

Estimación de parámetros en modelos moleculares de Fluidos Complejos usando técnicas estocásticas de optimización

Carlos Fernando Ospina Trujillo

Universidad Nacional de Colombia

17 de marzo de 2017

Comité evaluador

Coordinador: Delegado del comité asesor

Jurados: jurado 1
jurado 2
jurado 3

Directores: Juan C. Riaño Rojas
Felipe A. Perdomo Hurtado

Esquema de la presentación

Descripción del problema

Motivación

Referencias

Acercamiento a la solución

Modelo

Problema de ajuste

Método numérico

Results

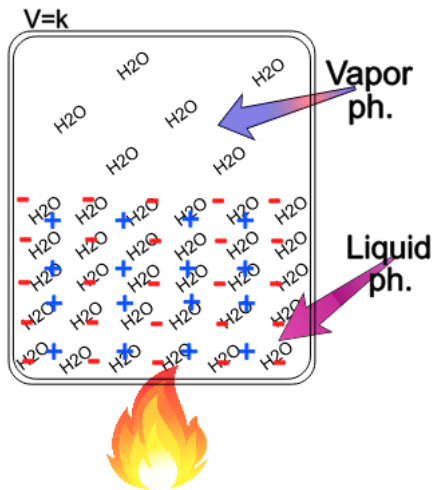
Conclusiones

Descripción del problema

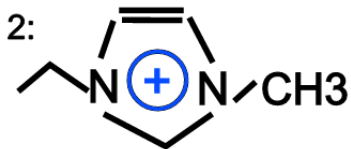
Usar técnicas de optimización estocástica para determinar algunos parámetros que describan un líquido iónico pero desde una perspectiva micromolecular.

- ▶ Técnicas estocásticas de optimización
- ▶ Modelo SAFT de la literatura
- ▶ Estimar los parámetros óptimos

Descripción del problema

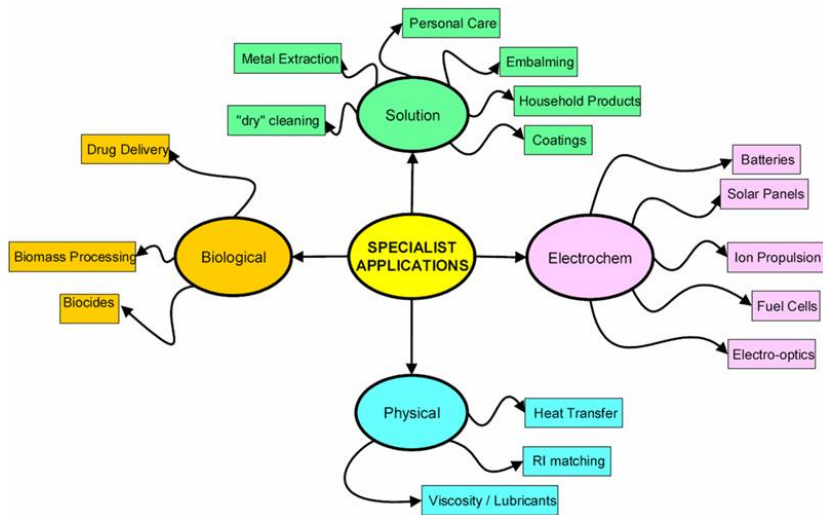


1: Water



3: Br^- Cl^- I^-

Motivación¹



¹Tomado de: <http://lem.ch.unito.it>
visitado el 12 de marzo, 2017

Referencias



Amparo Galindo, Alejandro Gil-Villegas, George Jackson, and Andrew N. Burgess.

SAFT-VRE: Phase behavior of electrolyte solutions with the statistical associating fluid theory for potentials of variable range.

The Journal of Physical Chemistry B, 103(46):10272–10281, 1999.



Felipe A. Perdomo and Alejandro Gil-Villegas.

Molecular thermodynamics of biodiesel fuel compounds.

Fluid Phase Equilibria, 293(2):182 – 189, 2010.



Felipe A. Perdomo, Beatriz M. Millán, and José L. Aragón.

