



TECHNISCHE  
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WIEN

## **165.144 Simulation of condensed matter**

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## Summary chapter 5

- For finite systems, one should directly sample in the ensemble of interest, e.g.
  - Micro-canonical (NVE) ensemble
  - Canonical (NVT) ensemble
  - Isobaric-isothermal (NPT) ensemble
- Pressure and/or temperature is held "constant" by a barostat or thermostat
- "Constant" means that the temperature or pressure fluctuates around a given mean with magnitudes determined by the heat capacity and isothermal compressibility
- Choice of the best barostat and thermostat depends on the use-case

**Remember, for an MD simulation, we need to know:**

- ① How atoms interact, i.e. given coordinates  $\vec{r}$ , obtain forces  $\vec{f}(\vec{r})$
- ② How atoms move, i.e. given forces  $\vec{f}$ , obtain coordinates at next time step  $\vec{r}(t + \Delta t)$



## Chapter 6: Interatomic potentials

## *n*-body potentials

Classic approach (as approximation of true, quantum-mechanical energy)

$$\begin{aligned}E_{\text{pot}}\{\vec{r}_I\} = & V_0 \\& + \sum_I V_1(\vec{r}_I) \\& + \sum_{I,J} V_2(\vec{r}_I, \vec{r}_J) \\& + \sum_{I,J,K} V_3(\vec{r}_I, \vec{r}_J, \vec{r}_K) \\& + \sum_{I,J,K,L} V_4(\vec{r}_I, \vec{r}_J, \vec{r}_K, \vec{r}_L) \\& + \dots\end{aligned}$$

The best choice of potential depends on the state of the system (gas, liquid, solid), and the type of bonds (covalent bonds, non-bonded interactions, crystal/metal lattices)

For non-bonded interactions, a two-body potential is usually a good description already. For bonded interaction, many more terms are needed!

## Two-body potentials $V_2(R)$

Noble gases:

- **Lennard-Jones potential 1924:**  $V_2(R) = 4\epsilon \left[ \left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]$  to model noble gases.
- **Buckingham potential 1938:**  $V_2(R) = Ae^{-BR} - \frac{C}{R^6}$  allows for a more flexible form than Lennard-Jones

Covalent (only diatomic) bonds:

- **Morse potential 1929:**  $V_2(R) = D_e \left[ \left(1 - e^{-\alpha(R-R_c)}\right)^2 - 1 \right]$  describes many diatomic systems well. Minimum at  $R_c$  with the potential energy  $-D_e$

## Two-body potentials $V_2(R)$

Solid state:

