User Specified non-bonded potentials in gromacs

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1   Introduction

On first appearances gromacs, unlike MD codes like LAMMPS or DL_POLY, appears to have very little flexibility with regards to the form of the inter-molecular interactions as one must either choose a Lennard Jones 12-6 potential or a Buckingham interaction in the [defaults] section of the topology file, which will subsequently be used throughout. There is, or so it would seem, no option to define a "wacky" non-bonded interaction or to have certain pairs of atom interacting through a buckingham term, while the remaining atoms interact through Lennard-Jones. Thankfully however both these options exist although the documentation on how precisely this should be done is split up in the manual. In the following therefore we will bring all this information together into a single document.

Firstly though a word of caution. Obviously Buckingham and Lennard Jones interactions are very standard descriptions for the non-bonded terms in atoms. Hence, unless you have a specific reason to believe that your special functional form is required it is often best to stay with these tried and trusted functions. In addition, although a mixture of Buckingham and Lennard-Jones terms provides a perfectly reasonable description of the essential physics, you enter a world where there are no longer any convenient mixing rules for the inter atomic forces. As a direct consequence there are going to be many more terms that must be fitted in the potential. In short don't do the following unless you are confident that you have a sensible potential and a reasonable way for obtaining the cross terms.

These caveats aside a few words on non-bonded potentials so as to define some terms. The inter molecular interactions between atoms can be split into three parts the electrostatic interaction, the dispersion interaction and the short range repulsion. With this in mind we can write the two body potential as:

$$V(r) = \frac{q_i q_j}{4\pi\epsilon_0} f(r) + Cg(r) + Ah(r) \tag{1}$$

where the first second and third terms are from the electrostatics, the dispersion and the short range repulsion respectively. The $f(r)$, $g(r)$ and $h(r)$ are then user defined functions, while A, C and the charges are the parameters of these functions. For the Lennard-Jones interaction these functions are:

$$f(r) = \frac{1}{r} \qquad g(r) = -\frac{1}{r^6} \qquad g(r) = \frac{1}{r^{12}} \tag{2}$$

while for Buckingham $f(r)$ and $g(r)$ are the same but $h(r) = Ae^{-Br}$, where B is an additional parameter. Gromacs, unless explicitly told otherwise (see section 3), will use the same $f(r)$, $g(r)$ and $h(r)$ for all the inter atomic interactions in the system. One then specifies the parameters (A, C and B) in the topology file and by changing these parameters you can reflect the differences in the interactions between different atomic types. The form of the interaction is specified in the [defaults] section of the topoology file as follows:

```
[ defaults ]
; nbfunc    comb-rule    gen-pairs    fudgeLJ    fudgeQQ
1               1            yes         0.5        0.8333
```

Here only the first two parameters in this line need concern us. By specifying 1 for the first we tell gromacs that we are using Lennard-Jones interactions rather than Buckingham terms (2=Buckingham). As a consequence gromacs assumes that two parameters are required for each of the non-bonded interactions (A and C in equation 1)[1]. The second term tells gromacs what mixing rules should be used and by extension how the parameters in the file should be interpreted. A 1 indicates that gromacs will interpret the parameters in

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[1] Obviously if we replace the 1 here by a 2 gromacs will expect us to provide A, B and C

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the topology file as C and A directly. 2 and 3 mean that we are providing the parameters for our Lennard Jones interactions in epsilon-sigma form:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \tag{3}$$

We thus providing the ϵ and σ in the topology file from which gromacs will calculate A and C using:

$$A = 4\epsilon\sigma^{12} \qquad\qquad C = 4\epsilon\sigma^6 \tag{4}$$

If you specify your own potentials these parameters must be both set equal to 1.

2 Changing the form of the global interaction

We now describe how to use tables to change the functions $f(r)$, $g(r)$ and $h(r)$ that gromacs uses to calculate inter-atomic interactions. First we will examine how to change the global $f(r)$, $g(r)$ and $h(r)$ and show an example in which all the atoms interact through a 9-6 interaction for which $f(r)$, $g(r)$ and $h(r)$ are equal to:

$$f(r) = \frac{1}{r} \qquad\qquad g(r) = -\frac{1}{r^6} \qquad\qquad g(r) = \frac{1}{r^9} \tag{5}$$

The mdp file in this file we must tell gromacs that it must read in a table to get $f(r)$, $g(r)$ and $h(r)$. This is a matter of simply including the following commands:

```
vdw-type = user
coulombtype = user
```

What is more the second of these is only required if we wish to change $f(r)$. In the example we are discussing we don't so we only need the first command [2]

The xvg/table file having told gromacs that it must read in a table containing $f(r)$, $g(r)$ and $h(r)$ we must now provide the table. This file

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[2]We must still specify one of the other options for coulombtype - these other options are beyond the scope of this document however.