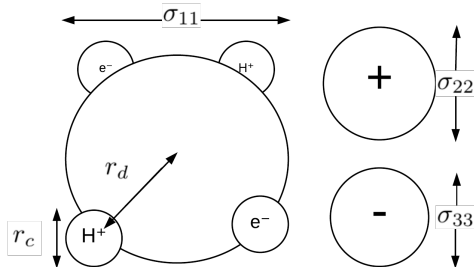
Predicting the physical-chemical properties of biodiesel fuels assessing the molecular structure with the SAFT- γ group contribution approach.

Energy, 72:274 – 290, 2014.

Modelo

water-water:

$$\mu(r) = \begin{cases} +\infty & \text{if } r < r_c, \\ \epsilon_{11}^{HB} & \text{if } r = r_c, \\ 0 & \text{if } r > r_c. \end{cases}$$



ion-ion (Coulomb):

$$F_{23} = \begin{cases} +\infty & \text{if } r < \bar{\sigma}_{avg}, \\ c \frac{q^+ q^-}{r^2} & \text{if } \bar{\sigma}_{avg} \leq r \leq \lambda_{23} \bar{\sigma}_{avg}, \\ 0 & \text{if } r \geq \lambda_{23} \bar{\sigma}_{avg}, \end{cases}$$

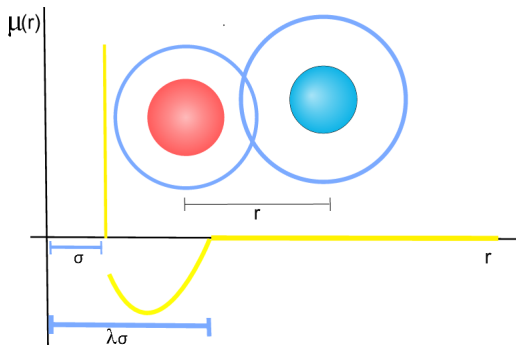
$$\bar{\sigma}_{avg} = \frac{\sigma_{22} + \sigma_{33}}{2}$$

$$\lambda_{ik} = \frac{\lambda_{ii} \sigma_{ii} + \lambda_{kk} \sigma_{kk}}{\sigma_{ii} + \sigma_{kk}}$$

Modelo

water-water:

$$\mu(r) = \begin{cases} +\infty & \text{if } r < r_c, \\ \epsilon_{11}^{HB} & \text{if } r = r_c, \\ 0 & \text{if } r > r_c. \end{cases}$$



ion-ion (Coulomb):

$$F_{23} = \begin{cases} +\infty & \text{if } r < \bar{\sigma}_{avg}, \\ c \frac{q^+ q^-}{r^2} & \text{if } \bar{\sigma}_{avg} \leq r \leq \lambda_{23} \bar{\sigma}_{avg}, \\ 0 & \text{if } r \geq \lambda_{23} \bar{\sigma}_{avg}, \end{cases}$$

$$\bar{\sigma}_{avg} = \frac{\sigma_{22} + \sigma_{33}}{2}$$

$$\lambda_{ik} = \frac{\lambda_{ii} \sigma_{ii} + \lambda_{kk} \sigma_{kk}}{\sigma_{ii} + \sigma_{kk}}$$

Modelo

En términos de la energía libre de Helmholtz:

$$\frac{A}{NkT} = \underbrace{\frac{A^{IDEAL}}{NkT}}_{\text{Energía libre del fluido ideal}} + \underbrace{\frac{A^{MONO}}{NkT}}_{\substack{\text{Interacción} \\ \text{seg.-seg.} \\ \text{Energ. libre residual de monómeros}}} + \underbrace{\frac{A^{ASSOC}}{NkT}}_{\text{Contribución asociación}} + \underbrace{\frac{A^{IONS}}{NkT}}_{\text{Energía libre interacción ión-ión}}$$

Modelo

$$\frac{A^{IDEAL}}{NkT} = \sum_{i=1}^n \underbrace{x_i}_{\substack{\text{fracc.} \\ \text{molar}}} \ln \left(\underbrace{\left(\frac{N_i/V}{\rho_i} \right)}_{\substack{\text{Long} \sim \\ \text{Broglie}}} \underbrace{\Lambda_i^3}_{\substack{\text{Long} \sim \\ \text{Broglie}}} \right) - 1$$

$$\frac{A^{MONO}}{NkT} = \left(\sum_{i=1}^n x_i \underbrace{m_i}_{=1} \right) \underbrace{\frac{A^M}{N_s kT}}_{\substack{\# \text{ seg.} \\ \text{esféricos}}} = \frac{A^M}{NkT} = a^M,$$

$$a^M = \underbrace{a^{HS}}_{\substack{\text{contrib. por} \\ \text{segmento}}} + \beta a_1 + \beta^2 a_2 + \dots,$$

