

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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Errata sheet

Elemento opcional da [ABNT](#) (2011, 4.2.1.2). Exemplo:

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.

Folha	Linha	Onde se lê	Leia-se
1	10	auto-conclavo	autoconclavo

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2018

*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, antecidas 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 SAFT- γ Mie Force Field

1.1 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:

$$U_{Mie}(r) = \epsilon \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a} \right)^{\left(\frac{\lambda_a}{\lambda_r - \lambda_a} \right)} \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right] \quad (1.1)$$

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_s 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 capable 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:

$$\frac{A}{N\kappa_b T} = a = a^{IDEAL} + a^{MONO} + a^{CHAIN} \quad (1.2)$$

1.1.1 Ideal Contribution

The ideal contribution for a mixture is given by:

$$a^{IDEAL} = \sum_{i=1}^{N_c} x_i \ln (\rho_i \Lambda_i^3) - 1 \quad (1.3)$$

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.

1.1.2 Monomer Contribution

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

$$a^{MONO} = \left(\sum_{i=1}^{N_c} x_i m_{s,i} \right) a^M \quad (1.4)$$

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):

$$a^M = a^{HS} + \beta a_1 + \beta a_2^2 + \beta a_3^3 \quad (1.5)$$

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

$$a^{HS} = \frac{6}{\pi \rho_s} \left[\left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1 - \zeta_3) + \frac{3\zeta_1\zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} \right] \quad (1.6)$$

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:

$$\zeta_l = \frac{\pi \rho_s}{6} \left(\sum_{i=1}^{N_c} x_{s,i} d_{ii}^l \right), l = 0, 1, 2, 3 \quad (1.7)$$

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

$$x_{s,i} = \frac{m_{s,i} x_i}{\sum_{k=1}^{N_c} m_{s,k} x_k} \quad (1.8)$$

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

$$d_{ii} = \int_0^{\sigma_{ii}} (1 - \exp(-\beta U_{ii}^{Mie}(r))) dr \quad (1.9)$$

The integral in Eq. (1.9) is normally obtained by means of Gauss-Legendre with a 5-point quadrature (PAPAIOANNOU et al., 2014). The detailing of the terms of Eq. (1.4) can be found in Lafitte et al. (2013).

1.1.3 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:

$$a^{CHAIN} = - \sum_{i=1}^{N_c} x_i (m_{s,i} - 1) \ln(g_{ii}^{Mie}(\sigma_{ii})) \quad (1.10)$$

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:

$$g_{ij}^{Mie}(\sigma_{ij}) = g_{d,ij}^{HS}(\sigma_{ij}) \exp[\beta \epsilon g_{1,ij}(\sigma_{ij}) / g_{d,ij}^{HS}(\sigma_{ij}) + (\beta \epsilon)^2 g_{2,ij}(\sigma_{ij}) / g_{d,ij}^{HS}(\sigma_{ij})] \quad (1.11)$$

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

1.1.4 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. (1.10) becomes:

$$a^{RING} = - \sum_{i=1}^{N_c} x_i m_{s,i} \ln(g_{ii}^{Mie}(\sigma_{ii})) \quad (1.12)$$

According to Lafitte et al. (2012), Eq. (1.12) 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 ring molecules. Recently Müller e Mejía (2017) tried to correct this inconsistency developing the ring free energy based on the work of Müller e Gubbins (1993) whom obtained rigorous expressions for molecular geometries of rings of $m_s = 3$ for hard fluids. The final expression for the dimensionless Helmholtz free energy is:

$$a^{RING} = - \sum_{i=1}^{N_c} x_i (m_{s,i} - 1 + \chi_i \eta_i) \ln(g_{ii}^{Mie}(\sigma_{ii})) \quad (1.13)$$

where $\eta_i = m_{s,i} \rho_i \sigma_{ii}^3 / 6$ is the packing fraction and χ_i is a parameter which depends on $m_{s,i}$ and the geometry of the ring of each component i . For a value of $\chi = 0$ Eq. (1.13) is equal to Eq. (1.10) and $\chi = 1.3827$ corresponds to a hard sphere system of triangles. Müller e Mejía (2017) also calculated values of ζ for the Saft-VR Mie EoS for the 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 estimated can be seen in the figure below:

