Thermodynamics of phase transitions for pure substances and mixtures

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Abstract

This paper presents in a concise way the mathematical models and experimental data of phase transitions of pure substances and solutions with new ansatz and calculation methods.
In chap.1 and chap.2 we deal with the theoretical basics of solutions and mixtures.
In chap.3 , the theory of equations-of-state is formulated, and in chap.4 the calculation results for four pure substances are presented and commented.
In chap.5, the equation-of-state and mixing rules for mixtures are formulated, and the calculation results for an example solution (benzene-ethanol) are discussed and compared with measured values.
Chap.6 deals with the theory of ionic solutions., and in chap. 7 we present the thermodynamics of solutions based on the Landau ansatz.
The paper introduces two novel methods.

- Exact algebraic solution for phase diagrams based on Peng-Robinson and Mie-Grueneisen equation-of-state
- A new ansatz for mixture phase diagrams based on the weighted sum of partial pressures

Contents

Introduction

Equations-of-state (eos) are an area, which is of considerable theoretical, but also technological importance.
Eos for fluid-gas phase are relatively well-understood, starting with the famous vdWaals equation.
There are several general extensions of vdWaals eos, which are in satisfactory agreement with measurements.
The best is arguably Peng-Robinson eos with 3 parameters and a precision of about 10%.
Beside this, there are much better individual numerical approximations for selected substances, e.g. water.
Eos for solids are few, most prominent is Mie-Grueneisen eos.
For saturation curves however, the situation is quite different.
For fluid-gas saturation curves, there is only one closed solution, namely Lekner's solution based on the vdWaals eos. For phase diagrams (solid-fluid-gas), there are only numerical parametric approximations for selected substances, based on direct measurement.
The Maxwell-Gibbs equation, which yields the exact solution for the saturation curve, is known in theory as the Maxwell-rule, but has not been solved for the Peng-Robinson and the Mie-Grueneisen eos.
In this paper, the Maxwell-Gibbs equation is solved for both fluid-gas and the solid phase in the form $p(E_{th})$, and is used to calculate the triple point and the phase diagram ($E_{th} = k_B T$ thermal energy, is used throughout this paper in place of temperature T).
As for binary mixtures, there exist only purely phenomenological ansatzes, there is no general theoretical treatment based on molecular data of the components.
In this paper we formulate a theoretical basis for binary solutions, based on the weighted sum of partial eos pressures, and including the 1-2-interaction of the components (i.e. non-ideal and irregular solutions).
Finally, we formulate an exact theoretical basis for binary solution eos, based on the Landau theory of phase transitions.

0.Flowcharts

Basics relation in statistics

$$Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right)$$ classical Boltzmann statistics

$$Z = \sum_i \frac{1}{\exp\left(\frac{E_i}{k_B T}\right)+1}$$ quantum fermion Fermi-Dirac statistics

$$Z = \sum_i \frac{1}{\exp\left(\frac{E_i}{k_B T}\right)-1}$$ quantum boson Bose-Einstein statistics

beta parameter $\beta = \frac{1}{k_B T}$

$$U = \langle E \rangle = -\frac{\partial \log Z}{\partial \beta} = k_B T^2 \frac{\partial \log Z}{\partial T}$$ mean energy

$$F = \langle E \rangle - TS = -k_B T \log Z$$ (Helmholtz) free energy

$$G = F + PV = \langle E \rangle - TS + PV = -\frac{1}{\beta}\frac{\partial (V \log Z)}{\partial V}$$ Gibbs energy

$$H = U + pV = -\left(\frac{1}{\beta}\frac{\partial \log Z}{\partial V} + \left(\frac{\partial \log Z}{\partial \beta}\right)\right)$$ enthalpy

$$S = \frac{\partial}{\partial T}\left(k_B T \log Z\right)$$ entropy

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2}\left\langle (\Delta E)^2 \right\rangle = k_B T\left(2\frac{\partial \log Z}{\partial T} + T\frac{\partial^2 \log Z}{\partial T^2}\right)$$ heat capacity

Thermodynamic classical ensembles

	Microcanonical	Canonical	Grand canonical
Fixed variables	N, V, E	N, V, T	μ, V, T
Microscopic features	Number of microstates W, with width ω $W = \sum_k f\left(\frac{H_k - E}{\omega}\right)$ $f(x) = \exp\left(-\pi x^2\right)$	Canonical partition function $Z = \sum_k exp\left(-\frac{E_k}{k_B T}\right)$ $Tr\left(exp\left(-\beta H\right)\right) =$ $\sum_k exp\left(-\beta E_k\right) = Z(\beta)$	Grand partition function $Z = \sum_k exp\left(-\frac{E_k - \mu N_k}{k_B T}\right)$ $Z\left(\beta, \mu_1, \mu_2, \ldots\right) = Tr\left(exp\left(\beta\left(\sum_k \mu_k N_k - H\right)\right)\right)$
Probability and density matrix	$\hat{\rho} = \frac{1}{W}\sum_k f\left(\frac{H_k - E}{\omega}\right)\lvert\psi_k\rangle\langle\psi_k\rvert$	$\rho = \frac{e^{-\beta H}}{Tr\, e^{-\beta H}}$ $p(E_m) = \frac{exp\left(-\beta E_m\right)}{\sum_k exp\left(-\beta E_k\right)}$	$\rho = \frac{e^{-\beta\left(H - \sum_i \mu_i N_i\right)}}{Tr\, e^{-\beta\left(H - \sum_i \mu_i N_i\right)}}$ $P(E_m) = \frac{e^{-\beta\left(E_m - \sum_i \mu_i N_i\right)}}{\sum_n e^{-\beta\left(E_n - \sum_i \mu_i N_i\right)}}$
Minimal principle	Boltzmann entropy $S = k_B \log W = \max$ v.Neumann entropy $S = -k_B Tr(\rho \ln \rho) = \max$	Helmholtz free energy $F = -k_B T \log Z = \min$	Grand potential $\Omega = -k_B T \log Z = \min$

Equations-of-state and mixing rules

ideal gas $p = \frac{1}{v\beta}$

vdWaals $p = \frac{1}{(v-b_1)\beta} - \frac{a_1}{v^2}$

mixing rules

$b_1 = \sum_i x_i b_{1,i}$, $a_1 = \sum_{i,j} x_i x_j a_{1,ij}$,

$a_{1,ij} = \sqrt{a_{1,i} a_{1,j}}$ geometric (GMA),

$a_{1,ij} = \frac{2\sqrt{a_{1,i} a_{1,j}} + a_{1,i} + a_{1,j}}{4}$ expanded geometric (EGA),

$a_{1,ij} = \left(a_{1,i} + a_{1,j}\right)/2$ simple arithmetic (SA)

Redlich–Kwong equation

$$p = \frac{1}{\beta(v-b_1)} - \frac{\sqrt{\beta}\, a_1}{v(v+b_1)},$$

$a_1 = \frac{0.42748}{p_c \beta^{2.5}}$, $b_1 = 0.08664 \frac{1}{p_c \beta_c}$

mixing rules PSRK

$$b_1 = \sum_i x_i b_{1,i} \ , \ \frac{a_1 \beta}{b_1} = \sum_i x_i \frac{a_{1,i}\beta}{b_{1,i}} + \frac{1}{A}\left(g^E \beta + \sum_i x_i \ln \frac{b_1}{b_{1,i}} \right),$$

$A = -0.64663$

Peng-Robinson equation

$$p = p(\beta, v, p_c, \beta_c) = \frac{1}{\beta(v-b_1)} - \frac{\left(1+\left(0.480+1.574\omega(p_c,\beta_c)-0.176\,\omega(p_c,\beta_c)^2\right)\left(1-\sqrt{\beta/\beta_c}\right)\right)^2 a_1}{v(v+b_1)+b_1(v-b_1)},$$

$a_1 = \frac{0.45723}{p_c \beta_c{}^2}$, $b_1 = 0.077796 \frac{1}{p_c \beta_c}$,

ω = acentric factor $\omega = -\log_{10}\left(\frac{p_{sat}(0.7T_c)}{p_c}\right) = \omega(p_c, \beta_c)$

mixing rules PSRK

$b_1 = \sum_i x_i b_{1,i}$, $A = -0.64663$

Comparison of eos and mixing rules results

Equation of state (EOS)	Mixing rule (MR)	% AAD
Van der Waals	GMA	46.8
	EGA	46.7
	SA	59.7
Redlich-Kwong	GMA	20.6
	EGA	20.5
	SA	29.9
Peng-Robinson	GMA	9.9
	EGA	9.9
	SA	18.9

General Landau theory

$Z=\int D\varphi\, dV \exp\left(-H\left(\vec{r},\varphi,\beta\right)\right)$, $H\left(\vec{r},\varphi,\beta\right)=E(\varphi)+\beta\, u\left(\vec{r}\right)$ is the thermodynamic Hamiltonian,

$E(\varphi)$ is the φ-induced Landau energy, $\beta\, u\left(\vec{r}\right)$ is the thermal intermolecular potential.

(first-order) fgs-systems: $\varphi\left(r,\theta,\lambda,\sigma;c_k\right)=\exp\left(-\frac{r}{\lambda}\right) f_{rdf}\left(r,\theta,\sigma;c_k\right)$, radial distribution function $f_{rdf}\left(r,\theta,\sigma;c_k\right)$

Solid-fluid-gas-solid system

$$Z=\int dV \exp\left(-\frac{r}{\lambda}\right)\varphi_{rdf}\left(\vec{r}\right)\exp\left(-\beta\, u\left(\vec{r}\right)\right)$$

Solid-fluid-gas-solid , first order transition (latent heat)
basic variables *T*, *V*, *N*

$\left(\frac{\partial F}{\partial v}\right)$ discontinuous, lat. heat $\Delta C>0$

$$Z=\int D\varphi\, dV \exp\left(-\beta\, u\left(\vec{r}\right)\right), D\varphi=\sum\frac{\partial\varphi}{\partial c_k}dc_k \ ,$$

$$H\left(\vec{r},\varphi,\beta\right)=\beta\, u\left(\vec{r}\right)$$

approximately $Z\approx\int\varphi\, dV \exp\left(-\beta\, u\left(\vec{r}\right)\right)$

$$\left(c_k\right)=\left(l_c,\alpha_k,l_{a,k},\alpha_{0k}\right)$$

$\varphi\sim\rho=\frac{1}{v}$, specific volume v

$$\varphi\left(\vec{r},\sigma,\lambda;c_k\right)=\exp\left(-\frac{r}{\lambda}\right)\varphi_{rdf}\left(r,\theta,\sigma;c_k\right)$$

$$\varphi_{rdf}\left(r,\theta,\sigma;c_k\right)=\Theta_H\left(r,\sigma\right)\left(1+\exp\left(-r/l_c\right)\left(\sum_k\alpha_k\cos\left(2\pi\frac{r-\sigma}{l_{a,k}}\right)\right)f_\theta\left(\theta,\alpha_{0k}\right)\right)$$

Θ_H step-up function

Binary solutions
rel. concentrations $\left(x_1,x_2\right)$, $x_1+x_2=1$,
potential $f\left(r/\sigma\right)$

$$u_{11}=\varepsilon_{11} f\left(r/\sigma_{11}\right),\ u_{12}=\varepsilon_{12} f\left(r/\sigma_{12}\right),$$

$$u_{22}=\varepsilon_{22} f\left(r/\sigma_{22}\right)$$

correlation function $g\left(\vec{r}/\sigma\right)$

$$g_{11}=g\left(\vec{r}/\sigma_{11}\right),\ g_{12}=g\left(\vec{r}/\sigma_{12}\right),$$

$$g_{22}=g\left(\vec{r}/\sigma_{22}\right),\ \sigma_{12}=\left(\sigma_{11}+\sigma_{22}\right)/2$$

$Z=Z_{11}Z_{12}Z_{22}$ product of the three component partition functions,
specific volume $v=V/N$, $\lambda=\left(v\right)^{1/3}$

$$Z_{11}=\left(\int D\varphi_{11}\, dv \exp\left(-\beta\,\varepsilon_{11}\, f\left(\vec{r}/\sigma_{11}\right)\right)\right)^{x_1^2} \ ,$$

$$Z_{22}=\left(\int D\varphi_{22}\, dv \exp\left(-\beta\,\varepsilon_{22}\, f\left(\vec{r}/\sigma_{22}\right)\right)\right)^{x_2^2} \ ,$$

$$Z_{12}=\left(\int D\varphi_{12}\, dv \exp\left(-\beta\,\varepsilon_{12}\, f\left(\vec{r}/\sigma_{12}\right)\right)\right)^{x_1x_2},$$

$$\sigma_{12}=\left(\sigma_1+\sigma_2\right)/2\ ,\ \varepsilon_{12}=\sqrt{\varepsilon_1\varepsilon_2}$$

Solid-fluid-gas $Z\left(\lambda,\beta;c_k\right)$
F-minimization Landau principle
Rescaling
radius $\sigma=1$, energy $\varepsilon=1$ in $u\left(\vec{r}\right)$
$\lambda\to\lambda/\sigma$, $r\to r/\sigma$
$u\to u/\varepsilon$, $p\to p\sigma^2/\varepsilon$

$$F\left(\lambda,\beta;c_k\right)=-\frac{1}{\beta}\log Z\left(\lambda,\beta;c_k\right)$$

$$F\left(\lambda,\beta;c_{0,k}\right)=\min\left(c_k\right)\to\varphi\left(c_{0,k}\right)=\varphi_0$$

$$Z\left(\lambda,\beta;c_{0,k}\right)=\max\left(c_k\right)\to\varphi\left(c_{0,k}\right)=\varphi_0$$

Solid-fluid-gas $Z\left(\lambda,\beta;c_k\right)$
Calculation of correlation function $\varphi_{rdf}\left(r,\theta;c_k\right)$
Rescaling
radius $\sigma=1$, energy $\varepsilon=1$ in $u\left(\vec{r}\right)$
$\lambda\to\lambda/\sigma$, $r\to r/\sigma$
$u\to u/\varepsilon$, $p\to p\sigma^2/\varepsilon$

HCOZ eq., ansatz $f\left(\vec{r};c_k\right)$

$$\log g\left(\vec{r}\right)+\beta u\left(\vec{r}\right)-\rho_0\left(1-g\left(\vec{r}\right)\right)I\left(g,\beta u\right)=0$$

$$I\left(g,\beta u\right)=\int\left(\left(1-g\left(R\right)\right)-\log g\left(R\right)-\beta u\left(R\right)\right)r_1^2\,dr_1\,\sin\theta\,d\theta\,d\phi$$

$$R\left(r,r_1\right)^2=r^2+r_1^2+2rr_1\cos\theta\cos\phi$$

→solution $g\left(r,\theta;c_{1,k}\right)$

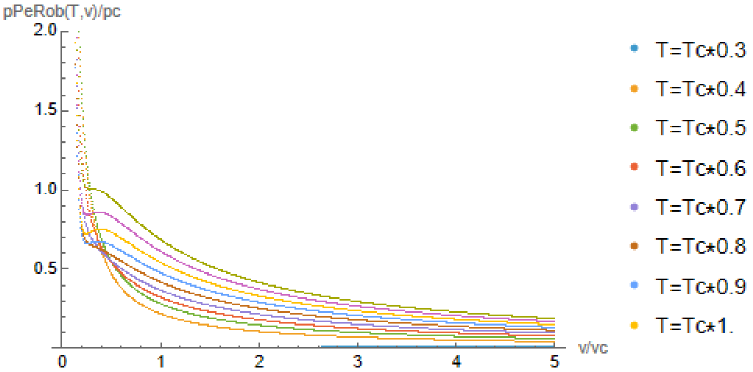
$$\varphi\left(r,\theta,\lambda;c_{1,k}\right)=\exp\left(-\frac{r}{\lambda}\right)g\left(r,\theta;c_{1,k}\right)$$

$$Z\left(\lambda,\beta;c_{1,k}\right)=\int\varphi\left(r,\theta,\lambda;c_{1,k}\right)dv\exp\left(-\beta u\left(\vec{r}\right)\right)$$

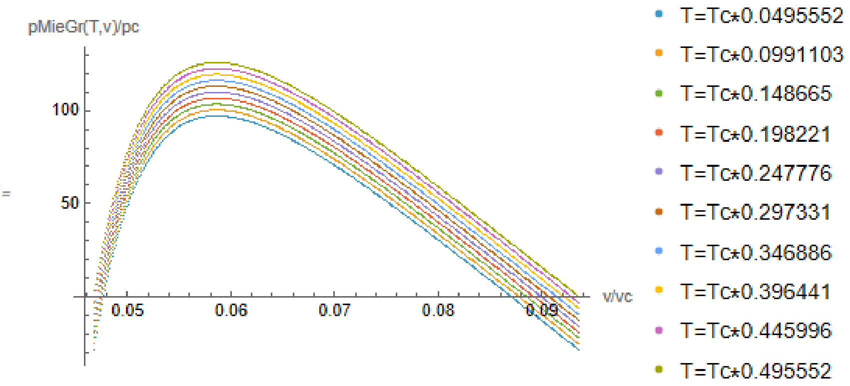
$$F\left(\lambda,\beta;c_{1,k}\right)=-\frac{1}{\beta}\log Z\left(\lambda,\beta;c_{1,k}\right)$$

Equation-of-state and phase diagram benzene

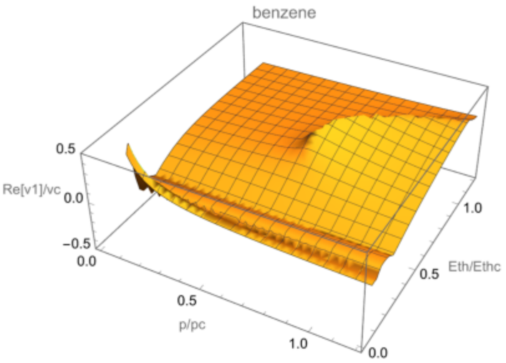
Peng-Robinson fluid-gas eos in relative coordinates

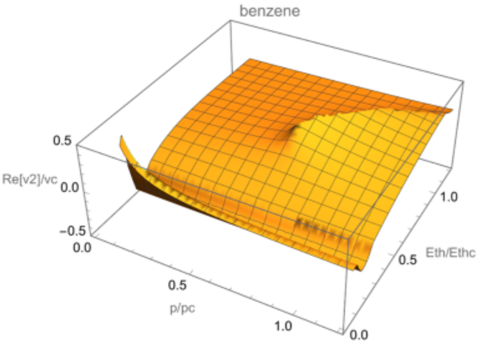


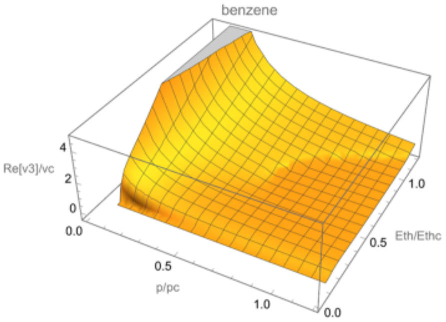
Mie-Grueneisen solid eos



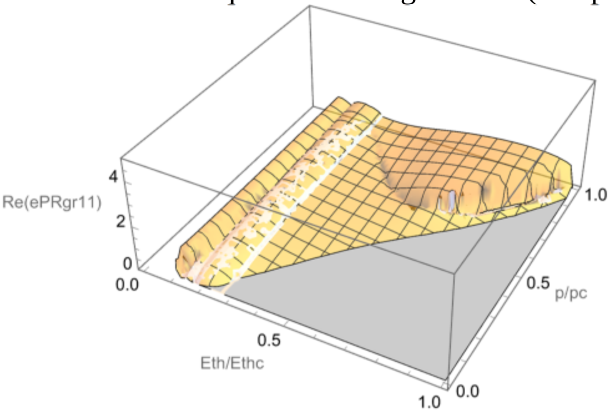
The three branches (real part) of the volume function $v = v(p, \beta)$ Peng-Robinson eos

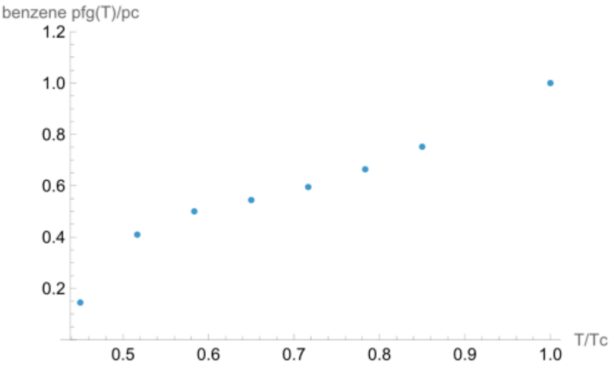




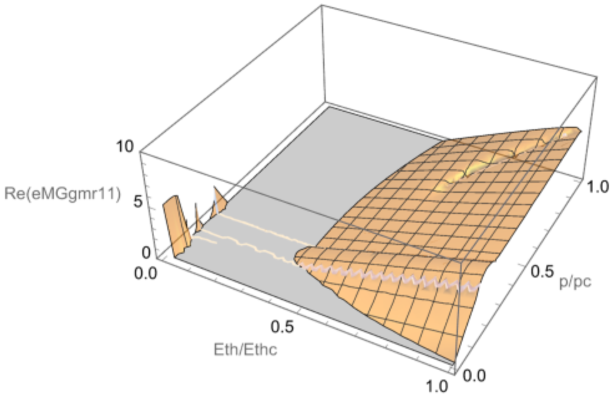


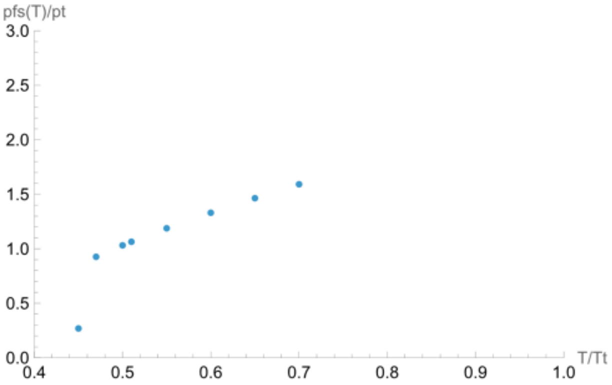
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



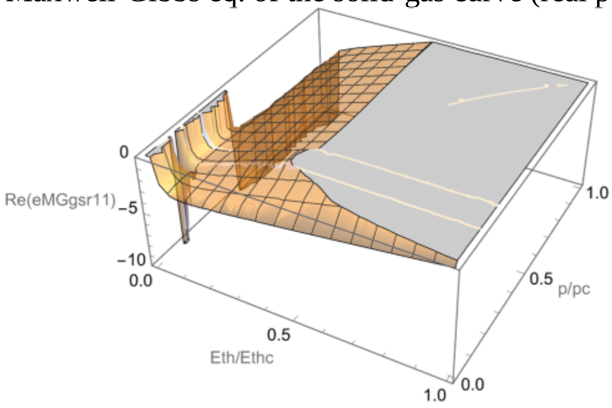


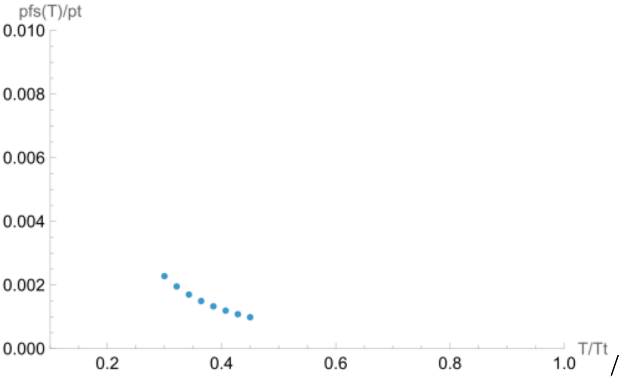
Maxwell-Gibbs eq. of the solid-fluid curve (real part)





Maxwell-Gibbs eq. of the solid-gas curve (real part)





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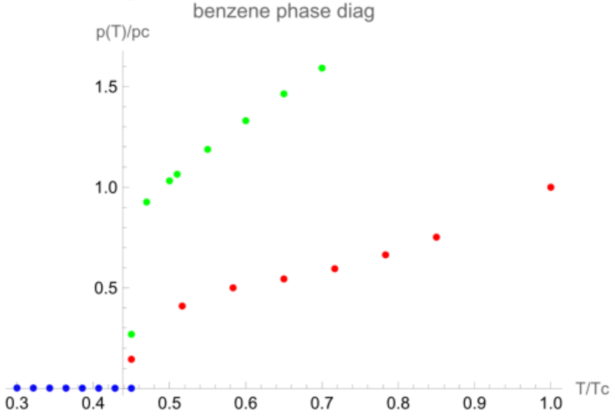
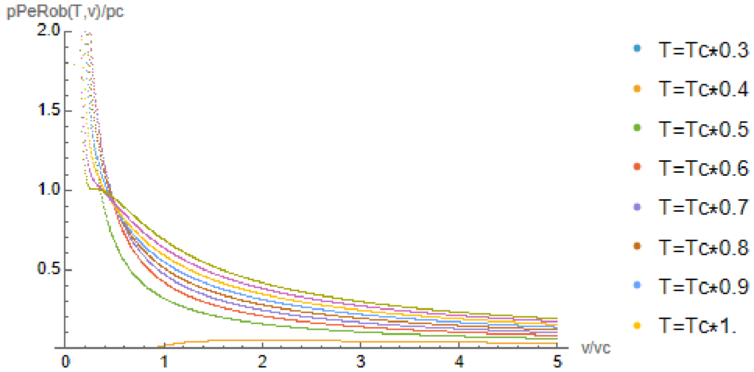
Phase diagram