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

Modelo

$$\frac{A^{ASSOC}}{NkT} = \sum_{i=1}^n x_i \left\{ \sum_{a \in s_i} \left(\ln X_{a,i} - \frac{X_{a,i}}{2} \right) + \frac{\#[s_i]}{2} \right\}.$$

$$X_{a,i} = \frac{1}{1 + \sum_{k=1}^n \sum_{b \in s_i, b \neq a} \rho x_k X_{b,k} \underbrace{\Delta_{a,b,i,k}}_{\substack{\text{Caracteriza} \\ \text{asociación}}}.$$

$$\frac{A^{ASSOC}}{NkT} = x_1 \left\{ 4 \left(\ln X_1 - \frac{X_1}{2} \right) + 2 \right\}$$

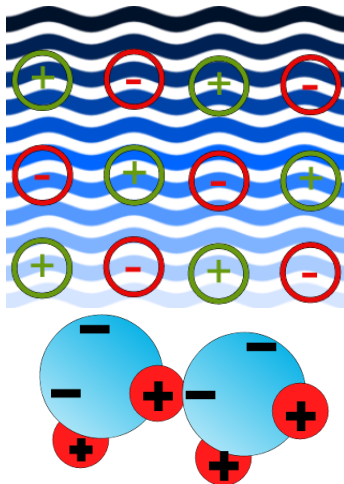
$$X_1 = \frac{-1 + \sqrt{1 + 8\rho x_1 \Delta_{11}}}{4\rho x_1 \Delta_{11}}$$

Modelo

$$\frac{A^{IONS}}{NkT} = \frac{3x^2 + 6x + 2 - 2(1 + 2x)^{3/2}}{12\pi\rho\tilde{\sigma}}$$

$$x = \underbrace{\kappa \sum_{i=2}^n \overbrace{\tilde{x}_i}^{\text{fracción corregida}} \sigma_{ij}}_{\tilde{\sigma}}$$

$$\kappa^2 = \frac{4\pi}{DkT} \sum_{i=2}^n \rho_i q_i^2$$



Problema de ajuste

Ajuste inicial:

$$\arg \min_{\Theta \in \Omega} \left\{ \overbrace{w_1 \sum_{i=1}^{n_1} \underbrace{\left(\frac{T_i^{\text{exp}} - T_i^{\text{calc}}}{T_i^{\text{exp}}} \right)^2}_{f_1}}^{\text{Función objetivo } f} + w_2 \sum_{k=1}^{n_2} \underbrace{\left(\frac{\rho_k^{\text{exp}} - \rho_k^{\text{calc}}}{\rho_k^{\text{exp}}} \right)^2}_{f_2} \right\}$$
$$\Theta = \{\sigma_{22}, \sigma_{33}, \lambda_{22}, \lambda_{33}, \epsilon_{22}, \epsilon_{33}\}$$

Problema de ajuste

¿Cómo determinar T^{calc} y ρ^{calc} ?

- ▶ $\frac{\mu}{kT} = \left[\frac{\partial(Na)}{\partial N_j} \right]_{j=1,2,3}$
- ▶ $\frac{P}{\rho kT} = \sum_{i=1}^n x_i \frac{\mu_i}{kT} - \frac{A}{NkT}$
- ▶ En fase vapor sólo hay solvente

$$\mu_{\text{water}}^L \left(\begin{array}{c} T^{calc} \\ \rho^L \\ \rho^V \end{array} ; \Theta \right) = \mu_{\text{water}}^V \underbrace{\left(\mu_{\text{water}}^L - \mu_{\text{water}}^V \right)^2 + \left(\mu_{\text{IL}}^L \right)^2 + \left(P^L - P^V \right)^2}_{f_{\text{aux},1}}$$
$$\mu_{\text{IL}}^L = \mu_{\text{IL}}^V = 0$$
$$P^L = P^V$$
$$\underbrace{1 - \frac{P}{\rho kT} \left(\sum_{i=1}^n x_i \frac{\mu_i}{kT} - \frac{A}{NkT} \right)^{-1}}_{f_{\text{aux},2}} = 0$$

Método numérico

El problema puede ser definido como uno de optimización continua:

$$\arg \min \{f(x) : x \in \Omega\}$$

donde f tiene dominio Ω .

