Contents

1 Model types

The database of "Molecular Models of the Boltzmann-Zuse Society" contains force fields for around 150 substances for low-molecular fluids, in particular for the fluid region. The models were developed over the last 20 years by members of the Boltzmann Zuse Society for Computational Molecular Engineering (BZS) and published here [put link to Literature side here]. They are known to describe vapour-liquid equilibrium data (saturated densities, vapour pressure, enthalpy of vaporization) well, to which they were parametrised (in most cases). In many cases, also predictions of other properties, like transport properties were tested and found to be in good agreement with experimental data. All force fields in the database are: rigid multi-centre Lennard-Jones 12-6 potentials with super-imposed point charges, dipoles, and quadrupoles. They can easily be combined for describing mixtures using mixing rules, e.g. the Lorentz-Berthelot rule.

In some cases, multiple models for the same substance were developed, e.g. for methane (one model as a simple Lennard-Jones fluid and one as Lennard-Jones truncated & shifted). The database also contains a set of ion models that can be used for modelling electrolyte systems.

2 Units

The force fields shown in the database are displayed in the following units system, cf. Tab. 2.

	symbol	unit	
length	σ	Å	Ångström
energy	ϵ/k_B	K	Kelvin
charge	q	e	Elementary charge
dipole	μ	D	Debye
angle	φ, ϑ	°	degree
mass	M	g/mol	molar mass
quadrupole	Q	DÅ	Buckingham

3 Z-Matrix

The geometry of the molecular models is displayed in the Z-matrix format [put here a reference]. The Z-matrix defines the structure of a molecular model not by Cartesian x, y, z-coordinates, but by internal coordinates. Removal of translational and rotational degrees of freedom, the necessary number of parameters for the definition of a molecular geometry is $3N - 6$ ($3N - 5$ for linear molecules).

Internal coordinates describe the location of the atoms with respect to each other. The position of an atom in space is uniquely described by three internal coordinates.

The Z-matrix is a list of internal coordinates that uniquely describes the structure of a molecule. The atoms – or interaction sites – of the molecule are successively positioned in relation to sites that were defined before. The position of each interaction site is defined by one distance (mostly the bond length), one angle and one dihedral angle and point from one site to the next.
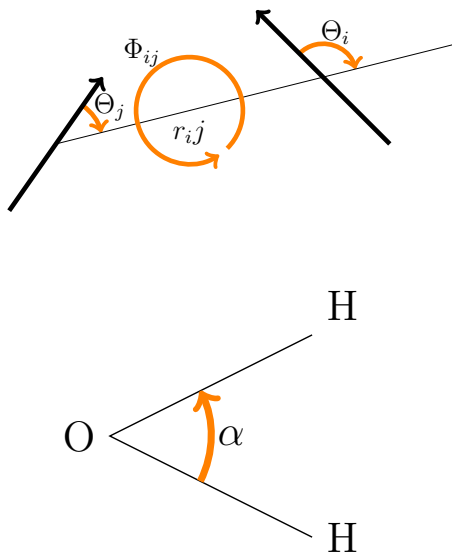
Figure 1: Angel and dihedral definition in Z-Matrix.

The general notation of the Z-Matrix is:

$$
\begin{pmatrix}
1 & Name_1 & - & - & - & - & - & - \\
2 & Name_2 & 1 & Distance_2 & - & - & - & - \\
3 & Name_3 & 2 & Distance_3 & 1 & Angle_3 & - & - \\
4 & Name_4 & 3 & Distance_4 & 2 & Angle_4 & 1 & Dihedral_4 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
n & Name_n & n-1 & Distance_n & n-2 & Angle_n & n-3 & Dihedral_n
\end{pmatrix}
\tag{1}
$$

Each line defines the position of one site with respect to the positions before defined. The *Site-ID* in the first column is used to uniquely identify each site. The *Site-name* in the second column describes, what atoms or quality (charge distribution) of the molecule the site models. Each line consists of three geometrical specifications (one distance, one angle, and one dihedral angle) and for each of these one corresponding reference ID. That ID indicates to which of the before defined sites the the distance, angle or dihedral angle stands in relation.