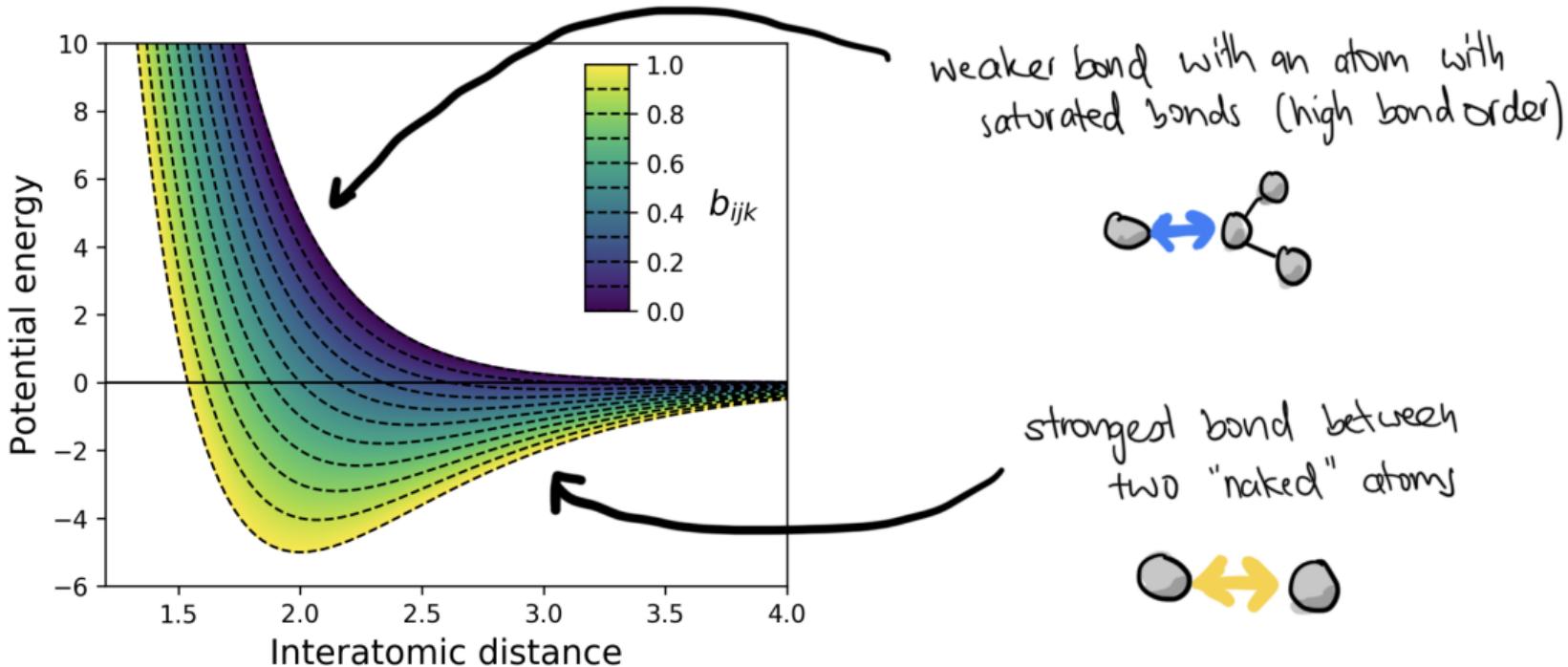
- **Stillinger-Weber potential 1985:**  $V_2(R) = A\epsilon \left[ B \left( \frac{\sigma}{R} \right)^p - \left( \frac{\sigma}{R} \right)^q \right] e^{\frac{\sigma}{R-a\sigma}}$  and  $V_3(R_{IJ}, R_{IK}, \theta_{IJK}) = \lambda\epsilon(\cos\theta_{IJK} - \cos\theta_0)^2 e^{\frac{\gamma\sigma}{R_{IJ}-a\sigma}} e^{\frac{\gamma\sigma}{R_{IK}-a\sigma}}$  to model solid and liquid phases of Si, GaN, 2D materials, etc.
- **Tersoff's bond-order potential 1988:**  $V_2(R_{IJ}) = f_c(R_{IJ})[f_r(R_{IJ} + b_{IJ}f_a(R_{IJ})]$  which is a two-body potential where the attractive part is modulated by the bond order  $b_{IJ}$  which depends on  $\theta_{IJK}$ :

$$f_r(R_{IJ}) = Ae^{-\lambda_1 R_{IJ}} \text{ and } f_a(R_{IJ}) = -Be^{-\lambda_2 R_{IJ}}$$

$$f_c(R_{IJ}) = \begin{cases} 1, & \text{if } R_{IJ} < C - D \\ \frac{1}{2} - \frac{1}{2}\sin\left(\frac{\pi}{2}\frac{R_{IJ}-C}{D}\right), & \text{if } C - D < R_{IJ} < C + D \\ 0, & \text{if } R_{IJ} > C + D \end{cases}$$

$$b_{IJ} = (1 + \beta^n \sum_K f_c(R_{IK}) \gamma \left[ 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (\cos\theta_{IJK} - \theta_0)^2} \right] e^{\lambda_3^m (R_{IJ} - R_{IK})^m})^{-\frac{1}{2n}}$$

# The general idea of bond-order potentials

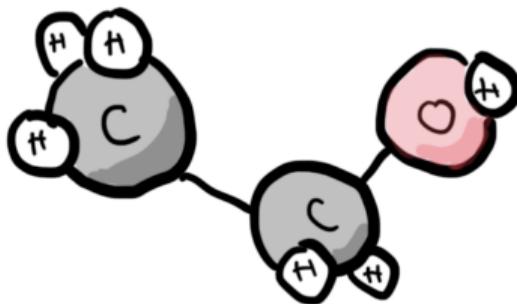


Source: [https://commons.wikimedia.org/wiki/File:Bond-order\\_interatomic\\_potential.png#/media/File:Bond-order\\_interatomic\\_potential.png](https://commons.wikimedia.org/wiki/File:Bond-order_interatomic_potential.png#/media/File:Bond-order_interatomic_potential.png)

