

Outline

- o Bubble/Dew Calculations using MRL

Making the function for G^E realistic:

- o 11.4 Van der Waals perspective
 - Van Laar
 - Scatchard/Hildebrand
 - Flory, Flory-Huggins
- o 11.5 Theory - Skip
- o 11.6 Local Composition Theory
 - Wilson
 - UNIQUAC
 - UNIFAC

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11.4 Van der Waals perspective

Regular Solutions ($V^E = 0, S^E = 0$)

energetics of mixing are described by the same energy equation for mixtures that we previously developed in discussing the simple basis for mixing rules.

$$U - U^{ig} = -\rho \sum \sum x_i x_j a_{ij} \quad \text{pg 322} \quad \frac{U - U^{ig}}{RT} = \frac{-a\rho}{RT}$$

Noting that $1/\rho = V = \sum x_i V_i$ according to “regular solution theory,”

$$a = \sum \sum x_i x_j a_{ij}$$

$$(U - U^{ig}) = \frac{-\sum \sum x_i x_j a_{ij}}{\sum x_i V_i}$$

For the pure fluid, taking the limit as $x_i \rightarrow 1$,

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$$(U - U^{ig})_i = -\frac{a_{ii}}{V_i} \Rightarrow (U^{is} - U^{ig}) = -\sum \frac{x_i a_{ii}}{V_i}$$

For a binary mixture, subtracting the ideal solution result to get the excess energy gives,

$$U^E = x_1 \frac{a_{11}}{V_1} + x_2 \frac{a_{22}}{V_2} - \left(\frac{x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}}{x_1 V_1 + x_2 V_2} \right)$$

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van Laar

$$Q \equiv \left[\frac{\sqrt{a_{11}}}{V_1} - \frac{\sqrt{a_{22}}}{V_2} \right]^2 \Rightarrow U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} Q$$

$$G^E = U^E = \frac{A_{12} A_{21} x_1 x_2}{(x_1 A_{12} + x_2 A_{21})} \quad 11.27$$

$$\ln \gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12} x_1}{A_{21} x_2} \right]^2}$$

$\ln \gamma_2$ 11.28
exchange subscripts

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Fitting Van Laar to a single experiment:

$$A_{12} = \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right]^2$$

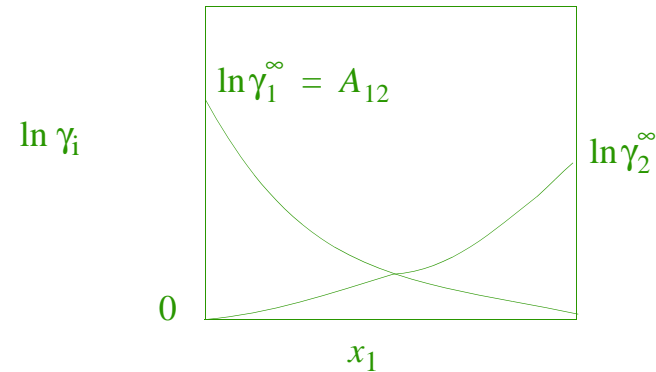
$$A_{21} = \ln \gamma_2 \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right]^2$$

Azeotrope point can be used. See example 11.6

$$y_i P = x_i \gamma_i P_i^{sat} \quad \gamma_i = \frac{y_i P}{x_i P_i^{sat}} = \frac{P}{P_i^{sat}}$$

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Infinite dilution can be used. See example 11.7



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Scatchard Hildebrand

$$a_{12} = \sqrt{a_{11} a_{22}}$$

$$U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} \left(\frac{a_{11}}{V_1^2} + \frac{a_{22}}{V_2^2} - 2 \sqrt{\frac{a_{11} a_{22}}{V_1^2 V_2^2}} \right)$$

$$U^E = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} \left(\frac{\sqrt{a_{11}}}{V_1} - \frac{\sqrt{a_{22}}}{V_2} \right)^2$$

$$G^E = U^E = \Phi_1 \Phi_2 \delta_1 - \delta_2 \mathbf{f}^2 (x_1 V_1 + x_2 V_2)$$

$$G^E = U^E = \Phi_1 \Phi_2 \delta_1 - \delta_2 \mathbf{f}^2 (x_1 V_1 + x_2 V_2)$$

$\Phi_i \equiv x_i V_i / \sum x_i V_i$ is known as the "volume fraction"

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$\delta_i \equiv \sqrt{a_{ii}} / V_i$ is known as the "solubility parameter"

$$\delta_i \equiv \sqrt{\frac{\Delta U^{vap}}{V_i}} = \sqrt{\frac{\Delta H^{vap} - RT}{V_i}}$$

This is a predictive technique valid for nonpolar substances. See table 11.1 for parameters.

