsilon$,

$$
A = -\frac{Q\kappa}{4\pi\epsilon(1+\kappa a)} ,
$$

ant the electrostatic potential is,

$$
\begin{aligned}
\phi_i &= \frac{Q}{4\pi\epsilon r} - \frac{Q\kappa}{4\pi\epsilon(1+\kappa a)} , \qquad r \leq a , \\
\phi_e &= \frac{Q}{4\pi\epsilon}\frac{\mathrm{e}^{\kappa a}}{1+\kappa a}\frac{\mathrm{e}^{-\kappa r}}{r} , \qquad r \geq a .
\end{aligned} \tag{33}
$$

The Helmholtz free energy due to electrostatic interaction between the colloid and the ions in solution evaluated charging the potential $\psi$ given by the second term in $\phi_i$,

$$
\psi = \phi_i - \phi_i(\kappa = 0) = -\frac{Q\kappa}{4\pi\epsilon(1+\kappa a)} . \tag{34}
$$

Therefor,

$$
\begin{aligned}
dF &= \psi dQ , \\
F &= \int \psi dQ = -\frac{\kappa}{4\pi\epsilon(1+\kappa a)} \int_0^Q QdQ , \\
F &= -\frac{Q^2}{8\pi\epsilon}\frac{\kappa}{1+\kappa a} .
\end{aligned} \tag{35}
$$

We note that $F \to 0$ if $\kappa \to 0$, as expected.

(b) Charge uniformly distributed at the volume of the sphere.

The electrostatic potential is given by,

$$
\begin{aligned}
\phi_i &= A + Br^2 , \qquad r \leq a , \\
\phi_e &= \frac{C\mathrm{e}^{-\kappa r}}{r} , \qquad r \geq a .
\end{aligned}
$$

The derivatives of $\phi$ are,

$$\frac{d\phi_i}{dr} = 2Br\,,$$
$$\frac{d\phi_e}{dr} = -\frac{\kappa C \mathrm{e}^{-\kappa r}}{r} - \frac{C\mathrm{e}^{-\kappa r}}{r^2}\,, \qquad r \geq a\,.$$

We have three constants to find. The constant $B$ is evaluated from Gauss law,

$$\oint E dS = \frac{Q_i}{\epsilon_i}\,.$$

We obtain, for $r < a$,

$$B = -\frac{Q}{8\pi\epsilon_i a^3}\,.$$

To determine $A$ and $C$ we use the boundary conditions,

$$\phi_i(a) = \phi_e(a)\,, \qquad \epsilon_i \frac{d\phi_i}{dr}(a) = \epsilon \frac{d\phi_e}{dr}(a)\,,$$

obtaining, with $\epsilon_i = \epsilon$,

$$A = \frac{Q}{8\pi\epsilon a}\frac{3+\kappa a}{1+\kappa a}\,,$$
$$C = \frac{Q\mathrm{e}^{\kappa a}}{4\pi\epsilon(1+\kappa a)}\,.$$

The electrostatic potential is then,

$$\phi_i = \frac{Q}{8\pi\epsilon a}\frac{3+\kappa a}{1+\kappa a} - \frac{Qr^2}{8\pi\epsilon a^3}\,, \qquad r \leq a\,,$$
$$\phi_e = \frac{Q}{4\pi\epsilon}\frac{\mathrm{e}^{\kappa a}}{1+\kappa a}\frac{\mathrm{e}^{-\kappa r}}{r}\,, \qquad r \geq a\,. \tag{36}$$

The electrostatic potential for $r \geq a$ is the same as before. The potential $\psi$ is,

$$\psi = \phi_i - \phi_i(\kappa = 0) = -\frac{Q\kappa}{4\pi\epsilon(1+\kappa a)}\,, \tag{37}$$

as before. Then we have the same free energy,

$$F = -\frac{Q^2}{8\pi\epsilon}\frac{\kappa}{1+\kappa a}\,. \tag{38}$$

(c) Charge uniformly distributed over the surface of the sphere.
The electrostatic potencial is,

$$\begin{aligned}
\phi_i &= A\,,\\
\phi_e &= \frac{B\mathrm{e}^{-\kappa r}}{r}\,, \qquad r \geq a\,.
\end{aligned}$$

