

# **A Second Order Dry Glass Reference Perturbation Theory for Modeling Sorption in Glassy Polymers: Applications to Systems Containing Light Gases, Alcohols, and Water Vapor**

## **Supplementary Information**

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## A. Derivation of the Second Order Dry Glass Reference Perturbation Theory

In the main manuscript, we expanded  $\mu_p$  as follows:

$$\mu_p(\{\rho_j\}, \rho_g(\{\rho_j\})) = \mu_p(\rho_g^0, \{\rho_j\} = 0) + \sum_i^n \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\{\rho_j\}=0} \rho_i + \frac{1}{2} \sum_i^n \sum_k^n \frac{\partial^2 \mu_p}{\partial \rho_i \partial \rho_k} \Big|_{\{\rho_j\}=0} \rho_i \rho_k + \dots \quad (1)$$

It is noteworthy to mention that the partial derivatives in equation 1 do NOT hold  $\rho_g$  constant. Using chain rule, the first order derivatives of  $\mu_p$  can be written as:

$$\frac{\partial \mu_p}{\partial \rho_i} \Big|_{\rho_j \neq i} = \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\rho_g, \rho_j \neq i} + \frac{\partial \mu_p}{\partial \rho_g} \Big|_{\{\rho_j\}} \frac{\partial \rho_g}{\partial \rho_i} \Big|_{\rho_j \neq i} \quad (2)$$

While the second-order derivatives are expressed as:

$$\frac{\partial^2 \mu_p}{\partial \rho_k \partial \rho_i} \Big|_{\rho_j \neq k} = \frac{\partial}{\partial \rho_k} \left( \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\rho_g, \rho_j \neq i} \right)_{\rho_j \neq k} + \frac{\partial}{\partial \rho_k} \left( \frac{\partial \mu_p}{\partial \rho_g} \Big|_{\{\rho_j\}} \right)_{\rho_j \neq k} \frac{\partial \rho_g}{\partial \rho_i} \Big|_{\rho_j \neq i} + \frac{\partial \mu_p}{\partial \rho_g} \Big|_{\{\rho_j\}} \frac{\partial^2 \rho_g}{\partial \rho_k \partial \rho_i} \Big|_{\rho_j \neq k} \quad (3)$$

Where :

$$\frac{\partial}{\partial \rho_k} \left( \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\rho_g, \rho_j \neq i} \right)_{\rho_j \neq k} = \frac{\partial^2 \mu_p}{\partial \rho_k \partial \rho_i} \Big|_{\rho_g, \rho_j \neq k} + \frac{\partial^2 \mu_p}{\partial \rho_g \partial \rho_i} \Big|_{\{\rho_j\}} \frac{\partial \rho_g}{\partial \rho_k} \Big|_{\rho_j \neq k} \quad (4)$$

We adopt the following notation for the limits of the derivatives taken at infinite dilution:

$$\lim_{\{\rho_j\} \rightarrow 0} \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\rho_j \neq i} = \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\{\rho_j\}=0} \quad (5)$$

$$\lim_{\{\rho_j\} \rightarrow 0} \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\rho_g, \rho_j \neq i} = \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\rho_g^0, \{\rho_j\}=0} \quad (6)$$

At infinite dilution, we defined the glassy density first-order derivatives as follows:

$$\frac{\partial \rho_g}{\partial \rho_i} \Big|_{\{\rho_j\}=0} = 0 \quad , \quad \forall i \quad (7)$$

Thus, the first and second order derivatives of  $\mu_p$  in equation 1 reduce to:

$$\frac{\partial \mu_p}{\partial \rho_i} \Big|_{\{\rho_j\}=0} = \frac{\partial \mu_p}{\partial \rho_i} \Big|_{\rho_g^0, \{\rho_j\}=0} \quad (8)$$

$$\left. \frac{\partial^2 \mu_p}{\partial \rho_k \partial \rho_i} \right|_{\{\rho_j\}=0} = \left. \frac{\partial^2 \mu_p}{\partial \rho_k \partial \rho_i} \right|_{\rho_g^0, \{\rho_j\}=0} + \left. \frac{\partial \mu_p}{\partial \rho_g} \right|_{\rho_g^0, \{\rho_j\}=0} \left. \frac{\partial^2 \rho_g}{\partial \rho_k \partial \rho_i} \right|_{\{\rho_j\}=0} \quad (9)$$

