

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

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

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

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Professor
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Rio de Janeiro
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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.

Keywords: latex. abntex. text editoration.

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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

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 :

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

where $\rho_s = \rho \sum_{i=1}^{N_c} x_i m_{s,i}$ 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 (PAPAIIOANNOU 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) (PAPAIIOANNOU 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 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. (1.11) 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. (1.11) 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:

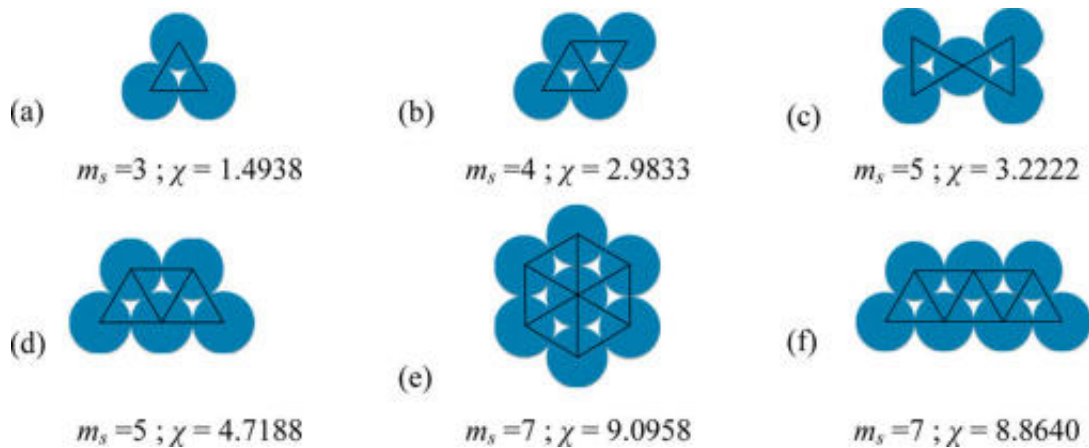


Figure 1.1.1 – Values for parameter χ according to the ring geometry (MÜLLER; MEJÍA, 2017)

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 Force Field is force field that uses a coarse graining top down methodology in your parameterization so the intermolecular parameters are obtained from macroscopic experimental data like fluid-phase equilibrium or superficial tension data. The idea is that the force field's parameters for the molecular simulation can be 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 Mie Potential.

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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.

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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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