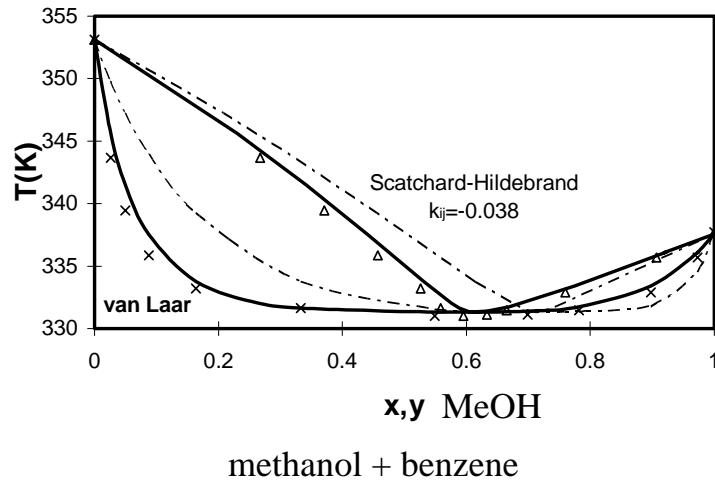
Also can make adjustable.

$$a_{12} = \sqrt{a_{11} a_{22}} (1 - k_{12})$$

$$RT \ln \gamma_1 = V_1 \Phi_2^2 [(\delta_1 - \delta_2)^2 + 2k_{12} \delta_1 \delta_2]$$

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Van Laar and Scatchard-Hildebrand



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Flory's Equation

Recall Ideal Solution result (pg 95)



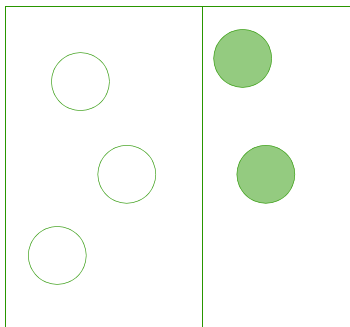
permit mixing

$$\Delta \underline{S}_1 = n_1 R \ln \frac{V_T}{V_1^i} = n_{tot} x_1 R \ln \frac{V_T}{V_1^i}$$

$$\Delta \underline{S}_2 = n_2 R \ln \frac{V_T}{V_2^i} = n_{tot} x_2 R \ln \frac{V_T}{V_2^i}$$

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$$\Delta \underline{S} = \Delta \underline{S}_1 + \Delta \underline{S}_2 = n_{tot} R \left(x_1 \ln \frac{V_T}{V_1^i} + x_2 \ln \frac{V_T}{V_2^i} \right)$$



free volume
(not occupied)

$$V_{f,i} = n_i V_i \lambda$$

$$V_f = (n_1 V_1 + n_2 V_2) \lambda$$

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$$\Delta \underline{S} = nR \left(x_1 \ln \left(\frac{(x_1 V_1 + x_2 V_2) \lambda}{x_1 V_1 \lambda} \right) + x_2 \ln \left(\frac{(x_1 V_1 + x_2 V_2) \lambda}{x_2 V_2 \lambda} \right) \right)$$

$$\Delta \underline{S}^{is} = nR (x_1 \ln x_1 + x_2 \ln x_2)$$

$$S^E = S - S^{is} = (S - \sum x_i S_i) - (S^{is} - \sum x_i S_i) = \Delta \underline{S} - \Delta \underline{S}^{is}$$

athermal

$$G^E = H^E - TS^E = RT \left(x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} \right)$$

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Flory-Huggins Model

$$G^E = RT \left(x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} \right) + \Phi_1 \Phi_2 (x_1 + x_2 R) \chi RT$$

Flory

$$R = \frac{V_2}{V_1}$$

Scatchard-Hildebrand

$$\chi = \frac{V_1 (\delta_1 - \delta_2)^2}{RT}$$

$$\chi = 0 \quad \text{athermal}$$

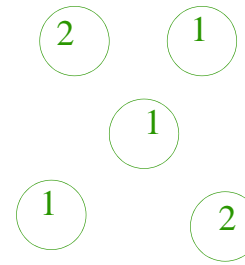
However χ usually nonzero even with $H^E = 0$
(compensate for error in Flory)

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11.6 Local composition models (nonrandom)

Common Features

- o Lattice Model - Fixed number of neighbors = 10
- o Uses $G^E = A^E$ approximation (good)
- o Local Composition



x_{21} - 2's around 1

x_{11} - 1's around 1

x_{12} - 1's around 2

x_{22} - 2's around 2

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$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \Omega_{21} \quad \frac{x_{12}}{x_{22}} = \frac{x_1}{x_2} \Omega_{12}$$

