

Isabela Quintela Matos

**Partition Coefficient Calculations of
Molecules Mimicking Asphaltenes Through
Molecular Simulation Using The
Coarse-Grained SAFT- γ Mie Force Field**

Rio de Janeiro

2018

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Dissertação de Mestrado apresentada ao
Programa de Pós-Graduação em Tecnologia de Processos Químicos e Bioquímicos,
Escola de Química, Universidade Federal
do Rio de Janeiro, como requisitos parcial à
obtenção do título de Mestre em Engenharia
Química.

Universidade Federal do Rio de Janeiro

Escola de Química

Programa de Pós-Graduação em Tecnologia de Processos Químicos e Bioquímicos

Supervisor: Charlles Rubber de Almeida Abreu

Co-supervisor: Papa Matar Ndiaye

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FERRIGNO, C. R. A. **Tratamento de neoplasias ósseas apendiculares com reim-
plantação de enxerto ósseo autólogo autoclavado associado ao plasma rico em pla-
quetas**: estudo crítico na cirurgia de preservação de membro em cães. 2011. 128 f. Tese
(Livre-Docência) - Faculdade de Medicina Veterinária e Zootecnia, Universidade de São
Paulo, São Paulo, 2011.

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*Este trabalho é dedicado às crianças adultas que,
quando pequenas, sonharam em se tornar cientistas.*

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¹ Os nomes dos integrantes do primeiro projeto *abnT_EX* foram extraídos de <http://codigolivres.org.br/projects/abntex/>

² <http://www.cpai.unb.br/>

³ <http://groups.google.com/group/latex-br>

⁴ <http://groups.google.com/group/abntex2> e <http://www.abntex.net.br/>

*“Não vos amoldeis às estruturas deste mundo,
mas transformai-vos pela renovação da mente,
a fim de distinguir qual é a vontade de Deus:
o que é bom, o que Lhe é agradável, o que é perfeito.
(Bíblia Sagrada, Romanos 12, 2)*

Abstract

Segundo a [ABNT \(2003, 3.1-3.2\)](#), o resumo deve ressaltar o objetivo, o método, os resultados e as conclusões do documento. A ordem e a extensão destes itens dependem do tipo de resumo (informativo ou indicativo) e do tratamento que cada item recebe no documento original. O resumo deve ser precedido da referência do documento, com exceção do resumo inserido no próprio documento. (...) As palavras-chave devem figurar logo abaixo do resumo, antecedidas da expressão Palavras-chave:, separadas entre si por ponto e finalizadas também por ponto.

Palavras-chave: latex. abntex. editoração de texto.

Abstract

This is the english abstract.

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Γ	Letra grega Gama
Λ	Lambda
ζ	Letra grega minúscula zeta
\in	Pertence

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1 Literature Review

1.1 Coarse Grained Force Fields

Molecular simulations can be carried out at different levels of descriptions. The detailed atomistic level or *ab initio* level is described by the laws of quantum mechanics. The system consists of a set of subatomic particulars in which Schrodinger's equation is solved for all of them. The next level is the atomistic description. It considers that the system is made up of atoms following the laws of statistical mechanics. Force fields at this level are based on pair potentials with Coulombic charged sites, which account for the molecular interactions. The contributions due to intramolecular interactions like bond-stretching, angle-bending and torsion are also usually accounted by these kind of force fields. When the scale of the simulations needs to be increased and the atomistic simulations become too computationally expensive, the coarse-grained (CG) description is more suited. It considers that the system is made up of pseudo atoms or beads that contain multiple atoms.

There is a obvious loss of information in grouping atoms, hence it is necessary to assure that the process of eliminating unnecessary or unimportant information ('coarse graining') doesn't affect the system's physical behavior. The coarse grained force fields based on this description are developed by mapping the atomistic model to define the pseudo atoms. This mapping is normally done by grouping similar functional groups. The level of coarse-graining also needs to be defined, up to 6 heavy atoms (non-hydrogen atoms) per bead in order to not loose much detail and maintain isotropic representations of the beads (SHINODA; DEVANE; KLEIN, 2007; MARRINK et al., 2007; HADLEY; MCCABE, 2012). The CG force field can be parametrized following two different approaches: bottoms up and top down. The bottoms up approach uses information of a more detailed scale such as the *ab initio* description or the atomistic description to obtain the information necessary to the parametrization. This method depends highly of the quality of the detailed model to succeed. Meanwhile, the top down methodology obtains the parameters from one larger scales. This information at larger scales could be experimentally observed data like thermodynamic properties or native-structure based properties.

