Mendeleev Communications

Mendeleev Commun., 2025, **35**, 221–223

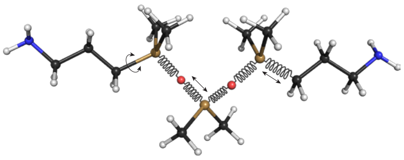
General AMBER force field parameters for modeling polyalkylsiloxane chains

Gennady I. Makarov* and Tatiana M. Makarova

South Ural State University (National Research University), 454080 Chelyabinsk,
Russian Federation. E-mail: makarovgi@susu.ru

DOI: 10.71267/mencom.7580

As a supplement to the widely used general AMBER force field, a set of parameters is proposed for molecular dynamics modeling of the structure and properties of polymer chains in polyalkylsiloxane matrices of materials capable of self-healing after stress loads.



$U = \sum k_1(l - l_0)^2 + \sum k_\theta(\theta - \theta_0)^2 + \sum k_\varphi[1 + \cos(n\varphi - \varphi_0)] + \ldots$

Keywords: siloxanes, GAFF, force field, polydimethylsiloxane, molecular mechanics.

Polyorganosiloxanes are widely used in engineering due to their chemical stability, biological inertness and wide range of operating temperatures. Moreover, most polymeric materials capable of spontaneously restoring their structure after stress loads are based on a polydimethylsiloxane matrix.[1,2] For example, Deriabin *et al.* created such a material based on a copolymer of α,ω-bis(3-aminopropyl)polydimethylsiloxane with pyridine-2,6-dicarboxylic acid, which coordinates nickel(II) ions.[3,4] Similar materials based on polydimethylsiloxane chains modified with dibenzoylmethane groups, which form complexes with metal ions, are also known.[5,6]

It is obvious that understanding how the structural organization of polyorganosiloxane materials is related to their properties would make it possible to improve them and predict their behavior under various conditions. However, as is usually the case for polymeric materials with only short-range order, the spatial structure of these polyorganosiloxanes cannot be directly studied by diffraction methods. Nevertheless, this is a feasible task for molecular dynamics (MD) modeling, which has been successfully used to study the structure of epoxy resin-based materials.[7,8]

MD modeling of any macromolecule involves creating its molecular mechanical model based on the appropriate force field, *i.e.*, the potential energy function of the modeled system in combination with a set of its parameters. There are several force fields that provide parameters for modeling compounds containing the Si–C covalent bond. First of all, these are ReaxFF extensions for solid SiC[9,10] or an alkyl monolayer on a silicon surface,[11] which, however, are rather different substances from organosiloxanes. Organosilicon compounds can also be modeled using the DREIDING[12] force field, which, however, has a rather simplified approach to assigning force constants, implying that the same values are assigned to all bonds with the same order, to all bond angles and to all torsion angles formed by atoms with the same hybridization, *i.e.*, the force constants are almost independent of the types of atoms. An interesting example of a force field developed for organosilicon molecules is PolCA,[13] which takes into account explicit polarization. The PolCA force field was developed to better predict the enthalpy of vaporization, free energy of solvation and other phase and electronic properties. However, in this force field, the aliphatic hydrogen atoms were not described explicitly, or in other words, each CH_x group was considered as a separate interaction site.

The general AMBER force field[14] (GAFF) is one of the widely used force fields because it enables high-performance MD simulations and covers a wide range of organic structures. The potential energy U_{pot} is represented in it as the sum of classical potentials that describe the vibration energy of interatomic bonds l, bond angles θ, torsion angles φ and the energy of dispersion and electrostatic interactions:

$$U_{pot} = \sum_{bond} \frac{k_1}{2}(l - l_0)^2 + \sum_{angle} \frac{k_\theta}{2}(\theta - \theta_0)^2 + \sum_{torsion} k_\varphi[1 + \cos(n\varphi - \varphi_0)] + \\ + \sum_{i,j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \sum_{i,j} \frac{q_i q_j}{\varepsilon r_{ij}}. \qquad (1)$$

In contrast to the above-mentioned force fields, GAFF allows one to construct a full-atom molecular-mechanical model that thoroughly considers the types of existing bonds, bond angles and torsion angles. At the same time, the simple form of the potential energy function of the simulated system, which does not take into account the polarization of atoms, ensures high simulation performance, which is necessary when simulating large polymer systems. MD simulation of such systems requires careful equilibration and multiple recalculations to average the influence of the starting structure, so high-performance computing is needed. Thus, the extension of GAFF to polyalkylsiloxane chains is necessary for conducting MD studies of self-healing materials based on polyalkylsiloxanes.