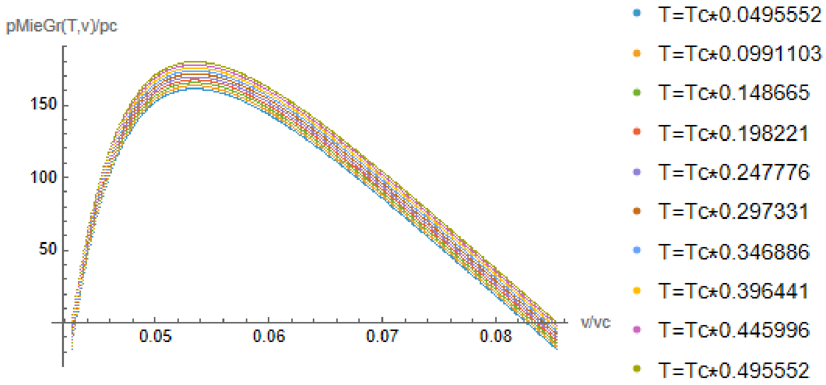


Equation-of-state and phase diagram ethanol

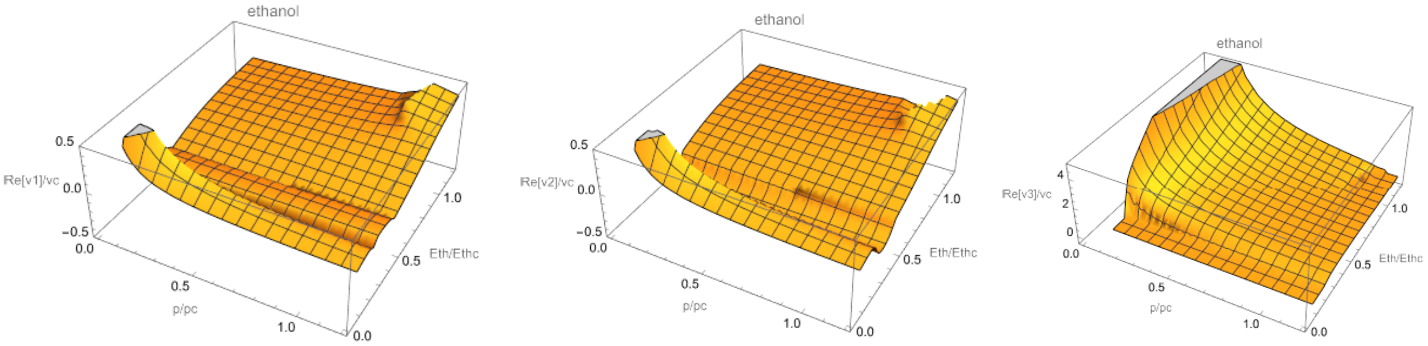
Peng-Robinson fluid-gas eos in relative coordinates



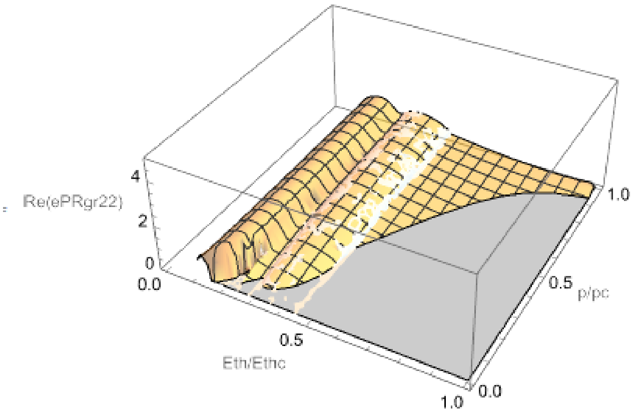
Mie-Grueneisen solid eos

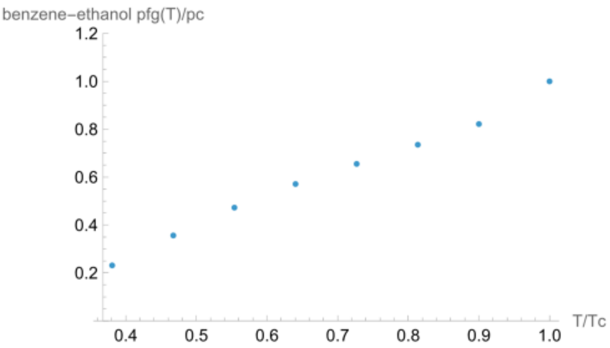


The three branches (real part) of the volume function $v = v(p, \beta)$ Peng-Robinson eos

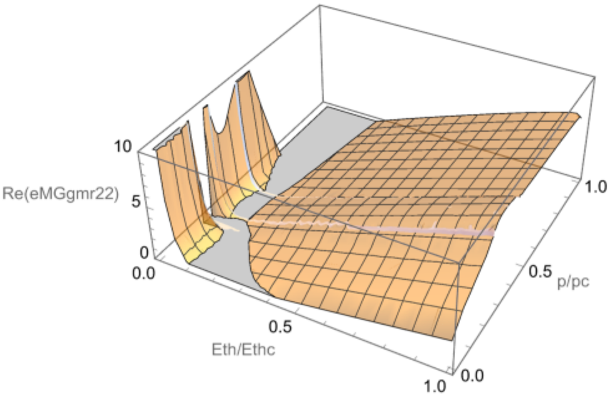


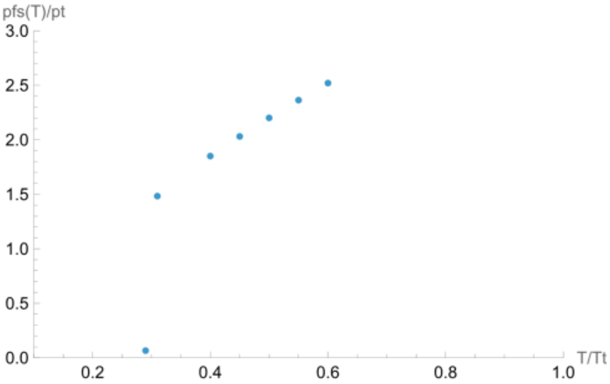
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



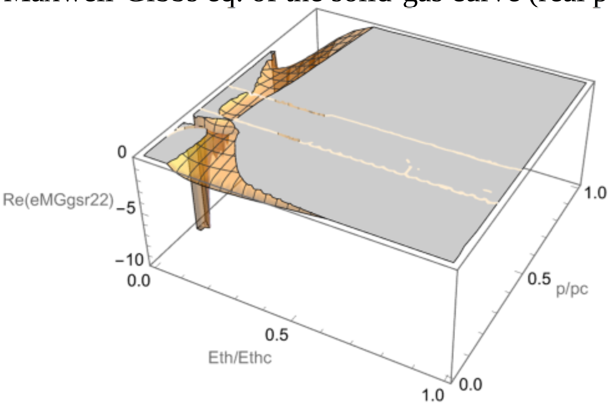


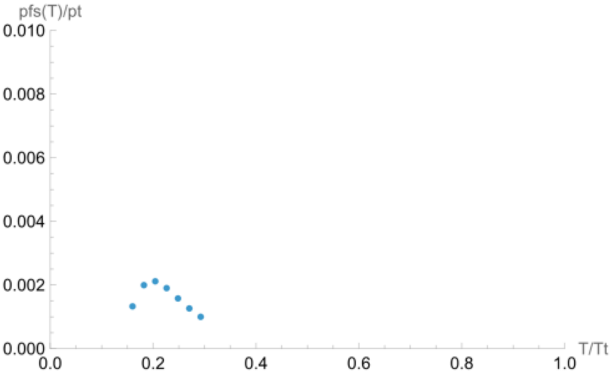
Maxwell-Gibbs eq. of the solid-fluid curve (real part)



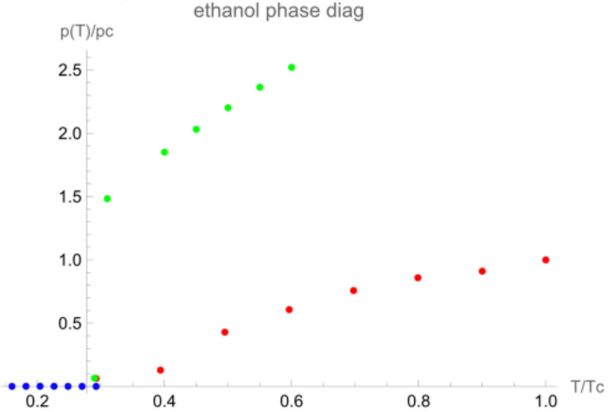


Maxwell-Gibbs eq. of the solid-gas curve (real part)

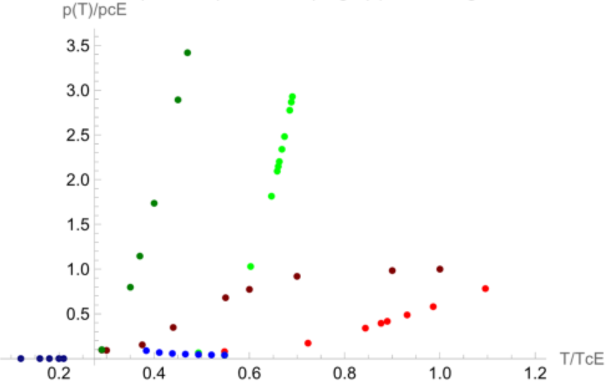




Phase diagram

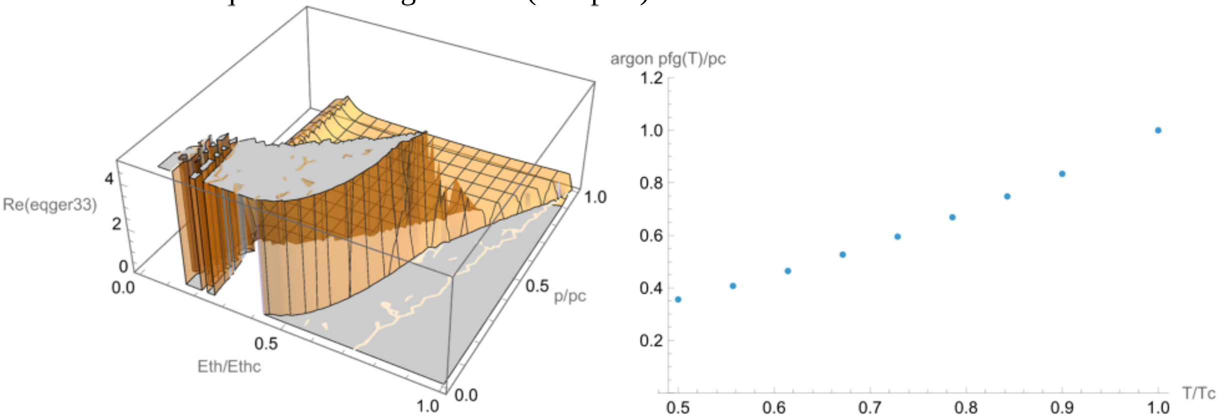


Phase diagram ethanol and benzene, rel. ethanol

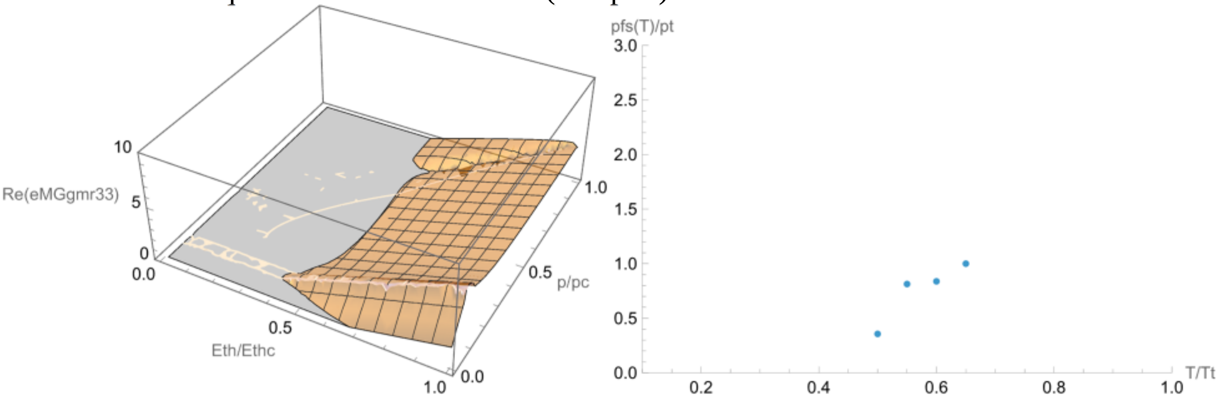


Equation-of-state and phase diagram argon

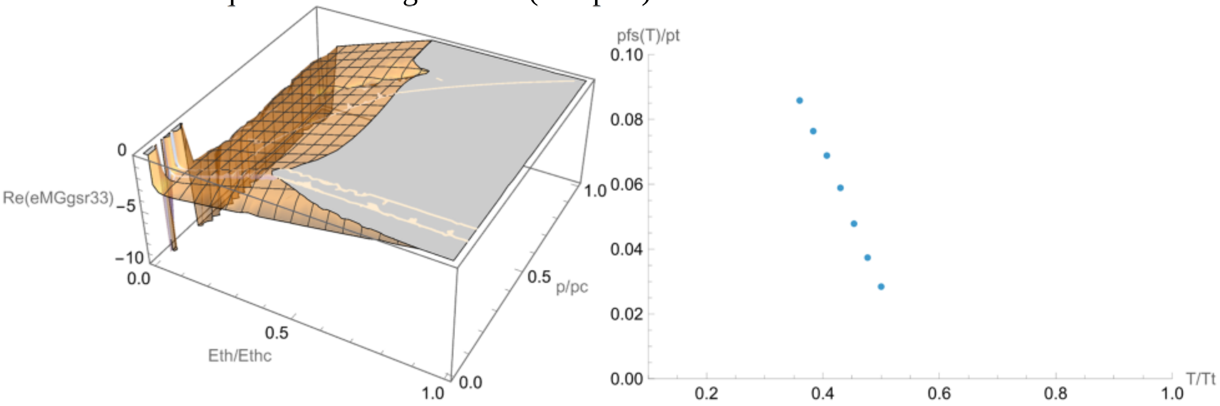
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



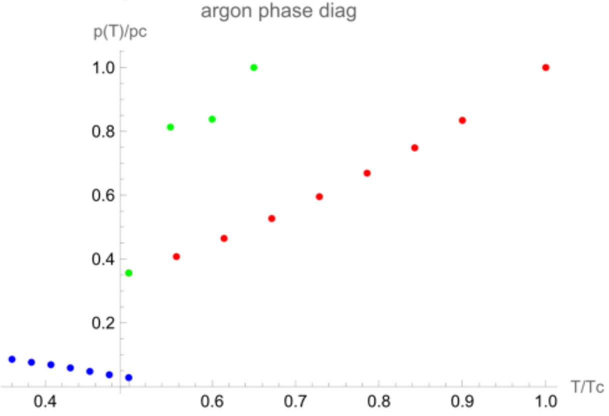
Maxwell-Gibbs eq. of the solid-fluid curve (real part)



Maxwell-Gibbs eq. of the solid-gas curve (real part)

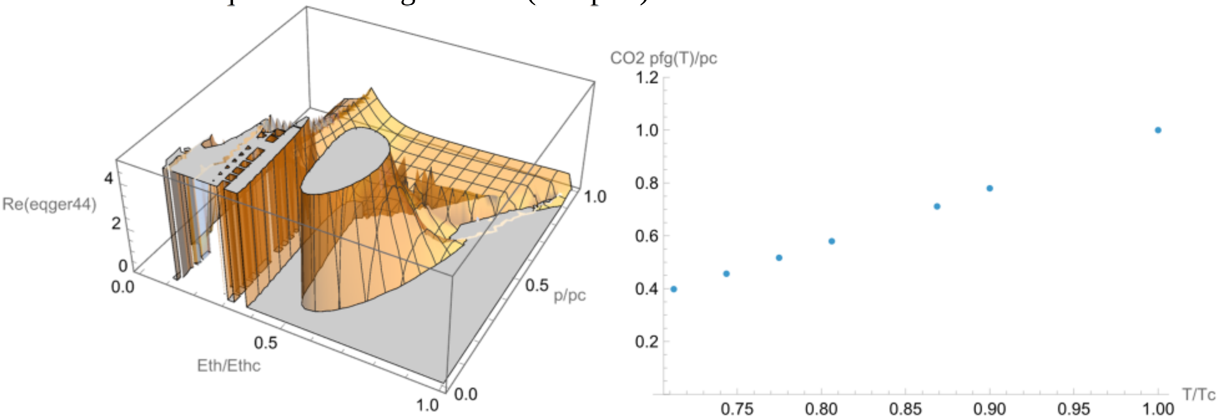


Phase diagram

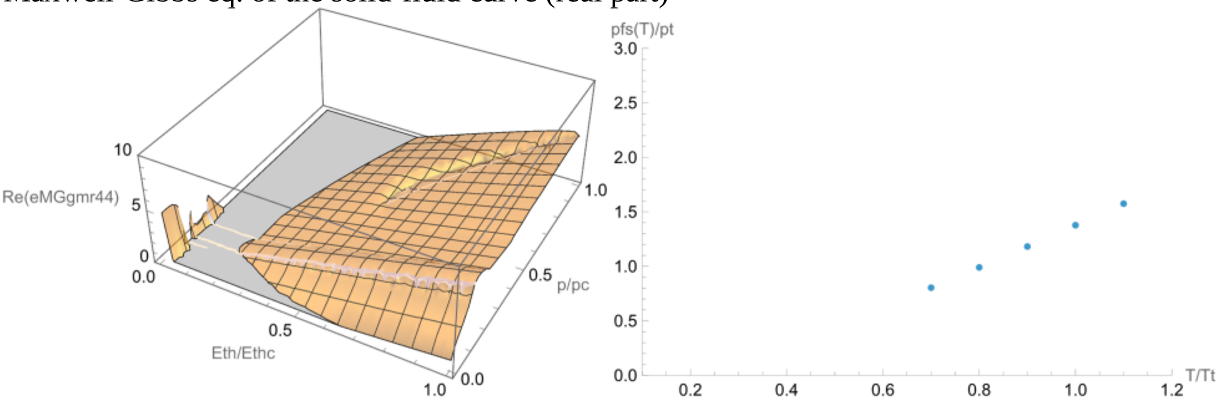


Equation-of-state and phase diagram carbon dioxide

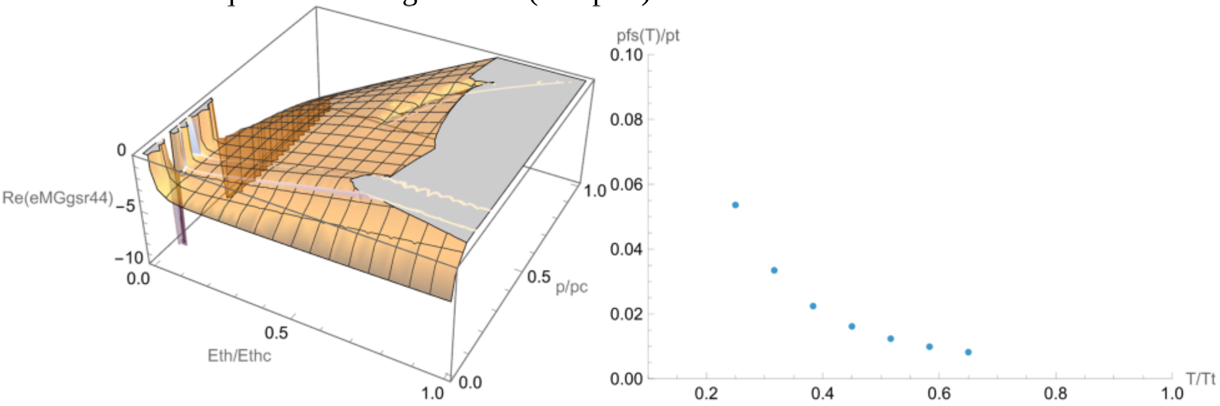
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



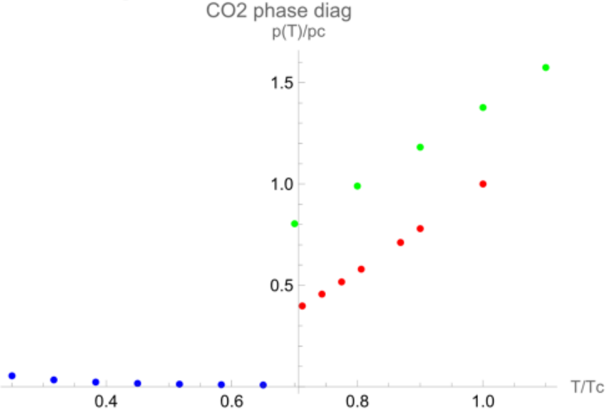
Maxwell-Gibbs eq. of the solid-fluid curve (real part)



Maxwell-Gibbs eq. of the solid-gas curve (real part)

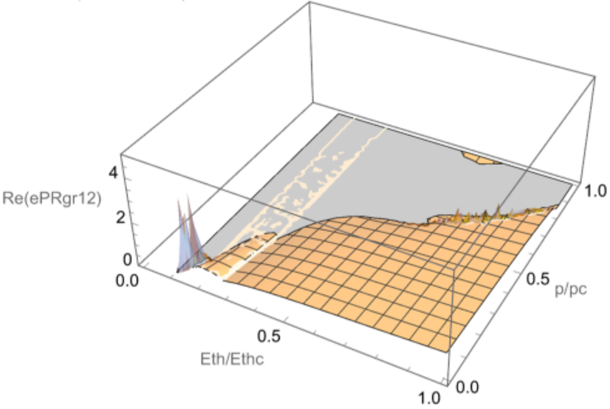


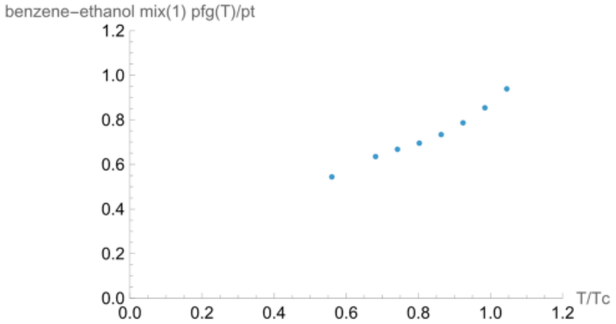
Phase diagram



Saturation curves for benzene-ethanol solutions
in relative coordinates rel. benzene-ethanol-1:1
rel. benzene concentration x_0=(1, 0.75, 0.5, 0.4, 0.25, 0.1, 0.)

Maxwell-Gibbs eq. of the fluid-gas curve (real part)
x_0=1 (benzene)





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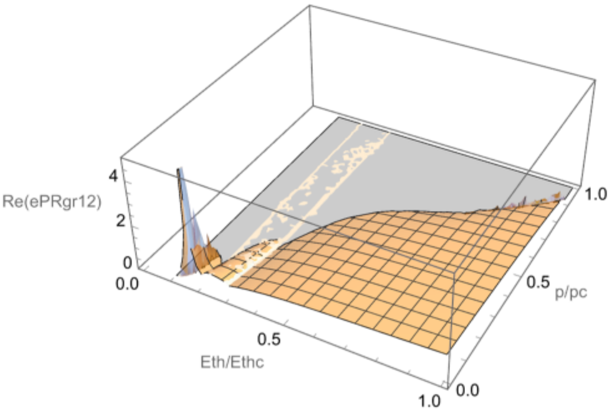

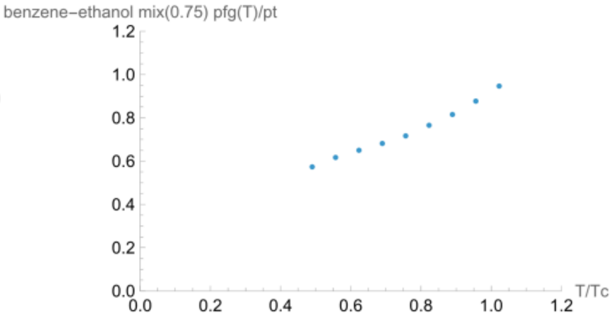

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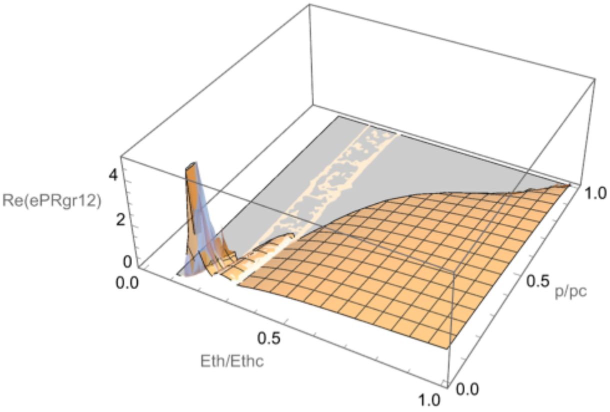
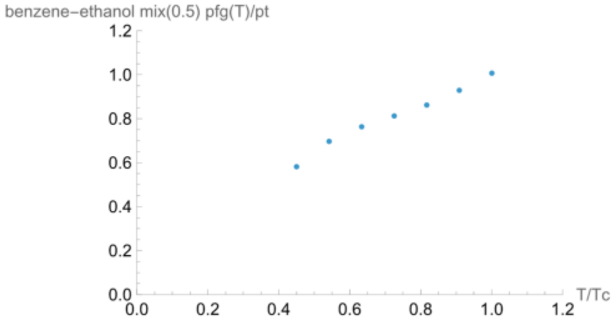
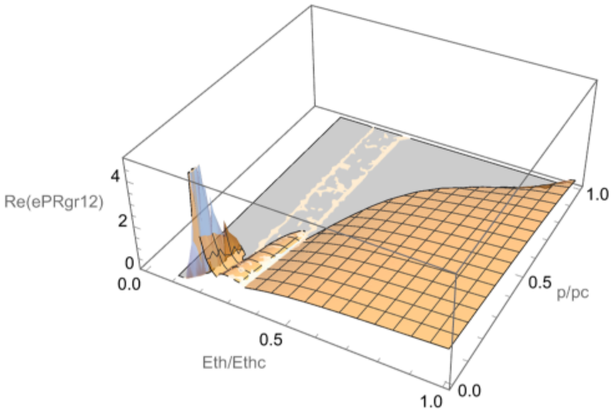
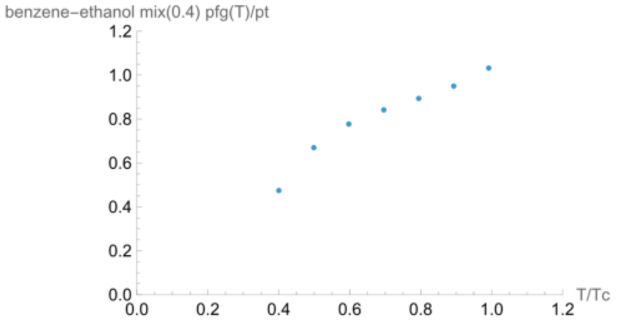




x_0=0.40





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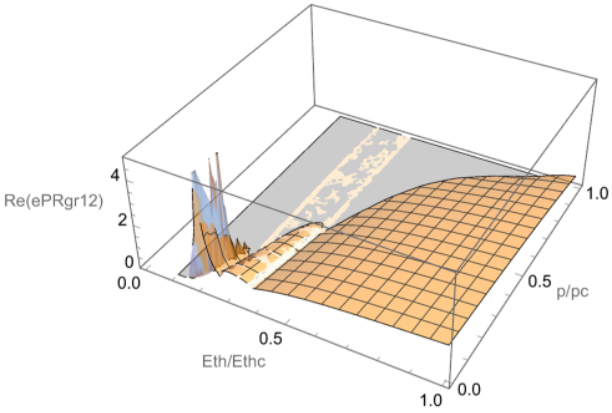
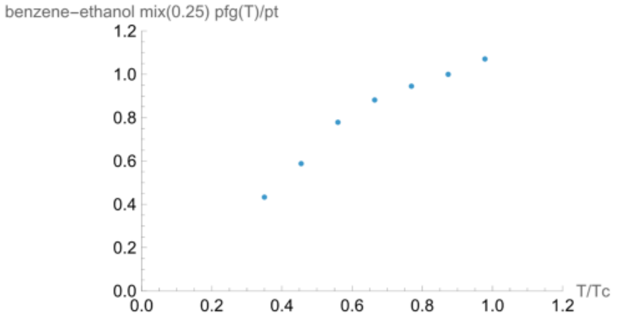
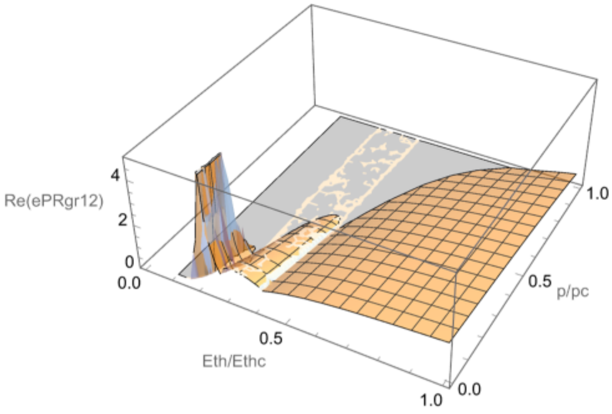
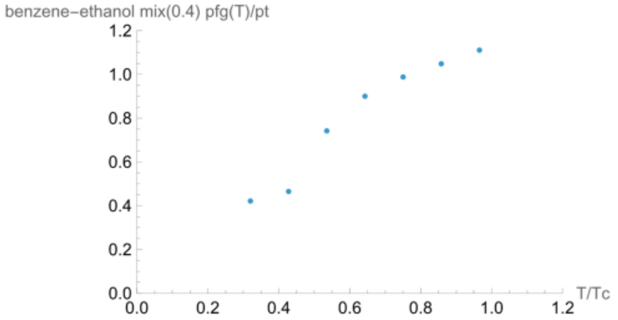