The main advantage of coarse-graining lies in the immense speed up of the simulation

Obviously, coarse graining comes at the cost of loosing electronic and atomistic details. Therefore it is crucial to identify the unimportant details and to preserve feature

that are essential for the description of the phenomenon on interest. In particular, CG mapping is critical for the accuracy, transferability, robustness, and computational efficiency of the CG model.

An early example of coarse-graining is the seminal work of Levitt and Warshel in 1975 [90], where the authors studied the folding of small proteins by obtaining atomistic potentials from the QM trajectories using MD simulations.

The pair potential is based on molecule specific parameters, such as the ranges of the repulsive and attractive interactions, the size of the bead and the energy parameter which characterises the strength of the attractive interaction.

At short distances, the potential is invariably repulsive and tends to infinity, whereas at larger separations, the potential is attractive and tends to zero so that the energy remains finite. The total potential energy is usually assumed as a sum of both, the repulsive and the attractive, contributions. Some of the commonly used pair potentials are illustrated in Figure 2.1 and briefly described below.

Using the versatile exponents has been shown to provide a significant improvement of the vapour pressure and the second-derivative thermodynamic properties of real fluids, such as speed of sound, heat capacity, and compressibility ([AVENDAÑO et al., 2011](#); [LAFITTE et al., 2013](#); [LAFITTE et al., 2006](#)).

In conventional statistical mechanics, it is common to replace time averages with ensemble averages. This hypothesis, currently referred to as the ergodic hypothesis, states that the time and the ensemble averages of two systems with the same state variables, e.g., N , V , and T are identical in infinite time and thermodynamic limits.

By contrast, commonly used bottom-up approaches often make use of temperature dependent parameters that have to be re-derived at various state points. The parameters obtained with our SAFT-gamma top-down methodology can be used as a direct input in molecular simulation. Unlike intermolecular interactions can also be obtained by using appropriate experimental data for the mixtures, but often combining rules are employed for some of the parameters as described in the next section.

The parameterisation of a force field is a non-trivial and a cumbersome task. Some of the main requirements on a force field include the accuracy, transferability, and robustness. Unfortunately, there is no generic force field that can reproduce all properties with a unique parameter set.

Mostly the intermolecular interactions and the torsional terms. In this work, our main focus lies on the dispersion interactions. The dispersion interactions are normally described by the intermolecular potentials presented in Section 2.1.2.

The LJ potential function forms the basis for a large number of widely used

molecular force fields, such as OPLS [73], TraPPE [74], NERD [75] force fields, and the TIP [76] and SPC [77] models of water, to mention but a few. The popular coarsegrained MARTINI force field [78] is also based on the LJ representation.

2 SAFT- γ Mie Force Field

2.1 SAFT-VR Mie EoS

The SAFT-VR Mie equation of state (LAFITTE et al., 2013) is the basis for the SAFT- γ Mie coarse grained force field (AVENDAÑO et al., 2011). This EoS was initially developed to describe chain molecule formed from fused Mie segments using the Mie attractive and repulsive potential. The Mie potential is a type of generalized Lennard-Jones potential that can be used to describe explicitly repulsive interactions of different hardness/softness and attractive interactions of different ranges, and is given by:

$$U_{Mie}(r) = \epsilon \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a} \right)^{\left(\frac{\lambda_a}{\lambda_r - \lambda_a} \right)} \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right] \quad (2.1)$$

where ϵ is the potential well depth, σ is the segment diameter, r is the distance between the spherical segments, λ_r is the repulsive exponent and λ_a is the attractive exponent. This equation uses the Barker e Henderson (1976) high perturbation expansion of the Helmholtz free energy up to third order and an improved expression for the radial distribution function (RDF) of Mie monomers at contact to obtain a equation able to give an accurate theoretical description of the vapor-liquid equilibria and second derivative properties (LAFITTE et al., 2013). For a non-associating fluid, the Helmholtz free energy is:

$$\frac{A}{N\kappa_b T} = a = a^{IDEAL} + a^{MONO} + a^{CHAIN} \quad (2.2)$$

2.1.1 Ideal Contribution

The ideal contribution for a mixture is given by:

$$a^{IDEAL} = \sum_{i=1}^{N_c} x_i \ln(\rho_i \Lambda_i^3) - 1 \quad (2.3)$$

where $x_i = N_i/N$ is the molar fraction of component i , $\rho_i = N_i/V$ is the number density, N_i is the number of molecules of each component and Λ_i^3 is de Broglie wavelength.