The derivatives of the potential are,

$$\begin{aligned}
\frac{d\phi_i}{dr} &= 0\,,\\
\frac{d\phi_e}{dr} &= -\frac{\kappa B\mathrm{e}^{-\kappa r}}{r} - \frac{B\mathrm{e}^{-\kappa r}}{r^2}\,, \qquad r \geq a\,.
\end{aligned}$$

The constants $A$ and $B$ are determined as before by the boundary conditions,

$$\phi_i(a) = \phi_e(a)\,, \qquad \epsilon E_n^e(a) - \epsilon_i E_n^i(a) = \sigma_q\,,$$

where $\sigma_q = Q/4\pi r^2$ is the surface charge density of the colloid. We obtain, using $\epsilon_i = \epsilon$,

$$\begin{aligned}
A &= \frac{Q}{4\pi\epsilon a}\frac{1}{1+\kappa a}\,,\\
B &= \frac{Q\mathrm{e}^{\kappa a}}{4\pi\epsilon(1+\kappa a)}\,.
\end{aligned}$$

The electrostatic potential is then,

$$\begin{aligned}
\phi_i &= \frac{Q}{4\pi\epsilon a}\frac{1}{1+\kappa a}\,, \qquad r \leq a\,,\\
\phi_e &= \frac{Q}{4\pi\epsilon}\frac{\mathrm{e}^{\kappa a}}{1+\kappa a}\frac{\mathrm{e}^{-\kappa r}}{r}\,, \qquad r \geq a\,.
\end{aligned} \tag{39}$$

The potential $\phi_e$ is the same, as expected. The potential $\psi$ is given by,

$$\psi = \phi_i - \phi_i(\kappa = 0) = -\frac{Q\kappa}{4\pi\epsilon(1+\kappa a)}\,, \tag{40}$$

as before. Therefore we obtain the same free energy,

$$F = -\frac{Q^2}{8\pi\epsilon}\frac{\kappa}{1+\kappa a}\,. \tag{41}$$

### 2.2 The polyion-polyion contribution

The equation (18) is our approximation for the interaction energy between spherical colloids in the ionic solution, considered as spherical shells. We note that this is not exactly the same form of the repulsive term of the DLVO potential [2, 19, 20, 24]. We will return to this point later. If all colloid molecules have the same charge and diameter, we may write,

$$\rho_s = \rho_s' = \frac{Z-n}{4\pi a^2}\,, \qquad \lambda = \frac{q^2}{4\pi\varepsilon}\,, \tag{42}$$

in which we consider a colloid with radius $a$ and $Z$ negative sites. At equilibrium there are $n$ associated positive ions at the colloid. Substituting in (18),

$$u = \frac{(Z-n)^2 q^2}{16\pi\varepsilon}\frac{(e^{\kappa a}-e^{-\kappa a})^2}{\kappa^2 a^2}\frac{e^{-\kappa z}}{z}\,. \tag{43}$$

We can verify that this expression, in the limit $\kappa \to 0$, reduces to,

$$u = \frac{(Z-n)^2 q^2}{4\pi\varepsilon z}\,, \qquad \kappa \to 0\,,$$

as expected. This interaction energy may be used to evaluate the van der Waals free energy [3, 5, 24, 39]. The contribution to the Helmholtz free energy due to polyion-polyion interaction is then,

$$\beta F_{pp} = \frac{1}{2}\rho_n^2 V \int \beta u d^3 r\,,$$

where $\rho_n$ is the number density of a polyion with $n$ positive associated ions. This forms what is called a *complex* of a polyion and $n$ associated counterions. We consider here all complexes with the same siza $n$, hence $\rho_n = \rho_p = N_p/V$. A complex size distribution may also be determined [17]. The result for $F_{pp}$ is,

$$\beta F_{pp} = \frac{\pi V}{2\kappa^4 a T^*}(Z-n)^2 \rho_n^2 (e^{\kappa a}-e^{-\kappa a})^2 e^{-2\kappa a}(1+2\kappa a)\,. \tag{44}$$