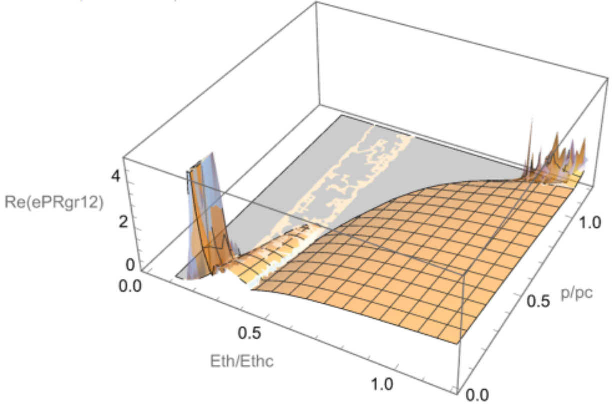


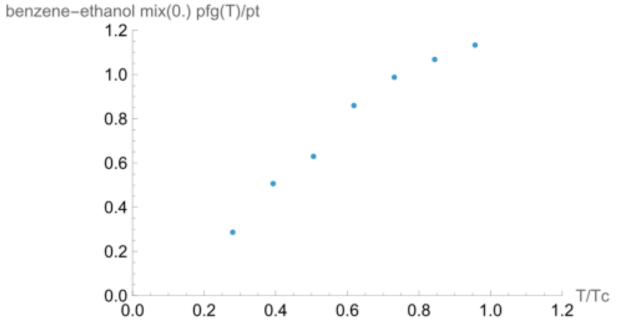
x_0=0.1



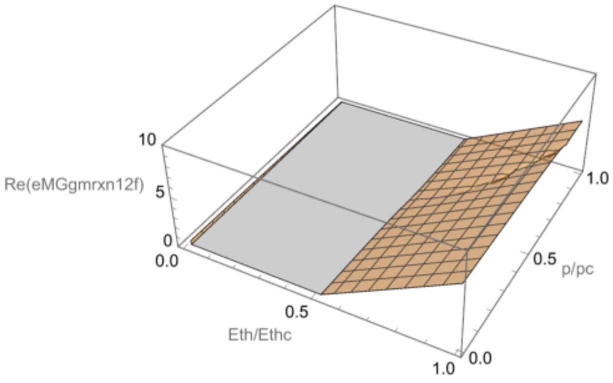


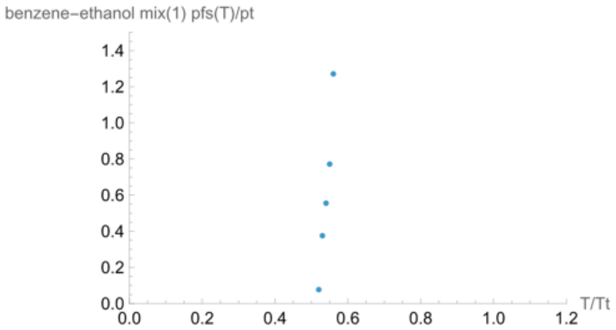
x_0=0 (ethanol)



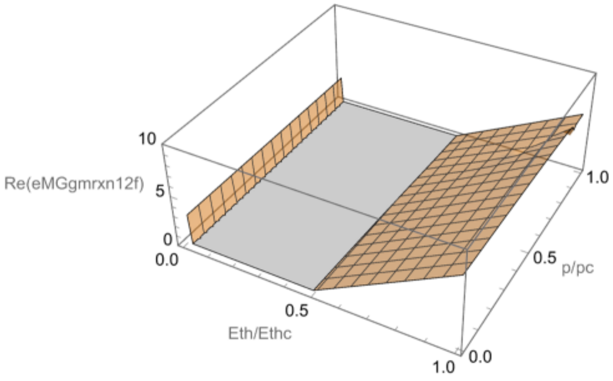


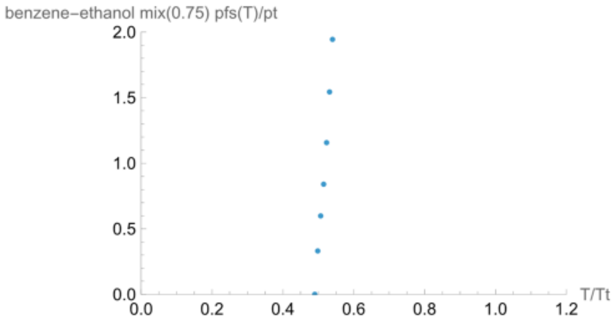
Maxwell-Gibbs eq. of the solid-fluid curve (real part)
x_0=1 (benzene)



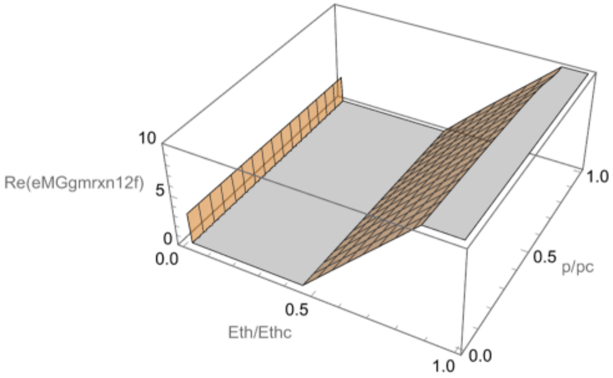


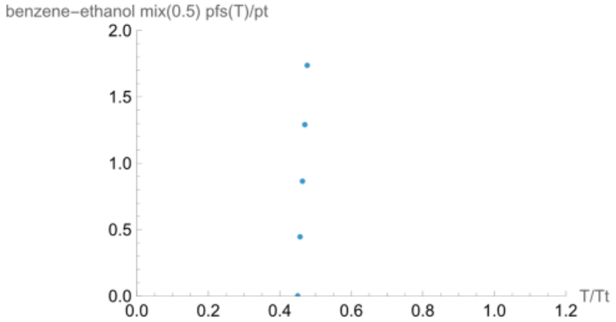
x_0=0.75



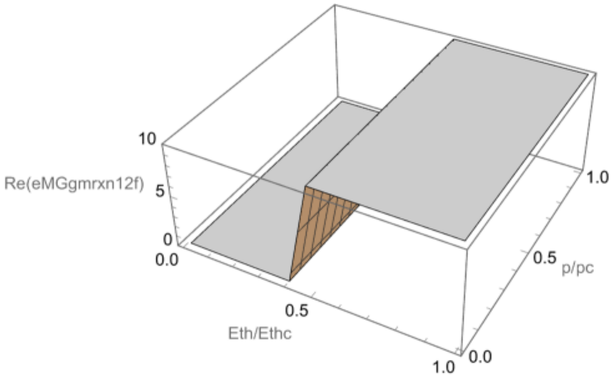


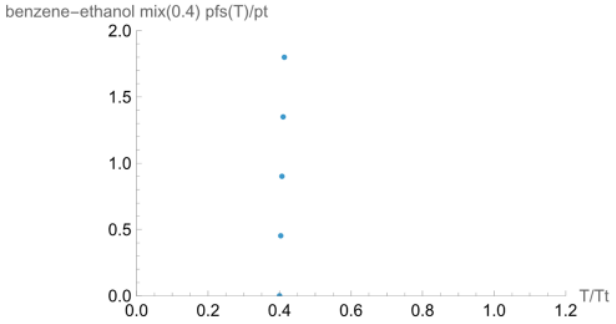
x_0=0.5



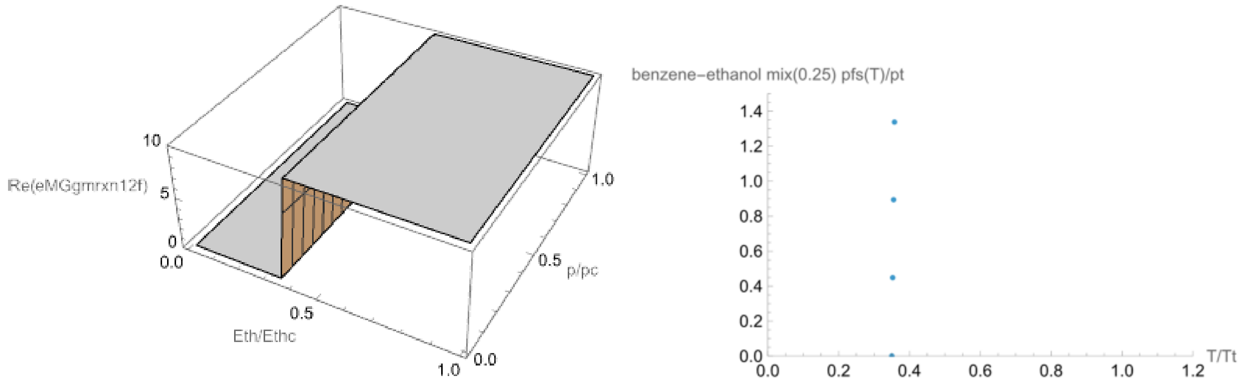


x_0=0.4

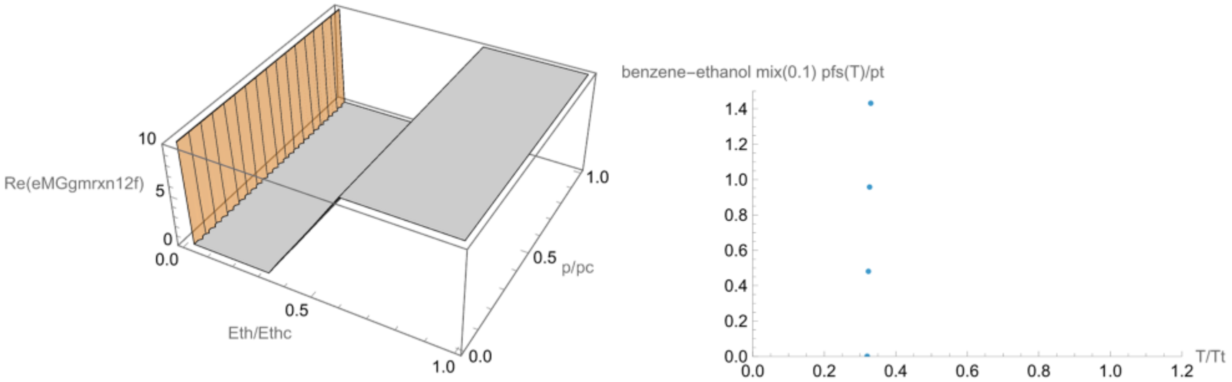




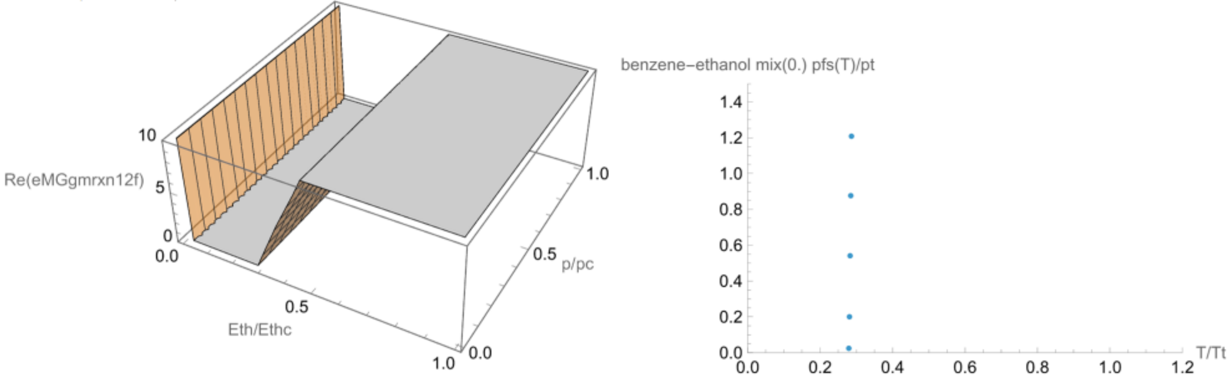
x_0=0.25



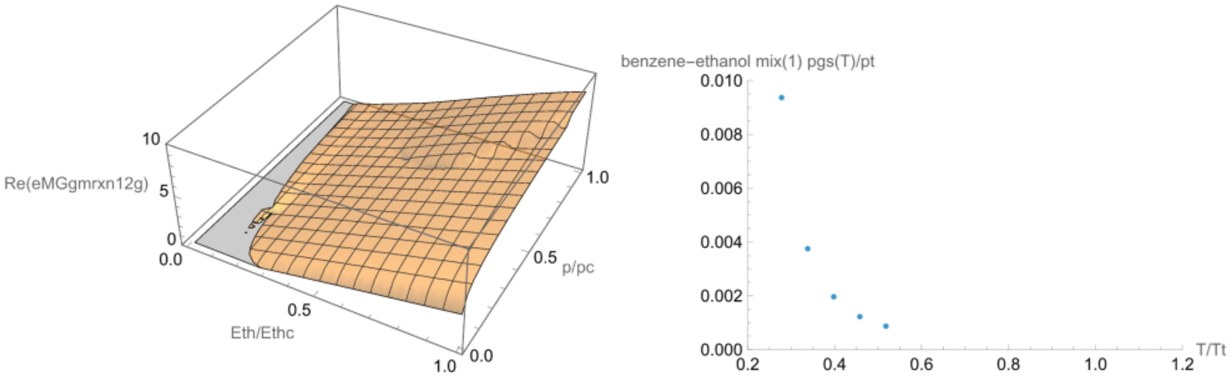
x_0=0.1



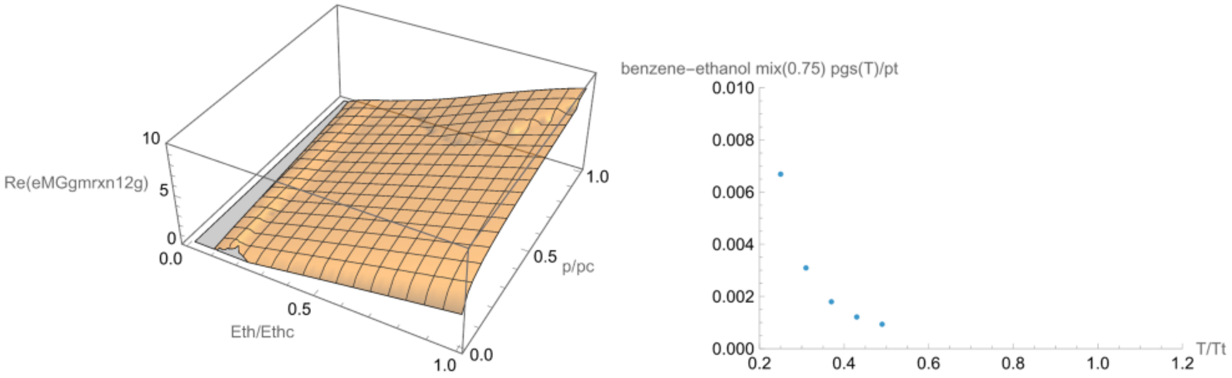
x_0=0 (ethanol)



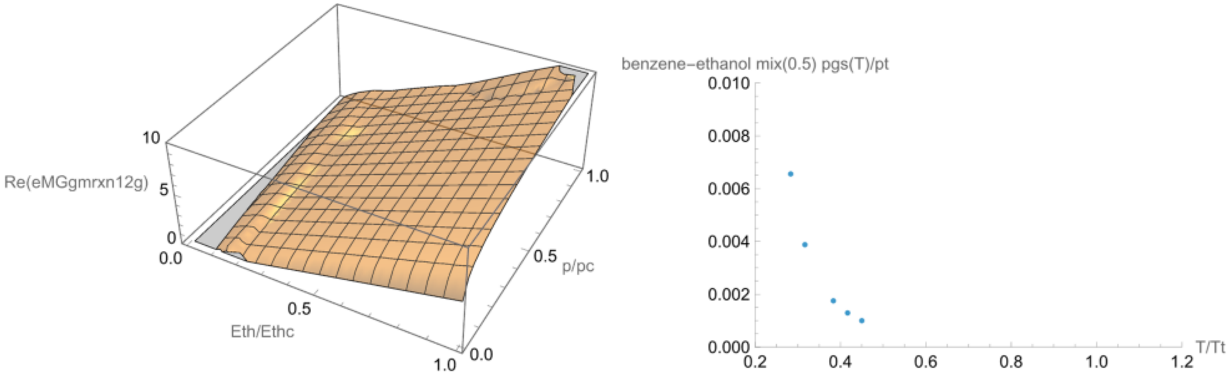
Maxwell-Gibbs eq. of the solid-gas curve (real part)
x_0=1 (benzene)



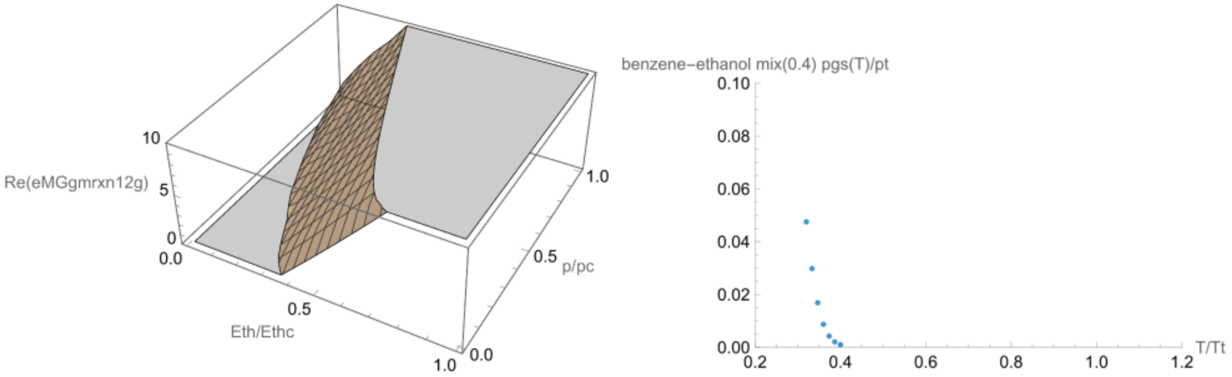
x_0=0.75



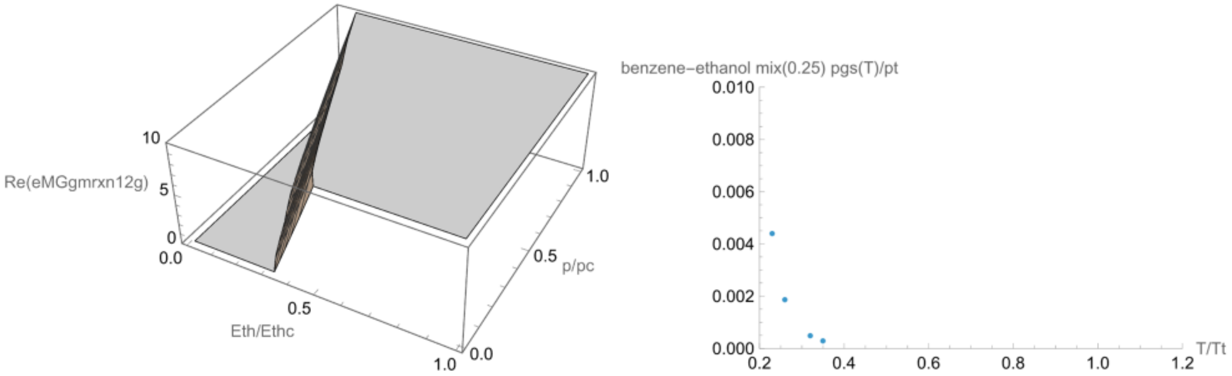
x_0=0.5



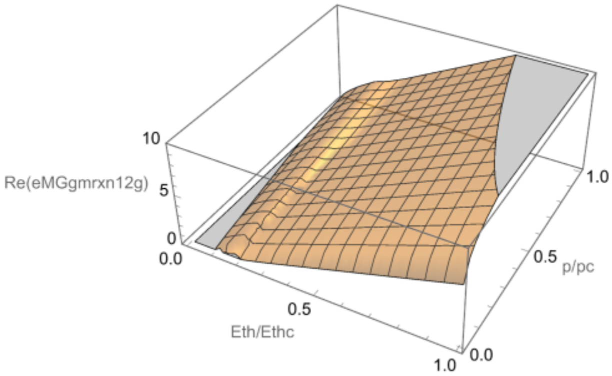
x_0=0.4

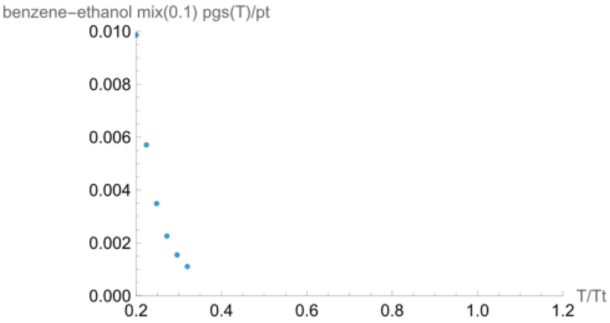


x_0=0.25

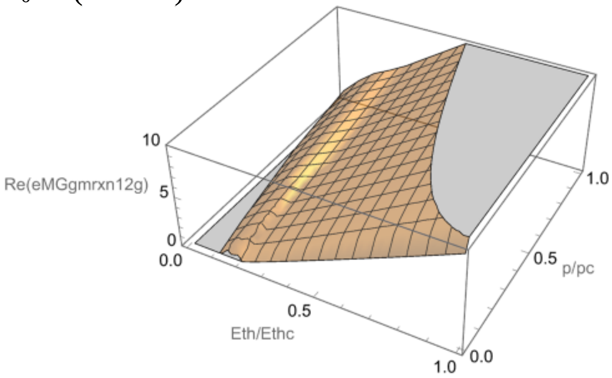


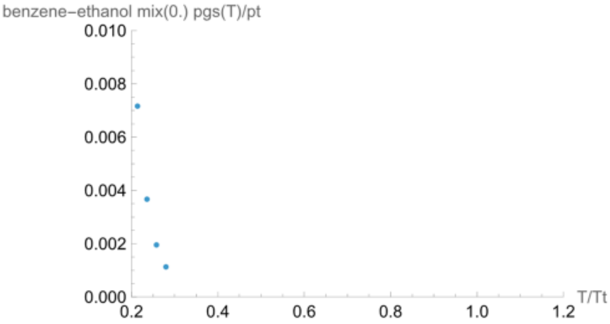
x_0=0.1


Re(eMGgmrxn12g)
10
5
0
0.0
0.5
Eth/Ethc
1.0
0.0
0.5
p/pc
1.0


benzene–ethanol mix(0.1) pgs(T)/pt
0.010
0.008
0.006
0.004
0.002
0.000
0.2
0.4
0.6
0.8
1.0
1.2
T/Tt

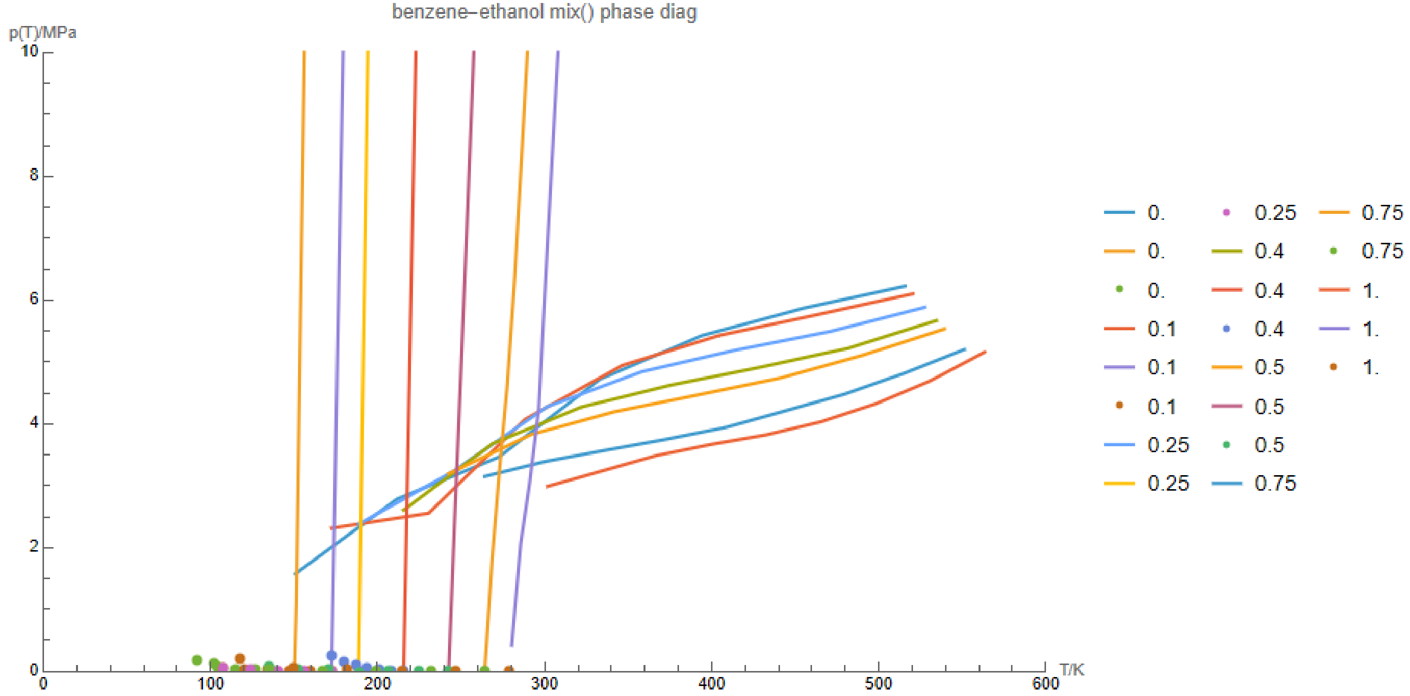
x_0=0 (ethanol)