2.1.2 Monomer Contribution

The monomer contribution describes the interactions between Mie segments and can be expressed for a mixture as:

$$a^{MONO} = \left(\sum_{i=1}^{N_c} x_i m_{s,i} \right) a^M \quad (2.4)$$

In the equation above, $m_{s,i}$ is the number of spherical segments making up the molecule i and a^M is the monomer dimensionless Helmholtz free energy and it is expressed as a third order perturbation expansion in the inverse temperature (BARKER; HENDERSON, 1976):

$$a^M = a^{HS} + \beta a_1 + \beta a_2^2 + \beta a_3^3 \quad (2.5)$$

where $\beta = \kappa_b T$ and a^{HS} is the hard-sphere dimensionless Helmholtz free energy for a mixture :

$$a^{HS} = \frac{6}{\pi \rho_s} \left[\left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1 - \zeta_3) + \frac{3\zeta_1\zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} \right] \quad (2.6)$$

The variable $\rho_s = \rho \sum_i^{N_c} x_i m_{s,i}$ is the total number density of spherical segments and ζ_l are the moments of the number density:

$$\zeta_l = \frac{\pi \rho_s}{6} \left(\sum_{i=1}^{N_c} x_{s,i} d_{ii}^l \right), l = 0, 1, 2, 3 \quad (2.7)$$

where $x_{s,i}$ is the mole fraction of the segments and is related through the mole fraction of component i (x_i) by:

$$x_{s,i} = \frac{m_{s,i} x_i}{\sum_{k=1}^{N_c} m_{s,k} x_k} \quad (2.8)$$

The effective hard-sphere diameter d_{ii} for the segments is:

$$d_{ii} = \int_0^{\sigma_{ii}} (1 - \exp(-\beta U_{ii}^{Mie}(r))) dr \quad (2.9)$$

The integral in Eq. (2.9) is normally obtained by means of Gauss-Legendre with a 5-point quadrature (PAPAIOANNOU et al., 2014). The detailing of the terms of Eq. (2.4) can be found in Lafitte et al. (2013).

2.1.3 Chain Contribution

The chain formation of m_s tangentially bonded Mie segments contribution is based on the first-order perturbation theory (TPT1) (PAPAIOANNOU et al., 2014) and can be expressed as:

$$a^{CHAIN} = - \sum_{i=1}^{N_c} x_i (m_{s,i} - 1) \ln(g_{ii}^{Mie}(\sigma_{ii})) \quad (2.10)$$

The $g_{ij}^{Mie}(\sigma_{ij})$ term correspond to the value of the radial distribution function (RDF) of the hypothetical Mie system evaluated at the effective diameter and can be obtained with the perturbation expansion:

$$g_{ij}^{Mie}(\sigma_{ij}) = g_{d,ij}^{HS}(\sigma_{ij}) \exp[\beta \epsilon g_{1,ij}(\sigma_{ij}) / g_{d,ij}^{HS}(\sigma_{ij}) + (\beta \epsilon)^2 g_{2,ij}(\sigma_{ij}) / g_{d,ij}^{HS}(\sigma_{ij})] \quad (2.11)$$

The other terms in the equations above are explicitly exposed in the original article (LAFITTE et al., 2013).