Método numérico

Hay diferentes métodos para resolver este tipo de problemas:

- ▶ Simulated Annealing
- ▶ Hide and Seek
- ▶ Improving Hit and Run
- ▶ Simplex Simulated Annealing

Método numérico

Simulated Annealing

- 1: Choose randomly an initial point $x_j \in \Omega$, with $j = 0$.
- 2: Choose a random point $x_{new} \in \Omega$, according to certain distribution.
- 3: Generate a random number ρ with uniform distribution from the interval $(0, 1)$.
- 4: According to the cooling schedule, do $T_{j+1} = \tau_{j+1}(x_0, \dots, x_j)$
- 5: Finally,

$$x_{j+1} = \begin{cases} x_{new} & \text{if } \rho < P(x_j, x_{new}, T_{j+1}), \\ x_j & \text{otherwise} \end{cases}$$

- 6: If any stopping criteria is satisfied stop, else return to the step 2.

Método numérico

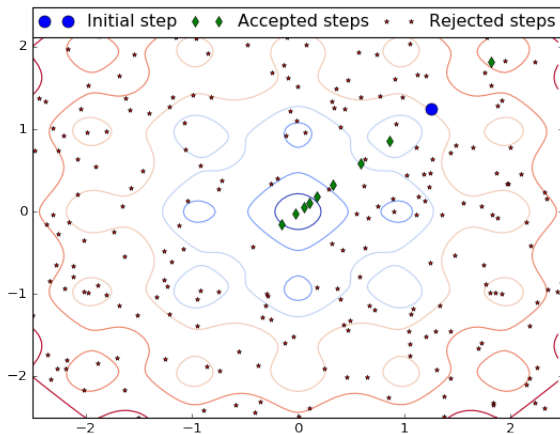


Figura 1: Sampling of Simulated Annealing to obtain the minimum value

Método numérico

Simplex Method

- 1: Sort the vertices as in equation 1.
- 2: Compute the centroid $x_0 = \sum_{i=1}^n x_i / n$.
- 3: Compute the reflected point $x_r = x_0 + \alpha(x_0 - x_{n+1})$.
- 4: **if** $f(x_1) \leq f(x_r) < f(x_n)$, **then**
- 5: **Reflection:** $x_{n+1} \leftarrow x_r$ and go to step 1.
- 6: **else if** $f(x_r) < f(x_1)$, **then**
- 7: compute $x_e = x_0 + \gamma(x_0 - x_{n+1})$.
- 8: **if** $f(x_e) < f(x_r)$ **then**
- 9: **Expansion:** $x_{n+1} \leftarrow x_e$ and go to step 1.
- 10: **else**
- 11: $x_{n+1} \leftarrow x_r$ and got to step 1.
- 12: **end if**
- 13: **else**
- 14: Compute the contracted point $x_c = x_0 + \rho(x_0 - x_{n+1})$,
- 15: **if** $f(x_c) < f(x_{n+1})$ **then**
- 16: **Contraction:** $x_{n+1} \leftarrow x_c$ and go to step 1.
- 17: **else**
- 18: **Reduction:** $x_i = x_1 + \sigma(x_i - x_1) \forall i \in \{2, \dots, n+1\}$ and go to step
- 19: **end if**
- 20: **end if**

Método numérico

$$\begin{aligned} f(x_1) &< \\ f(x_2) &< \\ &\vdots \\ f(x_{n+1}) &< \end{aligned} \quad (1)$$