must contain the values of $f(r)$, $g(r)$, $h(r)$ and their derivatives at a series of values of r. Gromacs will then use the cubic splines procedure described in section 6.7 of the manual to calculate the values of the functions for any value of r that occurs during the simulation. This file must be generated by the user. Each line consists of the values of the various functions for a particular r and consists of seven columns containing r, $f(r)$, $-f'(r)$, $g(r)$, $-g'(r)$, $h(r)$ and $-h'(r)$ [3]. Your table must contain must go from $r = 0$ to $r = r_c + 1$, where r_c is the largest cutoff distance specified in the mdp file. In addition, it is recommended that the spacing between the adjacent rs in your table should equal 0.002 nm or 0.0005 nm for the single and double precision versions of gromacs respectively. Some example tables can be found in share/gromacs/top.

For our 9-6 interaction example our table could be generated using the following short fortran code:

```
program gen_table
implicit none
real, parameter :: delr=0.002, rcut=1.0
real :: r
integer :: nbins, j

nbins=int( (rcut+1)/delr ) + 1

do j=0,nbins
    r=delr*j
    write(6,*) r, 1/r, 1/(r*r), −1/(r**6), −6/(r**7), 1/(r**9), 9/(r**10)
end do

end program
```

Care must be taken for $r = 0$ as the code above would obviously produce infinity or not a number for this case. To resolve this include an if condition that outputs a value of zero for $f(r)$, $-f'(r)$, $g(r)$, $-g'(r)$, $h(r)$ and $-h'(r)$ for very small r. This will have no effect on the dynamics as no atoms will ever be this close. Finally, note that we have provided meaningful data for $f(r)$ and $-f'(r)$ despite the fact that we are not using coulombtype=user. This is required as gromacs will complain otherwise.

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[3] According to the manual the spline procedure is different in gromacs 3 and so your table must contain r, $f(r)$, $f''(r)$, $g(r)$, $g''(r)$, $h(r)$ and $h''(r)$

The topology file the only remaining job required is to provide the A and C parameters for your potential. These must must be placed in the topology file. First, however ensure that you have set both nbfunc and comb-rule equal to one as described in the introduction. The parameters for interactions between atoms of the same type are then set in the [atomtypes] section, which comes immediately after the defaults section:

```
[ atomtypes ]
 ; name    bond_type    mass    charge    ptype      C         A
  Na          Na        22.99      1        A      1.0e-03   1.0e-06
  Cl          Cl        35.453    -1        A      2.0e-03   9.0e-06
```

As for the cross terms, unless you have specific reason to believe that gromacs will mix the terms correctly using mixing rule 1, you must provide these explicitly in the [nonbond_params] section immediately after the [atomtypes] section as follows:

```
[ nonbond_params ]
 ; i     j     func          C                  A
  Na    Cl     1      2.22213706E-03    3.43076954E-06
```

Please note that the parameters given above are complete guff and should not be used in any simulation of sodium chloride.

Running a calculation To run the above you then generate the binary input file using grompp in the normal way and then run mdrun with the -table flag as below:

```
grompp -f md.mdp - p topol.top -c conf.gro
mdrun -table table.xvg
```

When executed gromacs will look in the active directory and in share/gromacs/top for the xvg file specified after the table flag.

N.B. If there are 1-4 pair interactions in your molecule you must also separately specify which table is to be used to calculate them by using the -tablep extension. The fudgeLJ factor specified in the [defaults] section of your topology file is still taken into account in the calculation of these terms. As such unless the form of the $f(r)$, $g(r)$ and $h(r)$ functions is different for the pair interactions you may run using the following:

```
grompp -f md.mdp - p topol.top -c conf.gro
mdrun -table table.xvg -tablep table.xvg
```

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3 Specifying the form for a particular interaction

In the previous section we have seen how to change globally the $f(r)$, $g(r)$ and $h(r)$ functions. However, what if one simply wants to have a particular pair of atom types interacting with different $f(r)$, $g(r)$ and $h(r)$ functions. For example imagine we have sodium chloride in which the Na Na and Cl Cl interactions are given by buckingham terms while the Na Cl interaction has a Lennard Jones form. Gromacs is able to use tables to resolve this problem as well.

The mdp file Much like in the previous section we must first tell gromacs that it will be using a user-defined, tabulated potential using the following flags:

```
vdw-type = user
coulombtype = user
```

In addition though we are also required to define which $f(r)$, $g(r)$ and $h(r)$ functions are to be used for the various interactions. This is done using the following lines:

```
energygrps = Na Cl
energygrp_table = Na Na Cl Cl
```

The first of these tells gromacs that it must deal with the energies of all the atoms in the energy groups Na and Cl separately - we will return to this momentarily. The second line meanwhile tells gromacs that it must read in specific table files in order to get the $f(r)$, $g(r)$ and $h(r)$ functions for the Na Na and Cl Cl interactions. The remaining interactions (the Na Cl in this case) should be then be calculated using the default table file. If this default table file is called table.xvg then the table containing the Na Na interactions will be called table_Na_Na.xvg while the table containing the Cl Cl interactions will be called table_Cl_Cl.xvg.