2.1.4 Ring Contribution

There are two forms for the Helmholtz free energy for rings formed from m_s tangentially bonded segments in the literature. The first one (LAFITTE et al., 2012) considered that the difference between a chain and a ring molecule is that the latter one has one more bond that is connecting the first segment to the last. With this assumption, the Eq. (2.10) can be adapted to rings by:

$$a^{RING} = - \sum_{i=1}^{N_c} x_i m_{s,i} \ln(g_{ii}^{Mie}(\sigma_{ii})) \quad (2.12)$$

According to Lafitte et al. (2012), Eq. (2.12) needs an additional parametrization with molecular simulation data so the EoS can be used in molecular simulations, but this procedure is not the necessary for chain molecules. Recently Müller e Mejía (2017) tried to correct this inconsistency by means of developing the ring free energy based on the work of Müller e Gubbins (1993) who obtained rigorous expressions for molecular geometries of rings of $m_s = 3$ for hard fluids. The final expression developed for the ring dimensionless Helmholtz free energy is:

$$a^{RING} = - \sum_{i=1}^{N_c} x_i (m_{s,i} - 1 + \chi_i \eta_i) \ln(g_{ii}^{Mie}(\sigma_{ii})) \quad (2.13)$$

$\eta_i = m_{s,i} \rho_i \sigma_{ii}^3 / 6$ is the packing fraction and χ_i is a parameter which depends on $m_{s,i}$ and on the geometry of the ring of each component i . For a value of $\chi = 0$ Eq. (2.13) is equal to Eq. (2.10) and the system corresponds to a hard sphere system of triangles when $\chi = 1.3827$. Müller e Mejía (2017) also calculated values of ζ for values of $m_s = 3, m_s = 4, m_s = 5, m_s = 7$ with pseudo-experimental data from molecular dynamics (MD) for a defined pure fluid. The values of χ for each geometry estimated can be seen in the figure below:

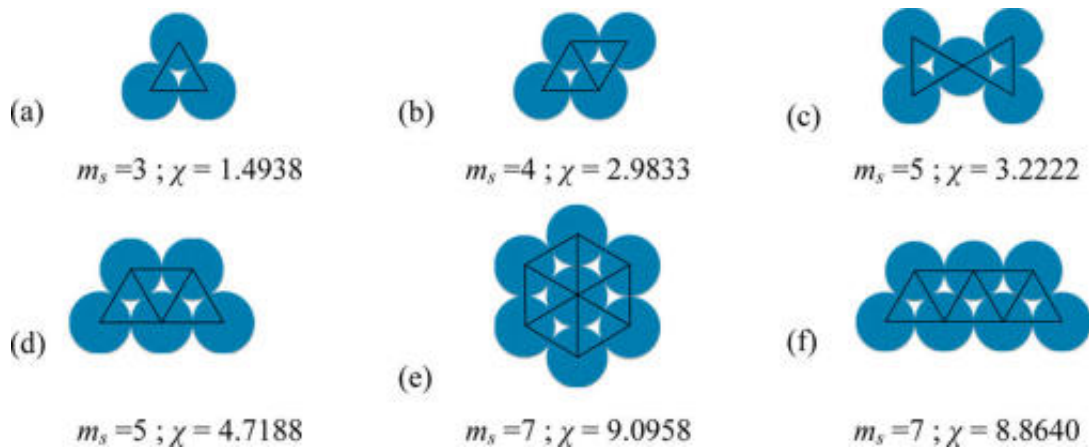


Figure 2.1.1 – Values for parameter χ according to the ring geometry (MÜLLER; MEJÍA, 2017)

2.1.5 Combining rules for the intermolecular potential parameters

Lafitte et al. (2013) also suggested mixing rules for the potential parameters based on Lorentz-Berthelot combining rules (ROWLINSON; SWINTON, 1982):

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (2.14)$$

$$\lambda_{k,ij} - 3 = \sqrt{(\lambda_{k,ii} - 3)(\lambda_{k,jj} - 3)}, k = r, a \quad (2.15)$$

$$\epsilon_{ij} = (1 - k_{ij}) \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (2.16)$$

The k_{ij} is a binary interaction parameter to correct the deviations of the Lorentz-Berthelot rule for chemically distinct compounds. This parameter can also be fitted to experimental data or pseudo experimental data.

2.2 Parameter Estimation for the SAFT- γ Mie Force Field

The SAFT- γ Mie is a force field that uses a coarse graining top down methodology in its parameterization. This methodology aims to obtain the intermolecular parameters from macroscopic experimental data like fluid-phase equilibrium or superficial tension data. The idea is that the force field's parameters estimated with the equation of state can be used on molecular simulations since both the SAFT-VR Mie EoS and the force field use the same explicit intermolecular potential model (Mie potential). This correspondence between models has already been seen for a variety of fluids in which this force field was parameterized and this success in the representation of the properties of real fluids can be imputed to the degrees of freedom of Mie Potential (HERDES; TOTTON; MÜLLER, 2015). This flexibility also provides an exploration of a very large parameter space without using a iterative simulation scheme (AVENDAÑO et al., 2011).