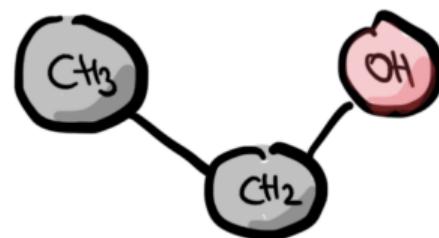
# Molecular mechanics

Molecular systems (with a bent toward organic molecules in fluid phases)

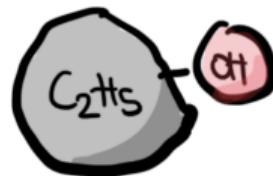
- Potential has bonded and non-bonded interactions
- Atoms have vdW radii, partial charges and possibly polarizabilities
- Molecules can be treated in an all-atom, united-atom (implicit hydrogen) or coarse-grained (multiple atom form a bead) fashion. Parts of the simulation can also be at the QM-level (QM-MM hybrid approach)



all-atom (AA)



united-atom (VA)



coarse-grained (CG)

# OPLS-AA 1996

The potential is a sum of bonded and non-bonded energy terms:  $V = V_{\text{bonded}} + V_{\text{non-bonded}}$

## Bonded terms:

- Bond-term  $V_{\text{bond}} = \sum_{\text{bonds } IJ} K_R(I, J)[R_{IJ} - R_{0,IJ}]^2$
- Angle-term  $V_{\text{angle}} = \sum_{\text{angles } IJK} K_\theta(I, J, K)[\theta_{IJK} - \theta_{0,IJK}]^2$
- Dihedral-term  $V_{\text{dihedral}} = \sum_{\text{dihedrals } IJKL} \frac{K_1}{2}[1 + \cos(\phi_{IJKL} - \phi_1)] + \frac{K_2}{2}[1 - \cos(2\phi_{IJKL} - \phi_2)] + \frac{K_3}{2}[1 + \cos(3\phi_{IJKL} - \phi_3)] + \frac{K_4}{2}[1 - \cos(4\phi_{IJKL} - \phi_4)]$

## Non-Bonded terms:

- Combined vdW and charge interactions:  $V_{\text{non-bonded}} = \sum_{I>J} f_{IJ} \left( \frac{A_{IJ}}{R_{IJ}^{12}} - \frac{C_{IJ}}{R_{IJ}^6} + \frac{q_I q_J e^2}{4\pi\epsilon R_{IJ}} \right)$   
with combining rules  $A_{IJ} = \sqrt{A_{ii} A_{jj}}$  and  $C_{IJ} = \sqrt{C_{ii} C_{jj}}$

$$f_{IJ} = \begin{cases} 1, & \text{if I and J are more than 3 bonds apart} \\ 0.5, & \text{if I and J are 3 bonds apart} \\ 0, & \text{if I and J are less than 3 bonds apart} \end{cases}$$

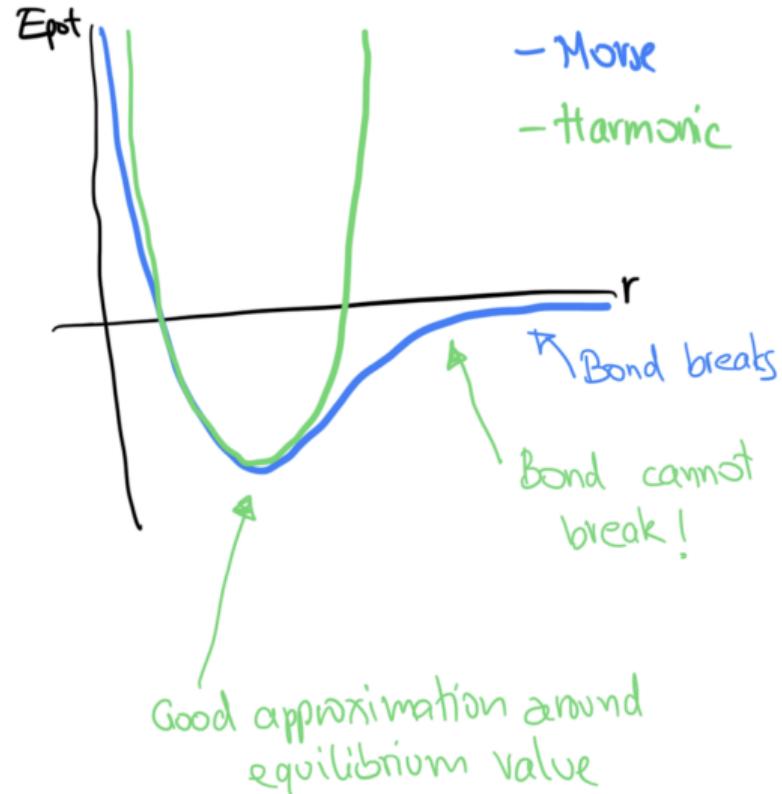
## Two-body terms in molecular potentials (= bonds)