The table files For our sodium chloride example gromacs now expects to find three table files when it is run; namely, table.xvg, table_Na_Na.xvg and table_Cl_Cl.xvg. These table files are set up in the exactly same manner described in section 2. It is important to note however that when a combination of Lennard Jones and Buckingham terms is required tabulated potentials

must be used for all the non-bonded interactions even for the Lennard Jones. In our sodium chloride example the following three tables are required:

$$
\begin{array}{llccll}
& & f(r) & g(r) & h(r) & \\
\text{table.xvg} & & \frac{1}{r} & -\frac{1}{r^6} & \frac{1}{r^{12}} & \text{For Na Cl} \\
\text{table\_Na\_Na.xvg} & & \frac{1}{r} & -\frac{1}{r^6} & e^{-B_{\text{NaNa}}r} & \text{For Na Na} \\
\text{table\_Cl\_Cl.xvg} & & \frac{1}{r} & -\frac{1}{r^6} & e^{-B_{\text{ClCl}}r} & \text{For Cl Cl}
\end{array}
$$

In addition, because, when tables are used gromacs always assumes the non-bonded interaction to be given by equation 1, separate tables are required for each of the buckingham terms as it is only in the table file that the different values for the B parameters are taken into account.

The index/ndx file The final job, prior to running gromacs, is to define the Na and Cl energy groups. These groups are defined in index file. For the following .gro file:

```
Some sodium chloride
8
    1SOD    Na    1    1.307    1.161    0.506
    2SOD    Na    2    1.374    1.105    0.468
    3SOD    Na    3    1.237    1.101    0.533
    4SOD    Na    4    1.306    1.149    0.505
    5CHL    Cl    5    0.095    1.090    0.514
    6CHL    Cl    6    0.004    1.106    0.490
    7CHL    Cl    7    0.100    1.116    0.606
    8CHL    Cl    8    0.086    1.095    0.521
```

The index file should read:

```
[ Na ]
1    2    3    4
[ Cl ]
5    6    7    8
```

as the first four atoms in the configuration are sodium while the remainder are chlorine.

Running The topology file is set up in the manner described in the previous section and the calculation is run by executing:

```
grompp -f md.mdp - p topol.top -c conf.gro -n index.ndx
mdrun -table table.xvg
```

with all the table files in the directory where mdrun is running.

4   Dealing with molecules

The previous sections have shown how powerful gromacs can be in handling inter atomic forces. If your system is molecular all of the above can be used as typically intermolecular interactions are calculated as a sum of interactions between the various atoms that make up the molecules. There is however one important caveat regarding how the molecules must be defined in the topology file, which we will illustrate through the following example.

Consider the the following extract from a topology file which defines a TIP3P water molecule:

```
[ atoms ]
;    at type   res nr   res name   at name   cg nr   charge      mass
1      OW        1         SOL        OW        1      -0.834    16.00000
2      HW        1         SOL        HW2       1       0.417     1.00800
3      HW        1         SOL        HW3       1       0.417     1.00800
```

Now imagine we set up our calculation so that the OW OW $f(r)$, $g(r)$ and $h(r)$ are different from the OW HW and HW HW $f(r)$, $g(r)$ and $h(r)$. To do this we would put the following in the mdp file:

```
vdw-type = user
energygrps = OW
energygrp_table = OW OW
```

and would set up the tables and index file in the manner described in the previous section. This setup would give a error when run through grommpp however. The reason for this is related to the way that gromacs deals with the calculation of neighbor lists and cutoffs. This is done through so called charge groups and the essential problem is that an energy groups must contain all contain either all or none of the atoms in any given change group. However, the charge groups are defined in the topology file in the column headed cg nr so by simply changing our molecule definition to:

```
[ atoms ]
;    at type   res nr   res name   at name   cg nr   charge      mass
1      OW        1         SOL        OW        1      -0.834    16.00000
2      HW        1         SOL        HW2       2       0.417     1.00800
3      HW        1         SOL        HW3       2       0.417     1.00800
```

we can bypass this problem and do the calculation in the manner required. Care must be taken when this procedure is carried out especially when one is using a cutoff or on the electrostatic interactions for the reasons described in section 3.4.2 of the manual. However, this should not be a problem if you are using pme or ewald electrostatics.

There is an additional problem if you are using constraints as you can now no longer use settles to constrain the water molecule and must define the constraints and use LINCS instead. In addition splitting the charge groups in this way means you can only use shake to enforce the constraints if you run without domain decomposition.