Each substance has initially five parameters to be estimated ($m_s, \sigma, \epsilon, \lambda_r$ and λ_a) according to Eq. (2.1). The number of segments are usually fixed in an integer value so it can be used in the coarse grained simulations. The attractive parameter can also be fixed since there is a high correlation between the attractive and repulsive parameter. Usually, the parameter is fixed in the London value of 6, which is expected to be a good representation of the dispersion scale of most simple fluids that don't have strong polar interactions (RAMRATTAN et al., 2015; HERDES; TOTTON; MÜLLER, 2015). There are two strategies to obtain the parameters of each substance: one is by fitting the Saft-Vr Mie EoS to experimental data as vapor pressure and liquid density and the

other is using correspondent state parametrization. The first one, generally, minimizes the following unweighted least-squares objective function:

$$\min_{\sigma, \epsilon, \lambda_r} F_{obj}(\sigma, \epsilon, \lambda_r) = \sum_{i=1}^{N_p} \left(\frac{P_v^{SAFT}(T_i, \sigma, \epsilon, \lambda_r) - P_v^{exp}(T_i)}{P_v^{exp}(T_i)} \right)^2 + \sum_{i=1}^{N_p} \left(\frac{\rho_l^{SAFT}(T_i, \sigma, \epsilon, \lambda_r) - \rho_l^{exp}(T_i)}{\rho_l^{exp}(T_i)} \right)^2 \quad (2.17)$$

where N_p is the number of experimental points, P_v is the vapor pressure and ρ_l is the saturated liquid density. The minimized properties can also change and other possible properties as superficial tension and speed of sound can also be taken into account. These multiple parameters make it necessary the use of a wide range of experimental data since multiple solutions can be found for the fit. So one need to be careful in deciding the level of coarse graining (i.e. the parameter m_s) and subsequent parameter space that will not result in some physical inconsistencies like a fluid with premature freezing.

Lafitte et al. (2012) suggested that the two corrections factors (c_σ and c_ϵ) should be estimated with simulation data when using Eq. (2.12) for the ring contribution. They are related to the EoS parameters by scaled parameters:

$$\sigma^{scaled} = c_\sigma \sigma^{SAFT} \quad (2.18)$$

$$\epsilon^{scaled} = c_\epsilon \epsilon^{SAFT} \quad (2.19)$$

According to Lafitte et al. (2012), these corrections are necessary because the approximations employed in the EoS theory generate discrepancies between molecular simulations and the EoS results for ring molecules modeled with Eq. (2.12). The objective function for this second estimation is given by:

$$\min_{c_\sigma, c_\epsilon} F_{obj}(c_\sigma, c_\epsilon) = \sum_{i=1}^{N_p} \left(\frac{P_v^{sim}(T_i, \sigma^{SAFT}, \epsilon^{SAFT}) - P_v^{SAFT}(T_i, \sigma^{scaled}, \epsilon^{scaled})}{P_v^{sim}(T_i, \sigma^{SAFT}, \epsilon^{SAFT})} \right)^2 + \sum_{i=1}^{N_p} \left(\frac{\rho_{liq}^{sim}(T_i, \sigma^{SAFT}, \epsilon^{SAFT}) - \rho_{liq}^{SAFT}(T_i, \sigma^{scaled}, \epsilon^{scaled})}{\rho_{liq}^{sim}(T_i, \sigma^{SAFT}, \epsilon^{SAFT})} \right)^2 \quad (2.20)$$

The repulsive parameter is maintained in the value found on the minimization of Eq. (2.17), so the refined values for the force field are:

$$\sigma^{sim} = \sigma^{SAFT} / c_\sigma \quad (2.21)$$

$$\epsilon^{scaled} = \epsilon^{SAFT} / c_\epsilon \quad (2.22)$$

It is interesting to point out that this new parametrization is not necessary when using Eq. (2.13) as the ring contribution. The other method to obtain the force field parameters is the correspondent state parametrization for the EoS SAFT-VR Mie (MEJÍA; HERDES; MÜLLER, 2014). This method considers that the unweighted volume average of the attractive contribution to the Mie intermolecular potential, a_1 , can be given a mean field approximation:

$$a_1 = 2\pi\rho\sigma^3\epsilon\alpha \quad (2.23)$$

The van der Waals constant, α , considering $\lambda_a = 6$ is related by the Mie exponents by:

$$\alpha = \frac{1}{\epsilon\sigma^3} \int_{\sigma}^{\infty} \phi(r)r^2 dr = \frac{\lambda_r}{3(\lambda_r - 3)} \left(\frac{\lambda_r}{6} \right)^{6/(\lambda_r - 6)} \quad (2.24)$$

