FORCE ON A UNIT CHARGE DUE TO IMAGE CHARGE EFFECTS

1. Redo the previous work

Since this work (checking assembly of Green's Function) was done two years ago, it should be reproduced to go to the next. The results are listed as follows:

Box size: 3.0×3.0×5.0

Green's Function: 30×30×30 grids (for channel)

FFT spacing: **0.10nm** in x,y,z-direction

Applied potential: **0V** was applied on both electrodes.

Electrodes: z = 0nm & **2.9nm**

Unit charge: a pair of unit charges are put between two electrodes; the distance between two unit charges is **0.5nm** (they have **the same z-position**).

Units (for all results): position/length (nm), force (kJ/mol/nm)

X	Y	Z			F_z
1.400	1.500	0.300	307.85855	-0.00001	-213.28143
1.400	1.500	0.400	371.16309	-0.00003	-84.59668
1.400	1.500	0.500	403.56107	0.00000	-38.51223
1.400	1.500	0.600	420.68997	0.00000	-19.38203
1.400	1.500	0.700	430.14474	0.00007	-10.47694
1.400	1.500	0.800	435.56601	0.00005	-5.95033
1.400	1.500	0.900	438.76471	0.00000	-3.49241
1.400	1.500	1.000	440.68753	0.00000	-2.08886
1.400	1.500	1.100	441.85120	0.00001	-1.25237
1.400	1.500	1.200	442.54645	0.00000	-0.72987
1.400	1.500	1.300	442.93756	0.00009	-0.38039
1.400	1.500	1.400	443.11337	0.00000	-0.11797
1.400	1.500	1.450	443.05411	0.00000	-0.00007

Analytic solution:

0.3 -210.042
0.4 -83.6164
0.5 -38.3320
0.6 -19.3820
0.7 -10.4982
0.8 -5.9657
0.9 -3.5016
1.0 -2.0943
1.1 -1.2554
1.2 -0.7316
1.3 -0.3813
1.4 -0.1182

2. simulation setup

1) box size (nm):
   2.75 2.75 5.5
2) Green's Function (GF) size (nm):
   2.75 2.75 3.3
3) FFT spacing 0.11nm, rc=1.1nm
4) Electrodes (parallel to xy-plane):
   lower one located at z=0;
   upper one located at z=3.3;
5) A Na^+ was put between two electrodes, and moved from 0.2~1.65nm along Z-direction
6) The position of compensated counter charge Cl- is fixed in the region z = (3.3,5.5) randomly.

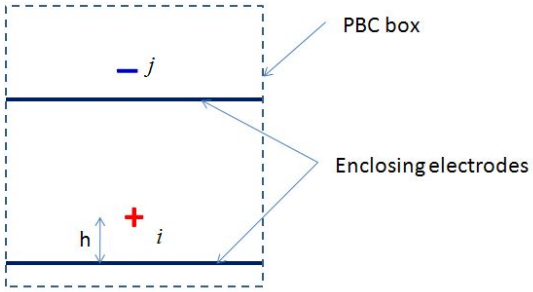

Figure 1. Setup the simulation system.

3. **Test 1:** Is the force acting on charge *i* independent of the position of the compensating charge j?

z(nm)	F_z (kJ/mol/nm)
0.200	-859.33002
0.200	-859.27649
0.200	-859.32739
0.200	-859.54803
0.200	-859.10400
0.200	-859.08789
0.200	-859.05774
0.200	-859.48535
0.300	-404.41959
0.300	-404.37933
0.900	-60.18221
0.900	-60.18124
0.900	-59.60311
0.900	-59.92646
0.900	-60.05145
0.900	-60.18885
0.900	-60.18614
0.900	-60.17764

In the above calculations, the position of compensated counter charge was tuned randomly. The above data indicates the force on the charge inside channel in z-direction is independent of the location of the compensated counter charge.

