Pygbe tutorial for the interaction between a charged particle and different types of surface.

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Contents

1 Introduction

This is a PyGBe tutorial for the interaction between a charge and different types of surface. We consider dielectric surfaces with different electric permittivites and charge densities. We also evaluate the effect of ionic or non-ionic solutions.

2 Methods

In most of the examples presented here the system consists in three different regions.

- **Region I**: It is the solvent (parent region), which is enclosing the other two regions (Region II and III). It is defined by its electric permitivity (ε) and Debye-Hückel parameter (κ).

- **Region II**: It consists in a rectangular prism of dimensions 10x1x10 nm^3. It is defined by its electric permitivity (ε'), Debye-Hückel parameter (κ') and surface charge density (σ).

- **Region III**: A small sphere enclosing a charge (radius=1Å). It is defined by its electric permitivity (ε"), inverse of Debye-Hückel parameter (κ") and charge (q). The charge takes a value of q=q_0e=+e if not otherwise indicated (q_0=1).

However, in calculations 9 and 10, Region II is defined using von Neumann boundary conditions ($\frac{\partial\phi(\vec{r})}{\partial\vec{n}}$)=constant where $\vec{n}$ is the normal vector to the surface. By setting this constant we characterize the electric field in the surface of Region II and consequently its surface charge.

The system is depicted in Figure 1. In the Results section we plot the binding energy between Region II (flat surface) and Region III (small sphere) as a function of distance.

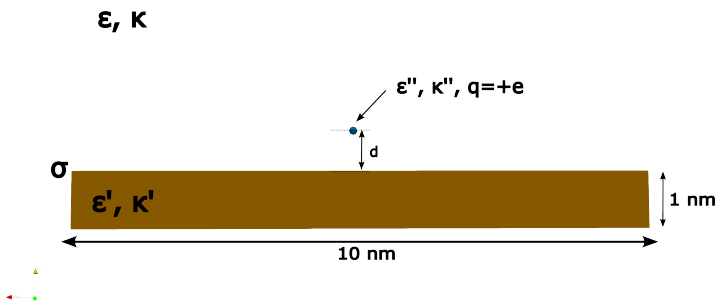

Figure 1: Scheme of the test system.

2.1 Structure of directories

In order to run a calculation using PyGBe, we need the input files and a proper organization of subdirectories and files inside the main folder of the calculation. Scheme in Figure 2

The configuration and parameter files used in the 10 calculations showed here are provided in https://github.com/marcdomingo2/pygbe_tutorial. A model for the PQR files for the sphere and the flat surface can also be found. A python script to generate the surface PQR file os also provided.

The files able to generate .phi0 (used when von Neumann boundary conditions are applied), .vert and .face files can be found in PyGBE GitHub (https://github.com/pygbe/pygbe/tree/master/preprocessing_tools). Region III

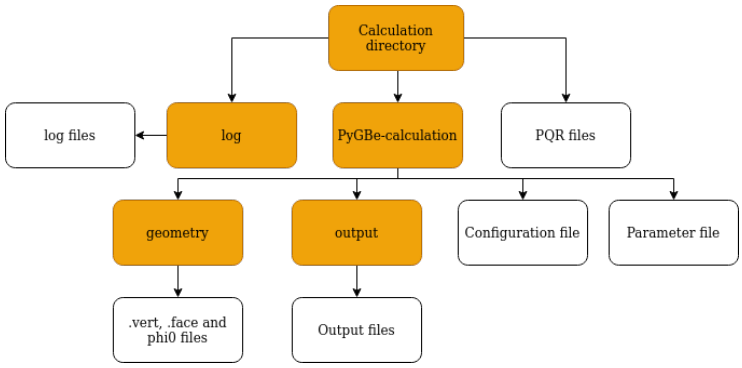

Figure 2: Flowchart of directories and files in a pygbe calculation.

mesh files are created using the file mesh_sphere.py. Region II files are created using mesh_brick file. We make use also of generate_phi0.py to generate .phi0 file for calculation 9 and 10.

The calculation is run from the "Calculation directory". More information on how to run the calculations can be found in the PyGBe documentation (http://pygbe.github.io/pygbe/docs/).