- o Two-fluid Theory

$$(U - U^{ig}) = x_1 (U - U^{ig})^{(1)} + x_2 (U - U^{ig})^{(2)}$$

$$U^E = \frac{N_A z}{2} \left[\frac{x_1 x_2 \Omega_{21} (\epsilon_{21} - \epsilon_{11})}{x_1 + x_2 \Omega_{21}} + \frac{x_2 x_1 \Omega_{12} (\epsilon_{12} - \epsilon_{22})}{x_1 \Omega_{12} + x_2} \right]$$

$$\frac{A^E}{RT} = \int \frac{-U^E}{RT} \frac{dT}{T} + C$$

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Wilson's equation

$$\Omega_{12} = \Lambda_{21} = \frac{V_1}{V_2} \exp\left(\frac{-A_{21}}{RT}\right)$$

integrate U^E to get $A^E = G^E$ (Eqn 11.85)

differentiate G^E to get γ expressions

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2} \right)$$

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UNIQUAC

$$\Omega_{ij} = \frac{q_i}{q_j} \exp\left(\frac{-N_A z(\epsilon_{ij} - \epsilon_{jj})}{2RT}\right) = \frac{q_i}{q_j} \exp\left(\frac{-a_{ij}}{T}\right) = \frac{q_i}{q_j} \tau_{ij}$$

q = surface area of molecule

$$r_i = \text{volume (look up)} \quad \sum_{\text{groups}} v_k R_k$$

$$q_i = \text{surface area (look up)} \quad \sum_{\text{groups}} v_k Q_k$$

$$\theta_i = \text{surface area fractions} \quad (x_i q_i) / (\sum x_i q_i)$$

$$\tau_{ij} = \exp\left(\frac{-a_{ij}}{T}\right) \text{ parameter}$$

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$$\frac{G^E}{RT} = x_1 \ln \frac{\Phi_1}{\phi_1} + x_2 \ln \frac{\Phi_2}{\phi_2} - 5 \left[q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2} \right] - q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_1 \tau_{12} + \theta_2)$$

Flory correction to Flory
} comb
} resid

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$$\ln \gamma_1 = \ln \frac{\Phi_1}{x_1} + \left(1 - \frac{\Phi_1}{x_1}\right) - 5q_1 \left[\ln \frac{\Phi_1}{\theta_1} + \left(1 - \frac{\Phi_1}{\theta_1}\right) \right] + q_1 \left[1 - \ln(\theta_1 + \theta_2 \tau_{21}) - \frac{\theta_1}{\theta_1 + \theta_2 \tau_{21}} - \frac{\theta_2 \tau_{12}}{\theta_1 \tau_{12} + \theta_2} \right]$$

$$\ln \gamma_2 = \ln \frac{\Phi_2}{x_2} + \left(1 - \frac{\Phi_2}{x_2}\right) - 5q_2 \left[\ln \frac{\Phi_2}{\theta_2} + \left(1 - \frac{\Phi_2}{\theta_2}\right) \right] + q_2 \left[1 - \ln(\theta_1 \tau_{12} + \theta_2) - \frac{\theta_1 \tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\theta_2}{\theta_1 \tau_{12} + \theta_2} \right]$$

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Group parameters for the UNIFAC and UNIQUAC equations.

AC in the table means aromatic carbon. (DIFFERS SLIGHTLY FROM TEXT)

Main Group	Sub-group	R(rel.vol.)	Q(rel.area)	Example
CH2	CH3	0.9011	0.8480	n-hexane: 4 CH2+2 CH3 isobutane: 1CH+3 CH3 neopentane: 1C+ 4 CH3
	CH2	0.6744	0.5400	
	CH	0.4469	0.2280	
	C	0.2195	0	
C=C	CH2=CH	1.2454	1.1760	1-hexene: 1 CH2=CH+3 CH2+1 CH3
	CH=CH	1.1167	0.8670	2-hexene: 1 CH=CH+2 CH2+2 CH3
ACH	CH2=C	1.1173	0.9880	benzene: 6ACH benzoic acid: 5ACH+1AC+1COOH toluene: 5ACH+1ACCH3 ethylbenzene: 5ACH+1ACCH2+1CH2
	CH=C	0.8886	0.6760	
	C=C	0.6605	0.4850	
	ACH	0.5313	0.4000	
	AC	0.3652	0.1200	
ACCH2	ACCH3	1.2663	0.9680	ethylbenzene: 5ACH+1ACCH2+1CH2
	ACCH2	1.0396	0.6600	
OH	ACCH	0.8121	0.3480	n-propanol: 1OH+1 CH3+2 CH2
	OH	1.0000	1.2000	