The DLVO potential [19] has also been used in colloid studies [24]. We include this possibility here for comparison. The interaction energy between two spherical colloids in DLVO theory is,

$$u_{DLVO} = \frac{q^2(Z-n)^2}{4\pi\varepsilon}\frac{e^{2\kappa a}}{(1+\kappa a)^2}\frac{e^{-\kappa r}}{r}\,. \tag{45}$$

The corresponding contribution to the free energy, evaluated with van der Waals theory, is [24],

$$\beta F_{DLVO} = \frac{2\pi a^3 V}{T^*}(Z-n)^2\rho_p^2 \frac{1+2\kappa a}{(\kappa a)^2(1+\kappa a)^2}\,. \tag{46}$$

The results with both interaction forms are shown below.

# 3 Resultados

We consider only the free salt case, that is, $\rho_s = 0$. In figure 10 we have the association isotherms as function of $Z$ for three different temperatures. In figure 11 we have the association fractions as function of $T^*$ for three different densities of polyions. In figure 12 we have $G \times p$ in dimensionless units for fixed $T^*$. We see a phase transition. Figure 13 shows the phase diagram $T^* \times \rho_p^*$ for the system without several excluded volume terms included. Figure 14 shows the $T^* \times m$ diagram corresponding to the diagrams in figure 13.

Figure 15 shows the phase diagrams for the system with free energy corresponding to the interaction between polyions given by (44), evaluated with the interaction between spherical shells (43). We also show the phase diagram using (46), corresponding to the interaction between polyions given by DLVO theory, equation (45), for comparison. In both curves we have not any excluded volume form.

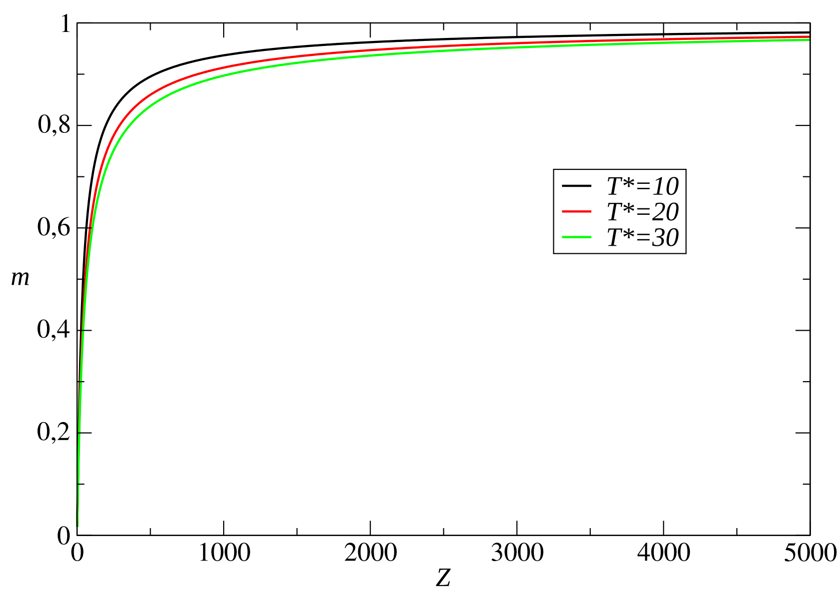


Fig. 10. Associated fraction as function of $Z$, for $\rho_p^* = 0,01$ and $\rho_s^* = 0$.