3 Results

Each row in Table 1 corresponds to a different calculation. The difference among this calculations consists in varying the electric permitivity, Debye-Hückel parameter, and surface charge in Regions I, II and III.

In each subsection we represent the free energy as a function of distance

Calculation	σ (e·nm^{-2})	ε	ε'	ε"	κ (nm^{-1})	κ' (nm^{-1})	κ" (nm^{-1})
1 Fig 3	0	80	1	80	0	0	0
2 Fig 4	0	80	10^6	80	0	0	0
3 Fig 5	0	80	1	80	1.25	0	0
4 Fig 6	0	80	10^6	80	1.25	0	0
5 Fig 7	0.3	80	1	80	1.25	0	1.25
6 (5 shifted) Fig 8	0.3	80	1	80	1.25	0	1.25
7 Fig 9	-0.3	80	1	80	1.25	0	1.25
8 (7 shifted) Fig 10	-0.3	80	1	80	1.25	0	1.25
9 Fig 11	0.3125	80	NA	80	1.25	NA	0
10 Fig 12	0.3125 (q=-e)	80	NA	80	1.25	NA	0

Table 1: Features for the different simulations

3.1 Calculation 1

As shown in Table 1, we consider a dielectric ε =1 in Region II. In order to calculate the energy of interaction between the charge and. This is done by th method of the image charge. The effext of the dielectric polarization due to the charge can be done by considering an image charge of charge q'=Δq. The force of attraction on the charge q towards the dielectric is then: $F = \frac{\Delta q^2}{16\pi\varepsilon\varepsilon_0 x^2}$. The demonstration can be found in [1]. By integrating the force we have $G = -\int_{+inf}^{d} F\,dx$:

$$G = \frac{\Delta q^2}{16\pi\varepsilon\varepsilon_0 d} = \frac{7.05 \cdot 10^{-31}}{d} J = \frac{1.01 \cdot 10^{-10}}{d} kcal/mol \tag{1}$$

where $\Delta(air) = \frac{\varepsilon-\varepsilon'}{\varepsilon+\varepsilon'} = 0.9753$

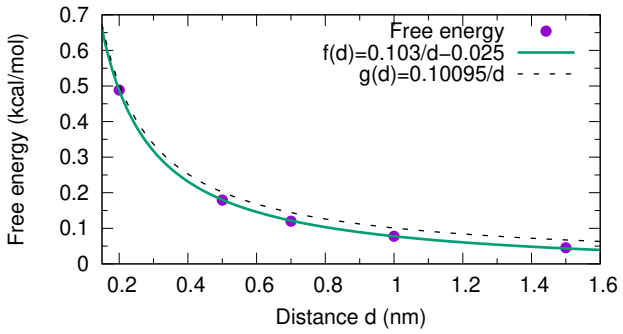

Figure 3: Free energy due to the dielectric flat surface as a function of the distance between Region II and III. Calculated points fitted via f(d)= a/d+b via a and b, where d is the distance between the charge and the plane. The free energy from calculated points are corrected imposing that it is 0 when $d \to +\infty$. Thedashed line is G calculated from Eq 1.

3.2 Calculation 2: metallic surface and small charged dielectric sphere in water (no salt)

It is the same case as the dielectric plane but in this case ε' tends to $+\infty$ (we are using a very high value of ε' so $\Delta \simeq -1$). In this situation $G = -\frac{1.03552 \cdot 10^{-10}}{d} kcal/mol$

In the following plot (Figure 4) I consider $\varepsilon' = 1000000$.

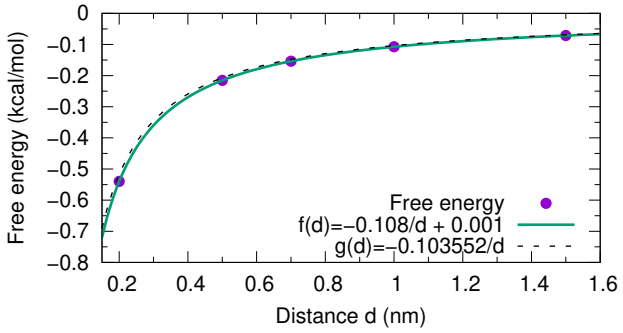

Figure 4: Free energy due to the metalic plane as a function of the distance between Region II and III. Calculated points fitted via f(d)= a/d+b via a and b, where d is the distance between the charge and the plane.