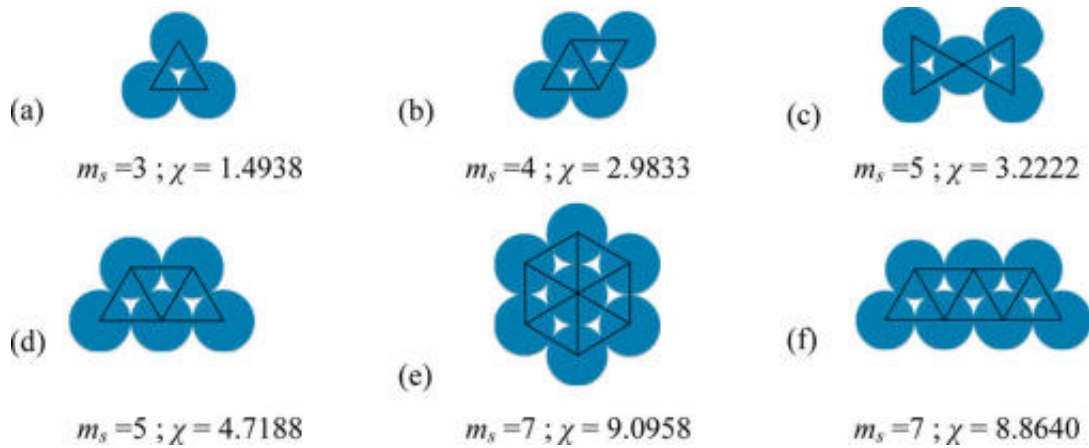


Figure 1.1.1 – Values for parameter χ according to the ring geometry (MÜLLER; MEJÍA, 2017)

1.1.5 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):

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (1.14)$$

$$\lambda_{k,ij} - 3 = \sqrt{(\lambda_{k,ii} - 3)(\lambda_{k,jj} - 3)}, k = r, a \quad (1.15)$$

$$\epsilon_{ij} = (1 - k_{ij}) \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (1.16)$$

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.

1.2 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 your parameterization. This methodology is 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 and, with this approach, one can explore a very large parameter space without using a iterative simulation scheme (AVENDAÑO et al., 2011). 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 can be imputed to the flexibility of the Mie potential due to its degrees of freedom to reproduce the properties of real fluids (HERDES; TOTTON; MÜLLER, 2015).

Each substance has initially five parameters to be estimated ($m_s, \sigma, \epsilon, \lambda_r$ and λ_a) according to Eq. (1.1). 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 in the London value of 6, which is expected to be a good representation of the dispersion scale of most simple fluids, (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:

$$\min_{\sigma, \epsilon, \lambda_r} F_{obj}(\sigma, \epsilon, \lambda_r) = \sum_{i=1}^{N_p} \left(\frac{P_v^{SAFT}(T_i, \sigma, \epsilon, \lambda_r) - P_v^{exp}(T_i)}{P_v^{exp}(T_i)} \right)^2 + \sum_{i=1}^{N_p} \left(\frac{\rho_l^{SAFT}(T_i, \sigma, \epsilon, \lambda_r) - \rho_l^{exp}(T_i)}{\rho_l^{exp}(T_i)} \right)^2 \quad (1.17)$$

