ELECTRONIC SUPPLEMENTARY INORMATION FOR 'SCREENING OF HIGHLY CHARGED IONS IN AN IONIC LIQUID; WHEN WILL ION PAIRS FORM?' BY R.M.LYNDEN-BELL

1. Calculation of uncerainties in the Free Energy curve.

The free energy curve is calculation from the observed curve of the force by equation (1) in the paper.:

$$A(z) - A(z') = -\int_{z'}^{z} (\Delta F(z)/2) dz. \tag{1}$$

The mean force, $\Delta F(z)$, is found for simulations at at a number of fixed values of z . The integration is carried out using the Trapezium rule

$$A(z_n) - A(z_0) = -\sum_{1}^{n} (\Delta F_i - \Delta F_{i-1})(z_i - z_{i-1})/4 \tag{2}$$

where one factor of one half comes from the rule and another factor from the definition of A.

To obtain the uncertainty one needs the variance of this quantity, knowing the variance σ_i^2 in the measurement of each average force ΔF_i. If we assume that the variances of the forces at different separations are uncorrelated (a good assumption in my opinion) and that the forces have normal distributions (a less good assumption that we shall discuss further) then the variance of the sum of forces from z=0 to z=n is

$$S_n^2 = \sigma_0^2 \delta_{01}^2/4 + \sum_{i=1}^{n-1} \sigma_i^2 (\delta_{i-1,i+1}/2)^2 + \sigma_n^2 \delta_{n-1,n}^2/4 \tag{3}$$

where $\delta_{IJ} = z_i - z_j$.

The standard error of each point in the free energy curve is then the square root of the variance of that point.

The variance of the forces were estimated from the results of several nanosecond runs.

The difficulty with this method is that the total run length at each may not be enough to estimate the variance accurately. In section 3.4 of the paper we have shown that for separations around 4Å the system has two solvation states with different numbers of anions. In these cases the variance is estimated from the differences between states.

2. Force Field parameters

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FIELD file in DL\_Poly format

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[dmim]Cl  with CD solute
UNITS kJ

molecules 3
Imidazolium
nummols 192
atoms 16
N          14.0          -0.267        2          0          1
C1         12.0           0.407        1          0          1
C2         12.0           0.105        2          0          1
C4         12.0           0.124        2          0          1
H1          1.0           0.097        1          0          1
H2          1.0           0.094        2          0          1
H4          1.0           0.064        6          0          1
constraints 6
    6   11     1.085
    6   12     1.085
    6   13     1.085
    7   14     1.085
    7   15     1.085
    7   16     1.085
angles 12
harm    2    7   14    293.00000 109.470000000
harm    2    7   15    293.00000 109.470000000
harm    2    7   16    293.00000 109.470000000
harm   14    7   15    293.00000 109.470000000
harm   14    7   16    293.00000 109.470000000
harm   15    7   16    293.00000 109.470000000
harm    1    6   11    293.00000 109.470000000
harm    1    6   12    293.00000 109.470000000
harm    1    6   13    293.00000 109.470000000
harm   11    6   12    293.00000 109.470000000
harm   11    6   13    293.00000 109.470000000
harm   12    6   13    293.00000 109.470000000
rigid 1
   10    1    2    3    4    5    6    7   8    9   10
finish
chloride
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nummols 192
atoms 1
Cl        37.0         -1.0         1         0         1
finish
CD
nummols 1
atoms 2
C         2000.0          2.0         0
D         2000.0         -2.0         0
finish
vdw  52
     C1       C1 buck   369737.     0.277778   2439.8
     C1       C2 buck   369737.     0.277778   2439.8
     C1       C4 buck   369737.     0.277778   2439.8
     C1       N  buck   369743.     0.271003   1833.2
     C1       H1 buck   66529.0     0.272480   576.9
     C1       H2 buck   66529.0     0.272480   576.9
     C1       H4 buck   66529.0     0.272480   576.9
     C2       C2 buck   369743.     0.277778   2439.8
     C2       C4 buck   369743.     0.277778   2439.8
     C2       N  buck   369743.     0.271003   1833.2
     C2       H1 buck   66529.0     0.272480   576.9
     C2       H2 buck   66529.0     0.272480   576.9
     C2       H4 buck   66529.0     0.272480   576.9
     C4       C4 buck   369743.     0.277778   2439.8
     C4       N  buck   369743.     0.271003   1833.2
     C4       H1 buck   66529.0     0.272480   576.9
     C4       H2 buck   66529.0     0.272480   576.9
     C4       H4 buck   66529.0     0.272480   576.9
     N        N  buck   254525.     0.264550   1378.4
     N        H1 buck   55198.0     0.265957   433.6
     N        H2 buck   55198.0     0.265957   433.6
     N        H4 buck   55198.0     0.265957   433.6
     H1       H1 buck   11971.0     0.267380   136.4
     H1       H2 buck   11971.0     0.267380   136.4
     H1       H4 buck   11971.0     0.267380   136.4
     H2       H2 buck   11971.0     0.267380   136.4
     H2       H4 buck   11971.0     0.267380   136.4
     H4       H4 buck   11971.0     0.267380   136.4
     Cl       Cl buck   924640.     0.284900   7740.2
     Cl       C1 buck   584700.     0.281294   4345.6
     Cl       C2 buck   584700.     0.281294   4345.6
     Cl       C4 buck   584700.     0.281294   4345.6
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     Cl      N  buck   485123.     0.274348   3266.3
     Cl      H1 buck   105208.     0.275862   1027.4
     Cl      H2 buck   105208.     0.275862   1027.4
     Cl      H4 buck   105208.     0.275862   1027.4
     C       Cl  lj   1.009        3.49
     C       C1  lj   0.664        3.56
     C       C2  lj   0.664        3.56
     C       C4  lj   0.7488       3.565
     C       N   lj   0.9335       3.49
     C       H1  lj   0.2773       3.07
     C       H2  lj   0.2773       3.07
     C       H4  lj   0.2837       3.12
     D       Cl  lj   1.009        3.49
     D       C1  lj   0.664        3.56
     D       C2  lj   0.664        3.56
     D       C4  lj   0.7488       3.565
     D       N   lj   0.9335       3.49
     D       H1  lj   0.2773       3.07
     D       H2  lj   0.2773       3.07
     D       H4  lj   0.2837       3.07
close

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