To resolve equation 9, the second order glassy density derivative at infinite dilution must be defined. In this work, we assume that it is determined as follows:

$$\left. \frac{\partial^2 \rho_g}{\partial \rho_k \partial \rho_i} \right|_{\{\rho_j\}=0} = -(1 - \gamma_{ik}) \frac{\left. \frac{\partial^2 \mu_p}{\partial \rho_k \partial \rho_i} \right|_{\rho_g^0, \{\rho_j\}=0}}{\left. \frac{\partial \mu_p}{\partial \rho_g} \right|_{\rho_g^0, \{\rho_j\}=0}} \quad (10)$$

Therefore:

$$\left. \frac{\partial^2 \mu_p}{\partial \rho_k \partial \rho_i} \right|_{\{\rho_j\}=0} = \gamma_{ik} \left. \frac{\partial^2 \mu_p}{\partial \rho_k \partial \rho_i} \right|_{\rho_g^0, \{\rho_j\}=0} \quad (11)$$

Where  $\gamma_{ik}$  is a second-order adjustable parameter. Finally, by truncating the expansion in equation 1 at the second order and substituting in equations 8 and 11, a quadratic approximation of the polymer's chemical potential around the dry polymer's density is obtained:

$$\mu_p(\{\rho_j\}, \rho_g(\{\rho_j\})) \approx \mu_p(\rho_g^0, \{\rho_j\} = 0) + \sum_i^n \left. \frac{\partial \mu_p}{\partial \rho_i} \right|_{\rho_g^0, \{\rho_j\}=0} \rho_i + \frac{1}{2} \sum_i^n \sum_k^n \gamma_{ik} \left. \frac{\partial^2 \mu_p}{\partial \rho_i \partial \rho_k} \right|_{\rho_g^0, \{\rho_j\}=0} \rho_i \rho_k \quad (12)$$

## B. Analytical Derivatives via Symbolic Differentiation for the PC-SAFT Equation of State

The analytical derivatives are generated using the symbolic mathematics package SymEngine [1] in Python. Once the symbolic expressions are obtained, they are converted into numerical functions using a C++ wrapper for fast computation. This approach eliminates the need to manually code individual derivatives. Instead, only the expression for the Helmholtz free energy is coded, and all other derivatives are automatically computed through symbolic differentiation.

## C. Resolving The Association Contribution to The Chemical Potential & Its Derivatives

The unbonded site fractions  $X_A^{(i)}$  and  $Y_B^{(i)}$  and their derivatives are required to determine the association free energy ( $\tilde{a}^{HB}$ ) and its derivatives. To resolve the site fraction quantities, the following equations are solved:

$$f_x^{(i)} = X_A^{(i)} \left( 1 + \sum_j \rho_j \Delta_{A_i B_j} Y_B^{(j)} \right) - 1 = 0 \quad (13)$$

$$f_y^{(i)} = Y_B^{(i)} \left( 1 + \sum_j \rho_j \Delta_{A_i B_j} X_A^{(j)} \right) - 1 = 0 \quad (14)$$

This set of equations can be concatenated into vector  $\mathbf{F}$ , which is a function of the site vector  $\mathbf{X}$  and the density vector  $\boldsymbol{\rho}$ :

$$\boldsymbol{\rho} = [\rho_1 \quad \dots \quad \rho_n]^T \quad (15)$$

$$\mathbf{X} = [X_A^{(1)} \quad \dots \quad X_A^{(n)} \quad Y_B^{(1)} \quad \dots \quad Y_B^{(n)}]^T \quad (16)$$

$$\mathbf{F}(\mathbf{X}, \boldsymbol{\rho}) = [f_x^{(1)} \quad \dots \quad f_x^{(n)} \quad f_y^{(1)} \quad \dots \quad f_y^{(n)}]^T = \mathbf{0} \quad (17)$$