True interaction: Morse

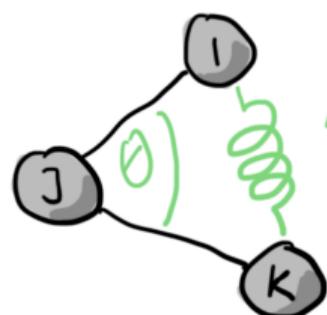
→ Taylor expansion around  $r_{\min}$ ,  
truncate after second order



$$\Delta E_{\text{pot}} = \frac{1}{2} K (l - l_0)^2$$



## Three-body terms in molecular potentials (= angles)



Approximate via harmonic term

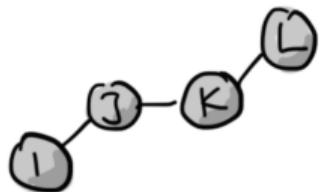
$$\Delta E_{\text{pot}} = \frac{1}{2} K (l - l_0)^2$$

$$l = \sqrt{R_{IJ}^2 + R_{KJ}^2 - R_{IJ} R_{KJ} \cos \theta}$$

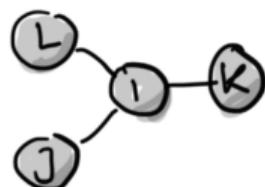
$$\Rightarrow \Delta E_{\text{pot}} \approx \frac{1}{2} K (\theta - \theta_0)^2$$

## Four-body terms in molecular potentials (= dihedral angles)

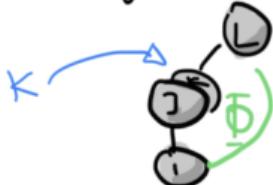
Proper dihedrals:



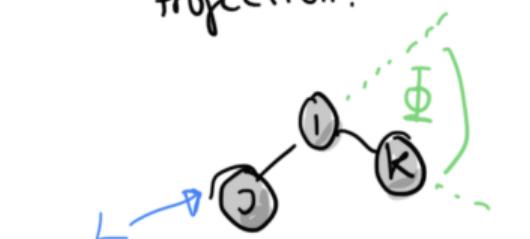
Improper dihedrals:



Projection:



Projection:

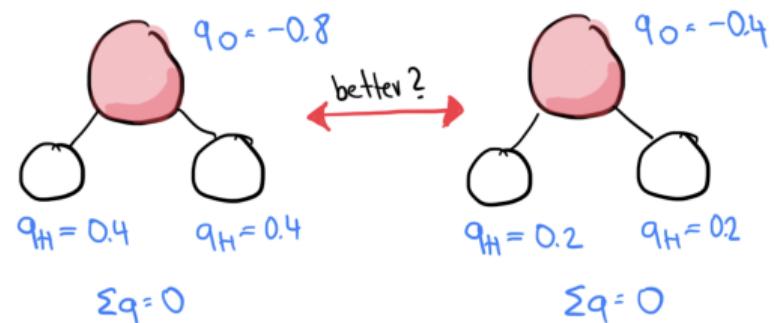


$\Rightarrow$  out-of-plane bending

# Partial charges

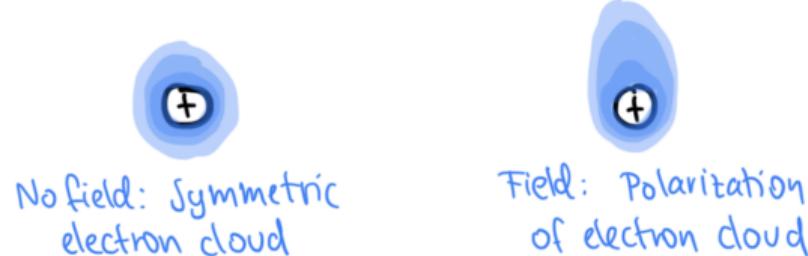
There is no physical quantity such as an "atomic charge", there are therefore many valid schemes to assign partial charges, e.g. (among many others)