The original GAFF did not include parameters for modeling polyorganosiloxanes, but Dong *et al.* extended it with parameters for modeling drug-like organosilicon compounds after performing extremely demanding work[15] to tune compatible (6–12)-potential parameters for silicon atoms and their bonded oxygen and carbon atoms (Table 1). Unfortunately, GAFF, as thus extended, does not include parameters for some of the covalent interactions present in the polyorganosiloxane chain. These include parameters for the harmonic potentials that govern the vibrations of the bonds between silicon atoms and the bridging oxygen atoms, or for the cosine potentials that affect the conformation of the polysiloxane core. We decided to calculate the missing GAFF parameters to be able to perform high-throughput MD simulations of siloxane materials using it. Thus, we introduced a new atom type ‘oss’ for the oxygen atoms connecting the silicon atoms in the polysiloxane chain (see Table 1).

Table 1 GAFF atom types used in the work of Dong *et al.*[15] to model polyalkylsiloxanes and their (6–12)-potential parameters.

Atom type		σ/nm	ε/kJ mol^{-1}
si	*sp*^{3} silicon	3.16804×10^{-1}	6.28020×10^{-2}
ci	*sp*^{3} carbon covalently bonded to silicon	3.56538×10^{-1}	4.73108×10^{-1}
ng	*sp*^{3} nitrogen covalently bonded to silicon	3.15913×10^{-1}	1.98036
oi	Hydroxyl oxygen covalently bonded to silicon	3.24287×10^{-1}	2.09340
oss	Oxygen covalently bonded to two silicon atoms	3.24287×10^{-1}	2.09340
hi	Hydrogen covalently bonded to silicon	2.59430×10^{-1}	3.97746×10^{-1}

To perform the calculations, we constructed two models, 1,5-bis(3-aminopropyl)-1,1,3,3,5,5-hexamethyltrisiloxane **1** and 1,1′-(ethane-1,2-diyl)bis(1,3,3,3-tetramethyldisiloxan-1-ol) **2**, simulating a segment of the polydimethylsiloxane chain (Figure 1), and carried out a deep optimization of their potential energies using the density functional theory (DFT) method with the M06-2X functional. In this case, from one calculation to another, we gradually increased the detailing of the basis set from 3-21G to 6-311++G(d,p), achieving a complete absence of imaginary frequencies of eigen vibrations. Quantum chemical calculations were performed using the ORCA 5.0.3 package.[16] For the optimized structure of the model siloxane, the **H** matrix of the second derivatives of energy with respect to the Cartesian coordinates x_i was calculated. Then the **H** matrix was projected into the space of redundant internal coordinates q_m, *i.e.*, bond lengths, bond and torsion angles:

$$\mathbf{H} = \{H_{ij}\},\ H_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}, \tag{2}$$

$$\mathbf{H} \rightarrow \mathbf{H}_{int},\ \mathbf{H}_{int} = \{k_{mn}\},\ k_{ij} = \frac{\partial^2 E}{\partial q_m \partial q_n}. \tag{3}$$

The diagonal elements $k_{nn} = k_n$ of the $\mathbf{H}_{int}$ matrix are nothing but the force constants of the corresponding harmonic potentials for the potential energies associated with the changes in bond lengths and bond angles [equation (1)]. The force constants and the equilibrium values of bond lengths and bond angles are presented in Tables 2 and 3. After that, the point charges were calculated for the model siloxane using the RESP[17] model, and then a molecular-mechanical model was constructed, which was used to further estimate the missing parameters k_φ of the cosine potentials for the torsion angles.