4. Force on a unit charge

The below data and figure are the forces (in z-direction) on a unit charge due to image charge effects changes with the distance of point charge from the lower electrode.

z(nm)	$F_{analytic}$	F_{MD}	Error_abs (kJ/mol/nm)	Error_relative
0.2000	859.3300	-877.8838	18.5538	0.0216
0.3000	-404.3793	-399.5922	4.7871	0.0118
0.4000	-236.7759	-234.0561	2.7198	0.0115
0.5000	-159.1746	-158.2549	0.9197	0.0058
0.6000	-116.9806	-117.1244	0.1438	0.0012
0.7000	-90.9588	-91.8176	0.8588	0.0094
0.8000	-73.2251	-74.5101	1.2850	0.0175
0.9000	-60.1822	-61.5210	1.3388	0.0222
1.0000	-50.0521	-50.9668	0.9147	0.0183
1.1000	-41.8968	-41.8255	0.0713	0.0017
1.2000	-34.5770	-33.5197	1.0573	0.0306
1.3000	-27.1924	-25.7126	1.4798	0.0544
1.4000	-19.6264	-18.2021	1.4243	0.0726
1.5000	-11.8686	-10.8628	1.0058	0.0847
1.6500	0	-0.0000	0.0000	0

Note that when using the attached code to compute the analytical solution, the number of charge images (denoted by G) should increase as the number of periodic images of original charge (denoted by M in the code) becomes large. In principle M and G should be infinitely large. It turns out the summation converges very slowly as M and G increases. The above results are obtained with M=32 and G=500. Further testing with M=50 and G=1200 shows results nearly identical to that produced by M32/G500 – suggesting that the value here can be trusted.

These results are also shown in Figure 2 and Figure 3.

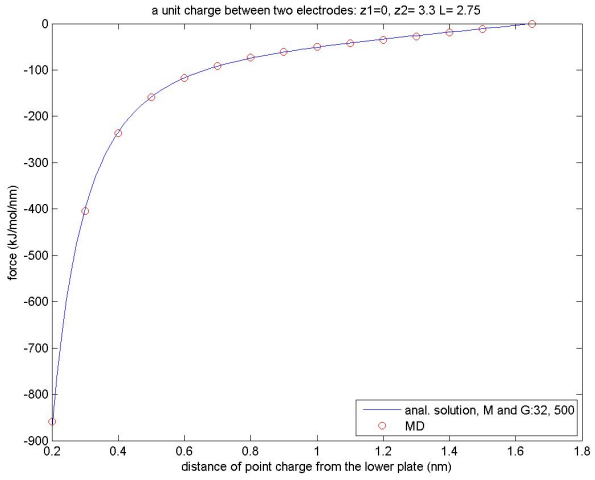

Figure 2. comparison of the force acting on charge *i* in Figure 1 as obtained from MD and from analytical solution.

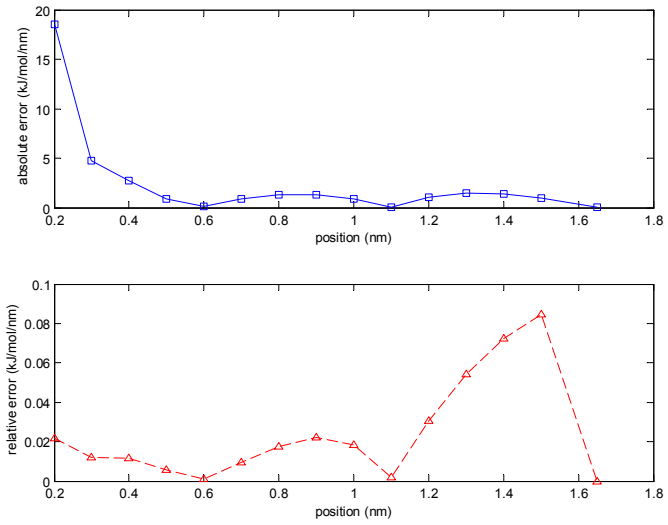

Figure 3. absolute and relative error of the force acting on the positive charge inside the electrode channel