Re(eMGgmrxn12g)
10
5
0
0.0
0.5
Eth/Ethc
1.0
0.0
0.5
p/pc
1.0

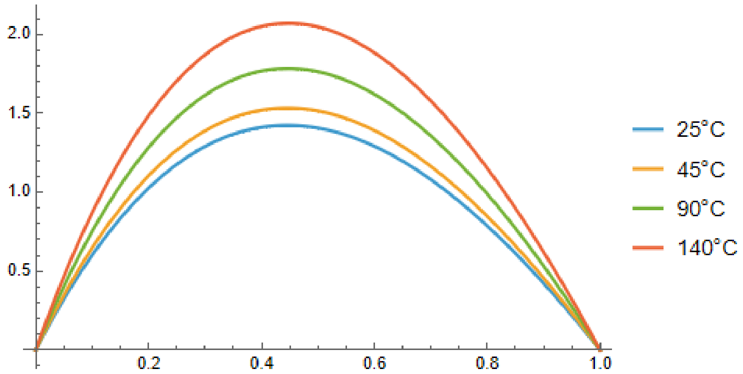

benzene–ethanol mix(0.) pgs(T)/pt
0.010
0.008
0.006
0.004
0.002
0.000
0.2
0.4
0.6
0.8
1.0
1.2
T/Tt

Phase diagrams, enthalpy, characteristic points of solutions benzene-ethanol

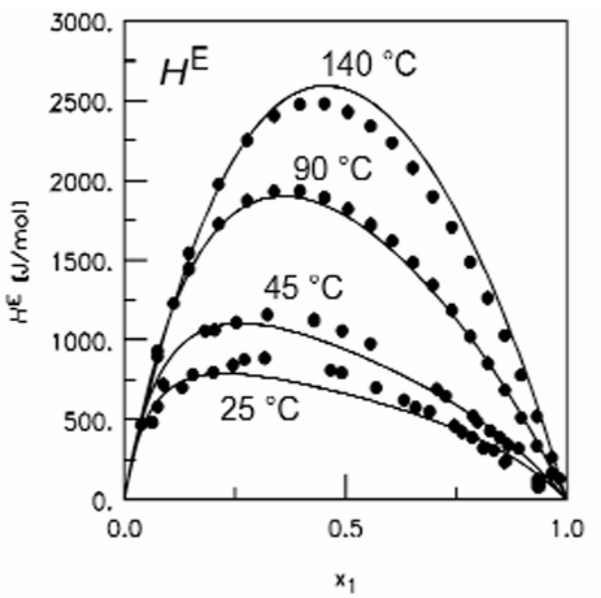
Phase diagrams



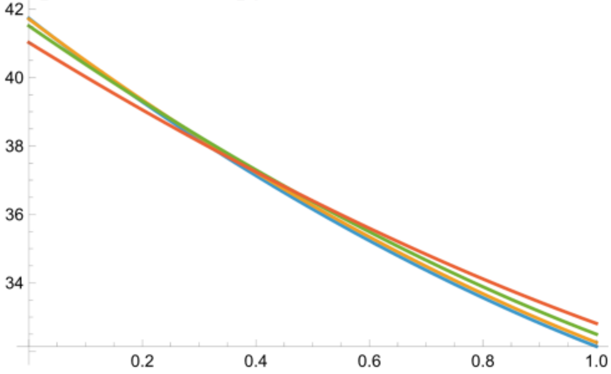
Excess enthalpy in kJ/mol vs. relative benzene concentration x_0



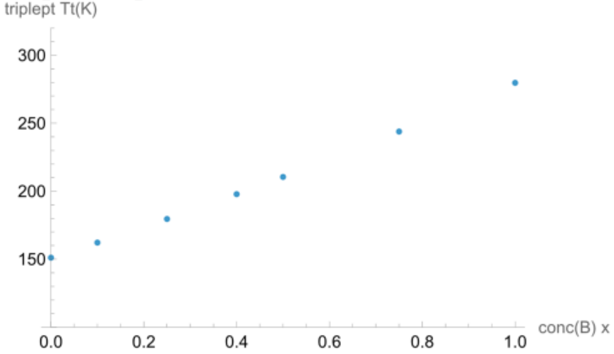
Excess enthalpy measured in J/mol



Vaporiation enthalpy in kJ/mol



Triple temperature in K



1.Basics of classical and quantum statistics

Statistical mechanics describes the thermodynamic behaviour of large systems ([12], [13], [14]).
Key features of a thermodynamic ensemble is its *partition function* (probability distribution) and its *macroscopic function* (extremal variable of the ensemble: e.g. entropy=max, free energy=min) . They are functions of the *thermodynamic state variables*: temperature, volume pressure, number of particles, chemical potential [8].
Fundamental variable is: partition function Z

$$Z=\sum_i \exp\left(-\frac{E_i}{k_B T}\right)$$ classical Boltzmann statistics

$$Z=\sum_i \frac{1}{\exp\left(\frac{E_i}{k_B T}\right)+1}$$ quantum fermion Fermi-Dirac statistics

$$Z=\sum_i \frac{1}{\exp\left(\frac{E_i}{k_B T}\right)-1}$$ quantum boson Bose-Einstein statistics

Important thermodynamic variables mean energy U , Helmholtz free energy F, Gibbs energy G, entropy S , heat capacity C_V .

$$U=\langle E\rangle=-\frac{\partial \log Z}{\partial \beta}=k_B T^2 \frac{\partial \log Z}{\partial T}$$ mean energy

$$F=\langle E\rangle-TS=-k_B T \log Z$$ Helmholtz free energy

$$G=F+PV=\langle E\rangle-TS+PV=-\frac{1}{\beta}\frac{\partial\left(V\log Z\right)}{\partial V}$$ Gibbs energy, with beta parameter $\beta=\frac{1}{k_B T}$

$$S=\frac{\partial}{\partial T}\left(k_B T\log Z\right)$$ entropy

$$C_v=\frac{\partial\langle E\rangle}{\partial T}=\frac{1}{k_B T^2}\left\langle\left(\Delta E\right)^2\right\rangle=k_B T\left(2\frac{\partial \log Z}{\partial T}+T\frac{\partial^2 \log Z}{\partial T^2}\right)$$ heat capacity

for $Z\approx W\exp\left(-\frac{\langle E\rangle}{k_B T}\right)$, $S=\frac{\partial}{\partial T}\left(k_B T\log Z\right)\approx\frac{\partial}{\partial T}\left(-\langle E\rangle+k_B T\log W\right)=k_B\log W$

which gives the famous Boltzmann aproximate formula $S\approx k_B\log W$

1.1 The three most important ensembles

The microcanonical ensemble describes [15] a system with *fixed energy and fixed number of particles*.
The canonical ensemble describes a system of *fixed number of particles* that is in thermal equilibrium with a heat bath of a fixed temperature.
The grand canonical ensemble describes a system with non-fixed particle numbers that is in thermal and chemical equilibrium with a thermodynamic reservoir with *fixed temperature and fixed number of particles*.

Thermodynamic classical and quantum ensembles with their partition function and the macroscopic function [30]

	Thermodynamic classical ensembles		
	Microcanonical	Canonical	Grand canonical
Fixed variables	N, V, E	N, V, T	μ, V, T
Microscopic features	Number of microstates W, with width ω $W=\sum_k f\left(\frac{H_k-E}{\omega}\right)$	Canonical partition function $Z=\sum_k exp\left(-\frac{E_k}{k_B T}\right)$	Grand partition function $Z=\sum_k exp\left(-\frac{E_k-\mu N_k}{k_B T}\right)$

	$f\left(x\right)=\exp\left(-\pi x^2\right)$	$Tr\left(exp\left(-\beta H\right)\right)=$ $\sum_k exp\left(-\beta E_k\right)=Z(\beta)$	$Z\left(\beta,\mu_1,\mu_2,\ldots\right)=Tr\left(exp\left(\beta\left(\sum_k \mu_k N_k-H\right)\right)\right)$
Probability and density matrix	$\hat{\rho}=\frac{1}{W}\sum_k f\left(\frac{H_k-E}{\omega}\right)\lvert\psi_k\rangle\langle\psi_k\rvert$	$\rho=\frac{e^{-\beta H}}{Tr\, e^{-\beta H}}$ $p(E_m)=\frac{exp\left(-\beta E_m\right)}{\sum_k exp\left(-\beta E_k\right)}$	$\rho=\frac{e^{-\beta\left(H-\sum_i \mu_i N_i\right)}}{Tr\, e^{-\beta\left(H-\sum_i \mu_i N_i\right)}}$ $P(E_m)=\frac{e^{-\beta\left(E_m-\sum_i \mu_i N_i\right)}}{\sum_n e^{-\beta\left(E_n-\sum_i \mu_i N_i\right)}}$
Minimal principle	Boltzmann entropy $S=k_B\log W=\max$ v.Neumann entropy $S=-k_B Tr(\rho\ln\rho)=\max$	Helmholtz free energy $F=-k_B T\log Z=\min$	Grand potential $\Omega=-k_B T\log Z=\min$

The macroscopic function obeys the minimum principle of statistics:
the macroscopic function attains an extremum in equilibrium
microcanonical: entropy is maximum
canonical: free energy is minimal
grand canonical: grand potential is minimal

The partition function describes the statistical properties of a system in thermodynamic equilibrium .
Partition functions are functions of the thermodynamic state variables .

For a canonical discrete ensemble the partition function reads

classical $Z=\sum_k g_k exp\left(-\beta E_k\right)$, $\beta=\frac{1}{k_B T}$, where g_j =degeneracy

quantum $Z=Tr\left(exp\left(-\beta\hat{H}\right)\right)$ or $Z=\sum_k\frac{g_k}{\exp\left(\frac{E_k}{k_B T}\right)\pm 1}$ (fermion + , boson -)

probability of state *s* reads $p_s=\frac{1}{Z}exp\left(-\beta E_s\right)$

The three probability distributions for the *average number in a state* ε: $N(\varepsilon)$ with degeneracy *g(ε)* and chemical potential *μ* are derived from the maximization of number of states $W(\nu_i)$ with occupation numbers ν_i of *N* particles for states with degeneracy g_r and energy levels η_r $r=1,2,\ldots N'$ under energy condition $\sum_r \nu_r\eta_r=E$ and particle number condition $\sum_r \nu_r=N$

fermions $S=n+1/2$ (Pauli principle) Fermi-Dirac statistics $W(\nu_i)=\prod_r\frac{g_r!}{\nu_r!(g_r-\nu_r)!}$ follows from Pauli-principle $\nu_r=0,1$ because the wave function is antisymmetric in particles $\Psi(\ldots\nu_i\ldots\nu_k\ldots)=-\Psi(\ldots\nu_k\ldots\nu_i\ldots)$:

$$N(\varepsilon)=\frac{g(\varepsilon)}{\exp\left(\frac{\varepsilon-\mu}{k_B T}\right)+1}$$

bosons $S = n$ Bose-Einstein statistics $W(\nu_i) = \prod_r \frac{(g_r + \nu_r - 1)!}{\nu_r!(g_r - 1)!}$ follows from $\nu_r = 0, 1, 2, ...$ because the wave function is symmetric in particles $\Psi(...\nu_i...\nu_k...) = \Psi(...\nu_k...\nu_i...)$:

$$N(\varepsilon) = \frac{g(\varepsilon)}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) - 1}$$

classical Boltzmann-Maxwell statistics $N(\varepsilon) = \exp\left(-\frac{\varepsilon}{k_B T}\right)$ is derived from both FD and BM statistics for high temperature $\exp\left(\frac{\varepsilon}{k_B T}\right) >> 1$

second principle of thermodynamics states that
$\frac{dS}{dt} \geq 0$ entropy is non-decreasing in time *t*,
or (Lorentz-invariant) $\frac{dS}{d\tau} \geq 0$ entropy is non-decreasing in proper time τ

1.2 Statistical mechanics basics

[15] chap. 2
Boltzmann theorem: The probability p_α of the system being found in the microstate α is proportional to

$$p_\alpha = \exp\left(-\frac{E_\alpha}{k_B T}\right)$$

Gibbs probability is $p_\alpha = \frac{1}{Z}\exp\left(-\frac{E_\alpha}{k_B T}\right)$, partition function $Z = \sum_\alpha \exp\left(-\frac{E_\alpha}{k_B T}\right)$, where the beta-parameter is $\beta = 1/k_B T$

the thermal average (X) of any property X of the system is then $\langle X \rangle = \sum_\alpha X_\alpha p_\alpha = \frac{1}{Z}\sum_\alpha X_\alpha \exp\left(-\frac{E_\alpha}{k_B T}\right)$

1.3 Thermodynamic quantities

[16] chap.4
Important thermodynamic quantities are

- mean energy $U \equiv \langle E \rangle = \sum_\alpha X_\alpha p_\alpha = \frac{1}{Z}\sum_\alpha E_\alpha \exp(-\beta E_\alpha) = -\left(\frac{\partial \log Z}{\partial \beta}\right)$
- heat capacity $C_v \equiv \left(\frac{\partial U}{\partial T}\right)_V = k_B \beta^2 \left(\frac{\partial^2 \log Z}{\partial \beta^2}\right)_V$, $C_v dT = T\, dS$, $C_v = -\beta\left(\frac{\partial S}{\partial \beta}\right)_V$

where entropy reads $S = -k_B \beta \left(\frac{\partial \log Z}{\partial \beta}\right)_V + k_B \log Z$

from this follows approximately $Z \approx \Omega \exp(-\beta U)$ and the famous Boltzmann formula $S \approx k_B \log \Omega$

where $\Omega = \Omega(U, U + \delta U)$ is the number of states ,

and with δU =stdev(U), $\delta U = T\left(k_B C_v\right)^{1/2}$ (see below)

- Helmholtz free energy $F(T, V, N) \equiv U - TS = -\frac{1}{\beta}\log Z$

$$dF = -S\, dT - p\, dV + \mu\, dN$$

- pressure p_i conjugate to volume v_i is $p \equiv -\left(\frac{\partial F}{\partial V}\right) = \frac{1}{\beta}\frac{\partial \log Z}{\partial V}$
- we introduce the average particle distance λ, and the specific volume $v = \frac{V}{N}$, where $v = \lambda^3$
- equation-of state (eos) $p\left(\lambda,\beta\right) = -\frac{\partial F}{\partial V} = \frac{1}{\beta}\frac{\partial \log Z}{\partial V} = \frac{1}{\beta}\frac{1}{3\lambda^2}\frac{1}{Z}\frac{\partial Z\left(\lambda,\beta\right)}{\partial \lambda}$, where the ideal gas law is

$$p = \frac{1}{v\beta} = \frac{1}{\lambda^3\beta}$$

- Gibbs free energy $G\left(T,p,N\right) \equiv F + pV = \mu N = -\frac{1}{\beta}\frac{\partial}{\partial V}\left(V \log Z\right)$

$$dG = -S\,dT + V\,dp + \mu\,dN$$

$$V = \frac{\partial G}{\partial p}$$

- Entropy $S = -k_B\beta\left(\frac{\partial \log Z}{\partial \beta}\right)_V + k_B \log Z$

$$S = -k_B\beta\left(\frac{\partial \log Z}{\partial \beta}\right)_V + k_B \log Z$$

$$S = -\left.\frac{\partial G}{\partial T}\right|_{p,N} = -\left.\frac{\partial G}{\partial T}\right|_{V,N}$$

- Enthalpy $H \equiv U + pV$

$$H = U + pV = G - F + U = -\frac{1}{\beta}\frac{\partial}{\partial V}\left(V \log Z\right) + \frac{1}{\beta}\log Z - \left(\frac{\partial \log Z}{\partial \beta}\right)$$

$$= -\left(\frac{1}{\beta}\frac{\partial \log Z}{\partial V} + \left(\frac{\partial \log Z}{\partial \beta}\right)\right)$$

$$dH = dU + d\left(pV\right),\ dH = T\,dS + V\,dp + \mu\,dN = dG + d\left(T\,S\right)$$

- compressibility $\kappa\left(\lambda,\beta\right) = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_T$,

from this follows heat capacity $C_V\left(\lambda,\beta\right) = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$

- chemical potential of a species $\mu_i = \left(\frac{\partial U}{\partial N_i}\right)$
- activity of a species (specific=per particle) $a_i = \exp\left(\frac{\mu_i - \mu_{0,i}}{k_B T}\right)$

or equivalently $\mu_i = \mu_{0,i} + k_B T \log a_i$

2. Basics of solutions

2.1 Basic equations

Partition function is $Z = Z(V, T, \mu_\alpha)$

with moles n_α of chemical species α , $x_\alpha = n_\alpha / n$ for the mole fraction of component α ,

$$dZ = (\partial Z / \partial V) dV + (\partial Z / \partial T) dT + \sum_\alpha (\partial Z / \partial \mu_\alpha) d\mu_\alpha$$

from this follows

$$(\partial Z / \partial p) dp + (\partial Z / \partial T) dT = \sum_\alpha n_\alpha d\mu_\alpha$$

$pdV - SdT = \sum_\alpha n_\alpha d\mu_\alpha$ Gibbs-Duhem equation [1] [2]

The chemical potential of component α is $\mu_\alpha \equiv \frac{\partial G}{\partial n_\alpha}(p, T, n_\alpha)$,

molar chemical potential of ideal gas is $\mu(T, p) = \mu_0(T) + RT \log(p / p_0)$,

where p is the pressure, p_0 is the reference pressure (1bar), and μ_0 is the reference chemical potential .

The ideal gas eos is for n mols $V = \partial G / \partial p = nRT / p$

free energy becomes $F = G - pV = n(\mu_0(T) - RT + RT \log(nRT / Vp_0))$

For perfect gas mixtures

$$F_{mix} = \sum_\alpha n_\alpha (\mu_{0,\alpha}(T) - RT + RT \log(n_\alpha RT / Vp_0))$$

$$G_{mix} = \sum_\alpha n_\alpha (\mu_{0,\alpha}(T) + RT \log(p_\alpha / p_0))$$

$H_{mix} = \frac{\partial(\mu / T)}{\partial(1/T)} = \frac{\partial(\mu\beta)}{\partial\beta}$ Gibbs–Helmholtz equation [1]

for a perfect mixture

$p = p\sum_\alpha x_\alpha = \sum_\alpha p_\alpha$ Dalton's law

where partial volume is $V_\alpha = \partial\mu_\alpha / \partial p = RT\, \partial \log p_\alpha / \partial p = RT / p$

Gibbs free energy of the mixture is ((p_α, p'_α) is the partial pressure before and after mixing)

$$\Delta_{mix} G = RT \sum_\alpha n_\alpha \log(p_\alpha / p'_\alpha)$$

and the entropy

$$\Delta_{mix} S = -\frac{\partial}{\partial T}\Delta_{mix} G = -R\sum_\alpha n_\alpha \log(p_\alpha / p'_\alpha)$$

A perfect solution is defined as having the same Gibbs energy of mixing as the perfect gas mixture

$$\Delta_{mix} S = -R \sum_\alpha x_\alpha \log(x_\alpha)$$

$$\Delta_{mix} \mu = RT \sum_\alpha x_\alpha \log(x_\alpha)$$

equivalently we have the partial pressure of perfect solution

$$\mu_\alpha(T, p) = \mu_{1,\alpha}(T, p) + RT \log(x_\alpha)$$

where $\mu_{1,\alpha}(T, p)$ is the partial chemical potential of pure component.

From μ(sol) = μ(vap) follows

$$\mu_{1,\alpha} + RT \log(x_\alpha) = \mu_{0,\alpha} + RT \log(p_\alpha / p_0) ,$$

so $\mu_{1,\alpha} = \mu_{0,\alpha} + RT \log(p_\alpha / p_0 x_\alpha) = \mu_{0,\alpha} + RT \log(K_{H,\alpha} / p_0)$, where $p_\alpha = K_{H,\alpha} x_\alpha$, $K_{H,\alpha} = \exp\left(\frac{\mu_{1,\alpha} - \mu_{0,\alpha}}{RT}\right)$ is Henry's constant, independent from x_α

For diluted binary solutions we have for the solvent $x_1 \approx 1$, $x_2 \ll 1$, $p_1 = K_{H,1}$,

and $p_1 \approx p_1^* x_1$ Raoult's law , exact for perfect solutions,

where $p_1^* = p_1^*(T,V)$ is the pressure of pure solvent.

Gas	K_H(water) in GPa	K_H(benzene) in GPa
CH4 methane	4.185	0.0569
C2H2 acetylene	0.135	
C2H4 ethylene	1.155	
C2H6 ethane	3.06	
air	7.295	
N2 nitrogen	8.765	0.239
O2 oxygen	4.438	
H2 hydrogen	7.16	0.367
He helium	12.66	
CO carbon monoxide	5.79	0.163
CO2 carbon dioxide	1.67	0.0144
H2S hydrogen sulfide	0.055	

Table [1] Henry's constant K_H for dissolved gases at T=25°C

2.2 Excess energy, freezing-boiling point shift

Excess values (compared to ideal solution) are given by [1] [4]

Excess Gibbs energy

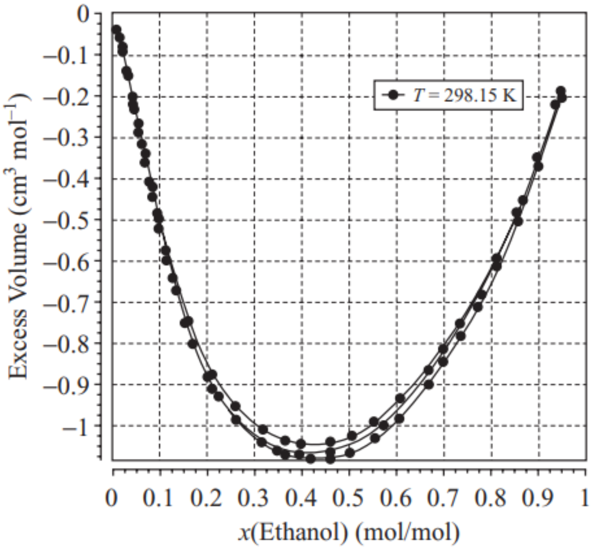
$$G_E = \sum_\alpha x_\alpha \left(\mu_\alpha - \mu_\alpha^*\right)$$

Excess volume

$$V_E = V_m - \sum_\alpha x_\alpha V_\alpha ,$$

where V_m is the volume of the mixture.