The search for missing k_φ was carried out using an approach similar to the published one:[18] we generated a set of conformers of the model siloxane **1** by changing those torsion angles for which it was necessary to find the energy barrier k_φ. We calculated the energy for each conformer using the same DFT M06-2X/6-311++G(d,p) method and then sequentially adjusted the missing parameters. To begin with, we calculated the change in the energy of the molecule caused by the rotation of the methyl group around the C–Si bond, which corresponds to a change in 6 torsion angles of the oss–si–ci–hc type and 3 torsion angles of the ci–si–ci–hc type and results in 72 conformations with a step of 5 degrees, while the remaining torsion angles were fixed. We assumed that the k_φ value for the potentials of these two types is the same, so the change in the potential energy U of the model siloxane can be considered as a change in the sum of 9 cosine potentials of the same type. Then the target parameter k_φ for torsion angles of the X–si–ci–hc type can be found by approximating the dependence $U(\varphi)$ with the cosine potential from equation (1), as shown in Figure 2.

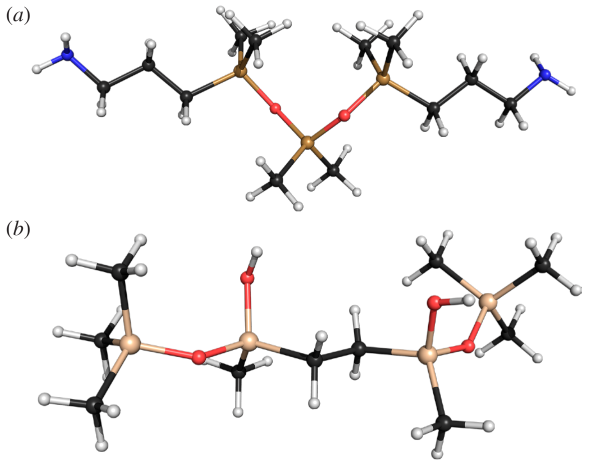


Figure 1 Model siloxanes (*a*) **1** and (*b*) **2** used to calculate the missing parameters of the force field. Silicon atoms are sand-colored, oxygen atoms are red, carbon atoms are black, and hydrogen atoms are white.

Table 2 Parameters of harmonic potentials for modeling bonds in polyalkylsiloxanes.

Atom types		l_0/nm	k_l/kJ mol^{-1} nm^{-2}
i	j		
si	oi	0.16740[a]	252462.56[a]
oi	ho	0.09730[a]	476641.28[a]
ci	hc	0.10936	318363.69
si	oss	0.16563	299464.63
si	ci	0.18719	172708.63
ci	c3	0.15412	263080.95
ci	ci	0.15515	265617.03

[a] The parameters are taken from Dong *et al.*[15]

Table 3 Parameters of harmonic potentials for modeling bond angles in polyalkylsiloxanes.

Atom types			θ_0/deg	k_θ/kJ mol^{-1} rad^{-2}
i	j	k		
ci	si	oi	106.420[a]	25.19[a]
si	oi	ho	116.370[a]	173.89[a]
ci	si	ci	109.696	379.81
hc	ci	hc	107.039	332.65
si	ci	hc	108.978	267.31
ci	si	oss	107.558	553.71
oss	si	oss	108.864	1033.58
oss	si	oi	109.641	658.87
si	oss	si	146.139	287.63
c3	c3	ci	113.585	910.99
c3	ci	hc	111.034	436.48
c3	ci	si	116.660	634.06
ci	c3	hc	110.133	528.62
ci	ci	si	112.581	412.35
ci	ci	hc	110.451	489.78

[a] The parameters are taken from Dong *et al.*[15]