3.3 Calculation 3: Dielectric surface and charged sphere (with salt)

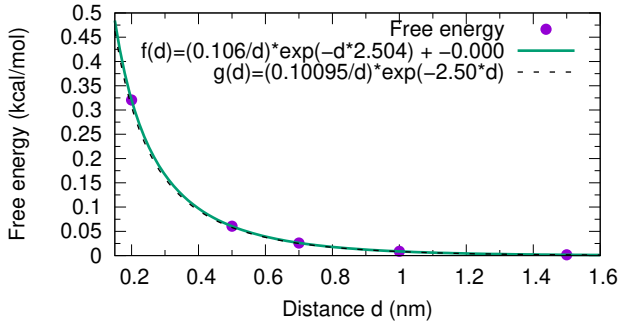

Figure 5: Free energy due to the dielectric plane as a function of the distance between Region II and III. Calculated points fitted via f(d)= a/d*exp(-cd)+b via a, b and c, where d is the distance between the charge and the plane. κ=0.125 Å^{-1}

.

We consider the case of system 1 but adding salt concentration in water. The

free energy as a function of distance can be calculated using Eq. 2 (equation 12 in [2]).

$$G \simeq \frac{q^2 e^{-2\kappa d}}{16\pi\varepsilon\varepsilon_0 d} = \frac{7.19 \cdot 10^{-31} e^{-2\kappa d}}{d} J = \frac{1.03 \cdot 10^{-10} e^{-2\kappa d}}{d} kcal/mol \qquad (2)$$

3.4 Calculation 4: Metallic surface and charged sphere (with salt)

We do the same but for a metallic surface:

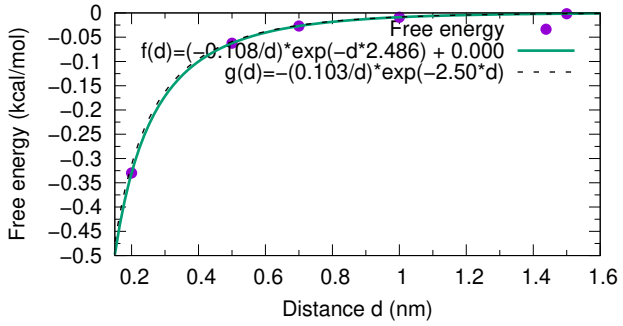

Figure 6: Free energy due to the dielectric plane as a function of the distance between Region II and III. Calculated points fitted via f(d)= a/d*exp(-cd)+b via a, b and c, where d is the distance between the charge and the plane. κ=0.125 Å^{-1}

3.5 Calculation 5 and 6: charged surface (σ = 0.03 e*nm^{-2})

Now we consider a surface charge density in Region II. To do so we place a grid of charges inside Region II, each of this charges owns a charge so that we reproduce the desired surface charge density. The PQR file grid is created using a python code (charge.sh). In this example, charges are located at 1 A of the Region II top layer.

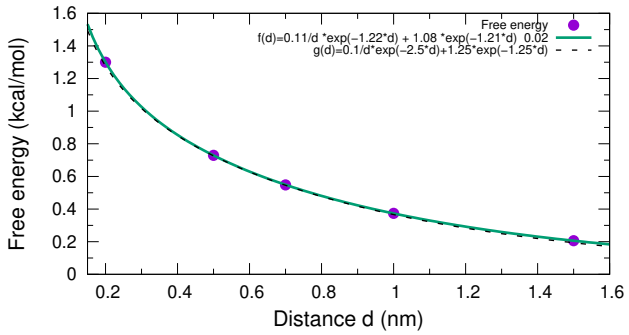

Figure 7: Free energy due to the charged sphere and surface as a function of the distance between Region II and III. Calculated points fitted via f(x)= a*exp(-b*d)+(c/d)*exp(-h*d)+j via a, b, c, h and j, where d is the distance between the charge and the plane. κ=0.125 Å^{-1}; σ=0.03 e*nm^{-2}.