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 others properties as superficial tension, speed of sound, compressibility can also be taken into account. This multiple parameters makes 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. (1.12) for the ring contribution. They are related to the EoS parameters by scaled parameters:

$$\sigma^{scaled} = c_\sigma \sigma^{SAFT} \quad (1.18)$$

$$\epsilon^{scaled} = c_\epsilon \epsilon^{SAFT} \quad (1.19)$$

According to Lafitte et al. (2012), this corrections is necessary because the approximations employed in the EoS theory generate discrepancies between molecular simulations and the EoS results for ring molecules modeled with Eq. (1.12). The objective function for this second estimation is given by:

$$\min_{c_\sigma, c_\epsilon} F_{obj}(c_\sigma, c_\epsilon) = \sum_{i=1}^{N_p} \left(\frac{P_v^{sim}(T_i, \sigma^{SAFT}, \epsilon^{SAFT}) - P_v^{SAFT}(T_i, \sigma^{scaled}, \epsilon^{scaled})}{P_v^{sim}(T_i, \sigma^{SAFT}, \epsilon^{SAFT})} \right)^2 + \sum_{i=1}^{N_p} \left(\frac{\rho_{liq}^{sim}(T_i, \sigma^{SAFT}, \epsilon^{SAFT}) - \rho_{liq}^{SAFT}(T_i, \sigma^{scaled}, \epsilon^{scaled})}{\rho_{liq}^{sim}(T_i, \sigma^{SAFT}, \epsilon^{SAFT})} \right)^2 \quad (1.20)$$

Maintaining the repulsive parameter in the value found on the minimization of Eq. (1.17), the refined values for the force field are:

$$\sigma^{sim} = \sigma^{SAFT} / c_\sigma \quad (1.21)$$

$$\epsilon^{scaled} = \epsilon^{SAFT} / c_\epsilon \quad (1.22)$$

It is interesting to add that this new parametrization is not necessary when using Eq. (1.13) as the ring contribution. The other method to obtain force field correspondent state parametrization for the EoS SAFT-VR Mie was developed by [Mejía, Herdes e 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:

$$a_1 = 2\pi\rho\sigma^3\epsilon\alpha \quad (1.23)$$

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

$$\alpha = \frac{1}{\epsilon\sigma^3} \int_{\sigma}^{\infty} \phi(r)r^2 dr = \frac{\lambda_r}{3(\lambda_r - 3)} \left(\frac{\lambda_r}{6} \right)^{6/(\lambda_r - 6)} \quad (1.24)$$

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:

$$\lambda_r = \frac{\sum_{i=0} a_i \omega^i}{1 + \sum_{i=1} b_i \omega^i} \quad (1.25)$$

a_i and b_i are dependent parameters of the number of segments and a table with its values area in the original paper ([MEJÍA; HERDES; MÜLLER, 2014](#)). Substituting λ_r into Eq. (1.24), the van der Waals constant can be found. The reduced critical potential T_c^* can also be related to α by a Padé series:

$$T_c^* = \frac{\sum_{i=0} c_i \alpha^i}{1 + \sum_{i=1} d_i \alpha^i} \quad (1.26)$$

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:

$$T_c^* = \frac{\kappa_b T_c}{\epsilon} \quad (1.27)$$

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 \(2014\)](#):

$$\rho_{T_r=0.7}^* = \frac{\sum_{i=0} j_i \alpha^i}{1 + \sum_{i=1} k_i \alpha^i} \quad (1.28)$$

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

$$\rho_{T_r=0.7}^* = \rho_{T_r=0.7} \sigma^3 N_{av} \quad (1.29)$$

where N_{av} is The Avogadro number. This correspondent state method has the advantage of only critical data, that it is available for a great range of fluids and one liquid density point and, 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} os Eq. (1.16) is necessary to adjust the mixture behaviour. 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. They did simulations in three values of k_{ij} and then refined the parameter 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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Morbi tincidunt posuere arcu. Cras venenatis est vitae dolor. Vivamus scelerisque semper mi. Donec ipsum arcu, consequat scelerisque, viverra id, dictum at, metus. Lorem ipsum dolor sit amet, consectetur adipiscing elit. Ut pede sem, tempus ut, porttitor bibendum, molestie eu, elit. Suspendisse potenti. Sed id lectus sit amet purus faucibus vehicula. Praesent sed sem non dui pharetra interdum. Nam viverra ultrices magna.

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Annex

ANNEX A – Morbi ultrices rutrum lorem.

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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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