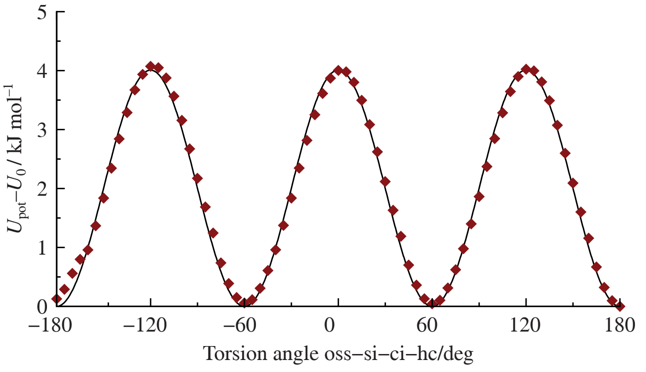


Figure 2 Approximation of the dependence of the energy of a molecule on the value of the torsion angle oss–si–ci–hc by a cosine potential.

Table 4 Parameters of cosine potentials for modeling torsion angles in polyalkylsiloxanes.

Atom types				φ_0/deg	k_φ/kJ mol^{-1}	n
i	j	k	l			
X	ci	c3	X	0.0[a]	2.4184[a]	3[a]
X	si	oi	X	0.0[a]	1.1443[a]	3[a]
X	si	ci	X	0.0[a]	1.4749[a]	3[a]
X	ci	ci	X	0.0	8.2250	3
oss	si	oss	si	0.0	0.6839	3
ci	si	oss	si	0.0	0.6839	3
oi	si	oss	si	0.0	0.0000	3
ci	si	ci	hc	0.0	0.2226	3
oss	si	ci	hc	0.0	0.2226	3
c3	ci	si	ci	0.0	0.7275	3
c3	ci	si	oss	0.0	0.7275	3

[a] The parameters are taken from Dong *et al.*[15] X denotes an atom of any type.

Then, for the thus obtained 72 conformations, differing in the oss–si–oss–si and si–oss–si–oss torsion angles with a step of 5 degrees, we calculated the potential energy values and combined these conformations into sets. After that, we adjusted k_φ of the oss–si–oss–si and ci–si–oss–si types, sequentially applying the genetic algorithm and the Nelder–Mead algorithm[19] in order to minimize the root-mean-square deviation Δ between the potential energies of model siloxanes calculated by quantum chemistry methods ($U_{\mathrm{QM,i}}$) and the potential energies calculated using the molecular-mechanical model with the target values of k_φ ($U_{\mathrm{MM,i}}$), as well as the values found for each i-th conformation out of N conformations:

$$\Delta = \sum_{\mathrm{i}}^{\mathrm{N}} (U_{\mathrm{QM,i}} - U_{\mathrm{MM,i}})^2. \qquad (4)$$

In this case, we assumed that the k_φ values for the oss–si–oss–si and ci–si–oss–si torsion angles are the same, since they describe rotation around the same Si–O bond. Then, k_φ was adjusted in exactly the same way for the c3–ci–si–ci and c3–ci–si–oss torsion angles.

The same procedures of generating the conformer and calculating its energy using quantum chemical calculations followed by Nelder–Mead fitting were performed with the model siloxane **2** to obtain k_φ for the oi–si–oss–si and X–ci–ci–X torsion angles. The parameters of the cosine potentials found in this way are presented in Table 4.

Thus, we have obtained a set of parameters for MD simulations of polyalkylsiloxanes that is compatible with GAFF. We hope that it will be useful to researchers interested in high-performance MD simulations of polymeric materials based on polyalkylsiloxanes.

This research was funded by the Ministry of Science and Higher Education of the Russian Federation (grant no. FENU 2024-0003).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7580.

References

1 Y. Yang and M. W. Urban, *Chem. Soc. Rev.*, 2013, **42**, 7446; https://doi.org/10.1039/c3cs60109a.

2 C.-H. Li, C. Wang, C. Keplinger, J.-L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X.-Z. You and Z. Bao, *Nat. Chem.*, 2016, **8**, 618; https://doi.org/10.1038/nchem.2492.

3 K. V. Deriabin, N. A. Ignatova, S. O. Kirichenko, A. S. Novikov and R. M. Islamova, *Polymer*, 2021, **212**, 123119; https://doi.org/10.1016/j.polymer.2020.123119.