Example: Excess volume V_E for a mixture of water-ethanol [1]



Freezing point, boiling point, osmotic pressre in binary mixtures

Freezing point depression is T_f=T*-Δ_fT,
we have
$\mu_1(s) = \mu_1(l) + RT\ln(x_1)$,

change in Gibbs energy $\Delta_f G \equiv \mu_1(l) - \mu_1(s)$, $-\frac{\Delta_f G}{RT} = \log(x_1)$

change in enthalpy $\Delta_f H = RT^2 \frac{\partial \ln(x_1)}{\partial T}$

from which follows $\Delta_f T = K_f x_2 = \frac{RT^{*2}}{\Delta_f H}$

Correspondingly, boiling point elevation is T_b=T*+Δ_bT ,

change in enthalpy is $\Delta_b T = K_b x_2 = \frac{RT^{*2}}{\Delta_b H}$

compound	**K_f (K kg/mol)**	**K_b (K kg/mol)**
acetic acid	3.9	3.07
benzene	5.12	2.53
CS2 carbon disulfide	3.8	2.37
CCl4 carbon tetrachloride	30	4.95
naphthalene	6.94	5.8
phenol	7.27	3.04
water	1.86	0.51
camphor	40	

Table: Cryoscopic constants K_f and ebullioscopic constants K_b for some compounds [1]

Osmotic (molar) pressure of a binary mixture $\Delta_O p$ is

$\Delta_O p = c_O RT$, $c_O = \frac{c_2}{x_1 V_1^* + x_2 V_2^*}$ Hoff's law

Thermodynamic variables for binary mixtures

Given a fluid with coordination number z , interaction energies w_{11} , w_{22} , w_{12} , molecule number N = N_1 + N_2 , we have [1] [2] [4]

internal energy change $\Delta U = w_{12} - (w_{11} + w_{22})/2$ =0 ,

entropy change $\Delta S = k_B \log(W) = -N k_B (x_1 \log x_1 + x_2 \log x_2)$,

free energy $F = U - TS$

the configurational partition function $Z = exp(-\beta F)$ reads

$$Z = \frac{N!}{N_1! N_2!} \exp\left(-\frac{\beta z}{2}\left(N_1 w_{11} + \frac{N_2 w_{22}}{2}\right)\right)$$

and the free energy becomes

$$F = -k_B T \log Z_m = z\left(\frac{N_1 w_{11}}{2} + \frac{N_2 w_{22}}{2}\right) + k_B T\left(N_1 \log N_1 + N_2 \log N_2\right)$$

With partial free energy

$$F_\alpha = -k_B T \log Z_\alpha = \frac{z N_\alpha w_{\alpha\alpha}}{2}$$

we obtain mixing free energy $\Delta F = F - (x_1 F_1 + x_1 F_1) = N k_B T (x_1 \log x_1 + x_2 \log x_2)$,

and the mixing entropy $\Delta S = -\frac{\partial \Delta F}{\partial T} = -N k_B (x_1 \log x_1 + x_2 \log x_2)$

the chemical potential $\mu_\alpha = \frac{\partial F}{\partial N_\alpha} = \frac{zw_{\alpha\alpha}}{2} + k_B T \log x_\alpha$, $\mu_\alpha - \mu_{0,\alpha} = k_B T \log x_\alpha$

The activity λ is given by $\mu_\alpha = k_B T \log \lambda_\alpha$, and we obtain $\frac{\lambda_\alpha}{\lambda_{0,\alpha}} = x_\alpha$

2.3 Ideal and regular molecular solutions

Different types of solutions are given by the table

ideal solution	$\Delta H=0$	$\Delta S=\Delta S_{ideal}$
athermal solution	$\Delta H=0$	$\Delta S\neq\Delta S_{ideal}$
regular solution	$\Delta H\neq 0$, $\Delta H = A x_1 x_2$	$\Delta S=\Delta S_{ideal}$
irregular solution	$\Delta H\neq 0$	$\Delta S\neq\Delta S_{ideal}$

Interchange energy is $w \equiv w_{12} - \frac{\left(w_{11}+w_{22}\right)}{2}$

$N = n N_A$, where N_A is the Avogadro number, *n* number of moles

change in interaction inner energy is after mixing

$$\Delta U = zN\left(x_1 x_2 w_{12} + \frac{x_1{}^2 w_{11}}{2} + \frac{x_2{}^2 w_{22}}{2} - \frac{x_1 w_{11}}{2} - \frac{x_2 w_{22}}{2} \right)$$

per mole inner energy $\Delta U_m = \frac{\Delta U}{n} = zN_A x_1 x_2 w$

for **ideal solution**

$$U_m = x_1 u_1 + x_2 u_2 = \frac{z\left(x_1 w_{11} + x_2 w_{22}\right)}{2}\,,\ \Delta H_m = \Delta U_m\ ,\ G_{ideal} = \sum_\alpha \left(n_\alpha \mu_{0,\alpha} + RTn_\alpha \log x_\alpha \right)$$

for **regular solution**

$$\Delta_{mix} S_m = -R\sum_\alpha x_\alpha \log\left(x_\alpha\right)\ ,\ S_E = \Delta_{mix} S_m = \Delta_{mix} S_{m,ideal}$$

$$\Delta_{mix} G_m = N_A\left(zwx_1x_2 + k_B T\left(x_1 \log x_1 + x_2 \log x_2 \right)\right)$$

excess Gibbs energy $G_E = \Delta_{mix} G - \Delta_{mix} G_{ideal} = N_A zwn_1 n_2 / \left(n_1 + n_2\right)$

Activity coefficient of regular solutions γ_α

From $G = \sum_\alpha n_\alpha \mu_\alpha$, $n_\alpha = x_\alpha N / N_A$, $\mu_\alpha = \mu_{0,\alpha} + RT \log\left(\gamma_\alpha x_\alpha\right)$

we obtain for activity coefficient γ_α

$$G = \sum_\alpha \left(n_\alpha \mu_{0,\alpha} + n_\alpha RT \log\left(\gamma_\alpha x_\alpha\right)\right)$$

which gives excess Gibbs energy $G_E = \Delta_{mix} G - \Delta_{mix} G_{ideal} = \sum_\alpha n_\alpha RT \log \gamma_\alpha = N_A zwn_1 n_2 / \left(n_1 + n_2\right)$

so $\partial G_E / \partial n_\alpha = RT \log \gamma_\alpha$, $\log \gamma_1 = \beta zwx_2{}^2$, $\log \gamma_2 = \beta zwx_1{}^2$

Total pressure becomes $p = p_1^* x_1 \exp\left(\beta zwx_2{}^2\right) + p_2^* x_2 \exp\left(\beta zwx_1{}^2\right)$,

where as usual p_1^* and p_2^* are the pressure of the pure component.

Phase separation and vapor pressure

The critical point for phase separation can be obtained from

$$\frac{\partial \mu_1}{\partial x_1} = 0\,, \frac{\partial^2 \mu_1}{\partial x_1{}^2} = 0\,, \frac{\partial \mu_2}{\partial x_2} = 0\,, \frac{\partial^2 \mu_2}{\partial x_2{}^2} = 0\,,$$

follows

$x_1 = 0.5$, $x_2 = 0.5$, $\beta_{cr} = 2 / zw$

$x_1 = x_2 = 0.5$, $(\beta zw)_{cr} = 2$, $T_{cr} = z\, w/2\, k$

activity coefficient $\gamma_{cr} = 1.649$, activity $a_{cr} = \gamma x = 0.824$,

critical pressure $p_{cr} = a_{cr}\left(p_1^* + p_2^*\right) = 0.824\left(p_1^* + p_2^*\right)$, compared to $p=\left(p_1^*+p_2^*\right)$ for insoluble liquids.

Regular solutions with correlation functions and volume fractions

- General energy calculation [1] [4]

The volume is

$$V=\left(n_1V_1\ +n_2V_2\ \right)$$

with volume fractions $\phi_i=x_iV_i\ \ /\left(x_1V_1\ +x_2V_2\ \right)$,

inner energy in dependence of correlation function is (radial-symmetrical potential *u*, radial distribution function *g*)

$$U=\left\langle E_{kin}\right\rangle+\left\langle E_{pot}\right\rangle=\frac{3Nk_BT}{2}+\frac{N^2}{2V}\int_0^\infty u\left(r\right)g\left(r\right)4\pi r^2dr$$

with average potential energy

$$\left\langle E_{pot}\right\rangle=V2\pi N_A{}^2\left(\frac{\phi_1{}^2}{V_1^2}\int_0^\infty u_{11}\left(r\right)g_{11}\left(r\right)4\pi r^2dr+\frac{\phi_2{}^2}{V_2^2}\int_0^\infty u_{22}\left(r\right)g_{22}\left(r\right)4\pi r^2dr+\frac{2\phi_1\phi_2}{V_1V_2}\int_0^\infty u_{12}\left(r\right)g_{12}\left(r\right)4\pi r^2dr\right)$$

Subtracting the energy of the separate components

$$U_1+U_2=V2\pi N_A{}^2\left(\frac{\phi_1\phi_2}{V_1^2}\int_0^\infty u_{11}\left(r\right)g_{11}\left(r\right)4\pi r^2dr+\frac{\phi_1\phi_2}{V_2^2}\int_0^\infty u_{22}\left(r\right)g_{22}\left(r\right)4\pi r^2dr\right)$$

gives mixing energy

$$\Delta_{mix}U=\left\langle E_{pot}\right\rangle-\left(U_1+U_2\right)=V2\pi N_A{}^2\left(\begin{aligned}&\frac{\phi_1{}^2}{V_1^2}\int_0^\infty u_{11}\left(r\right)g_{11}\left(r\right)4\pi r^2dr+\frac{\phi_2{}^2}{V_2^2}\int_0^\infty u_{22}\left(r\right)g_{22}\left(r\right)4\pi r^2dr\\&+\phi_1\phi_2\left(\frac{2}{V_1V_2}\int_0^\infty u_{12}\left(r\right)g_{12}\left(r\right)4\pi r^2dr-\frac{1}{V_1^2}\int_0^\infty u_{11}\left(r\right)g_{11}\left(r\right)4\pi r^2dr-\frac{1}{V_2^2}\int_0^\infty u_{22}\left(r\right)g_{22}\left(r\right)4\pi r^2dr\right)\end{aligned}\right)$$

We introduce scaling with energy scale ε and length scale σ,

$$u_{ij}\left(r\right)=\varepsilon_{ij}u_0\left(r/\sigma_{ij}\right)\ ,\ g_{ij}\left(r\right)=g_0\left(r/\sigma_{ij}\right)$$

and obtain

$$\Delta_{mix}U=V2\pi N_A{}^2\phi_1\phi_2\left(\int_0^\infty u_0\left(r\right)g_0\left(r\right)4\pi r^2dr\right)\left(\frac{2\varepsilon_{12}\sigma_{12}{}^3}{V_1V_2}-\frac{\varepsilon_{11}\sigma_{11}{}^3}{V_1^2}-\frac{\varepsilon_{22}\sigma_{22}{}^3}{V_2^2}\right)$$

Experimental approximation

Redlich–Kister expansion of excess Gibbs energy is a Taylor series in $\left(x_1-x_2\right)$ with coefficients (A,B,C) [1] [4]:

$$G_E=x_1x_2\left(A+B\left(x_1-x_2\right)+C\left(x_1-x_2\right)^2+...\right)$$

for ideal solution A=0, B=0, C=0 , G_E=0, γ_1=1, γ_2=1

$A=B=C=\cdots=0,\ G^E=0,\ RT\ln\gamma_1=RT\ln\gamma_2=0$ and $\gamma_1=\gamma_2=1$

for regular solution B=0, C=0 , $G_E=Ax_1x_2$, $RT\log\gamma_1=Ax_2{}^2$, $RT\log\gamma_2=Ax_1{}^2$

for deviation from regular C=0 , $G_E=x_1x_2\left(A+B\left(x_1-x_2\right)\right)$ Margules equation

$$RT\log\gamma_1=Ax_2{}^2,\ RT\log\gamma_2=Ax_1{}^2$$

components	T_0(K)	A/RT_0	B/RT_0	C/RT_0
ethanol/methylcyclohexane	305	2.118	-0.239	0.375
methylcyclohexane/acetone	318	1.6907	-0.0001	0.1832
pyridine/acetone	303	0.1919	0.00050	0.0075
chloroform/furan	303	-0.1083	-0.0177	0.0071
pyridine/ chloroform	303	-1.0271	0.2270	0.0930
chloroform/1-4-dioxan	303	-1,2006	-0.4131	0.0318

Table Excess Gibbs function parameters for various solutions [1]

3. Equations-of-state

3.1 Fluid-gas equations-of-state

vdWaals eos

The well-known vdWaals equation-of-state (eos) for real gas reads in molar variables

$$p=\frac{RT}{\left(V_m-b\right)}-\frac{a}{V_m{}^2}$$

and in specific (per particle) variables

$$p=\frac{1}{\left(v-b_1\right)\beta}-\frac{a_1}{v^2}$$

with critical parameters

$$\frac{1}{\beta_c}=kT_c=\frac{8a}{27b}\ ,\ v_c=3b\ ,\ p_c=\frac{a}{27b^2}$$

we obtain $a=27b^2p_c=\dfrac{27b}{8\beta_c}$,

so $b=\dfrac{1}{8\beta_c p_c}$, $a=\dfrac{27}{64\beta_c{}^2 p_c}$

With molecular parameters we obtain

$$a=a_{W0}\varepsilon\sigma^3$$

for Lennard-Jones potential $u_{LJ}\left(r,\sigma,\varepsilon\right)=4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right)$, $a_{W0}=23.4$ [18],

for dipole-dipole potential $u_{DD}\left(r,\sigma,\theta\right)=4\varepsilon\left(\Theta_L\left(r,\sigma,\Delta r\right)-\frac{\Theta_H\left(r,\sigma,\Delta r\right)}{\left(\left(r/\sigma\right)^3+\Delta r\right)}\cos\left(\theta\right)\right)$, $\Delta r=0.1\sigma$, $a_{W0}=25.7$ [18]

Parameter mixing rules

[11]

Parameter mixing rules determine the vdW parameters of the solution with component concentrations x_i from the component parameters a_i b_i , in simplest form

$$b_1=\sum_i x_i b_{1,i}\ ,\ a_1=\sum_{i,j} x_i x_j a_{1,ij}\ ,$$

$a_{1,ij}=\sqrt{a_{1,i}a_{1,j}}$ geometric (GMA), $a_{1,ij}=\dfrac{2\sqrt{a_{1,i}a_{1,j}}+a_{1,i}+a_{1,j}}{4}$ expanded geometric (EGA),

$p=\dfrac{1}{\beta\left(v-b_1\right)}-\dfrac{\sqrt{\beta}\ a_1}{v\left(v+b_1\right)}$ simple arithmetic (SA)

Molecular mixing rules

[27]

Parameter mixing rules calculate the molecular parameters ε_{ij} (characteristic energy) and σ_{ij} (effective hard-core radius) for the partial pressure p_{ij} from the component parameters $\varepsilon_i=a_i/\sigma_i{}^3$ and $\sigma_i=\left(3b_i/2\right)^{1/3}$, the resulting partial pressure is then

$p_{ij}=\dfrac{1}{\left(v-2\sigma_{ij}{}^3/3\right)\beta}-\dfrac{\varepsilon_{ij}\sigma_{ij}{}^3}{v^2}$, and the total pressure is $p=\sum_{i,j}x_i x_j p_{ij}$.

A widely used rule is Lorentz-Berthelot

$$\sigma_{ij} = \left(\sigma_i + \sigma_j\right)/2 \ , \ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

which generates the simple GMA parameter mixing rule above.
An improved rule is Halgren HHG rule [27]

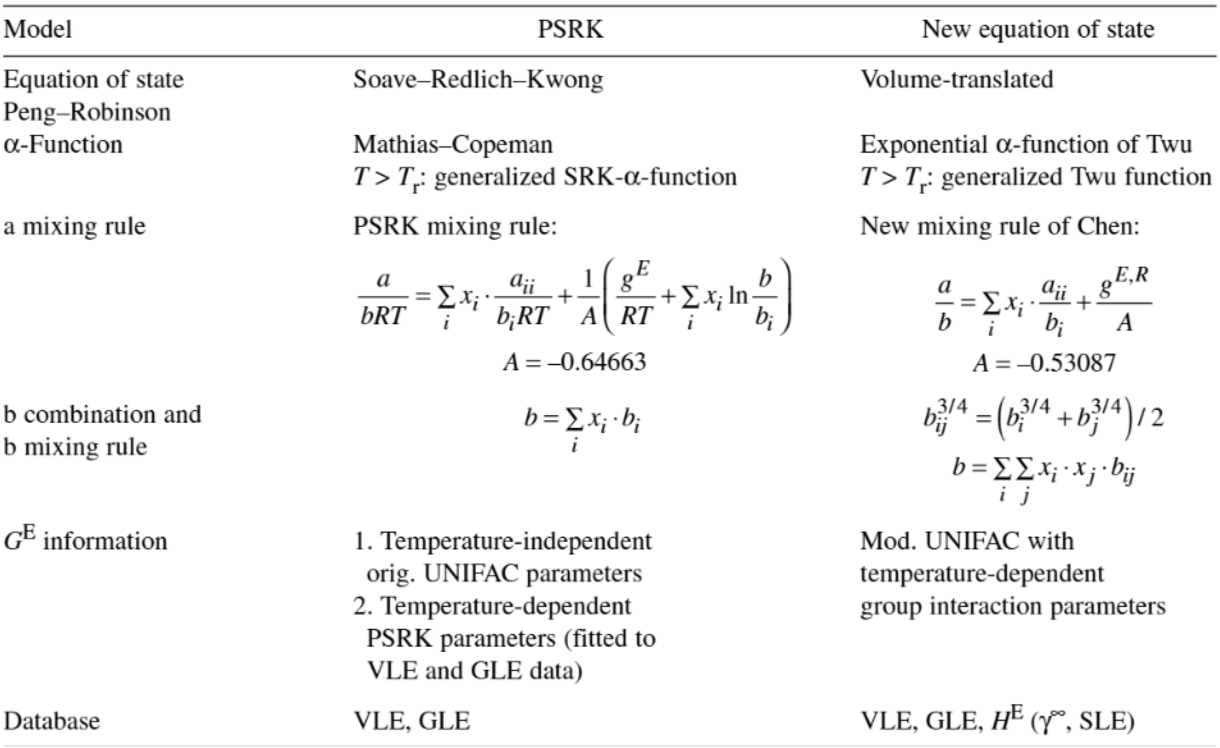
$$\sigma_{ij} = \frac{\sigma_i^{\ 3} + \sigma_j^{\ 3}}{\sigma_i^{\ 2} + \sigma_j^{\ 2}} \ , \ \varepsilon_{ij} = \frac{4\varepsilon_i \varepsilon_j}{\left(\sqrt{\varepsilon_i} + \sqrt{\varepsilon_j}\right)^2}$$

A fit to experimental data gives the experimental Al-Matar rule [27]

$$\sigma_{ij} = \left(\frac{0.5640\sigma_i^{\ 6} + 0.9464\sigma_i^{\ 3}\sigma_j^{\ 3} + 0.4896\sigma_j^{\ 6}}{2}\right)^{1/6}$$

$$\varepsilon_{ij} = \left(\frac{0.0799\varepsilon_i + 1.9129\sqrt{\varepsilon_i \varepsilon_j} + 0.0071\varepsilon_j}{2}\right)\left(\frac{\sigma_i^{\ 3}\sigma_j^{\ 3}}{\sigma_{ij}^{\ 6}}\right)$$

PSRK model (Predictive Soave-Redlich-Kwong)
[6]
The PSRK model provides reliable predictions of VLE (vapor-liquid-equilibria) and gas solubilities. Therefore, the PSRK model was implemented in the different process simulators and is well accepted as a predictive thermodynamic model for the synthesis and design of the different processes in the chemical, gas proc-essing, and petroleum industries. But also the group contribution equation of state PSRK shows a few weaknesses. Because the SRK (Soave-Redlich-Kwong) equation of state is used in PSRK, poor results are calculated for liquid densities of the pure compounds and the mixtures.
Better results are achieved with the improved Peng-Robinson eos.



Model	PSRK	New equation of state
Equation of state Peng–Robinson	Soave–Redlich–Kwong	Volume-translated
α-Function	Mathias–Copeman $T > T_r$: generalized SRK-α-function	Exponential α-function of Twu $T > T_r$: generalized Twu function
a mixing rule	PSRK mixing rule: $\frac{a}{bRT} = \sum_i x_i \cdot \frac{a_{ii}}{b_i RT} + \frac{1}{A}\left(\frac{g^E}{RT} + \sum_i x_i \ln \frac{b}{b_i}\right)$ $A = -0.64663$	New mixing rule of Chen: $\frac{a}{b} = \sum_i x_i \cdot \frac{a_{ii}}{b_i} + \frac{g^{E,R}}{A}$ $A = -0.53087$
b combination and b mixing rule	$b = \sum_i x_i \cdot b_i$	$b_{ij}^{3/4} = \left(b_i^{3/4} + b_j^{3/4}\right)/2$ $b = \sum_i \sum_j x_i \cdot x_j \cdot b_{ij}$
G^E information	1. Temperature-independent orig. UNIFAC parameters 2. Temperature-dependent PSRK parameters (fitted to VLE and GLE data)	Mod. UNIFAC with temperature-dependent group interaction parameters
Database	VLE, GLE	VLE, GLE, H^E (γ^∞, SLE)

Main differences between the new group contribution equation of state (Gmelich) and the PSRK model.

Redlich–Kwong equation
[9]
The Redlich–Kwong equation is a real-gas equation and is formulated as (extended vdWaals)

$$p = \frac{RT}{\left(V_m - b\right)} - \frac{a}{\sqrt{T}\, V_m \left(V_m + b\right)}$$

where V$_m$=V/N$_A$ is the molar volume , a , b are the generalized vdWaals constants, the constants *a, b* depend on critical values of the gas:

$$a = 0.42748 \frac{R^2 T_c^{\,2.5}}{p_c} \ , \ b = 0.08664 \frac{RT_c}{p_c}$$

The equation can be formulated in specific (per particle) volume *v=V/N* , $a_1 = \frac{0.42748}{p_c \beta^{5/2}}$,

with specific generalized vdWaals parameters $b_1 = \frac{b}{N_A}$, $a_1 = \frac{a}{N_A}\sqrt{k_B}$

$$b_1 = 0.08664 \frac{1}{p_c \beta_c} \ , \ b_1 = 0.08664 \frac{1}{p_c \beta_c}$$

PSRK Mixing rule

$$b = \sum_i x_i b_i \ , \ \frac{a}{bRT} = \sum_i x_i \frac{a_{ii}}{b_i RT} + \frac{1}{A}\left(\frac{g^E}{RT} + \sum_i x_i \ln \frac{b}{b_i} \right) \ , \ A = -0.64663$$

specific variables

$$b_1 = \sum_i x_i b_{1,i} \ , \ \frac{a_1 \beta}{b_1} = \sum_i x_i \frac{a_{1,i} \beta}{b_{1,i}} + \frac{1}{A}\left(g^E \beta + \sum_i x_i \ln \frac{b_1}{b_{1,i}} \right) ,$$

where g^E is the excess Gibbs energy.

Peng-Robinson equation

[10]

The Peng-Robinson equation is an improvement of the Redlich–Kwong equation in the form

$$p = p\left(\beta, v, p_c, \beta_c, \omega\right) = \frac{1}{\beta\left(v - b\right)} - \frac{\alpha\, a}{v\left(v + b\right) + b\left(v - b\right)}$$

where

$$a = \frac{0.45723}{p_c \beta_c^{\,2}} \ , \ \alpha = \left(1 + \left(0.480 + 1.574\omega - 0.176\,\omega^2\right)\left(1 - \sqrt{\beta / \beta_c}\right)\right)^2 \ , \ b = 0.077796 \frac{1}{p_c \beta_c}$$

ω is the acentric factor $\omega = -\log_{10}\left(\frac{p_{sat}\left(0.7 T_c\right)}{p_c} \right)$

with critical parameters

$$\beta_c = \frac{b}{a}\frac{0.45723}{0.077796} = 5.8773 \frac{b}{a} \ , \ p_c = \frac{0.077796}{b \beta_c} = \frac{0.077796}{5.8773}\frac{a}{b^2} = 0.013236 \frac{a}{b^2}$$

with vdWaals parameters

$$\frac{1}{\beta_c} = kT_c = \frac{8 a_W}{27 b_W} \ , \ v_c = 3 b_W \ , \ p_c = \frac{a_W}{27 b_W^{\,2}}$$

$$b_W = \frac{2\pi\sigma^3}{3} = \frac{1}{8\beta_c p_c} = \frac{0.125}{0.077796} b = 1.607 b \ . \ a_W = a_{W0}\varepsilon\sigma^3 = \frac{27}{64 \beta_c^{\,2} p_c} = \frac{0.4219}{\beta_c^{\,2} p_c} ,$$

so $a = \frac{0.45723}{p_c \beta_c^{\,2}} = 1.083 a_W$, $b = 0.077796 \frac{1}{p_c \beta_c} = 0.62223 b_W$

Now we can reformulate the eos with

$$\beta_c = 5.8773\frac{b_1}{a_1} = 5.8773\frac{0.62223}{1.083}\frac{b_W}{a_W} = 3.37676\frac{b_W}{a_W} = \frac{3.37676}{a_{W0}\varepsilon\sigma^3}\frac{2\pi\sigma^3}{3} = \frac{7.07227}{a_{W0}\varepsilon},$$

$$p_c = 0.013236\frac{a}{b^2} = 0.013236\frac{1.083a_W}{0.62223^2 b_W{}^2} = 0.03702\frac{a_{W0}\varepsilon\sigma^3}{\sigma^6\left(2\pi/3\right)^2} = 0.00844a_{W0}\frac{\varepsilon}{\sigma^3},$$

$$p = p\left(\beta, v, \omega, \varepsilon, \sigma\right) = \frac{1}{\beta\left(v-b\right)} - \frac{\alpha\, a}{v\left(v+b\right)+b\left(v-b\right)}$$

$$a = 1.083a_{W0}\varepsilon\sigma^3,\ b = 0.62223b_W = 0.62223\frac{2\pi\sigma^3}{3} = 1.303\sigma^3$$

$$\alpha = \left(1+\left(0.480+1.574\omega-0.176\omega^2\right)\left(1-\sqrt{0.141\frac{a}{b}\beta}\right)\right)^2$$

Values of ω [20]:
ω=-0.302 vdWaals,
ω=0.304 acetone
ω=-0.644 ethanol
ω=0. argon
ω=0.353 benzene

The material parameters here are the critical parameters p_c, β_c , and the acentric factor ω .

Chen mixing rule [26]

$$b_1 = \sum_{i,j} x_i x_j b_{1,ij}\ ,\ b_{1,ij}{}^{3/4} = \left(b_{1,i}{}^{3/4} + b_{1,j}{}^{3/4}\right)/2\,,\ \frac{a_1}{b_1} = \sum_i x_i\frac{a_{1,ii}}{b_{1,i}} + \frac{g^E_{res}}{A}\ ,\ A = -0.53087\,,$$

where g^E_{res} is the residual excess Gibbs energy.

Thermodynamic variables for Peng-Robinson
[5]

$$p = p\left(\beta, v, p_c, \beta_c, \omega\right) = \frac{1}{\beta\left(v-b\right)} - \frac{\alpha\, a}{v\left(v+b\right)+b\left(v-b\right)}$$

free energy F

$$F = -\int p\left(v,T\right)dv = -\frac{1}{\beta}log\left(v-b\right) - \alpha(\omega,\beta)a\left(\operatorname{arctanh}\left(\frac{b+v}{\sqrt{2b}}\right) - \operatorname{arctanh}\left(\sqrt{2b}\right)\right)$$

including a T-term, the complete expression is

$$F = -\int p\left(v,T\right)dv = -\frac{1}{\beta}\left(1-\frac{3}{2}\log\beta + \log\left(v-b\right)\right) - \alpha a\left(\operatorname{arctanh}\left(\frac{b+v}{\sqrt{2b}}\right) - \operatorname{arctanh}\left(\sqrt{2b}\right)\right)$$

partition function

$$Z = \exp\left(-\beta F\right) = \beta^{3/2}\left(v-b\right)\exp\left(\alpha(\omega,\beta)a\beta\left(\operatorname{arctanh}\left(\frac{b+v}{\sqrt{2b}}\right) - \operatorname{arctanh}\left(\sqrt{2b}\right)\right)\right)$$

Gibbs energy G

$$G = F + pv = -\frac{1}{\beta}\left(1-\frac{3}{2}\log\beta + \log\left(v-b\right)\right) - \alpha a\left(\operatorname{arctanh}\left(\frac{b+v}{\sqrt{2b}}\right) - \operatorname{arctanh}\left(\sqrt{2b}\right)\right) + p\,v$$

The material parameters here are the critical parameters p_c, β_c , and the acentric factor ω .
The acentric factor ω is an independent third parameter alongside a, b .

The parameters are functions of the critical values: ω , $a=a(p_c,\beta_c)$, $b=b(p_c,\beta_c)$.