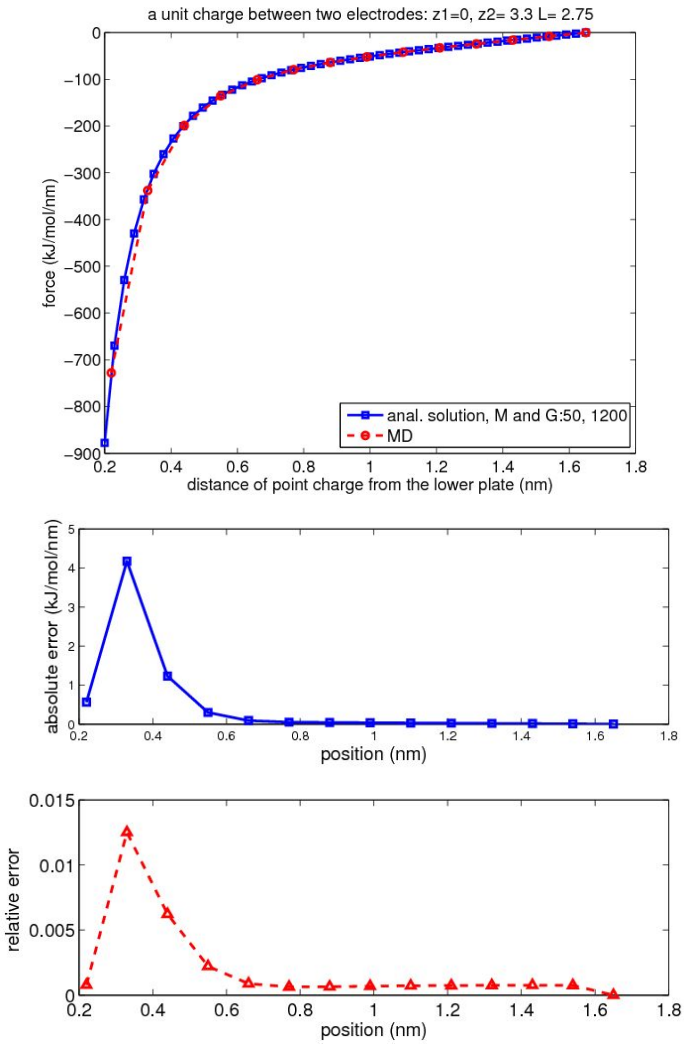

Figure 4. same plots as Figures 2 and 3 except that MD points are on FFT grids

5. $\mathbf{\Phi_r}$ and $\mathbf{\Phi_k}$ on the lower electrode

the charges have the location as I (1.500 1.500 0.400) and j (1.500 1.500 5.390), $\mathbf{\Phi_r}$ and $\mathbf{\Phi_k}$ on the lower electrode are plotted as follows,

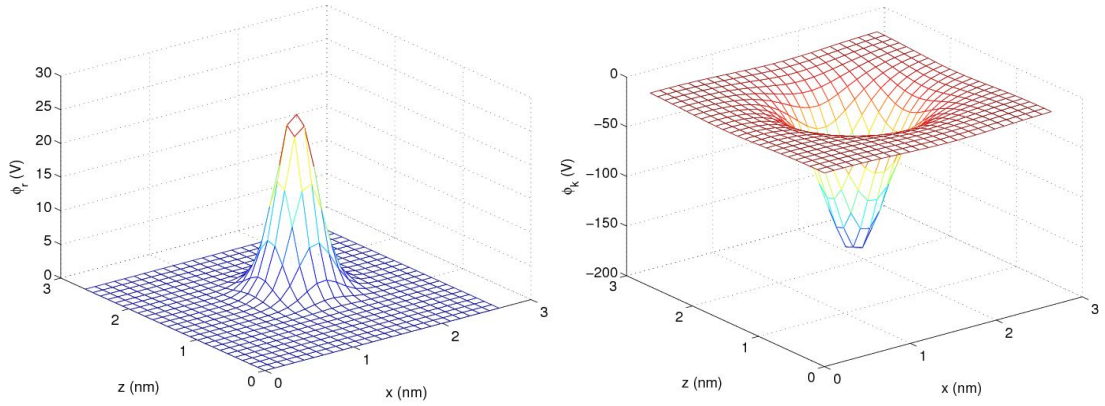

Figure 5: $\mathbf{\Phi_r}$ (the left) and $\mathbf{\Phi_k}$ (the right) on the lower electrode with 0.11nm FFT spacing