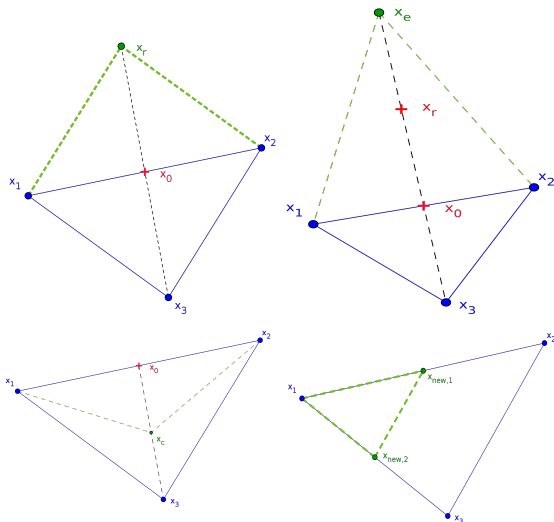


Figura 2: Movements of the Simplex Method

Método numérico

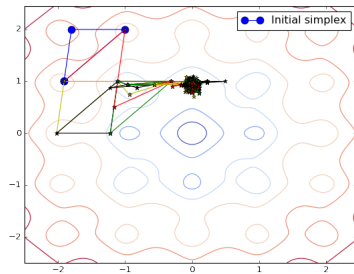
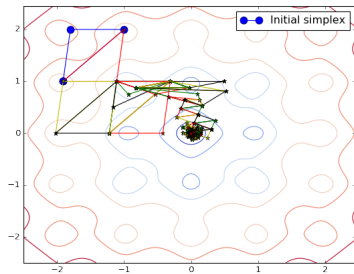
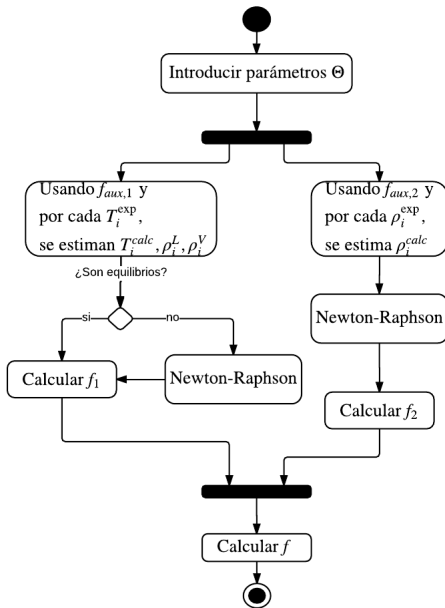


Figura 3: Algunas aproximaciones del Simplex Method

Método numérico

El model presenta un alto grado de sensibilidad, por lo tanto, fue necesario construir un esquema que proporcione evaluaciones precisas de la función objetivo.



Método numérico

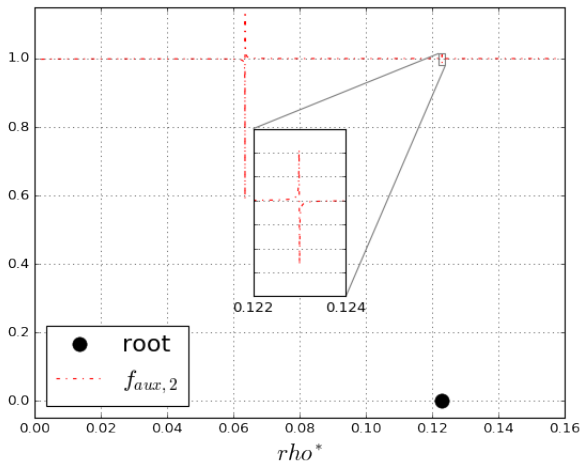


Figura 4: Uno de los inconvenientes...