Note that  $n$  here also includes the polymer. In a nested loop,  $\boldsymbol{\rho}$  is solved in the outer loop, while  $\mathbf{X}$  is solved in the inner loop. Once the inner loop converges to solution  $\mathbf{X}^*$ , the derivative of  $\mathbf{X}^*$  with respect to  $\boldsymbol{\rho}$  can be computed from the following system of linear equations:

$$\left. \frac{\partial \mathbf{F}}{\partial \mathbf{X}} \right|_{\mathbf{X}^*} \left. \frac{\partial \mathbf{X}}{\partial \boldsymbol{\rho}} \right|_{\mathbf{X}^*} + \left. \frac{\partial \mathbf{F}}{\partial \boldsymbol{\rho}} \right|_{\mathbf{X}^*} = \mathbf{0} \quad (18)$$

From there, the association contribution to the chemical potentials ( $\boldsymbol{\mu}^{HB} \in \mathbb{R}^{1 \times n}$ ) can be calculated:

$$\frac{1}{kT} \boldsymbol{\mu}^{HB} = \left( \frac{\partial(\rho \tilde{a}^{HB})}{\partial \mathbf{X}} \right)_{\boldsymbol{\rho}} \frac{\partial \mathbf{X}}{\partial \boldsymbol{\rho}} + \left( \frac{\partial(\rho \tilde{a}^{HB})}{\partial \boldsymbol{\rho}} \right)_{\mathbf{X}} \quad (19)$$

For our purposes, we only require the derivatives of  $\mu_p^{HB}$  (i.e. the polymer's association chemical potential), thus, the Jacobian of  $\mu_p^{HB}$  is:

$$\mathbf{J} = \left( \frac{\partial \mu_p^{HB}}{\partial \mathbf{X}} \right)_{\boldsymbol{\rho}} \frac{\partial \mathbf{X}}{\partial \boldsymbol{\rho}} + \left( \frac{\partial \mu_p^{HB}}{\partial \boldsymbol{\rho}} \right)_{\mathbf{X}} \quad (20)$$

The Hessian matrix, on the other hand, is computed as follows:

$$\mathbf{M} = \mathbf{J}^T \quad (21)$$

$$\mathbf{H} = \left( \frac{\partial \mathbf{M}}{\partial \mathbf{X}} \right)_{\boldsymbol{\rho}} \frac{\partial \mathbf{X}}{\partial \boldsymbol{\rho}} + \left( \frac{\partial \mathbf{M}}{\partial \boldsymbol{\rho}} \right)_{\mathbf{X}} \quad (22)$$

In this work, the approximation  $X_A^{(i)} = Y_B^{(i)}$  was made. This assumption is reasonable for the systems investigated, as both site types in component  $i$  are equally likely to form a bond. This simplification reduces the complexity of computing the association contribution. For further details, see references [2] and [3].

## References

- [1] J. Ma, N. Sai, L. Keegan, I. Fernando, P. Schmitteckert, R. Nordgren, A. Edgington, B. Dahlgren, T. Barrett, SymEngine, 2021. URL: <https://github.com/symengine/symengine>.
- [2] S. H. Huang, M. Radosz, Equation of state for small, large, polydisperse, and associating molecules, *Industrial & Engineering Chemistry Research* 29 (1990) 2284–2294.
- [3] K. Mejbri, A. Taieb, A. Bellagi, Phase equilibria calculation of binary and ternary mixtures of associating fluids applying PC-SAFT equation of state, *The Journal of Supercritical Fluids* 104 (2015) 132–144.