4 K. V. Deriabin, M. A. Dziuba, A. A. Rashevskii, I. E. Kolesnikov, A. V. Korzhov, V. A. Sharov, A. Vorobyev, A. A. Vereshchagin, A. S. Chernukha, J. Tian, O. V. Levin, I. S. Mukhin and R. M. Islamova, *ACS Appl. Polym. Mater.*, 2023, **5**, 892; https://doi.org/10.1021/acsapm.2c01822.

5 E. E. Kim, Yu. N. Kononevich, A. A. Anisimov, M. I. Buzin, V. G. Vasil'ev, A. A. Korlyukov, D. S. Ionov, D. A. Khanin, E. V. Shtykova, V. V. Volkov and A. M. Muzafarov, *React. Funct. Polym.*, 2021, **164**, 104896; https://doi.org/10.1016/j.reactfunctpolym.2021.104896.

6 E. E. Kim, Y. N. Kononevich, Y. S. Dyuzhikova, D. S. Ionov, D. A. Khanin, G. G. Nikiforova, O. I. Shchegolikhina, V. G. Vasil'ev and A. M. Muzafarov, *Polymers*, 2022, **14**, 2554; https://doi.org/10.3390/polym14132554.

7 R. Unger, U. Braun, J. Fankhänel, B. Daum, B. Arash and R. Rolfes, *Comput. Mater. Sci.*, 2019, **161**, 223; https://doi.org/10.1016/j.commatsci.2019.01.054.

8 G. Makarov, O. Borodina, T. Makarova, A. Ignatova, N. Olivenko, E. Bartashevich and S. Sapozhnikov, *J. Phys. Chem. A*, 2023, **127**, 3894; https://doi.org/10.1021/acs.jpca.3c00425.

9 D. A. Newsome, D. Sengupta, H. Foroutan, M. F. Russo and A. C. T. van Duin, *J. Phys. Chem. C*, 2012, **116**, 16111; https://doi.org/10.1021/jp306391p.

10 F. Niefind, Q. Mao, N. Nayir, M. Kowalik, J.-J. Ahn, A. J. Winchester, C. Dong, R. A. Maniyara, J. A. Robinson, A. C. T. van Duin and S. Pookpanratana, *Small*, 2024, **20**, 2306554; https://doi.org/10.1002/smll.202306554.

11 F. A. Soria, W. Zhang, P. A. Paredes-Olivera, A. C. T. van Duin and E. M. Patrito, *J. Phys. Chem. C*, 2018, **122**, 23515; https://doi.org/10.1021/acs.jpcc.8b07075.

12 S. L. Mayo, B. D. Olafson and W. A. Goddard, *J. Phys. Chem.*, 1990, **94**, 8897; https://doi.org/10.1021/j100389a010.

13 M. Jorge, A. W. Milne, M. C. Barrera and J. R. B. Gomes, *ACS Phys. Chem. Au*, 2021, **1**, 54; https://doi.org/10.1021/acsphyschemau.1c00014.

14 J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman and D. A. Case, *J. Comput. Chem.*, 2004, **25**, 1157; https://doi.org/10.1002/jcc.20035.

15 X. Dong, X. Yuan, Z. Song and Q. Wang, *Phys. Chem. Chem. Phys.*, 2021, **23**, 12582; https://doi.org/10.1039/d1cp01169c.

16 F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2022, **12**, e1606; https://doi.org/10.1002/wcms.1606.

17 C. I. Bayly, P. Cieplak, W. Cornell and P. A. Kollman, *J. Phys. Chem.*, 1993, **97**, 10269; https://doi.org/10.1021/j100142a004.

18 J. Wang and P. A. Kollman, *J. Comput. Chem.*, 2001, **22**, 1219; https://doi.org/10.1002/jcc.1079.

19 J. A. Nelder and R. Mead, *The Computer Journal*, 1965, **7**, 308; https://doi.org/10.1093/comjnl/7.4.308.

Received: 30th July 2024; Com. 24/7580