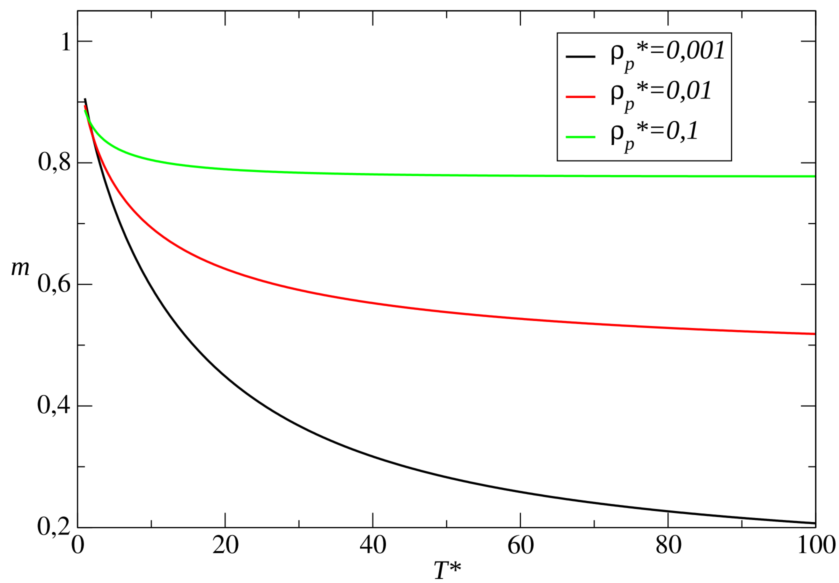


Fig. 11. Associated fraction as function of $T^*$, for $\rho_s^* = 0$, $Z = 100$ and different densities of colloids.

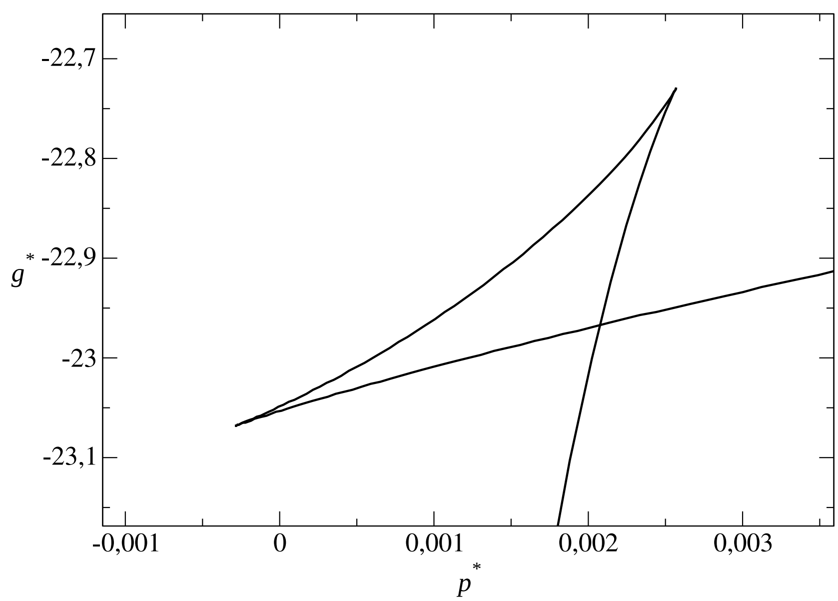


Fig. 12. Graphic of $g^* \times p^*$ for the system with $Z = 100$, $\rho_s^* = 0$ and $T^* = 0,2$, without excluded volume terms.

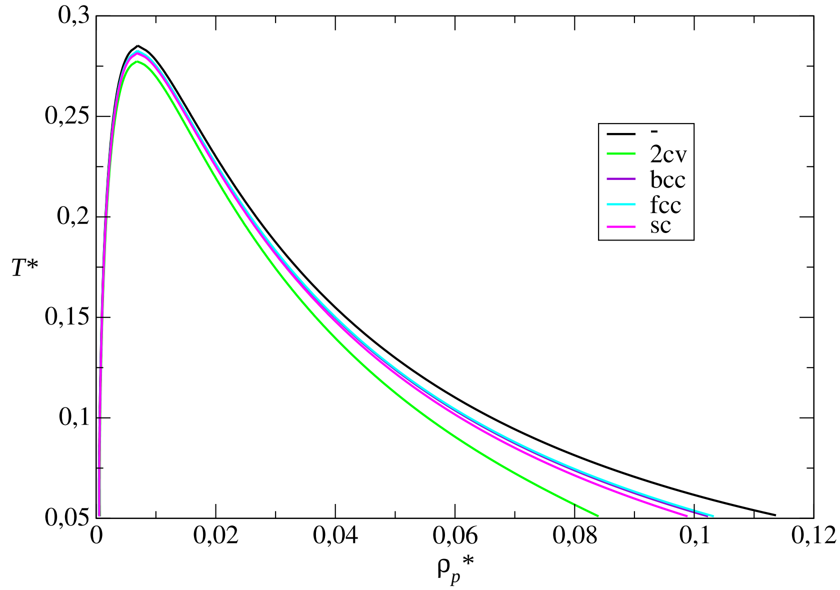


Fig. 13. Phase diagram for the system with $Z = 100$ and $\rho_s^* = 0$.