The analytical expression for the free energy (G) is calculated as shown in Equation 3. It consists of two terms: G_{self} which is due to the dielectric discontinuity in Region II and G_σ which is due to the surface charge density σ (G_σ is calculated as in equation 10 in [2]).

$$G = G_{self} + G_\sigma = \frac{q^2 e^{-2\kappa d}}{16\pi\varepsilon\varepsilon_0 d} + \frac{2e^{-\kappa d}}{\mu\kappa} = ... = \frac{1.03 \cdot 10^{-10} \cdot e^{-2\kappa d}}{d} + 1.3e^{-\kappa d} kcal/mol \tag{3}$$

where μ is the Gouy-Chapman length ($\mu = \frac{e}{2\pi q_0 l_B \sigma}$), where l_B is the Bjerrum length ($l_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_B T}$)

Now we do the same calculation but charges are located at 0.05A of the border between Region II and Region I.

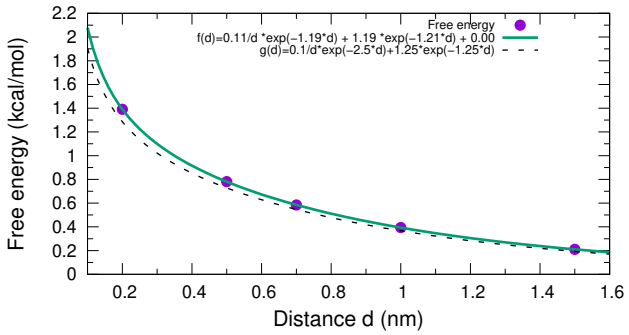

Figure 8: Free energy due to the charged sphere and surface as a function of the distance between Region II and III. Calculated points fitted via f(x)= a*exp(-b*d)+(c/d)*exp(-h*d)+j via a, b, c, h and j, where d is the distance between the charge and the plane. κ=0.125 $Å^{-1}$; σ=0.03 e*nm^{-2}.

3.6 Calculation 7 and 8: charged surface (σ = -0.03 e*nm^{-2}) [Rel Q1]

In this example, charges are located at 1 A from the Region II top layer. The results show a considerable mismatch between the theoretical curve and the calculated points (Figure 9). This mismatch is later corrected by shifting the grid of charges bery close to top layer in Region II (charges are located at 0.05A of the border between Region II and Region I). Results are shown in Figure 10.

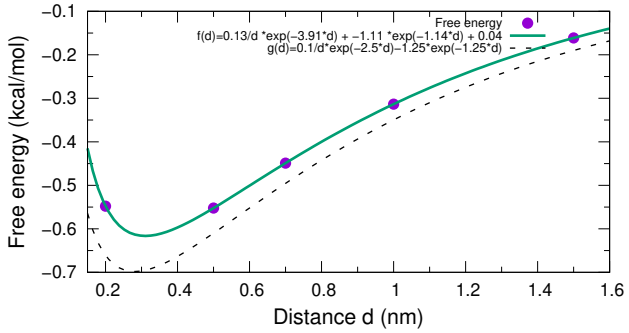

Figure 9: Free energy due to the charged sphere and surface as a function of the distance between Region II and III. Calculated points fitted via f(x)= a*exp(-b*d)+(c/d)*exp(-h*d)+j via a, b, c, h and j, where d is the distance between the charge and the plane. κ=0.125 Å^{-1}; σ=-0.03 e*nm^{-2}.

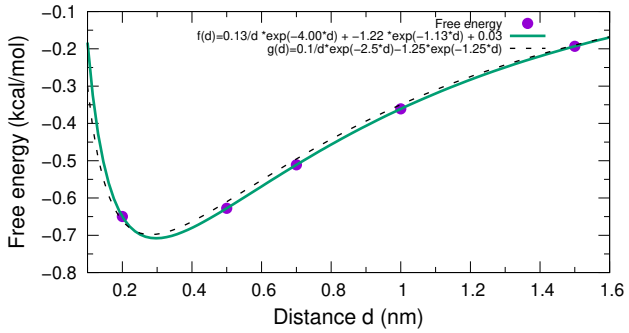

Figure 10: Free energy due to the charged sphere and surface as a function of the distance between Region II and III. Calculated points fitted via f(x)= a*exp(-b*d)+(c/d)*exp(-h*d)+j via a, b, c, h and j, where d is the distance between the charge and the plane. κ=0.125 Å^{-1}; σ=-0.03 e*nm^{-2}.