The parametrization in this method starts by using the experimental acentric factor, ω , for each molecule with a fixed value of m_s to obtain the value of the repulsive exponent with the following Padé series:

$$\lambda_r = \frac{\sum_{i=0} a_i \omega^i}{1 + \sum_{i=1} b_i \omega^i} \quad (2.25)$$

a_i and b_i are dependent parameters of the number of segments and a table with its values is presented in the original paper (MEJÍA; HERDES; MÜLLER, 2014). Substituting λ_r into Eq. (2.24), the van der Waals constant can be found. The reduced critical potential T_c^* can also be related to α by a Padé series:

$$T_c^* = \frac{\sum_{i=0} c_i \alpha^i}{1 + \sum_{i=1} d_i \alpha^i} \quad (2.26)$$

The values of c_i and d_i are also available in the original paper. The reduced temperature of the equation above is used in conjunction with the experimental critical temperature, T_c , to find the energy parameter with the relation below:

$$T_c^* = \frac{\kappa_b T_c}{\epsilon} \quad (2.27)$$

The diameter parameter, however, is not obtained with the critical properties, but with the reduced liquid density, $\rho_{T_r=0.7}$, at the reduced temperature, T_r , of 0.7. This

density is also obtained with a Padé series using parameters obtained by [Mejía, Herdes e Müller \(2014\)](#):

$$\rho_{T_r=0.7}^* = \frac{\sum_{i=0} j_i \alpha^i}{1 + \sum_{i=1} k_i \alpha^i} \quad (2.28)$$

The relation among the equation above, σ and the experimental density is given by:

$$\rho_{T_r=0.7}^* = \rho_{T_r=0.7} \sigma^3 N_{av} \quad (2.29)$$

where N_{av} is The Avogadro number. This correspondent state method has the advantage of only requiring critical data, that it is available for a great range of fluids, and one liquid density point. In addition to that, there is an available online parameter database obtained with this strategy ([ERVIK; MEJÍA; MÜLLER, 2016](#)).

The binary interaction parameter k_{ij} of Eq. (2.16) is necessary to adjust the mixture behaviour of chemically distinct components. Normally, it is fitted to experimental binary vapor liquid equilibrium or superficial tension data with the SAFT-VR Mie EoS ([MÜLLER; MEJÍA, 2017](#); [LOBANOVA et al., 2016](#)). However, [Ervik et al. \(2016\)](#) used molecular simulation results to fit the parameter to the superficial tension data of the mixture water-toluene. The strategy followed by them was to do simulations in three values of k_{ij} and then refine the parameter value until a value in good agreement with the experimental data was found.

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Appendix

APPENDIX A – Quisque libero justo

Quisque facilisis auctor sapien. Pellentesque gravida hendrerit lectus. Mauris rutrum sodales sapien. Fusce hendrerit sem vel lorem. Integer pellentesque massa vel augue. Integer elit tortor, feugiat quis, sagittis et, ornare non, lacus. Vestibulum posuere pellentesque eros. Quisque venenatis ipsum dictum nulla. Aliquam quis quam non metus eleifend interdum. Nam eget sapien ac mauris malesuada adipiscing. Etiam eleifend neque sed quam. Nulla facilisi. Proin a ligula. Sed id dui eu nibh egestas tincidunt. Suspendisse arcu.

APPENDIX B – Nullam elementum urna vel imperdiet sodales elit ipsum pharetra ligula ac pretium ante justo a nulla curabitur tristique arcu eu metus

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Annex

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ANNEX B – Cras non urna sed feugiat cum sociis natoque penatibus et magnis dis parturient montes nascetur ridiculus mus

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ANNEX C – Fusce facilisis lacinia dui

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