Resultados

Cuadro 1:
Parámetros
estimados

	+	-
σ_{ii}^*	2.43	2.183
λ_{ii}^*	1.264	2.523
ϵ_{ii}^*	1.643	2.391

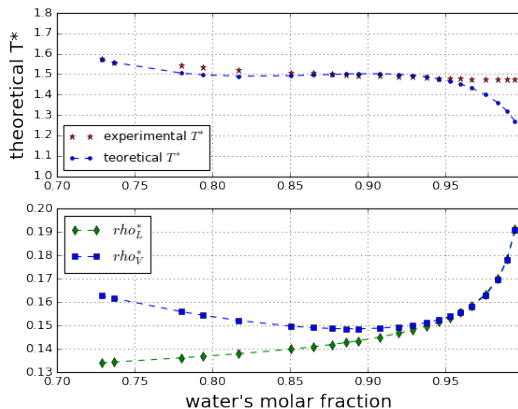


Figura 5: Ajuste

Resultados

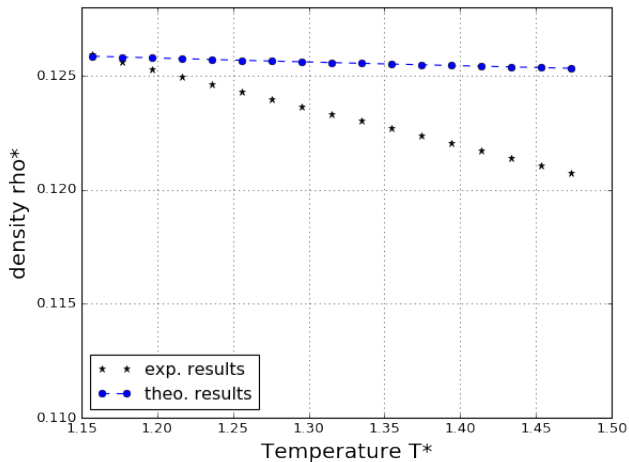


Figura 6: Densidad vs. Temperatura

Resultados

Cuadro 2:
Prediciendo la
densidad...

	+	-
σ_{ii}^*	2.327	2.258
λ_{ii}^*	1.246	2.631
ϵ_{ii}^*	1.647	2.38

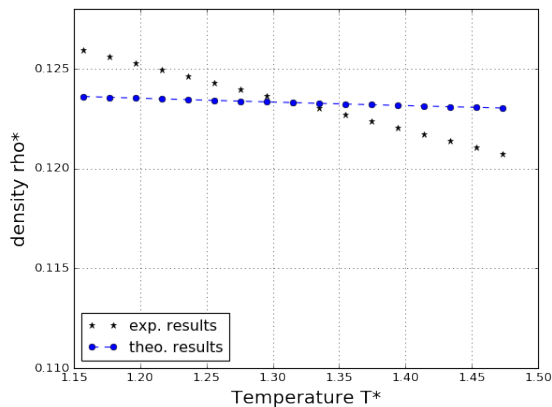


Figura 7: Ajuste de densidad

Resultados

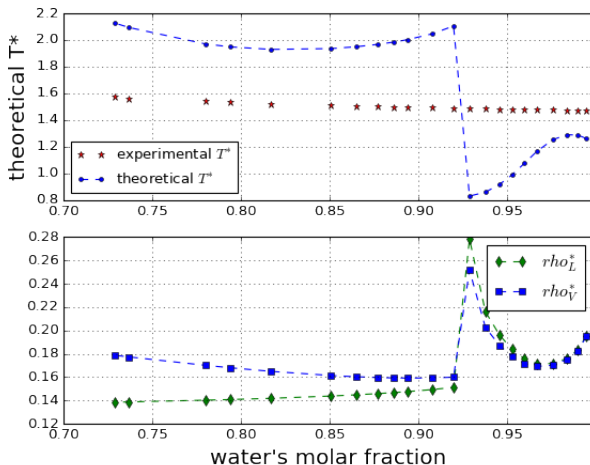


Figura 8: Predicción de los valores de equilibrio

Resultados

Cuadro 3: Con menos datos experimentales

	+	-
σ_{ii}^*	2.443	2.186
λ_{ii}^*	1.232	2.598
ϵ_{ii}^*	1.667	2.279

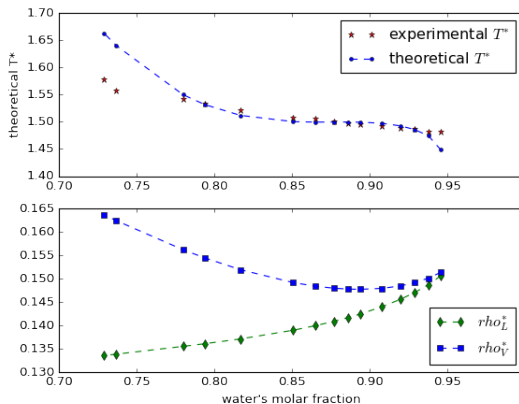


Figura 9: Valores de equilibrio

Conclusiones

- ▶ Uso de técnicas estocásticas
- ▶ Modelo
- ▶ Parámetros