The analytical expression for the free energy (G) is calculated as shown in Equation 4. The difference between Equation 3 and Equation 4 is the sign of G_σ due to the positive or negative surface charge density in Region II.

$$G = G_{self} + G_{\sigma} = \frac{q^2 e^{-2\kappa d}}{16\pi\varepsilon\varepsilon_0 d} - \frac{2e^{-\kappa d}}{\mu\kappa} = ... = \frac{1.03 \cdot 10^{-10} \cdot e^{-2\kappa d}}{d} - 1.3e^{-\kappa d} kcal/mol \tag{4}$$

3.7 Calculation 9: charged surface (σ = 0.03125 e*nm^{-2})

In Region II we set von Neumann boundary condition in the borders of Region II. In this example, we set $\frac{\partial\phi(\vec{r})}{\partial\vec{n}} = -4 \cdot 10^{-5}$ in units of electron charge and angstrom^2 which corresponds to a surface charge density of σ = 0.03125 e*nm^{-2} (just in the top face of Region II. In the other 5 faces, it is set to 0). In order to generate this boundary condition we use python code (https://github.com/pygbe/pygbe/blob/master/preprocessing_tools/generate_phi0.py)

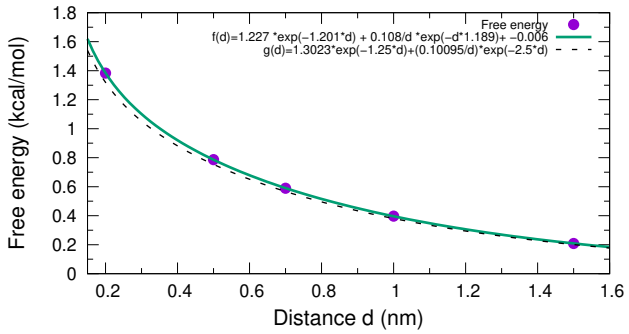

Figure 11: Free energy due to the charged sphere and surface as a function of the distance between Region II and III. Calculated points fitted via f(x)= a*exp(-b*d)+(c/d)*exp(-h*d)+j via a, b, c, h and j, where d is the distance between the charge and the plane. κ=0.125 Å^{-1}; σ=0.03125 e*nm^{-2}.

3.8 Calculation 10: charged surface (σ = 0.03125 e*nm^{-2}), q=-e

Here, we have the same system as in calculation 9 but the point charged is negatively charge (q=-e).

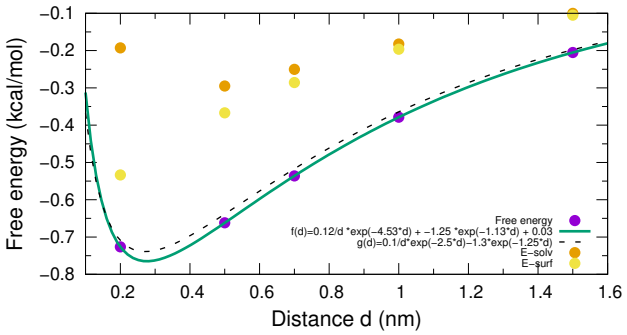

Figure 12: Free energy due to the charged sphere and surface as a function of the distance between Region II and III. Calculated points fitted via f(x)= a*exp(-b*d)+(c/d)*exp(-h*d)+j via a, b, c, h and j, where d is the distance between the charge and the plane. κ=0.125 $Å^{-1}$; σ=0.03 e*nm^{-2}.

References

[1] Brebis Bleaney B. I. Bleaney. *Electricity and Magnetism*. Vol. 1. 55-56. New York: Oxford University Press, 1976.

[2] Matej Kanduč et al. "Dressed counterions: Polyvalent and monovalent ions at charged dielectric interfaces". en. In: *Physical Review E* 84.1 (July 2011), p. 011502. ISSN: 1539-3755, 1550-2376. DOI: 10.1103/PhysRevE.84.011502. URL: https://link.aps.org/doi/10.1103/PhysRevE.84.011502 (visited on 06/30/2023).