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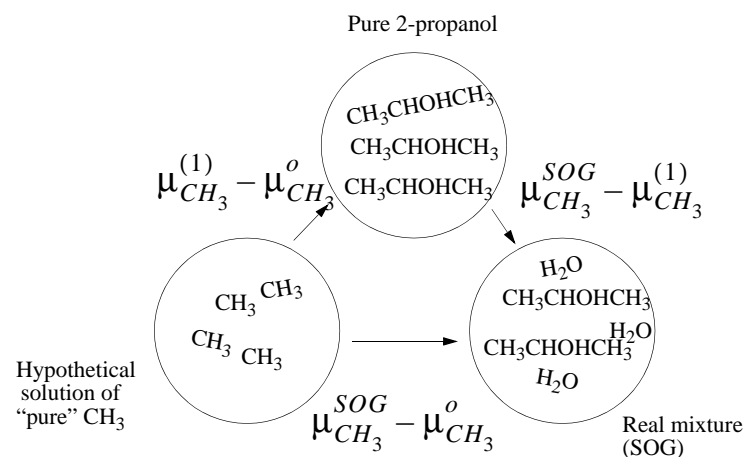
Group parameters for the UNIFAC and UNIQUAC equations.

AC in the table means aromatic carbon. (DIFFERS SLIGHTLY FROM TEXT)

CH3O	CH3OH	1.4311	1.4320	methanol is an independent group
H				
water	H2O	0.9200	1.4000	water is an independent group
furfural	furfural	3.1680	2.4810	furfural is an independent group
DOH	(CH2OH) ₂	2.4088	2.2480	ethylene glycol is an independent group
ACOH	ACOH	0.8952	0.6800	phenol: 1ACOH+5ACH
CH2CO	CH3CO	1.6724	1.4880	dimethylketone: 1 CH3CO+CH3
	CH2CO	1.4457	1.1800	diethylketone=1 CH2CO+2 CH3+1 CH2
CHO	CHO	0.9980	0.9480	acetaldehyde: 1CHO+1 CH3
CCOO	CH2COO	1.9031	1.7280	methyl acetate: 1 CH3COO+1 CH3
	CH2COO	1.6764	1.4200	methyl propanate: 1 CH2COO+2 CH3
COOH	COOH	1.31013	1.2240	benzoic acid: 5ACH+1AC+1COOH

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UNIFAC



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$$\ln \gamma_k = \ln \gamma_k^{COMB} + \ln \gamma_k^{RES}$$

$\ln \gamma_k^{COMB}$ as UNIQUAC

$$\frac{\mu_{CH_3}^{SOG} - \mu_{CH_3}^{(1)}}{RT} = \frac{\mu_{CH_3}^{SOG} - \mu_{CH_3}^o}{RT} - \frac{\mu_{CH_3}^{(1)} - \mu_{CH_3}^o}{RT} = \ln \Gamma_{CH_3} - \ln \Gamma_{CH_3}^{(1)}$$

$$\begin{aligned} \text{IPA} \quad \mu_1 &= 2\mu_{CH_3}^{SOG} + \mu_{CH}^{SOG} + \mu_{OH}^{SOG} && \text{mixture} \\ \mu_1^o &= 2\mu_{CH_3}^{(1)} + \mu_{CH}^{(1)} + \mu_{OH}^{(1)} && \text{pure IPA} \end{aligned}$$

$$\ln \gamma_1^{resid} = \frac{\mu_1 - \mu_1^o}{RT} = \sum_m v_m^{(1)} [\ln \Gamma_m - \ln \Gamma_m^{(1)}]$$

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	Group Variable	Molecular Variable
volume	R	r
surface area	Q	q
activity coefficient	Γ	γ
surface fraction	Θ	θ
energy variable	Ψ_{ij}	τ_{ij}
energy parameter	a_{ij}	a_{ij}
mole fraction	X	x

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compare to UNIQUAC eqns

$$\ln \Gamma_m = Q_m \left[1 - \ln \sum_i \Theta_i \Psi_{im} - \sum_j \frac{\Theta_j \Psi_{mj}}{\sum_i \Theta_i \Psi_{ij}} \right]$$

$$\Theta_j = (\text{surface area fraction of group } j) \equiv \frac{X_j Q_j}{\sum_i X_i Q_i}$$

$$\Psi_{mj} = \frac{\exp\left(\frac{-a_{mj}}{T}\right) \sum_i v_j^{(i)} x_i}{\sum_{\text{molecules } i} \sum_{\text{groups } k} v_k^{(i)} x_i} X_j$$