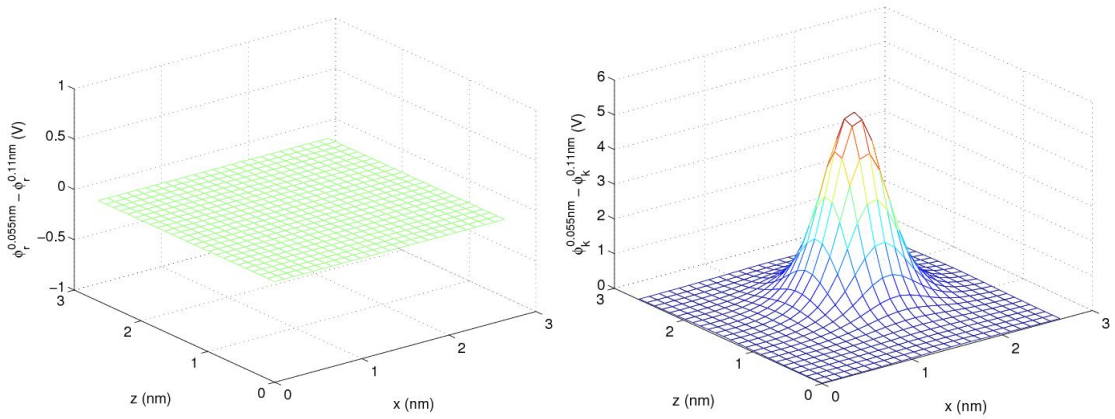

Figure 6: difference of $\mathbf{\Phi_r}$ (the left, ideally ZERO) and $\mathbf{\Phi_k}$ (the right) on the lower electrode when FFT spacing is 0.055nm and 0.11nm.

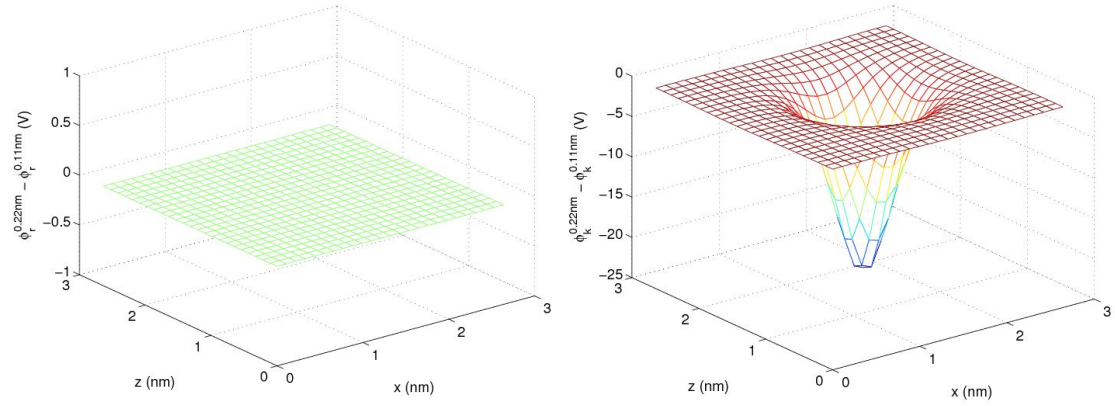

Figure 7: difference of $\mathbf{\Phi_r}$ (the left, ideally ZERO) and $\mathbf{\Phi_k}$ (the right) on the lower electrode when FFT spacing is 0.22nm and 0.11nm.

NOTE: Figure 5~7 $\mathbf{\Phi_r}$ is not right, because no PBC is considered for charge outside the channel. After correction of PME part in the code (adding PBC for charge outside the channel), results are shown below.

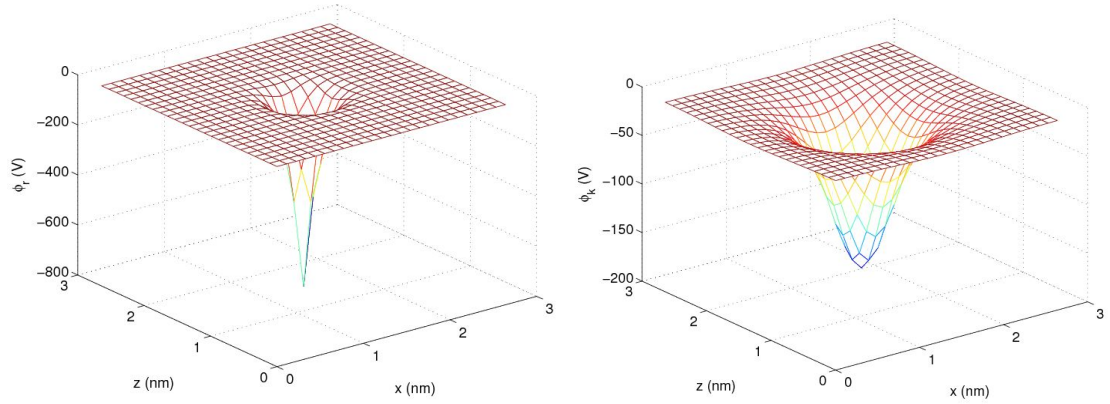

Figure 8: $\mathbf{\Phi_r}$ (the left) and **$\mathbf{\Phi_k}$** (the right) on the lower electrode with 0.11nm FFT spacing