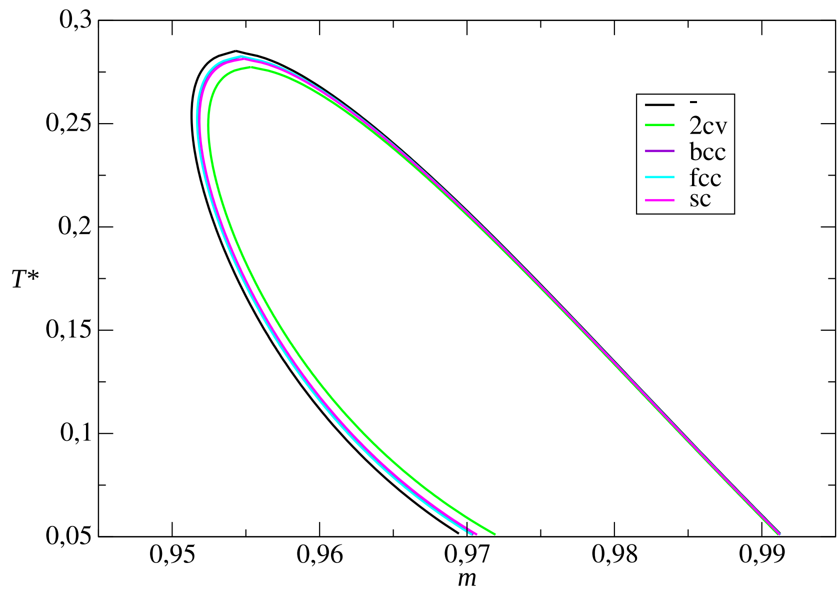


Fig. 14. Association fractions corresponding to the diagrams in figure 13.

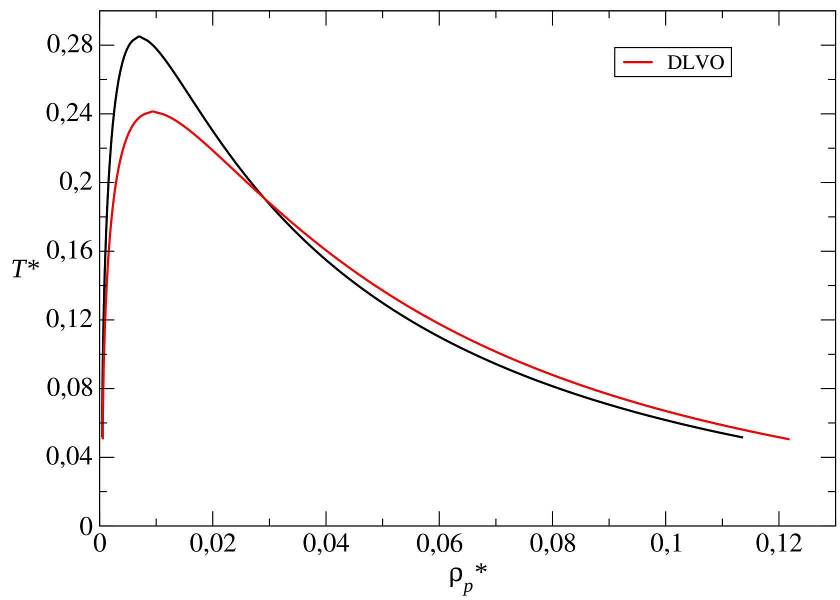


Fig. 15. Phase diagrams for the system with free energy corresponding to the interaction between polyions given by (44) (black line), evaluated with the interaction between spherical shells (43). The red lineis the phase diagram using (46), corresponding to the interaction between polyions given by DLVO theory, equation (45).

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