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*        Supplemental Parameters for CGenFF SAM Surface Residues
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! ************************************************************************
! Listed below are parameters not appearing in the CGenFF 2a5 parameter set that
! are needed to simulate the SAM residues POXY, TFCO, and PEGH found in the file
! top_sams_cgenff.inp.  These parameters come from three sources (labeled
! CGenFF, NHLBI, and CLEMSON) which will be described below.
!
! The CGenFF parameter set used in this study was the CGenFF version 2a data set
! which was obtained through private communication with Alex MacKerell in late
! January of 2009.  When version 2a5 was made available we cross-checked the 2a
! parameters for the SAM residues and found only one difference (in POXY).
!
! POXY Parameterization:
! ----------------------
! The phenoxy functionalized SAM residue (POXY) introduced an oxygen atom type
! "OG301P" just for the purpose of using the CGenFF v2a ethoxybenzene ether
! oxygen bond stretching parameter CG321 OG301.  In CGenFF v2a this parameter
! was commented out and was totally absent in v2a5--replaced by diethylether
! oxygen derived parameters.  The remaining bond angle, torsion, and Lennard
! Jones parameters for OG301P are identical to the CGenFF v2a and v2a5 values
! for OG301 and are given the parameter origin label "CGenFF" below (along with
! the CGenFF atom type coupling that the parameters were taken from).
!
! PEGH Parameterization:
! ----------------------
! When trying to build the oligo ethylene glycol functionalized SAM residue
! (PEGH), the CGenFF v2a and v2a5 force fields contained a PEGM monomer but not
! a glycol cap.  Thus, our OEG parameters for the O-C-C-O torsion and glycol end
! patch were obtained from the June 2007 version of the CHARMM32 ether force
! field in par_all35_ethers-nhlbi.prm.  These parameters were provided via email
! correspondence with R.M. Venable as supplemental material to:
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!   Hwankyu Lee, Richard M Venable, Alexander D MacKerell Jr., Richard W Pastor
!   Molecular dynamics studies of polyethylene oxide and polyethylene glycol:
!   Hydrodynamic radius and shape anisotropy
!   Biophysical Journal 95(4):1590-1599 (2008).
! Lee, et al., derived the glycol end patch from the hexapyranose files in:
!   Olgun Guvench, Shannon N. Greene, Ganesh Kamath, John W. Brady, Richard M.
!   Venable, Richard W. Pastor, Alexander D. Mackerell Jr.
!   Additive empirical force field for hexopyranose monosaccharides
!   J Comput Chem 29(15):2543-64 (2008).
! which included ethylene glycol as a model compound.
! Reference for CHARMM32 ether force field:
!   Vorobyov, I., Anisimov, V.M., Greene, S., Venable, R.M., Moser, A.,
!   Pastor, R.W., and MacKerell, A.D., Jr.
!   Additive and Classical Drude Polarizable Force Fields for Linear and
!   Cyclic Ethers
!   J Chem Theory Comput 3(3):1120-1133 (2007).
! The CGenFF atom type OG311 did not match the atom type corresponding to the
! PEG hydroxyl oxygen OC311 in this publication and so we added it to our CGenFF
! atom type list with the name "OPEG."  All parameters taken from
! par_all35_ethers-nhlbi.prm are given the parameter origin label "NHLBI" below.
! If the parameters were identical to those in CGenFF, their parameter origin
! label is "CGenFF."
!
! TFCO Parameterization:
! ----------------------
! Most of the CGenFF force field parameters for the -O-CH2-CF3 trifluoroethoxy
! group came from trifluoroethanol, which is chemically different from the
! -CH2-O-CH2-CF3 endcap in TFCO.  After scanning the literature, we chose to make
! parameter fits to MP2 calculations on n-butyl trifluoroethyl ether.  When the
! MP2 energy profile of a bond/dihedral angle for trifluoroethanol matched (or
! was a close fit with) the MP2 energy profile of n-butyl trifluoroethyl ether,
! the trifluoroethanol CGenFF parameters were used for TFCO (these are labeled
! "CLEMSON validated by MP2").  If the n-butyl trifluoroethyl ether MP2 energy
! profile was significantly different from trifluoroethanol (or if CGenFF lacked
! a particular torsion angle like CG302 CG321 OG301 CG321), our fitted
! parameters were used (these are labeled "CLEMSON MP2 fit").
!
! Dihedral parameters introduced by our group to the CGenFF data set were fit
! according to the procedure outlined in:
!   O. Guvench and A. D. MacKerell Jr.
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!   Automated conformational energy fitting for force-field development
!   J Mol Model 14:667-679 (2008).
! using the Python script fit_dihedral.py, which is available for download at
! http://mackerell.umaryland.edu.  QM energies used in the fitting were computed
! at the MP2/6-31G(d) level for the SAM residues using Spartan'08 for Mac.  The
! MP2 data were from relaxed potential energy scans of the dihedral surfaces in
! question as depicted in the above referenced paper.  In these adiabatic scans,
! the dihedral angle investigated was locked to a specific value by the dihedral
! constraint function in Spartan and allowed to relax to its preferred
! MP2/6-31G(d) geometry under that constraint.
! ******************************************************************************