Table 3 shows the structure of isobutane in the Z-matrix format as an example. The forth line indicates, that the site #4 has a distance of 1.881 Åto site #3, an angle of 87.9092 ° between site $\{\#2 - \#3 - \#4\}$ and a dihedral angle of -21.6121 ° between the sites $\{\#1 - \#2 - \#3 - \#4\}$.

Site-ID	Site-name	Ref.	Distance / Å	Ref.	Angle / °	Ref.	Dihedral / °
1	CH(1)	-	-	-	-	-	-
2	CH(2)	1	1.8811	-	-	-	-
3	CH(3)	2	1.8811	1	87.909	-	-
4	CH(4)	3	1.8811	2	87.9092	1	-21.6121

The following points hold for the nomenclature of the Z-matrix geometries:

1. The first site of each molecular model does not need any coordinates (one can say that it sets the origin). The second site only needs a distance to the first atom, since the orientation in space is arbitrary. The third site needs one distance and one angle to be uniquely defined. From the forth site on, besides the distance and the angle, the dihedral states, how the new site lies in space.

2. Overlapping sites: if a site lies at the same spot like an other it is enough to reference the already defined site. No further information is needed, e. g. the 'C$_7$H$_8$_I'-model for Toluene. All the point quadrupoles lie exactly on the above defines Lennard-Jones sites.

3. Orientation of point-dipole and point-quadrupole: The orientation of those sites is denoted by a unity vector. It's basis is located on the site of the point-dipole or point-quadrupole respectively. This orientation-vector is given by an extra line in the Z-matrix named *dir.*, which follows the line where the position of dipole or quadrupole is defined. See the 'C$_3$H$_6$O'-model for Acetone as an example.

4. In cases where the model reduces the molecular structure so much, that a unique assignment of atoms to the sites is not unique anymore, the sites are labled $\mathcal{V}$, $\mathcal{W}$, $\mathcal{X}$, $\mathcal{Y}$, $\mathcal{Z}$ etc. (for example the 'CCl$_4$_I' model for Carbon tetrachloride with two Lennard-Jones sites and one quadrupole).

4 Interaction Potentials

All models in the database "Molecular Models of the Boltzmann-Zuse Society" consist of Lennard-Jones 12-6 interaction sites, point charges, point-dipoles and point quadrupoles. The last two are computationally much cheaper compared to the corresponding configuration of point charges. Since point multipoles are not supported by some molecular dynamics simulation codes, we use the approach [put link to section underneath] of [but reference of Engin here] to transform point-dipoles and point quadrupoles straightforwardly to two or three point charges respectively.

JL 12-6 Repulsion and dispersion interaction between two particles i, j of the same kind at a distance r is modelled throughout the database by the standard Lennard-Jones 12-6 potential

$$u_{ij}^{\mathrm{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{2}$$

The potential model itself consists of two parts – the first part with the positive sing represents the repulsion and the negative the attraction. The potential has of two parameters: The size parameter σ with a dimension of length defines the distance where the potential energy is zero and the energy-parameter ε, which defines the depth of the potential and thereby sets the dispersion energy.
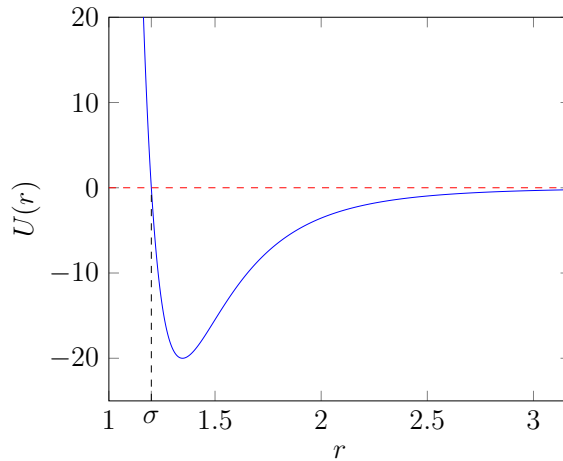

Figure 2: Lennard-Jones potential between two particles.