- Formal charges
- Restrained fit to the electrostatic potential (RESP)
- Mulliken charges
- Bader charges

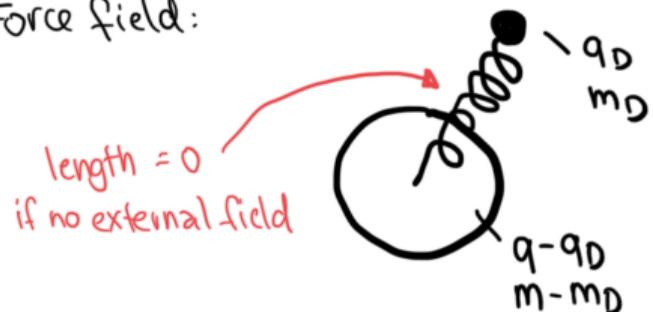


# Polarizability

In reality atoms react to an external field:



Force field:



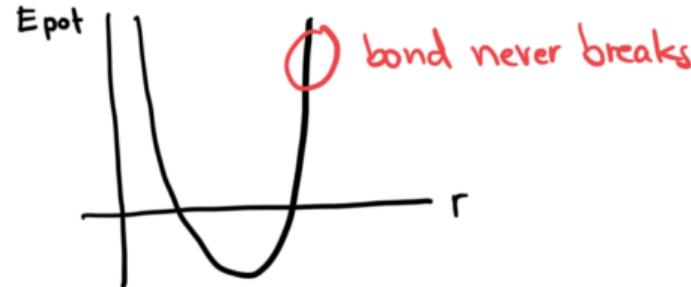
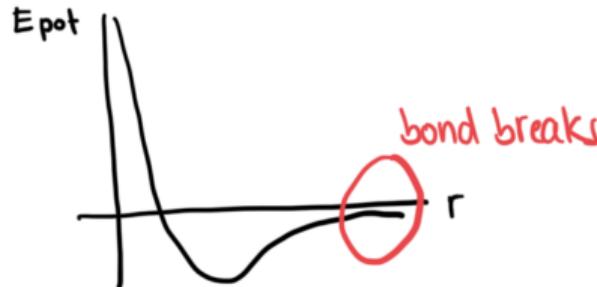
← "Drude particle"

= artificial particle that can only interact through  $q_D$ , attached via harmonic force

Usually: Force constant same for all Drude particles, and  $q_D$  dependent on the atomic polarizability

# Reactive (molecular) force fields

For LJ, Buckingham, Morse-type FFs, reactivity is not a problem:



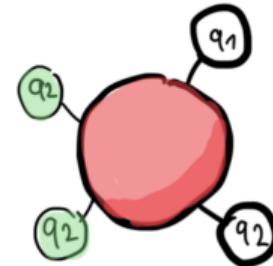
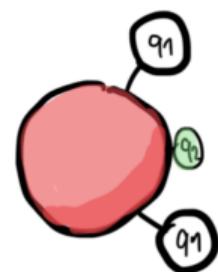
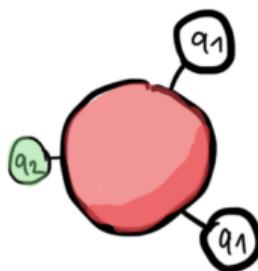
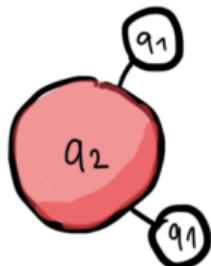
But for molecular force fields, because we change the Morse term to an harmonic term, all bonds become unbreakable

## Possible solutions:

- General reactive force fields based on bond-order potentials, for example ReaxFF
- Force fields without enforced functional form, e.g. from machine learning
- For simple cases, e.g. protonation reactions, one can also work with ghost atoms