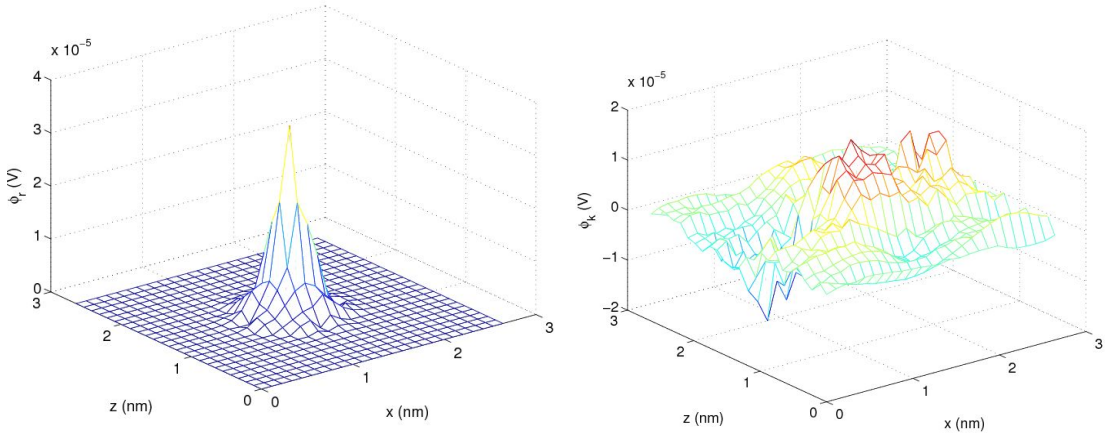

Figure 9: $\mathbf{\Phi_r}$ (the left) and **$\mathbf{\Phi_k}$** (the right) on the lower electrode with 0.11nm FFT spacing Z_j = -0.40nm (symmetric with charge i by the lower electrode)

1) Z_j = 5.39nm has the exactly same results as Z_j = -0.11nm
2) The dependence still exists (shown by the following data), just the distance between i and j becomes smaller (<0.8nm).
3) In Figures 5~8 the right figures also show that **$\mathbf{\Phi_k}$** calculated by FFT in Gromacs changes (~10%) as FFT spacing changes.
4) Figure 9 shows **$\mathbf{\Phi_r}$** (the left) and **$\mathbf{\Phi_k}$** (the right) as charge i and j are symmetric by the lower electrode, which can reveal the magnitude of numerical error Gromacs gives.

xj	yj	zj	zi	Fix	Fiy	Fiz
1.320	**1.320**	**4.400**	**0.550**	**-0.00011**	**-0.00014**	**-135.31509**
1.320	1.320	5.090	0.550	-0.97418	-0.97434	-134.23184
1.320	1.320	5.040	0.550	-0.97697	-0.97738	-134.65819
1.320	1.320	5.170	0.550	-0.96670	-0.96670	-133.18433
1.320	1.320	5.280	0.550	-0.94613	-0.94607	-130.00829

1.320	1.320	5.390	0.550	-0.92783	-0.92799	-119.94485
1.320	1.320	5.450	0.550	-1.21822	-1.21840	-108.71744
1.320	1.320	5.490	0.550	-1.78761	-1.78771	-113.42480

1.320	1.320	4.400	0.220	0.00002	-0.00004	-727.97711
1.320	1.320	4.950	0.220	0.00007	-0.00013	-725.00122
1.320	1.320	5.000	0.220	0.00004	-0.00003	-721.72998
1.430	1.320	5.000	0.220	-1.13495	-0.00001	-722.41742
1.540	1.320	5.000	0.220	-1.68351	-0.00018	-724.07733
1.650	1.320	5.000	0.220	-1.57740	-0.00006	-725.84711
1.760	1.320	5.000	0.220	-1.15000	-0.00004	-727.10065
1.870	1.320	5.000	0.220	-0.72270	-0.00001	-727.74908
1.980	1.320	5.000	0.220	-0.42087	-0.00014	-728.00134
2.090	1.320	5.000	0.220	-0.23889	-0.00005	-728.06982
2.200	1.320	5.000	0.220	-0.13553	-0.00005	-728.07336
2.310	1.320	5.000	0.220	-0.07730	0.00002	-728.06146
2.420	1.320	5.000	0.220	-0.04347	-0.00005	-728.04877