For the **unlike Interaction** – the interaction of two sites with different ε and/ or σ – mixing rules can be applied. The extensive study of the influence of different mixing rules by Schnabel et al. [Schnabel, 2007] showed, that the mixture bubble density is accurately obtained using the arithmetic mean of the two size parameters σ_k, σ_l as proposed by the Lorentz combining rule (3). That results in $\eta_{kl} = 1$ being a very accurate description of the unlike size parameter. The vapor pressure turn out to be dependent on both unlike Lennard-Jones parameters. It is therefore recommended by Schnabel et al. to adjust the unlike Lennard-Jones energy parameter to the vapour pressure.

$$\sigma_{kl} = \eta_{kl} \frac{\sigma_k + \sigma_l}{2} \tag{3}$$

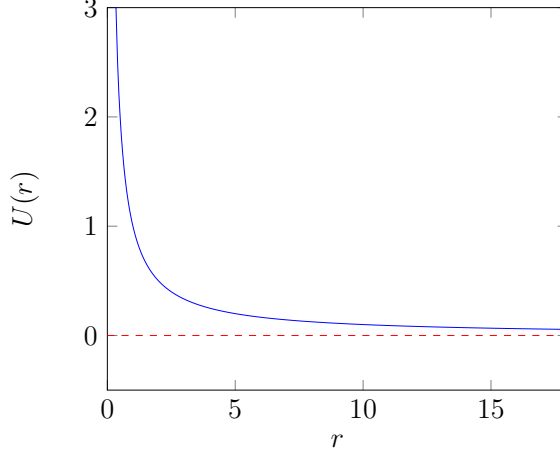$$\varepsilon_{kl} = \xi_{kl} \sqrt{\varepsilon_k \varepsilon_l} \tag{4}$$

Figure 3: Coulomb potential between two particles.

Charge Point charges are first order electrostatic interaction sites. They are indicated in the database with an 'e'. The electrostatic interaction between two point charges q_i and q_j is given by Coulomb's law:

$$u_{ij}^{\text{ee}}(r_{ij}) = \frac{1}{4\epsilon_0 \pi} \frac{q_i q_j}{r_{ij}} \tag{5}$$

with q the magnitude of the charge and r_{ij} the distance between tow charges

Dipole A point dipole describes the electrostatic field of two point charges with equal magnitude, but opposite sign at a mutual distance $a \to 0$. It is labelled throughout the database with a 'd'. The magnitude of a dipole moment is defined by $\mu = qa$. The electrostatic interaction between two point dipoles with the moments μ_i and μ_j at a distance r_{ij} is given by:

$$u_{ij}^{\text{dd}}(r_{ij}, \theta_i, \theta_j, \Phi_{ij}, \mu_i, \mu_j) = \frac{1}{4\pi\epsilon_0} \frac{\mu_i \mu_j}{r_{ij}^3} \left[(\sin(\theta_i)\sin(\theta_j)\cos(\phi_{ij}) - 2\cos(\theta_i)\cos(\theta_j) \right], \tag{6}$$

where the angles θ_i, θ_j and ϕ_{ij} indicate the relative angular orientation of the two point dipoles.

Quadrupole A linear point quadrupole describes the electrostatic field (sf. fig. 4) induced either by two collinear point dipoles with the same moment, but opposite orientation at a distance $a \to 0$ or three point charges. Point quadrupoles are labelled as 'q' in the database. The magnitude of a point-quadrupole Q is defined as $Q = 2qd^2$, where q is the magnitude of the three similar charges and d their distance. The interaction potential is given by:

$$u_{ij}^{\text{qq}}(r_{ij}, \theta_i, \theta_j, \Phi_{ij}, Q_i, Q_j) = \frac{1}{4\pi\epsilon_0} \frac{3}{4} \frac{Q_i Q_j}{r_{ij}^5} \left[1 - 5((\cos(\theta_i)^2 + \cos(\theta_i)^2) - 15(\cos(\theta_i))^2(\cos(\theta_j))^2 + 2(\sin(\theta_i)\sin(\theta_j) \right.$$
$$\tag{7}$$

where the angles θ_i, θ_j and ϕ_{ij} indicate the relative angular orientation of the two point quadrupoles.