With reduced variables $T_r=\frac{T}{T_c}$, $v_r=\frac{v}{v_c}$, $p_r=\frac{p}{p_c}$

Peng-Robinson equation in reduced variables depends only on material-specific ω , whereas *a* and *b* are material-independent

$$p=p(\beta,v,\omega)=\frac{1}{\beta(v-b)}-\frac{\alpha(\omega,\beta)a}{v(v+b)+b(v-b)}$$

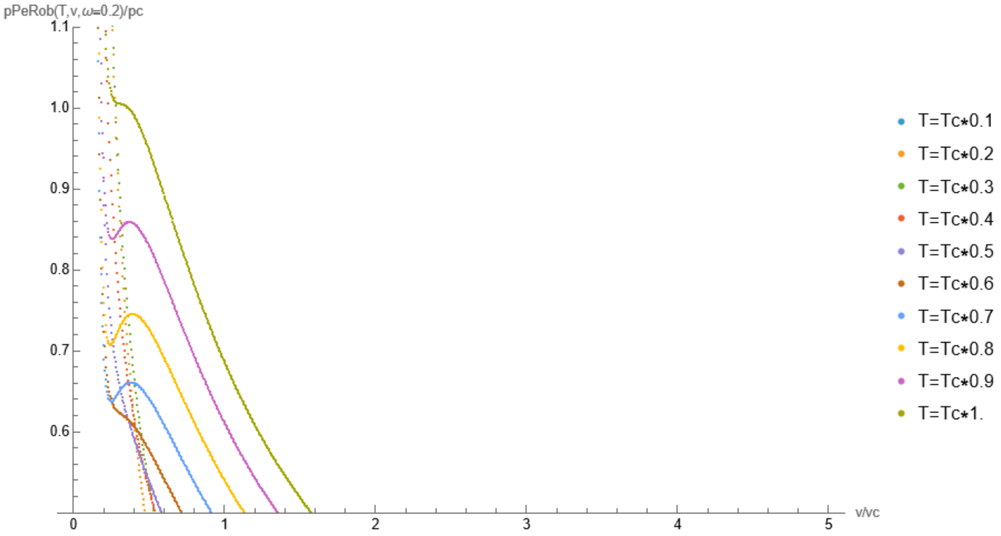
where

$a=0.45723$, $b=0.077796$

$$\alpha=\left(1+\left(0.480+1.574\omega-0.176\omega^2\right)\left(1-\sqrt{\beta}\right)\right)^2$$

ω is the acentric factor $\omega=-\log_{10}\left(p_{sat}(1/0.7)\right)$

Below, a the p(v) curves for different temperature values are shown for $\omega=0.2$ (carbon dioxide) [18]



Tait–Tammann equation of state

The Tait–Tammann equation [17] is adapted and intensely tested for water, it is an extension of the vdWaals equation in exponential form, for pressure p (bar) in dependence of $w=1/\rho$ (m^3/ kg) and temperature T (degree K).

$$p=(p_0+B)\exp\left(-\frac{w-w_0}{C_0w_0}\right)-B,\ \ p_0=p(w_0,T_0)\ \text{normal pressure},\ \ w=1/\rho$$

where C_0 is a material constant, for water $C_0=0.315$

$B=B_0+B_1(T-T_0)$, with material constants B_0, B_1 , for water $B_0=2996\,bar$, $B_1=7.555\ bar\,K^{-1}$

With the introduction of molecular mass m_0, it can be reformulated in standard variables (per particle) $p=P/N$, $v=V/N$, $\beta=1/k_BT$ in the form

$$p=(p_0+b)\exp\left(-\frac{v-v_0}{C_0v_0}\right)-b\ ,\ \ p_0=p(v_0,\beta_0),\ b=B\frac{m_0}{1kg}$$

- Comparison of eos and mixing rules results

Equation of state (EOS)	Mixing rule (MR)	% AAD
Van der Waals	GMA	46.8
	EGA	46.7
	SA	59.7
Redlich-Kwong	GMA	20.6
	EGA	20.5
	SA	29.9
Peng-Robinson	GMA	9.9
	EGA	9.9
	SA	18.9

Absolute average deviation for GMA, EGA, and SA for ammonia – water binary system [11]

The above table gives an assessment of precision for different eos, the best relative error has the Peng-Robinson eos (about 10%).

3.2 Solid equations-of-state

Mie-Grueneisen eos

[21]

The Mie-Grueneisen eos has the form

$$p-p_0=\frac{\rho_0 v_s^2(\eta-1)\left(\eta-\frac{\Gamma_0}{2}(\eta-1)\right)}{\left(\eta-s(\eta-1)\right)^2}+\Gamma_0 E\ ,\ \eta=\frac{\rho}{\rho_0}$$

where v_s is the bulk speed of sound, ρ_0 is the initial density (reference state), ρ is the current density, Γ_0 is Grueneisen's gamma at the reference state, $s=dv_s/dv_p$ is the Hugoniot coefficient, v_s is the shock wave velocity,v_p is the particle velocity, and *E* is the internal energy density.

The internal energy density *e* can be computed using

$$E=\frac{1}{V_0}\int C_v dT\approx c_v\left(T-T_0\right)$$

From the Dulong-Petit law follows $c_v=n\frac{n_{dof}}{2}k_B$, $E\approx\frac{n_{dof}}{2}\frac{k_B\left(T-T_0\right)}{v}$,

where *n*=particle density, n_{dof} =number of degrees-of -freedom ; for solids $n_{dof}\approx 6\ \ c_v\approx 3nk_B$, so

$E=3k_B\left(T-T_0\right)=3\left(E_{th}-E_{th,0}\right)$ per particle.

Also, as speed of sound $v_s=\sqrt{\frac{Y}{\rho}}$, *Y*=Young modulus, we obtain

$$p-p_0=\frac{Y(\eta-1)\left(\eta-\frac{\Gamma_0}{2}(\eta-1)\right)}{\eta\left(\eta-s(\eta-1)\right)^2}+3\Gamma_0\frac{\left(E_{th}-E_{th,0}\right)}{v_0}$$

, where the Young modulus is slightly dependent on particle density $\rho=1/v$,

$Y=y_1\rho-y_2$ per particle .

With these relations, the Mie-Grueneisen eos reads per particle

$$p(\eta,\beta)=p_0+\frac{\left(y_1\eta/v_0-y_2\right)(\eta-1)\left(\eta-\frac{\Gamma_0}{2}(\eta-1)\right)}{\eta\left(\eta-s(\eta-1)\right)^2}+3\frac{\Gamma_0}{v_0}\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)$$

, where $\eta=\frac{v_0}{v}$

The equation is derived from the Mie ansatz $p-p_0=\Gamma_0\left(E-E_0\right)$.

In solids, as opposed to fluids/gasses, the molecules are located on a crystal lattice with a lattice constant *a*.

For the intermolecular potential $u=u\left(\vec{r},\sigma,\varepsilon\right)$ with repulsive (hardcore) radius σ , characteristic (well depth) energy ε , and well-minimum radius r_0, the solid’s lattice constant becomes $a=2r_0$ (fcc) resp. $a=2r_0/\sqrt{3}$ (bcc).

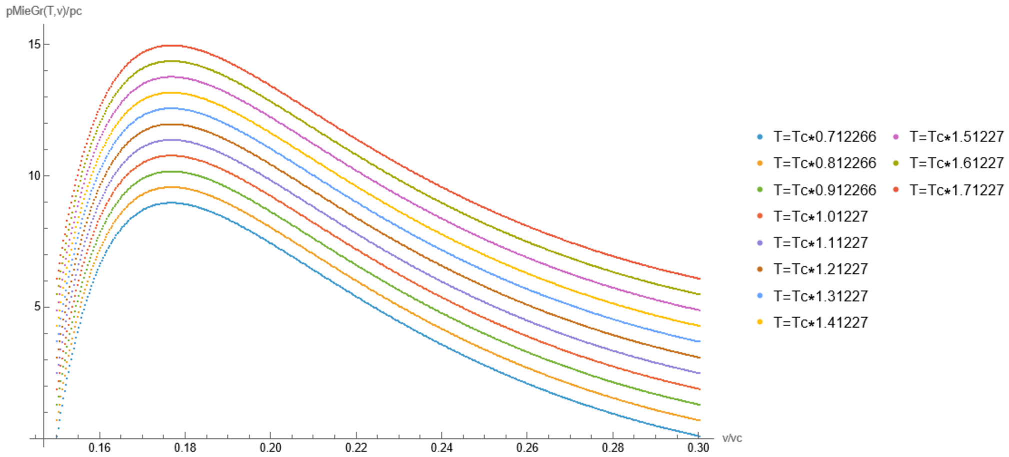
At the well-minimum, the potential has the form of a harmonic oscillator

$$u_0\left(r\right)=\frac{1}{2}\frac{\partial^2 u\left(r=r_0\right)}{\partial r^2}\left(r-r_0\right)^2 \text{ , i.e. } Y\approx\frac{1}{r_0}\frac{\partial^2 u\left(r=r_0\right)}{\partial r^2} \text{ from } \left(\frac{K}{A}=\frac{\partial u_0\left(r\right)}{{r_0}^2\partial r}\right)=\frac{1}{r_0}\frac{\partial^2 u\left(r=r_0\right)}{\partial r^2}\frac{\left(r-r_0\right)}{r_0}$$

From the crystal lattice ansatz follows $\Gamma_0\approx 2$ and $s\approx 3/2$, which is confirmed experimentally.

The Mie-Grueneisen eos is derived from the crystal lattice ansatz and from the Hugoniot equations for the conservation of mass, momentum, and energy [21] [22].

Below, the Mie-Grueneisen eos is shown [18] for different temperatures for carbon dioxide , with $y_1=8.44$, $y_2=17.4$ [20]



Thermodynamic variables for Mie-Grueneisen eos

[5]

$$p\left(v,\beta\right)=p_0+\frac{\left(y_1-y_2 v\right)\left(v_0-v\right)\left(v_0-\frac{\Gamma_0}{2}\left(v_0-v\right)\right)}{v_0\left(v_0-s\left(v_0-v\right)\right)^2}+3\frac{\Gamma_0}{v_0}\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)$$

free energy F

$$F=-\int p\left(v,\beta\right)dv=-\frac{1}{\beta}\left(1-\frac{3}{2}\log\beta\right)-v\left(p_0+3\frac{\Gamma_0}{v_0}\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)\right)-\frac{v_0\left(\left(s-1\right)v_0 y_2-s y_1\right)\left(s-\Gamma_0\right)}{s^4\left(s-1\right)\left(s\left(v-v_0\right)+v_0\right)}$$

$$-\frac{\Gamma_0 y_2\left(s\left(v-v_0\right)+v_0\right)^2}{2s^4 v_0}+\frac{\left(s\left(v-v_0\right)+v_0\right)\left(s\Gamma_0\left(y_1+3v_0 y_2\right)-s v_0 y_2\left(\Gamma_0+1\right)\right)}{s^4 v_0}-$$

$$\frac{\left(s^2\left(v_0 y_2-y_1\right)+2s y_1\Gamma_0+3v_0 y_2\Gamma_0-2s v_0 y_2\left(\Gamma_0+1\right)\right)\log\left(s\left(v-v_0\right)+v_0\right)}{s^4}$$

Gibbs energy G

$$G = F + pv = -\frac{1}{\beta}\left(1-\frac{3}{2}\log\beta\right) - v\left(p_0 + 3\frac{\Gamma_0}{v_0}\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)\right) - \frac{v_0\left((s-1)v_0y_2 - sy_1\right)(s-\Gamma_0)}{s^4(s-1)\left(s(v-v_0)+v_0\right)}$$

$$-\frac{\Gamma_0 y_2\left(s(v-v_0)+v_0\right)^2}{2s^4v_0} + \frac{\left(s(v-v_0)+v_0\right)\left(s\Gamma_0(y_1+3v_0y_2) - sv_0y_2(\Gamma_0+1)\right)}{s^4v_0} -$$

$$\frac{\left(s^2(v_0y_2-y_1) + 2sy_1\Gamma_0 + 3v_0y_2\Gamma_0 - 2sv_0y_2(\Gamma_0+1)\right)\log\left(s(v-v_0)+v_0\right)}{s^4} +$$

$$vp_0 + \frac{v(y_1-y_2v)(v_0-v)\left(v_0 - \frac{\Gamma_0}{2}(v_0-v)\right)}{v_0\left(v_0 - s(v_0-v)\right)^2} + 3\frac{\Gamma_0}{v_0}v\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)$$

$$G = F + pv = -\frac{1}{\beta}\left(1-\frac{3}{2}\log\beta\right) - v\left(p_0 + 3\frac{\Gamma_0}{v_0}\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)\right) - \frac{v_0\left((s-1)v_0y_2 - sy_1\right)(s-\Gamma_0)}{s^3(s-1)\left(s(v-v_0)+v_0\right)}$$

$$-\frac{\Gamma_0 y_2\left(s(v-v_0)+v_0\right)}{s^3} + \frac{y_1(\Gamma_0-1)\log(sv)}{(s-1)^2} +$$

$$\frac{\left(s^3(y_1-v_0y_2) + 2v_0y_2\Gamma_0 + 2s^2\left(-\Gamma_0y_1 + v_0y_2(\Gamma_0+1)\right) + s\left(\Gamma_0y_1 - v_0y_2(1+4\Gamma_0)\right)\right)\log\left(s(v-v_0)+v_0\right)}{s^3(s-1)^2} +$$

$$vp_0 + \frac{(y_1-y_2v)(v_0-v)\left(v_0 - \frac{\Gamma_0}{2}(v_0-v)\right)}{\left(v_0 - s(v_0-v)\right)^2} + 3\frac{\Gamma_0}{v_0}v\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)$$

3.3 Fluid-gas transition

[14]

The vdWaals eos is

$$p = \frac{kT}{v-b} - \frac{a}{v^2} \;,\; v = \frac{V}{N}$$

The critical temperature T$_c$ in the liquid-gas transition results from

$\frac{dp}{dv} = 0$ $\frac{d^2p}{dv^2} = 0$, follows $p_c(v-v_c)^3 = 0$

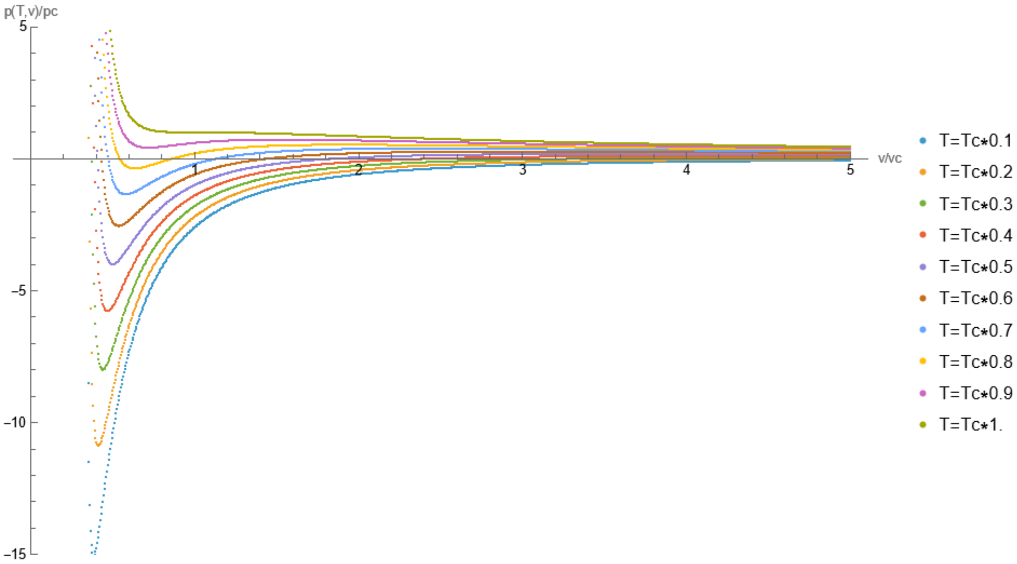
$$kT_c = \frac{8a}{27b} \;,\; v_c = 3b \;,\; p_c = \frac{a}{27b^2}$$

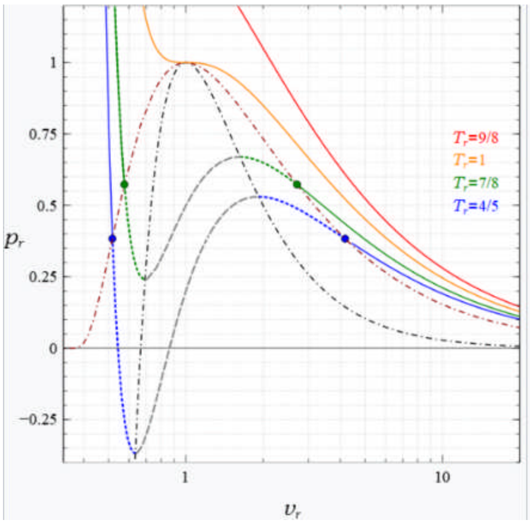
With reduced variables $T_r = \frac{T}{T_c}$, $v_r = \frac{v}{v_c}$, $p_r = \frac{p}{p_c}$

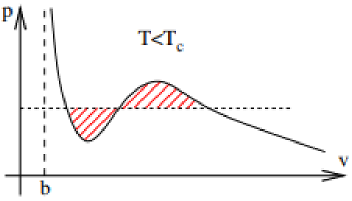
vdWaals equation becomes universal $p_r = \frac{8}{3}\frac{T_r}{v_r - 1/3} - \frac{3}{v_r{}^2}$, and also and the compressibility ratio is universal

$\frac{p_c v_c}{k_B T_c} = \frac{3}{8} = 0.375$.

Below are shown four isotherms of the universal vdWaals equation in relative coordinates with the spinodal curve $\frac{\partial p}{\partial v} = 0$ (black dash-dot curve) and the saturation curve (red dash-dot curve). The critical point lies at the turning point $\frac{\partial^2 p}{\partial v^2} = 0$ on the orange isotherm [14] [18].







The saturation curve (left wing=fluid, right wing=gas) left (low volume) wing ends at the triple point, its points are determined by Maxwell's equal-area rule [14]

$$G(v_1,T)=G(v_2,T)\ ,\ p=p(v_1,T)\ ,\ p=p(v_2,T)$$

Saturation curve vdWaals

For vdWaals fluid-gas the saturation curve can be calculated in closed form from Maxwell's equal-area rule [23], using relative variables , and the universal vdWaals form $p_{vdW}(v,\beta)=\frac{8}{3\beta}\frac{1}{v-1/3}-\frac{3}{v^2}$

$$p=\frac{8}{3\beta}\frac{1}{v_f-1/3}-\frac{3}{{v_f}^2}\ ,\ p=\frac{8}{3\beta}\frac{1}{v_g-1/3}-\frac{3}{{v_g}^2}$$

$$G_f=G_g\ ,\ eqgr(v_f,v_b)=0$$

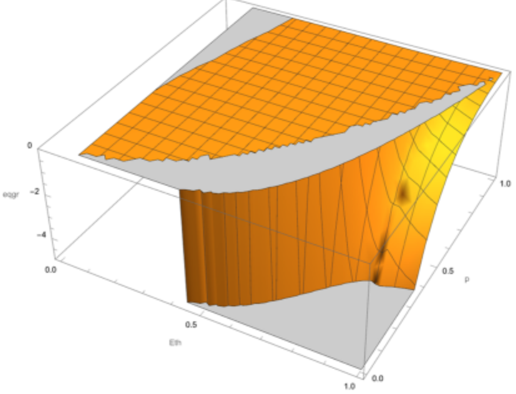
$$eqgr(v_f,v_g,\beta)=-\log\frac{v_g-1/3}{v_f-1/3}+\frac{9}{4}\beta\left(\frac{1}{v_f}-\frac{1}{v_g}\right)+\frac{v_g}{(v_g-1/3)}-\frac{v_f}{(v_f-1/3)}$$ Maxwell-Gibbs equation

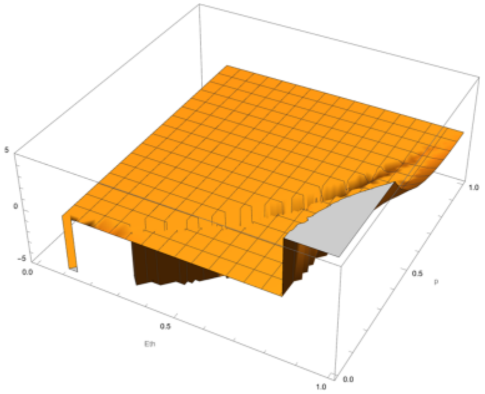
These are two equations for the variables p,T,v_f,v_g , from which v_f,v_g can be eliminated, giving the saturation curve in the form $p_{sat}(E_{th})$, where $E_{th}=\frac{T}{T_c}$ is the relative temperature, and *p* is the relative pressure relative to p_c .

The vdWaals equation is cubic in *v*, we insert the smallest and the largest of the three roots into v_f,v_g (second and third Cardano's root)

$v_f = v_{vdW,2}(p,\beta)$, $v_g = v_{v_{vdW,3}}(p,\beta)$, and obtain the condition function $eqgr(p, E_{th})$.

The condition function (real and imaginary part) has the form [18]

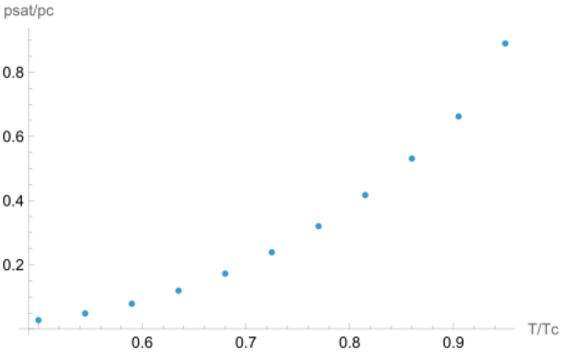




where in the real part (left) the edge of the grey area marks the zero-condition, and in the imaginary part (right) the “wall” is the boundary of the real-valued region in the upper left half.

The saturation curve runs along the “wall” on the edge of the grey area, and ends at the end of the shaded part of the “wall” at about $T=0.5T_c$, which is the triple point.

$p_{sat}(E_{th})$ is calculated numerically [18] in relative coordinates



Analytic solution for saturation curve

Lekner [23] found an analytic parametric solution for the vdWaals saturation curve, without use of the the cubic roots of the eos. The solution is analytic, but does not allow to determine the triple point.

Starting with the ansatz

$$\rho = v^* / (v - v^*)$$

we obtain the G-equation in the form

$$\log\left(\frac{\rho_f}{\rho_g}\right) = \frac{(\rho_f - \rho_g)(\rho_f + \rho_g + 2)}{\rho_f + \rho_g + 2\rho_f \rho_g}$$

which yields the solution

$$f(y) = \frac{y \cosh y - \sinh y}{\sinh y \cosh y - y}$$

$$\rho_f(y) = f(y) \exp(y)/2 \ , \ \rho_g(y) = f(y)\exp(-y)/2$$

$$v_f = v^*(1 + 1/\rho_f) \ , \ v_g = v^*(1 + 1/\rho_g)$$

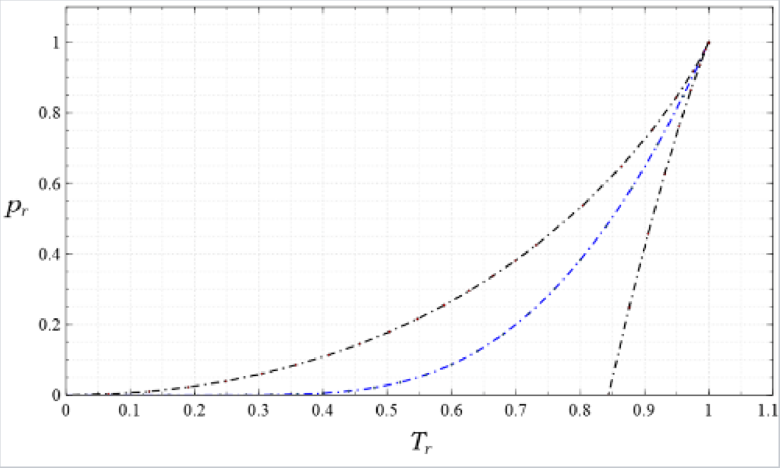
$$p = p^* \frac{v^{*2}\left(v_f v_g - v^*(v_f + v_g)\right)}{v_f^{\,2} v_g^{\,2}} \ , \ T = T^* \frac{v^*(v_f + v_g)(v_f - v^*)(v_g - v^*)}{v_f^{\,2} v_g^{\,2}}$$

As a result, one obtains the saturation curve in dependence of the parameter $0 \le y \le \infty$,

critical point $y = 0$: $f(0) = 1$, $\rho_f(0) = \rho_g(0) = 1/2$, $T(0) = 8T^*/27$, $p(0) = p^*/27$, $v_f(0) = v_g(0) = 3v^*$

triple point: $y=\infty$, $f(y)\sim 2(y-1)\exp(-y)$, $\rho_f(y)\sim(y-1)$, $\rho_g(y)\sim 2(y-1)\exp(-2y)$, $v_f(\infty)=v^*$, $v_g(\infty)\to\infty$, $T(\infty)=0$, $p(\infty)=0$

The saturation curve $(T(y),p(y))$ parametric in *y* is shown below in the middle in relative coordinates [68], the outer curves are the two spinoidal curves (first and third cubic root of *p*).



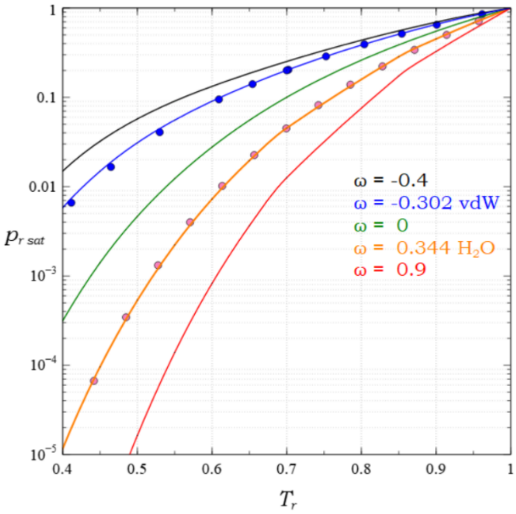
Approximate saturation curve

For approximate solutions, the ansatz which $p_r=p(v_r,T_r,\phi)$ has been suggested , where ϕ is a substance-dependent dimensionless parameter, $\phi=\frac{p_c v_c}{k_B T_c}$, a better candidate is $\omega=-\log_{10}\left(p_r\left(T_r=0.7\right)\right)$

The approximate saturation curve is [50]

$$\log\left(p_{rs}\right)=5.37\left(1-\frac{1}{T_r}\right)+\omega\left(7.49-11.18\,T_r^3+3.69\,T_r^6+17.93\log T_r\right)$$

with $\omega=-\log_{10}\left(p_r\left(T_r=0.7\right)\right)$



The family of saturation curves, showing the vdW curve as a member (blue curve). The blue dots are calculated from Lekner's solution. The orange dots are calculated from data in the ASME Steam Tables [24] .