BONDS
!! ******************************************************************************
!! V(bond) = Kb*(b - b0)**2                                    *
!!                                                 *
!!  Kb: kcal/mol/A**2                                    *
!!  b0: A                                          *
!! ********************************************************************************  **********  ****************
!! I     J     Kb      b0    ! DESCRIPTION                          SAMS USING  PARAMETER ORIGIN
!! ********************************************************************************  **********  ****************
  CG321  OG301P 428.00  1.4200 ! ETOB, Ethoxybenzene, chayan              POXY       CGenFF2a: CG321 OG301
  CG2R61 OG301P 230.00  1.3820 ! COMPDS PEDRO                             POXY       CGenFF: CG321 OG301
  CG321  OPEG   428.00  1.4200 ! methanol vib fit EMB 11/21/89           PEGH       CGenFF: CG321 OG311
  OPEG   HGP1   545.00  0.9600 ! 11/89 methanol vib fit; og tested on MeOH EtOH  PEGH       CGenFF: OG311 HGP1

ANGLES
!! ******************************************************************************
!! V(angle) = Ktheta*(Theta-Theta0)**2                          *
!!                                                 *
!!  Ktheta: kcal/mol/rad**2                              *
!!  Theta0: degrees                                   *
!!  No Urey-Bradley parameters were required for these bond angles.          *
!! ********************************************************************************  **********  ****************
!! I     J     K     Ktheta  Theta0   ! DESCRIPTION                  SAMS USING  PARAMETER ORIGIN
!! ********************************************************************************  **********  ****************
  CG321  CG321  OG301P  45.00  111.50   ! diethylether, alex              POXY       CGenFF: CG321 CG321 OG301
  OG301P CG321  HGA2    45.90  108.89   ! ETOB, Ethoxybenzene, chayan       POXY       CGenFF: OG301 CG321 HGA2
  CG2R61 OG301P CG321   65.00  108.00   ! ETOB, Ethoxybenzene, chayan       POXY       CGenFF: CG2R61 OG301 CG321
  CG2R61 CG2R61 OG301P 110.00  120.00   ! BIPHENYL ANALOGS                  POXY       CGenFF: CG2R61 CG2R61 OG301
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OG301  CG321  HGA2    60.00  109.50   ! phosphate, alex                  TFCO, PEGH  NHLBI : HCA2 CC32A OC30A
CG302  CG321  OG301   75.00  110.10   ! TFE, trifluoroethanol              TFCO       CGenFF: CG302 CG321 OG311
                          !                                        CLEMSON validated by MP2/6-31G(d)
OPEG   CG321  CG321   75.70  110.10   ! MeOH, EMB, 10/10/89                PEGH       CGENFF: CG321 CG321 OG311
HGA2   CG321  OPEG    55.00  108.89   ! EtOH RMV Aug07                     PEGH       CGENFF: OG311 CG321 HGA2
CG321  OPEG   HGP1    50.00  106.00   ! OG sugar COH, RMV Aug07             PEGH       CGENFF: CG321 OG311 HGP1