1.320	1.320	5.170	0.220	-0.00002	-0.00005	-669.23364
1.430	1.320	5.170	0.220	-10.96276	-0.00002	-676.53876
1.540	1.320	5.170	0.220	-14.88824	0.00001	-693.90723
1.650	1.320	5.170	0.220	-12.14024	0.00004	-711.06696
1.760	1.320	5.170	0.220	-7.43669	-0.00005	-721.73737
1.870	1.320	5.170	0.220	-3.89014	0.00004	-726.48633
1.980	1.320	5.170	0.220	-1.93225	-0.00004	-728.07166
2.090	1.320	5.170	0.220	-0.98108	-0.00004	-728.43512
2.200	1.320	5.170	0.220	-0.52317	-0.00004	-728.43982
2.310	1.320	5.170	0.220	-0.28995	-0.00005	-728.37445

The above data indicates that rij should be large than 0.79/0.78nm

Description:

1) **In** section 4, the figure 4 shows the comparison of the forces (in z-direction) on a unit charge due to image charge effects from analytic calculation and MD simulation with **putting the points exactly on the FFT grids,** which can give a very good results.

2) In section 5, figure 5~7 represent that $\mathbf{\Phi_r}$ and $\mathbf{\Phi_k}$ were plotted with changing FFT spacing (0.055, 0.11, and 0.22nm) and using the same Green's Function (30×30×31 grids) and same MD simulation box size (2.75×2.75×5.5).

1) and 2) indicate that the overlap of charge and FFT grid would give a good results, which means that our interpolation introduce such difference (even though that difference is acceptable)?

3) force-0.11nmFFT.dat shows the force changes as moving charge i or the counter charge j:

i) PART 1 is for keeping the counter charge j at (1.320 1.320 4.400) and moving charge i from 0.2nm~1.65nm

If charge j is far from charge i, MD results agree with analytic solution.

ii) PART 2 is for keeping the charge i at (1.500 1.500 0.250) and moving charge j

Location of charge j would affect the force on charge i, if their distance is within one cutoff.

iii) PART 3 is for keeping the charge i at (1.500 1.500 0. 660) and moving charge j with different FFT spacing (0.055, 0.11, and 0.22nm)

FFT spacing affects very little the force on charge i.

6. Tested by finer FFT gracing

simulation setup with finer FFT gracing, which is expected to give a more accurate results.

1) Box size (nm):

3.0 3.0 5.0

2) Green's Function (GF) size (nm):

3.0 3.0 2.95 (60×60×60 grids)

3) FFT spacing 0.05nm, rc=1.0nm

4) Electrodes (parallel to xy-plane):

lower one located at z=0;

upper one located at z=2.95nm;

5) A Na^+ was put between two electrodes, and moved from 0.2~1.475nm along Z-direction

The position of compensated counter charge Cl- is fixed in the region z = (2.95, 5.0) randomly.

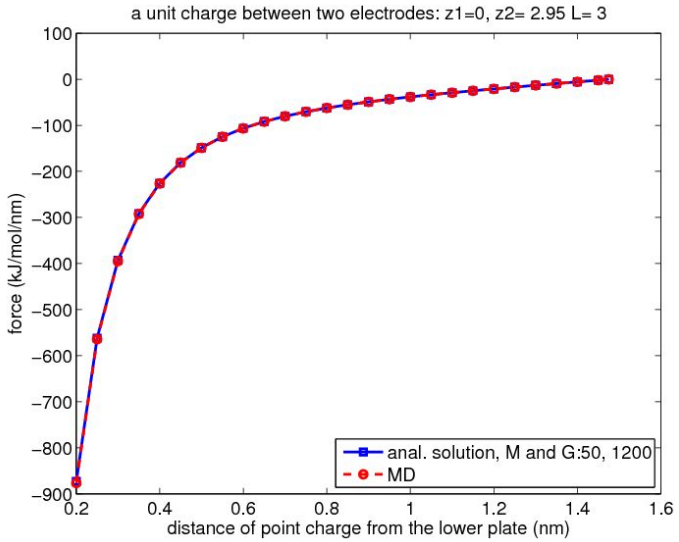

Figure 4. comparison of the force acting on charge *I* from MD and from analytical solution.