# A potential for water

There are nearly 50 water potentials reported in literature, which follow the general forms



eg SPC, SPC/E,  
TIP3P

eg PPC

eg TIP4P,  
SWM4-NDP

eg TIP5P

planar

tetrahedral

# A potential for water

Calculated physical properties of the water models						
Model	Dipole moment e	Dielectric constant	self-diffusion, $10^{-5} \text{ cm}^2/\text{s}$	Average configurational energy, $\text{kJ} \cdot \text{mol}^{-1}$	Density maximum, °C	Expansion coefficient, $10^{-4} \text{ °C}^{-1}$
SSD	2.35 [511]	72 [511]	2.13 [511]	-40.2 [511]	-13 [511]	-
SPC	2.27 [181]	65 [185]	3.85 [182]	-41.0 [185]	-45 [983]	7.3 [704] **
SPC/E	2.35 [3]	71 [3]	2.49 [182]	-41.5 [3]	-38 [183]	5.14 [994]
SPC/Fw	2.39 [994]	79.63 [994]	2.32 [994]	-	-	4.98 [994]
PPC	2.52 [3]	77 [3]	2.6 [3]	-43.2 [3]	+4 [184]	-
TIP3P	2.35 [180]	82 [3]	5.19 [182]	-41.1 [180]	-91 [985]	9.2 [180]
TIP3P/Fw	2.57 [994]	193 [994]	3.53 [994]	-	-	7.81 [994]
JAMOeba	2.78 [2031]	80.7 [2031]	2.54 [2031]	-	4 [2031]	2.5 [2031]
JAMOeba	2.80 [2401]	76.3 [2401]	2.41 [2401]	-	-	3.38 [2401]
OCT **	1.85 [1251]	-	1.5 [1251]	-42.7 [1251]	+10 [1251]	3.5 [1251]
TIP4P	2.18 [3,180]	53 a [3]	3.29 [182]	-41.8 [180]	-25 [180]	4.4 [180]
TIP4P-Ew	2.32 [649]	62.9 [649]	2.4 [649]	-46.5 [649]	+1 [649]	3.1 [649]
TIP4P-FQ	2.64 [197]	79 [197]	1.93 [197]	-41.4 [201]	+7 [197]	-
TIP4P/2005	2.305 [984]	60 [984]	2.08 [984]	-	+5 [984]	2.8 [984]
TIP4P/2005f	2.319 [1765]	55.3 [1765]	1.93 [1765]	-	+7 [1765]	-
TIP4P/E	2.4345 [2444]	78.3 [2444]	2.10 [2444]	-	+4 [2444]	-
OPC	2.48 [2168]	78.4 [2168]	2.3 [2168]	-	-1 [2168]	2.7 [2168]
OPC3	2.43 [2722]	78.4 [2722]	2.3 [2722]	-	-13 [2722]	4.3 [2722]
SWFLEX-AI	2.69 [201]	116 [201]	3.66 [201]	-41.7 [201]	-	-
COS/G3 **	2.57 [704]	88 [704]	2.6 [704]	-41.1 [704]	-78 [1939]	7.0 [704]
COS/D2	2.55 [1617]	78.9 [1617]	2.2 [1617]	-41.8 [1617]	-	4.9 [1617]
GCPM	2.723 [859]	84.3 [859]	2.26 [859]	-44.8 [859]	-13 [859]	-
SWM4-NDP	2.461 [933]	79 [933]	2.33 [933]	-41.5 [933]	<53 [1999]	-
BK3	2.644 [2080]	79 [2080]	2.28 [2080]	-43.32 [2080]	+4 [2080]	3.01 [2080]
SWM6	2.431 [1999]	78.1 [1999]	2.14 [1999]	-41.5 [1999]	-48 [1999]	-
TIP5P	2.29 [180]	81.5 [180]	2.62 [182]	-41.3 [180]	+4 [180]	6.3 [180]
TIP5P-Ew	2.29 [619]	92 [619]	2.8 [619]	-	+8 [619]	4.9 [619]
TTM2-F	2.67 [1027]	67.2 [1027]	1.4 [1027]	-45.1 [1027]	-	-
POL5/TZ	2.712 [256]	98 [256]	1.81 [256]	-41.5 [256]	+25 [256]	-
Six-site *	1.89 [491]	33 [491]	-	-	+14 [491]	2.4 [491]
MB-pol	[3133]	-	68.4	2.3	-10	3.5
Experimental	2.95	78.4	2.30	-41.5 [180]	+3.984	2.53

All the data is at 25 °C and 1 atm, except \* at 20 °C and \*\* at 27 °C.