Saturation curve Peng-Robinson

For Peng-Robinson fluid-gas the saturation curve can be calculated in closed form from Maxwell’s equal-area rule [5]

$a=0.45723$, $b=0.077796$

$$\alpha=\left(1+\left(0.480+1.574\omega-0.176\omega^2\right)\left(1-\sqrt{\beta}\right)\right)^2$$

$$p = p_{PR}\left(v_f,\beta\right) = \frac{1}{\beta\left(v_f - b\right)} - \frac{\alpha\, a}{v_f\left(v_f + b\right) + b\left(v_f - b\right)}$$

$$p = p_{PR}\left(v_g,\beta\right) = \frac{1}{\beta\left(v_g - b\right)} - \frac{\alpha\, a}{v_g\left(v_g + b\right) + b\left(v_g - b\right)}$$

$$G_f = G_g \ , \ eqgr\left(v_f, v_b\right) = 0$$

$$eqgr\left(v_f, v_b, \beta, \omega\right) = -\left(\log\frac{v_g - b}{v_f - b}\right) - \alpha(\omega,\beta)\beta a\left(\operatorname{arctanh}\left(\frac{b + v_g}{\sqrt{2b}}\right) - \operatorname{arctanh}\left(\frac{b + v_f}{\sqrt{2b}}\right)\right) + \left(\frac{v_g}{\left(v_g - b\right)} - \frac{v_f}{\left(v_f - b\right)} - a\beta\left(\frac{1}{v_g} - \frac{1}{v_f}\right)\right)$$

These are two equations for the variables p, T, v_f, v_g, from which v_f, v_g can be eliminated, giving the saturation curve in the form $p_{sat}\left(E_{th}\right)$, where $E_{th} = \frac{T}{T_c}$ is the relative temperature, and *p* is the relative pressure relative to p_c.

The Peng-Robinson equation is cubic in *v*, we insert the smallest and the largest of the three roots into v_f, v_g (second and third Cardano's root) : $v_f = v_{PR,2}\left(p,\beta\right)$, $v_g = v_{PR,3}\left(p,\beta\right)$, and obtain the condition function $eqgr\left(p, E_{th}\right)$ and the Maxwell-Gibbs equation $eqgr\left(p, E_{th}\right) = 0$.

Maxwell-Gibbs equation gives a solution $p_{sat}\left(E_{th}\right)$, where $eqgr\left(p, E_{th}\right)$ is real ($\operatorname{Im}\left(eqgr\left(p, E_{th}\right)\right) = 0$), because otherwise we have two equations (real part and imaginary part =zero) for two variables, which yields a point instead of a curve.

- Triple point

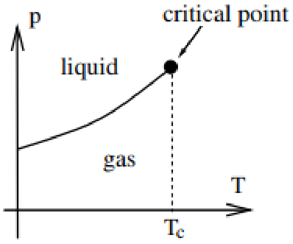
For sufficiently low value $E_{th} = E_{th,t} < E_{th,c}$, $eqgr\left(p, E_{th}\right)$ becomes complex, and the saturation curve ends at triple point $E_{th,t}$.

- Critical point

The upper end point of the saturation curve is the critical point $E_{th,c}$, where the pressure as a turning point

$$\frac{\partial^2 p\left(E_{th}, v\right)}{\partial v^2} = 0$$

Clausius-Clapeyron equation



For first order phase transition fluid-gas with *s* discontinuous we have with Gibbs free energy G and entropy S we have

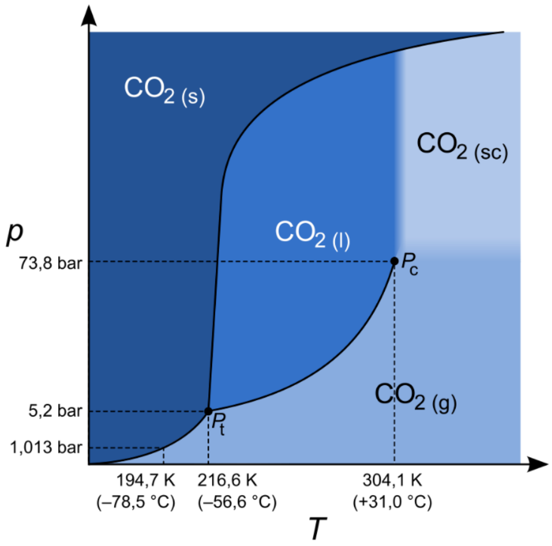
$G\left(V_f, T\right) = G\left(V_g, T\right)$ gives $\frac{dp}{dT} = \frac{S_g - S_f}{V_g - V_f}$, with latent heat $Q_{gf} = T\left(S_g - S_f\right)$,

we obtain $\frac{dp}{dT} = \frac{Q_{gf}}{T\left(V_g - V_f\right)}$, and using $\left(V_g - V_f\right) \approx V_g$, $pV_g = k_B T$, gives $\frac{dp}{dT} = \frac{Q_{gf}\, p}{k_B T^2}$, or

$p\left(T\right) = p_0 \exp\left(-\frac{Q_{gf}}{k_B T}\right)$, which is the Clausius-Clapeyron equation.

3.4 Solid-fluid, solid-gas transition

We calculate the phase diagram for solid-fluid-gaseous carbon dioxide using the Peng-Robinson eos for fluid-gas and the Mie-Grueneisen eos for solid-fluid transition. The substance in consideration is here carbon dioxide.
It has the phase diagram[20]



Saturation curve fluid-gas

We use the Peng-Robinson eos with $\omega = 0.2$ for CO2 [25]

$a = 0.45723$, $b = 0.077796$

$$\alpha = \left(1+\left(0.480+1.574\omega-0.176\,\omega^2\right)\left(1-\sqrt{\beta}\right)\right)^2$$

with the Maxwell condition for the volume variables v_f, v_g .

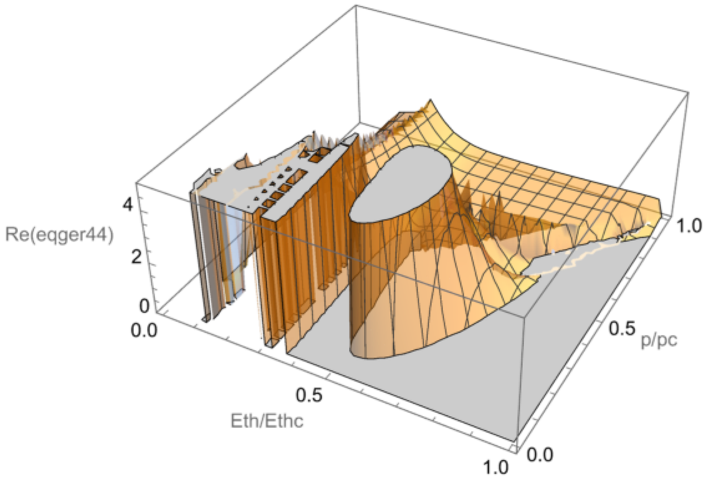
$p = p_{PR}\left(v_f,\beta\right) = \dfrac{1}{\beta\left(v_f-b\right)} - \dfrac{\alpha\, a}{v_f\left(v_f+b\right)+b\left(v_f-b\right)}$, solution $v_f = v_{PR,2}\left(p\right)$ second Cardano’s root

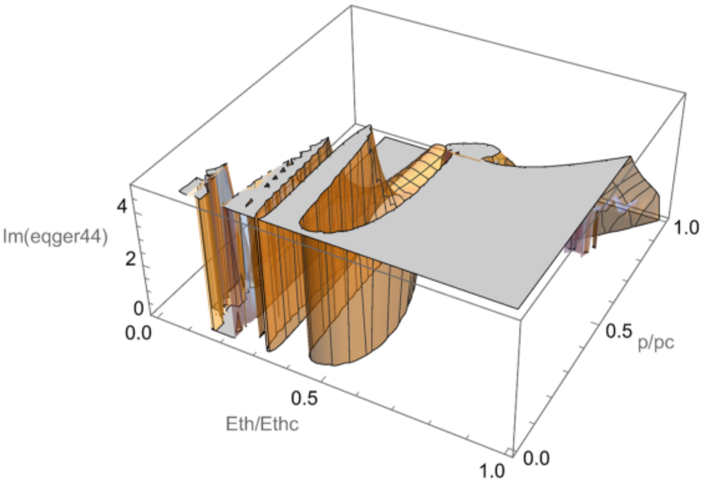
$p = p_{PR}\left(v_g,\beta\right) = \dfrac{1}{\beta\left(v_g-b\right)} - \dfrac{\alpha\, a}{v_g\left(v_g+b\right)+b\left(v_g-b\right)}$, solution $v_g = v_{PR,3}\left(p\right)$ third Cardano’s root

$$G_f = G_g \;,\; eqgr\left(v_f, v_g, \beta, \omega\right) \equiv G_{PR}\left(v_g,\beta\right) - G_{PR}\left(v_f,\beta\right) = 0$$

$$eqgr\left(v_f, v_b, \beta, \omega\right) = -\left(\log\frac{v_g-b}{v_f-b}\right) - \alpha(\omega,\beta)\beta a\left(\operatorname{arctanh}\left(\frac{b+v_g}{\sqrt{2b}}\right) - \operatorname{arctanh}\left(\frac{b+v_f}{\sqrt{2b}}\right)\right) + \left(\frac{v_g}{\left(v_g-b\right)} - \frac{v_f}{\left(v_f-b\right)} - a\beta\left(\frac{1}{v_g} - \frac{1}{v_f}\right)\right)$$

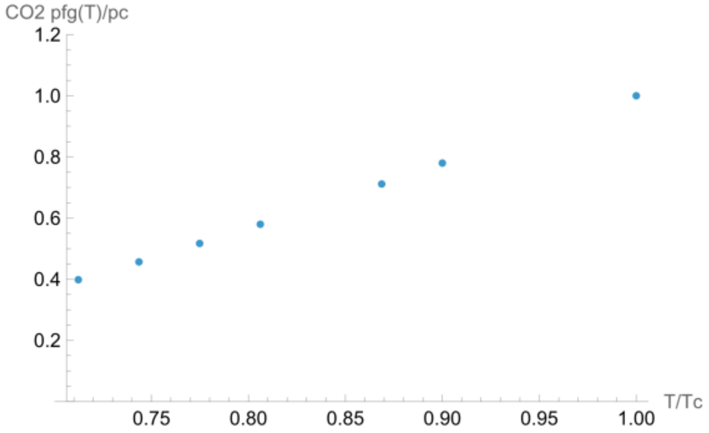
We obtain for the Maxwell-Gibbs equation $eqgr\left(\beta, p\right)$ [19]





where in the real part (left) the edge of the grey area marks the zero-condition, and the imaginary part (right) is zero in the area under consideration.

$p_{sat}\left(E_{th}\right)$ is calculated numerically [18] in relative coordinates



Saturation curve solid-fluid (melting curve)

We use the Mie-Grueneisen eos for CO2 for the volume variable v_s

$$p_{MG}\left(v,\beta\right)=p_0+\frac{\left(y_1-y_2v\right)\left(v_0-v\right)\left(v_0-\frac{\Gamma_0}{2}\left(v_0-v\right)\right)}{v_0\left(v_0-s\left(v_0-v\right)\right)^2}+3\Gamma_0\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)$$

with the Young Modulus in relative coordinates $Y\left(v\right)=\left(y_1/v-y_2\right)$, with $y_1=0.844$, $y_2=1.74$ for CO2 [20]

and the Peng-Robinson eos $p_{PR}\left(v,\beta\right)=\frac{1}{\beta\left(v-b\right)}-\frac{\alpha\, a}{v\left(v+b\right)+b\left(v-b\right)}$ for the volume variable v_f ,

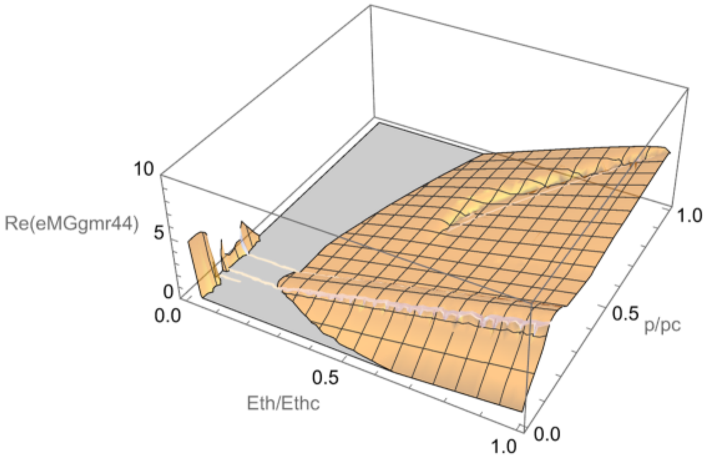
$p=p_{MG}\left(v_s,\beta\right)$, $p=p_{PR}\left(v_f,\beta\right)$,

solution $v_f=v_{PR,3}\left(p\right)$ third Cardano's root of Peng-Robinson eos, and solution $v_s=v_{MG,1}\left(p\right)$ first Cardano's root of Mie-Grueneisen eos,

and the Maxwell condition for the volume variables v_s,v_f

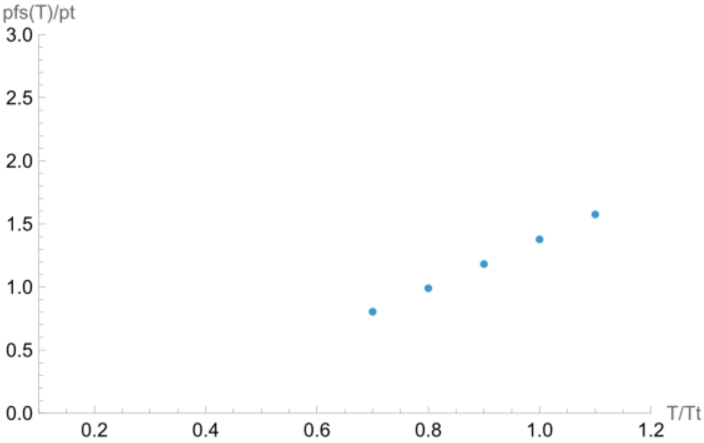
$G_f=G_s$, $eqgmr\left(v_f,v_s,\beta\right)\equiv G_{PR}\left(v_f,\beta\right)-G_{MG}\left(v_s,\beta\right)=0$

We obtain for the Maxwell-Gibbs equation $eqgmr\left(\beta,p\right)=0$ [19] the real part



The melting curve lies at the steep left edge of the "boot".

$p_{sat}\left(E_{th}\right)$ is calculated numerically [14] in relative coordinates



As depicted in the measured phase diagram above, the solid-fluid curve rises steeply near the triple point to about the critical pressure p_c, and then bends off towards about $2p_c$ near the critical temperature T_c .

Saturation curve solid-gas (sublimation curve)

We use the Mie-Grueneisen eos for CO2 for the volume variable v_s

$$p_{MG}(v,\beta)=p_0+\frac{(y_1-y_2v)(v_0-v)\left(v_0-\frac{\Gamma_0}{2}(v_0-v)\right)}{v_0\left(v_0-s(v_0-v)\right)^2}+3\Gamma_0\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)$$

with the Young Modulus in relative coordinates $Y(v)=(y_1/v-y_2)$, with $y_1=0.844$, $y_2=1.74$ for CO2 [20]

and the Peng-Robinson eos $p_{PR}(v,\beta)=\frac{1}{\beta(v-b)}-\frac{\alpha\, a}{v(v+b)+b(v-b)}$ for the volume variable v_g ,

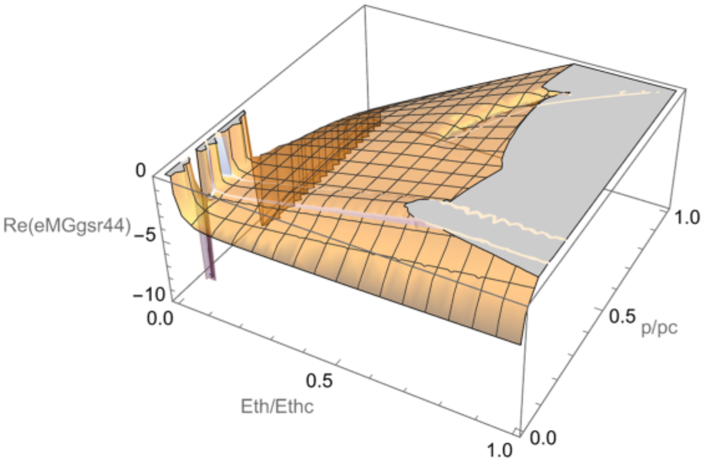
$$p=p_{MG}(v_s,\beta)\ ,\ p=p_{PR}(v_g,\beta),$$

solution $v_g=v_{PR,3}(p)$ third Cardano’s root of Peng-Robinson eos, and solution $v_s=v_{MG,3}(p)$ third Cardano’s root of Mie-Grueneisen eos,

and the Maxwell condition for the volume variables v_s, v_g

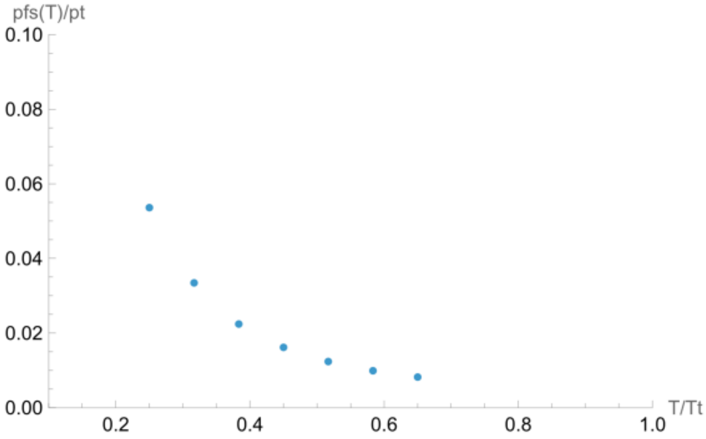
$$G_g=G_s\ ,\ eqgmg(v_g,v_s,\beta)\equiv G_{PR}(v_g,\beta)-G_{MG}(v_s,\beta)=0$$

We obtain for the Maxwell-Gibbs equation $eqgmg(\beta,p)$ [18] the real part



The sublimation curve lies at the bottom of the “boot”.

$p_{sat}(E_{th})$ is calculated numerically [18] in relative coordinates



In the measured phase diagram above the sublimation curve rises slightly until T_{tr}, here the sublimation curve has a slight maximum near $T = 0.33 T_c$.

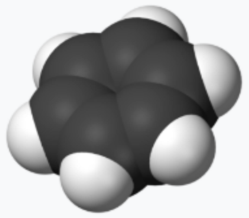
4. Equations-of-state: calculation results

4.1 Benzene

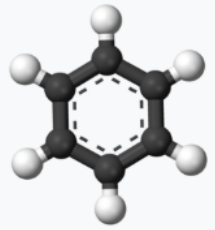
4.1.1 Material data of benzene

The important material data of benzene are as follows [20].

Benzene is an organic chemical compound with the molecular formula C6H6. The benzene molecule is composed of six carbon atoms joined in a planar hexagonal ring. The intermolecular potential is of Lennard-Jones type.



Space-filling model



Ball and stick model

vdWaals parameters

aW=18.24 L^2·bar/mol^2 = 52.16 eV A^3

bW=0.1193 L/mol = 198 A^3

p0=aW/bW^2= 1.33 meV/ A^3

where $a = \dfrac{0.45723}{p_c \beta_c{}^2} = 1.083 a_W$, $b = 0.077796 \dfrac{1}{p_c \beta_c} = 0.62223 b_W$

$\sigma \approx 3.70$ Å, $\epsilon / k_B \approx 400$ K.

ε σ parameters

$\sigma(Benzene) = 3.7\dot{A}$, $\varepsilon(Benzene) = k_B 400K = (4/3)0.0259 = 0.0345eV$

crit. Tc=562K (289°C), pc=4.89MPa , λc=7.47A

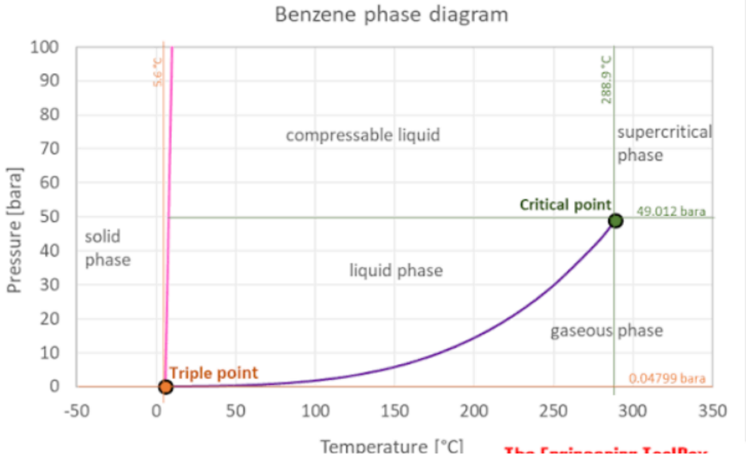
$\beta_c = 1/0.0485eV^{-1} = 20.6eV^{-1}$, $p_c = 30.5\mu eV\ A^{-3} = 0.0229 p_0$, $\lambda_c = 7.47A$

triple Tt=278.5K , pt=4.83kPa, λtf=5.31A, λts=5.33A , λtg=75A

$\beta_t = 1/0.0240eV^{-1} = 41.6eV^{-1}$, $p_t = 30.1 \times 10^{-3} \mu eV\ A^{-3}$, $\lambda_{tf} = 5.31A$, $\lambda_{ts} = 5.33A$, $\lambda_{tg} = 75A$

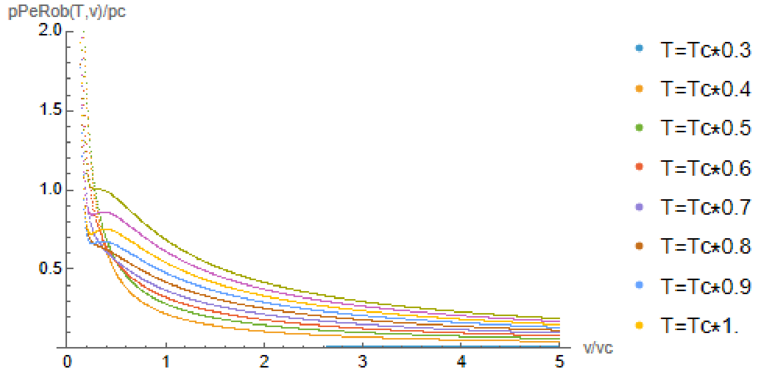
Y= $2GPa = 12500 \mu eV / A^3$

$\omega = 0.212$

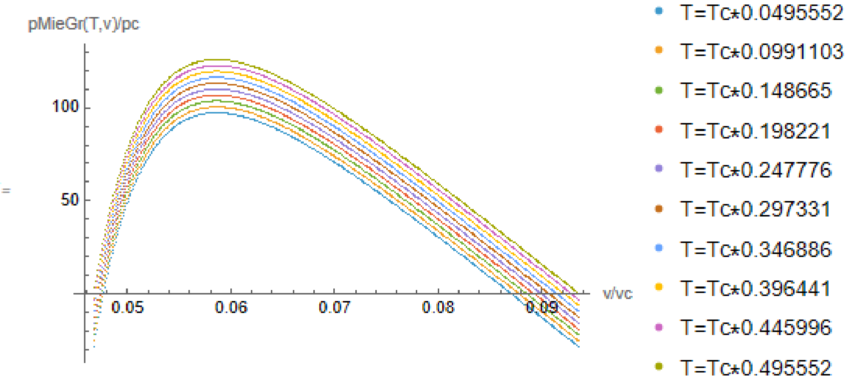


4.1.2 Equation-of-state and phase diagram benzene

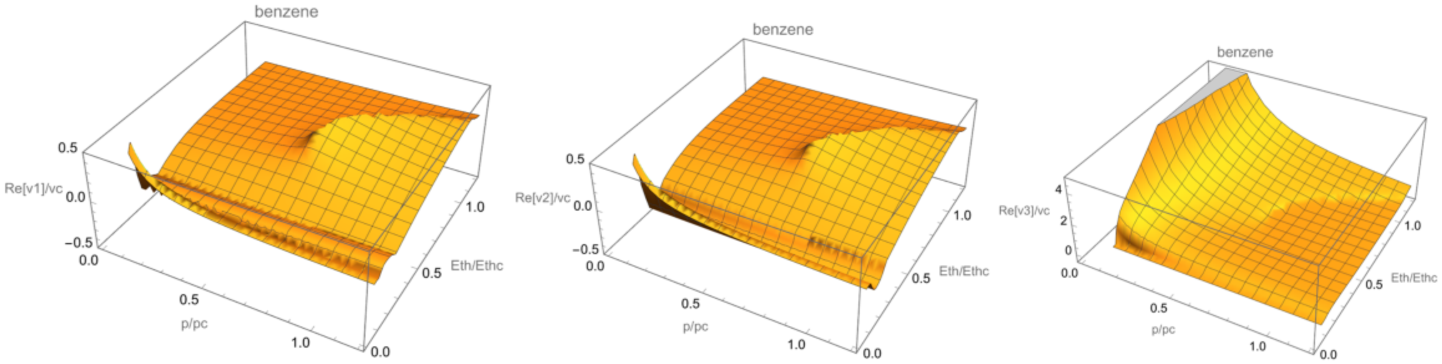
Peng-Robinson fluid-gas eos in relative coordinates



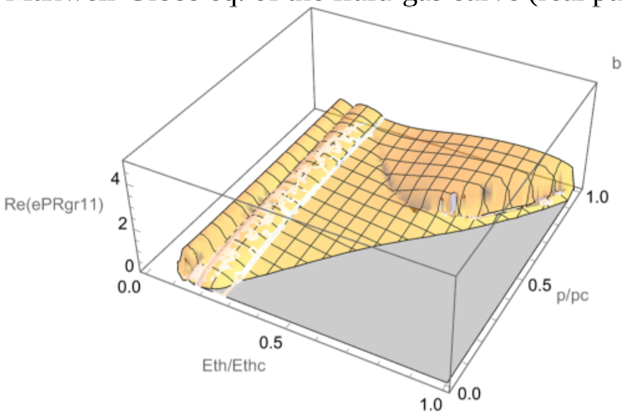
Mie-Grueneisen solid eos

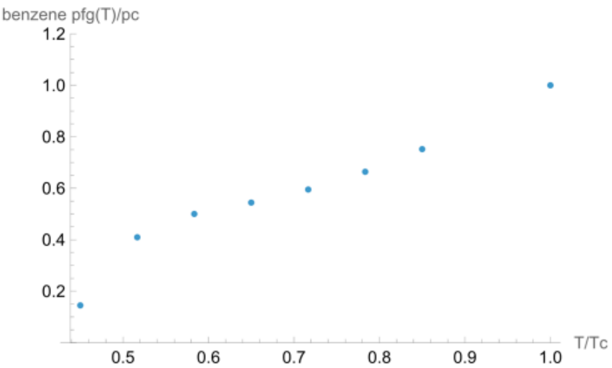


The three branches (real part) of the volume function $v = v(p, \beta)$ Peng-Robinson eos