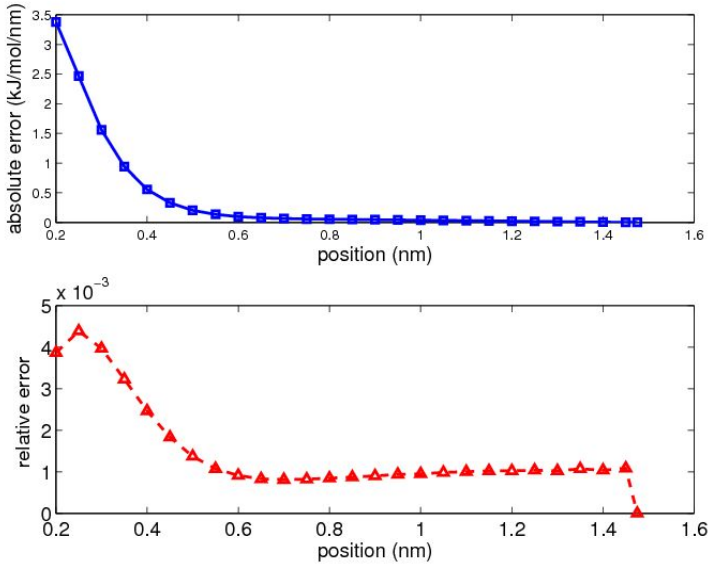

Figure 5. absolute and relative error of the force acting on the positive charge inside the electrode channel

As figures 4 and 5 are obtained by fix the counter charge at (1.500 1.500 4.000), which show the MD results are perfectly consistent with analytic solutions!

Double-check of the independence of the position of the compensating charge

1) The unit charge inside channel was fixed at (1.500 1.500 0.250), and the counter charge was moving outside the channel. The results are listed force-0.05nmFFT.dat (PART 2).
2) The data indicate that, dislike 0.10nm FFT spacing, for 0.05nm FFT spacing, the force is sensitive to the location of the counter charge when such counter charge in within the cutoff of the unit charge inside channel.

7. Conclusions:

The algorithm is tested in a two-charge system (one positive charge enclosed by two electrodes and one negative compensating charge outside the electrode). The results show that

Where should be the counter charge j

- Since Φ_r decays exponentially with distance, one must capture such variation with fine grid. Hence, when the counter charge j is close to the electrode, its contribution to Φ_r on the electrode is large and this can cause large errors.
- Under test of channel simulation, the counter charge j should be $r_{cutoff}/2$ away from the electrode, so that the error is acceptable (error <2%). The data in Page 6/7 reveal that the distance between charge i and counter charge j should be larger than 0.8nm, which can give a neglected error.
- Still suggest that better put the counter charge at the symmetric location outside the channel.

Comparison of force on charge i from MD simulations and analytic calculations

- The force acting on the charge inside the electrode computed from MD simulation agrees with analytical solution within about 1kJ/mol/nm at position 0.4nm from the electrode. At even closer distance, the absolute error becomes large, but the relative error is small, e.g., less than 2%. Since at position away from the electrode, the force should be accurate within ~1kJ/mol/nm (accuracy of typical MD force), and at position close, the relative error is small, the error is acceptable even with the present implementation.
- If the charge i is on the FFT grids, this method would give a very good results (within 1%)
- The accuracy of **both** Φ_r and Φ_k depends on FFT spacing
- Finer FFT grids would bring a better results, especially, for charge i is not on FFT grids

Unresolved issue

- Why Φ_k obviously depends on FFT spacing (Figure 9 the magnitude of numerical error Gromacs gives is quite smanll: ~10^{-5})

- The data in Page 6/7 reveal that the distance between charge i and counter charge j should be larger than 0.8nm, which can give a neglected error. Looks like such distance also accounts for the location of counter charge j.

Based on the above observation, we conclude that the method works at least for the simple geometry investigated here.