DIHEDRALS
!! ***************************************************************************
!! V(dihedral) = Kchi*(1 + cos(n*chi - delta))                    *
!!                                                 *
!!   Kchi: kcal/mol                                  *
!!     n: multiplicity                              *
!!  delta: degrees                                  *
!! ***************************************************************************  **********  *****************
!! I     J     K     L     Kchi    n  delta ! DESCRIPTION                SAMS USING  PARAMETER ORIGIN
!! ***************************************************************************  **********  *****************
CG321  CG321  CG321  OG301P 0.1600  1 180.00 ! methylpropylether, 2/12/05,ATM  POXY       CGenFF: CG321 CG321 CG321 OG301
CG321  CG321  CG321  OG301P 0.3900  2   0.00 ! methylpropylether              POXY       CGenFF: CG321 CG321 CG321 OG301
OG301P CG321  CG321  HGA2   0.1900  3   0.00 ! alkane, 4/98, yin & mackerell   POXY       CGenFF: OG301 CG321 CG321 OG301
CG321  CG321  OG301P CG2R61 2.4000  1 180.00 ! PNTM, Pentamidine/ETOB, ...     POXY       CGenFF: CG321 CG321 OG301 CG2R61
CG321  CG321  OG301P CG2R61 1.0000  2 180.00 !  ...Ethoxybenzene, chayan, sz   POXY       CGenFF: CG321 CG321 OG301 CG2R61
HGA2   CG321  OG301P CG2R61 0.0950  3   0.00 ! ETOB, Ethoxybenzene, chayan     POXY       CGenFF: HGA2 CG321 OG301 CG2R61
CG2R61 CG2R61 OG301P CG321  1.6200  2 180.00 ! ETOB, Ethoxybenzene, chayan     POXY       CGenFF: CG2R61 CG2R61 OG301 CG321
CG2R61 CG2R61 OG301P CG321  0.1900  4 180.00 ! ETOB, Ethoxybenzene, chayan     POXY       CGenFF: CG2R61 CG2R61 OG301 CG321
CG2R61 CG2R61 CG2R61 OG301P 3.1000  2 180.00 ! BIPHENYL ANALOGS                POXY       CGenFF: CG2R61 CG2R61 CG2R61 OG301
OG301P CG2R61 CG2R61 HGR61  2.4000  2 180.00 ! BIPHENYL ANALOGS Kenno:4.2->2.4 POXY       CGenFF: OG301 CG2R61 CG2R61 HGR61
CG302  CG321  OG301  CG321  0.68    1 180.00 ! n-butyl trifluoroethyl ether    TFCO       CLEMSON MP2/6-31G(d) fit
CG302  CG321  OG301  CG321  0.45    2   0.00 ! n-butyl trifluoroethyl ether    TFCO       CLEMSON MP2/6-31G(d) fit
CG302  CG321  OG301  CG321  0.30    3   0.00 ! n-butyl trifluoroethyl ether    TFCO       CLEMSON MP2/6-31G(d) fit
OG301  CG321  CG302  FGA3   0.2500  3   0.00 ! TFE, Trifluoroethanol           TFCO       CGenFF: FGA3 CG302 CG321 OG311
                          !                                        CLEMSON validated by MP2/6-31G(d)
FGA3   CG302  CG321  HGA2   0.1580  3   0.00 ! TFE, Trifluoroethanol           TFCO       CGenFF: FGA3 CG302 CG321 HGA2
                          !                                        CLEMSON validated by MP2/6-31G(d)
OG301  CG321  CG321  OG301  0.5900  1 180.00 ! 1,2 dimethoxyethane, 06/07      PEGH       NHLBI : OC30A CC32A CC32A OC30A
OG301  CG321  CG321  OG301  1.1600  2   0.00 ! 1,2 dimethoxyethane, HKL       PEGH       NHLBI : OC30A CC32A CC32A OC30A
OPEG   CG321  CG321  OG301  2.6500  1 180.00 ! glycol RMV Aug07               PEGH       NHLBI : OC311 CC32A CC32A OC30A
OPEG   CG321  CG321  OG301  0.0000  2   0.00 ! glycol RMV Aug07               PEGH       NHLBI : OC311 CC32A CC32A OC30A
OPEG   CG321  CG321  OG301  0.1300  3 180.00 ! glycol RMV Aug07               PEGH       NHLBI : OC311 CC32A CC32A OC30A
HGP1   OPEG   CG321  CG321  0.4000  1 180.00 ! og ethylene glycol             PEGH       NHLBI : HCP1 OC311 CC32A CC32A
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HGP1   OPEG   CG321  CG321  0.0100  2   0.00 ! "  *** NOT suitable for        PEGH       NHLBI : HCP1 OC311 CC32A CC32A
HGP1   OPEG   CG321  CG321  0.2600  3   0.00 ! "  *** HO-C-C-C- type alcohols  PEGH       NHLBI : HCP1 OC311 CC32A CC32A
HGA2   CG321  CG321  OPEG   0.1400  3   0.00 ! glycol RMV Aug07              PEGH       NHLBI : HCA2 CC32A CC32A OC311
HGP1   OPEG   CG321  HGA2   0.1800  3   0.00 ! og methanol                   PEGH       NHLBI : HCP1 OC311 CC32A HCA2

NONBONDED
!! ***************************************************************************
!! V(Lennard-Jones) = Eps_i,j[(Rmin_i,j/r_i,j)**12 - 2*(Rmin_i,j/r_i,j)**6]    *
!!                                                                             *
!!  epsilon: kcal/mol, Eps_i,j = sqrt(eps_i * eps_j)                           *
!!   Rmin/2: A, Rmin_i,j = (Rmin_i + Rmin_j)/2                                 *
!!                                                                             *
!! The second and fifth columns, marked #, are ignored.                        *
!! No "1-4" eps and Rmin/2 parameters were given for these atom types.         *
!! ***************************************************************************  **********  *****************
!! atom   #   eps     Rmin/2 #   eps   Rmin/2 ! DESCRIPTION                    SAMS USING  PARAMETER ORIGIN
!!                        1-4   1-4    !
!! ***************************************************************************  **********  *****************
OG301P 0.0 -0.1000 1.6500              ! ether; LJ from THP, sng 1/06      POXY       CGenFF: OG301
OPEG   0.0 -0.1921 1.7650              ! og MeOH and EtOH 1/06; RMV Aug07  PEGH       CGenFF: OG311 = NHLBI: OC311

HBOND CUTHB 0.5
END
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