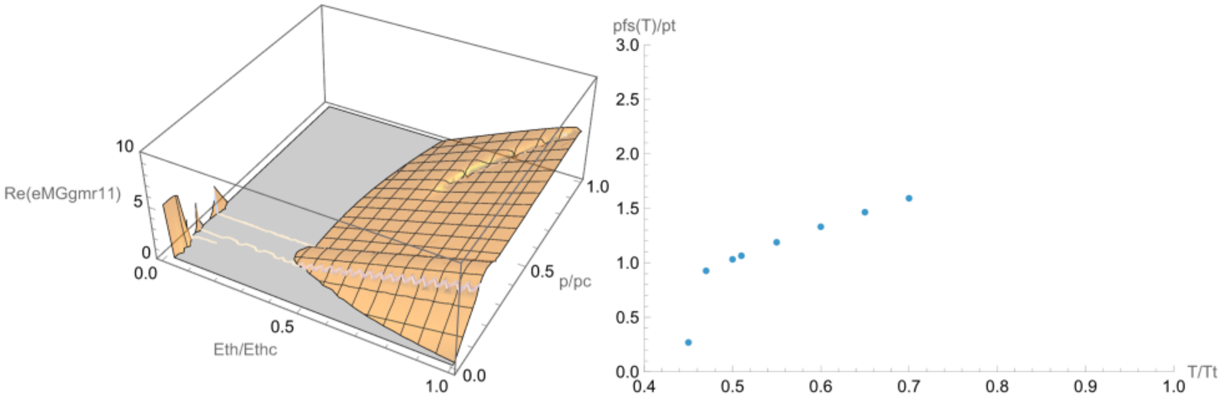


Maxwell-Gibbs eq. of the fluid-gas curve (real part)

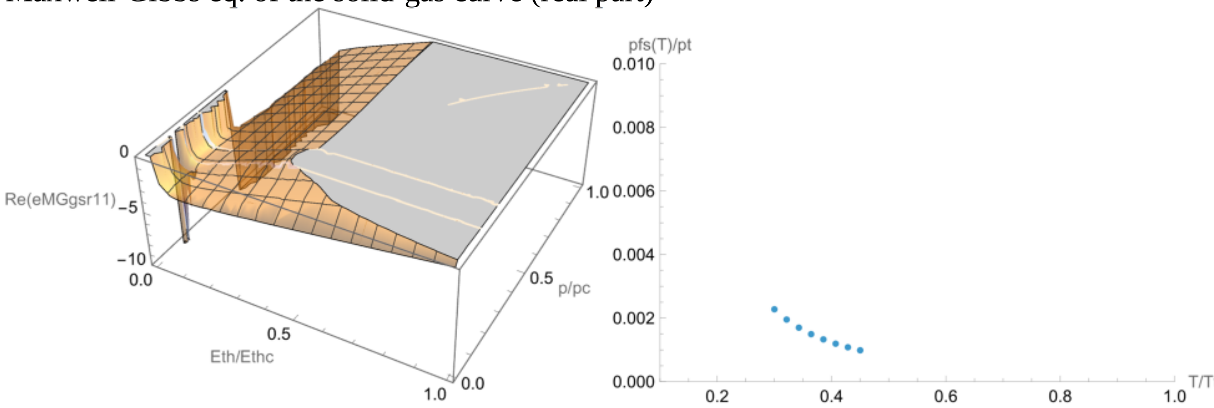




Maxwell-Gibbs eq. of the solid-fluid curve (real part)



Maxwell-Gibbs eq. of the solid-gas curve (real part)



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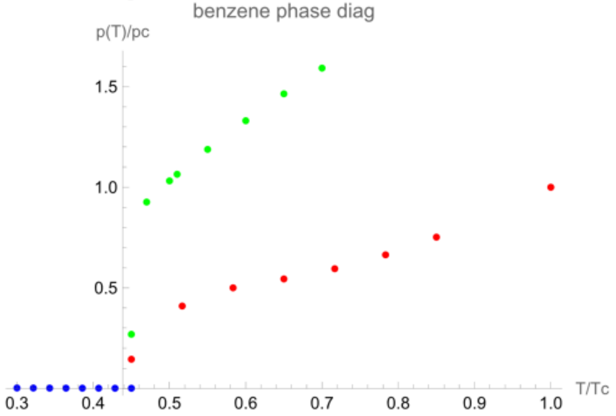
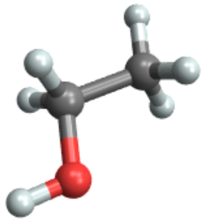
Phase diagram



4.2 Ethanol

4.2.1 Material data of ethanol

The important material data of ethanol are as follows [20].
Ethanol is an alcohol with the formula CH3-CH2-OH, and has a dipole intermolecular potential, mainly from H-H covalent bond.



vdWaals parameters
aW=12.56 L^2·bar/mol^2 = 35.9 eV A^3
bW=0.0871 L/mol = 144.6 A^3

where $a=\frac{0.45723}{p_c\beta_c^{\,2}}=1.083a_W$, $b=0.077796\frac{1}{p_c\beta_c}=0.62223b_W$

p0=aW/bW^2= 1.717 meV/ A^3

ε σ parameters

$\varepsilon_h\left(Eth\right)=0.0542eV$, $\sigma\left(Eth\right)=2.6\dot{A}$

crit. $T_c=513K$, $p_c=6.25MPa$, $\lambda_c=6.55\dot{A}$

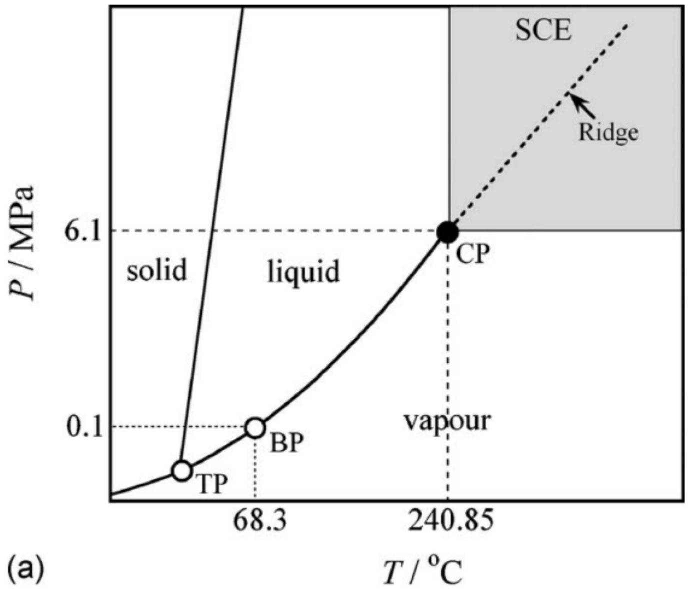
crit. $\beta=1/0.0445eV^{-1}=22.5eV^{-1}$, $p_c=39\mu eV\ A^{-3}=0.0227p_0$, $\lambda_c=6.55\dot{A}$

triple $T_t=150K$, $\beta=1/0.013eV^{-1}=77eV^{-1}$, $p_t=4.3\times10^{-10}MPa=26.9\times10^{-10}\mu eVA^{-3}$,

$\lambda_{tf}=4.6\dot{A}$, $\lambda_{ts}=4.4\dot{A}$

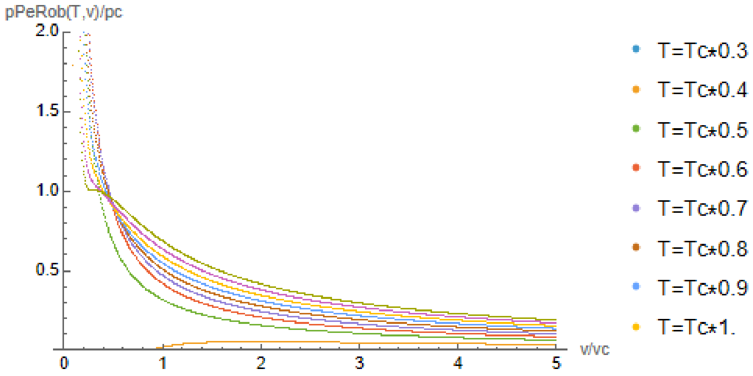
Y= $\rho_0 v_s^{\,2}=3.66GPa=22838\mu eV/A^3$

$\omega=0.62$

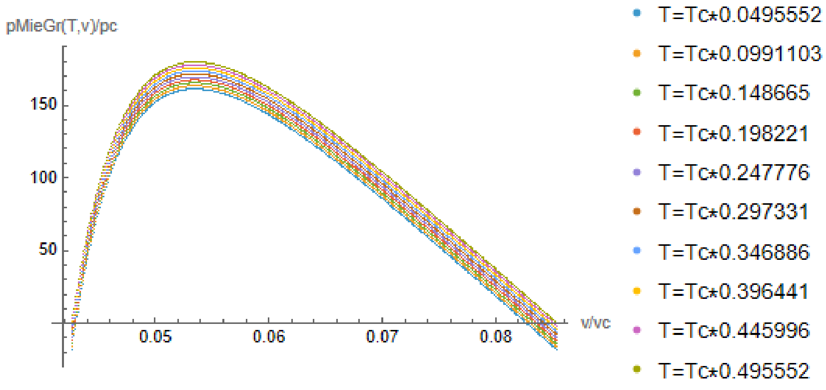


4.2.2 Equation-of-state and phase diagram ethanol

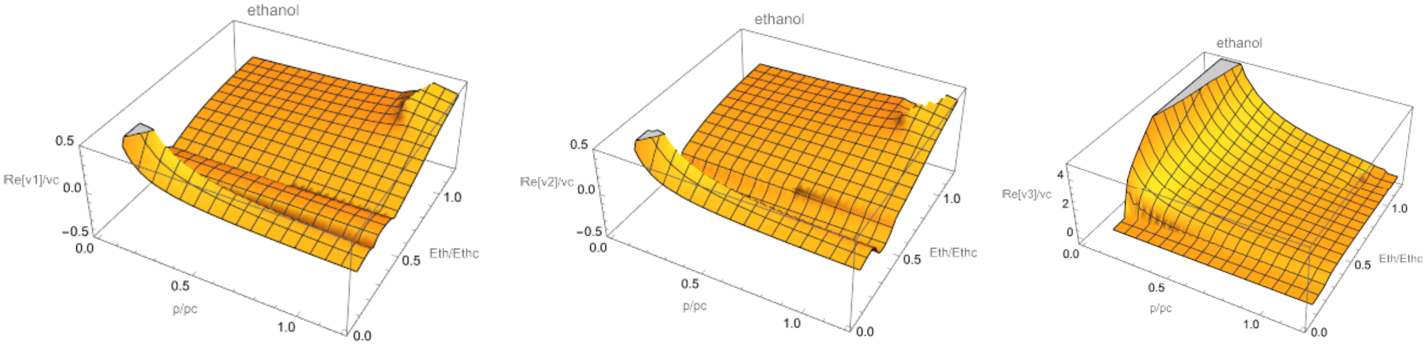
Peng-Robinson fluid-gas eos in relative coordinates



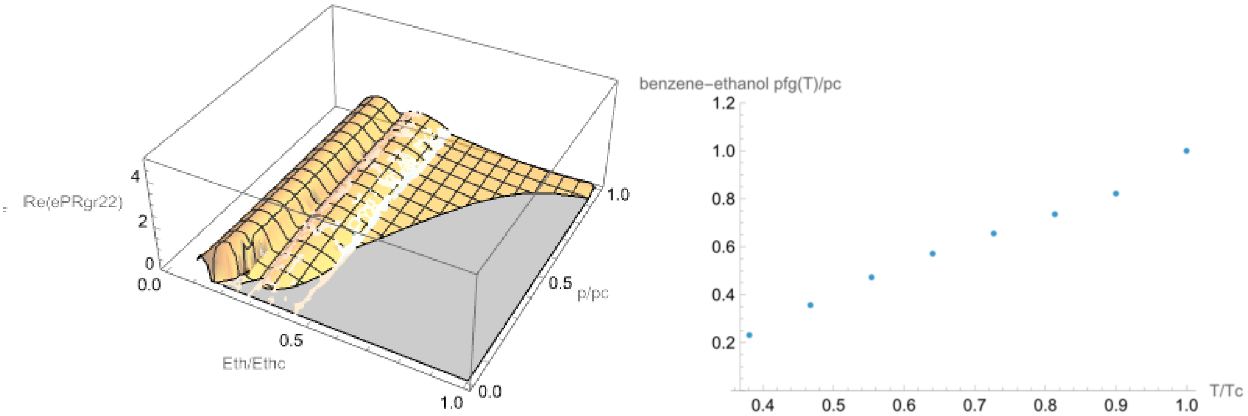
Mie-Grueneisen solid eos



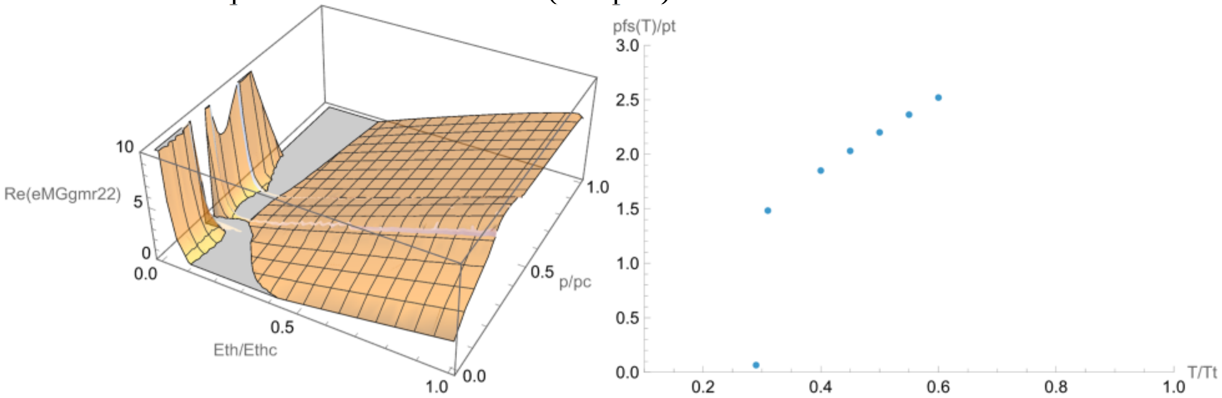
The three branches (real part) of the volume function $v = v(p, \beta)$ Peng-Robinson eos



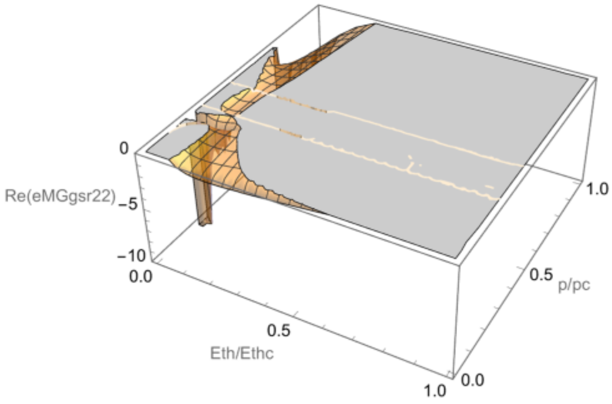
Maxwell-Gibbs eq. of the fluid-gas curve (real part)

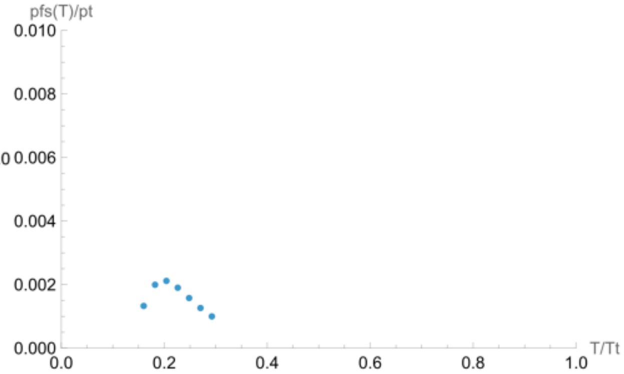


Maxwell-Gibbs eq. of the solid-fluid curve (real part)

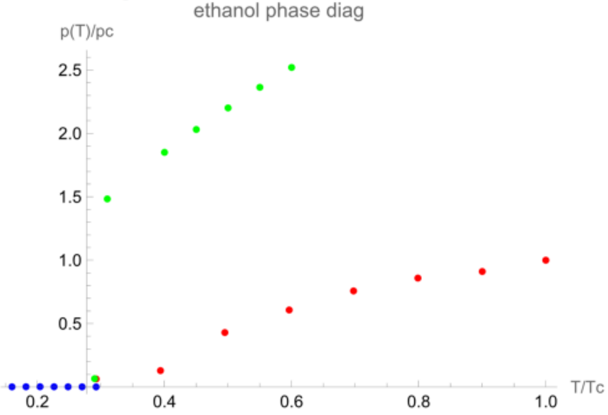


Maxwell-Gibbs eq. of the solid-gas curve (real part)

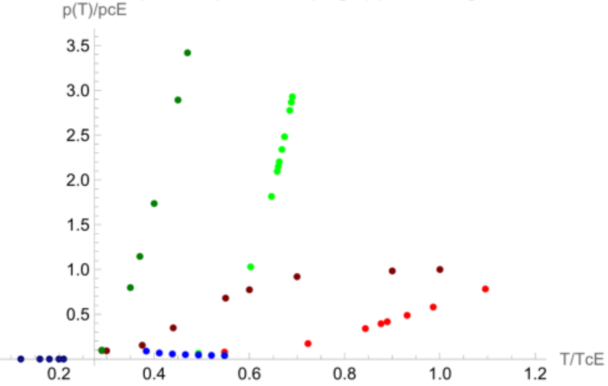




Phase diagram



Phase diagram ethanol and benzene, rel. ethanol



4.3 Argon

4.3.1 Material data of argon

The important material data of argon are as follows [20].

Argon belongs to the noble gasses, is practically chemically inactive, and its intermolecular potential is of Lennard-Jones type, it is even a typical Lennard-Jones substance.

vdWaals parameters

aW=1.355 L^2·bar/mol^2 = 3.87 eV A^3

bW=0.03201 L/mol = 53 A^3

p0=aW/bW^2= 1.378 meV/ A^3

where $a = \frac{0.45723}{p_c \beta_c^{\;2}} = 1.083 a_W$, $b = 0.077796 \frac{1}{p_c \beta_c} = 0.62223 b_W$

ε σ parameters

$\sigma(Ar) = 3.4\dot{A}$, $\varepsilon(Ar) = 0.0123 eV$

crit. $T = 150.8K$, $p_c = 4.83MPa = 0.0218\,p_0$, $\lambda_c = 5.0A$

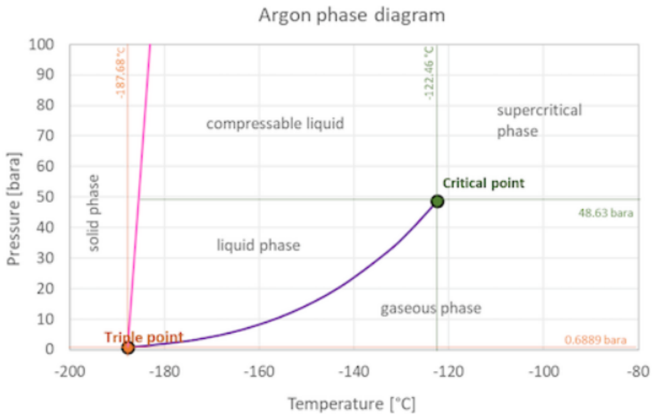
$\beta_c = 1/0.0130eV^{-1} = 76.8eV^{-1}$, $p_c = 30.1\mu eV\ A^{-3}$

triple $T_t = 83.7K$, $p_t = 0.068MPa$, $v_{tf} = 47.2A^3$

$\beta_t = 1/0.0072eV^{-1} = 138.4eV^{-1}$, $p_t = 0.42\mu eV\ A^{-3}$, $\lambda_{tf} = 3.6A$, $\lambda_{tg} = 25.8A$

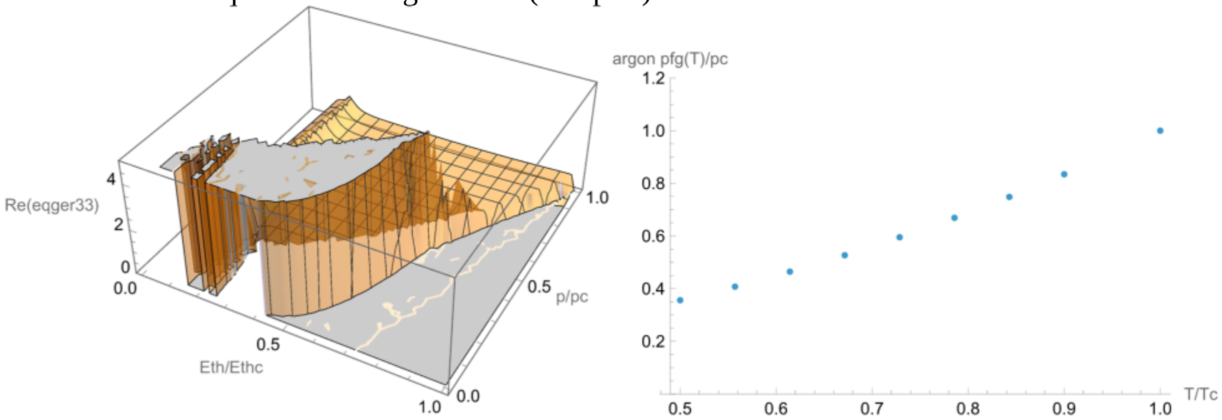
ω=0.001

Y=1.6GPa=9.98 meV/A^3

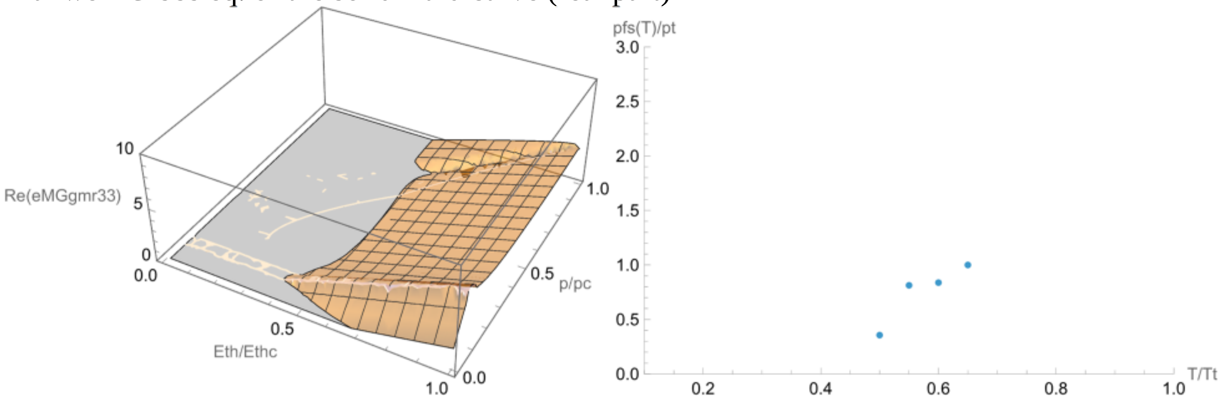


4.3.2 Equation-of-state and phase diagram argon

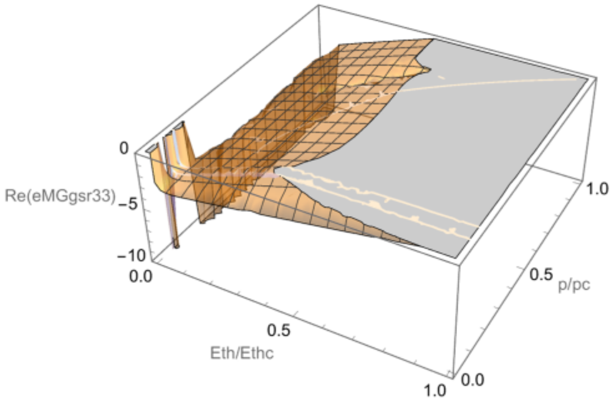
Maxwell-Gibbs eq. of the fluid-gas curve (real part)

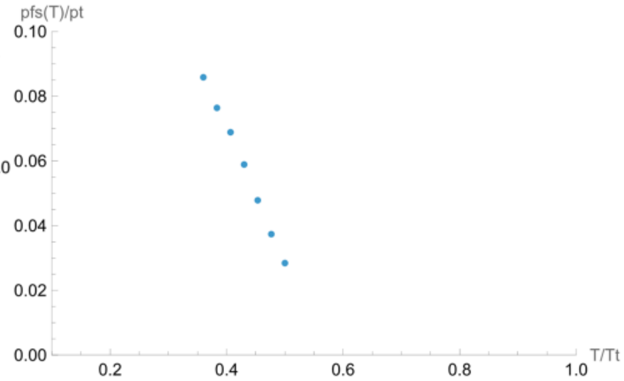


Maxwell-Gibbs eq. of the solid-fluid curve (real part)

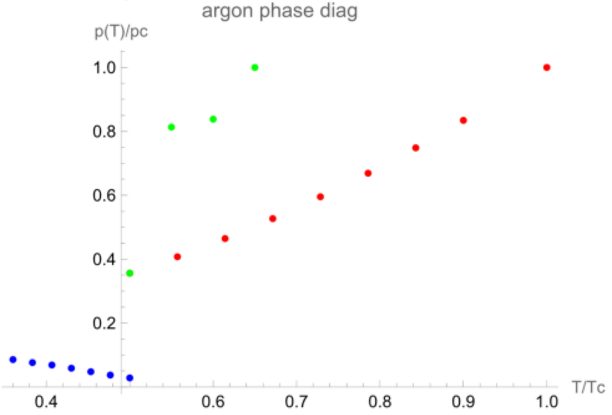


Maxwell-Gibbs eq. of the solid-gas curve (real part)





Phase diagram



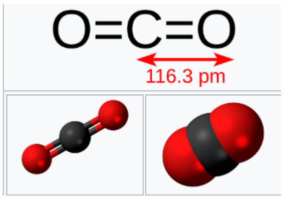
4.4 Carbon dioxide

4.4.1 Material data of carbon dioxide

The important material data of carbon dioxide are as follows [20].

Carbon dioxide is a chemical compound with the chemical formula CO2, made up of molecules that each have one carbon atom covalently double bonded to two oxygen atoms [71].

Carbon dioxide has the intermolcular potential of Lennard-Jones type, from O-O covalent binding.



vdWaals parameters

aW=3.6 L^2·bar/mol^2 = 10.3 eV A^3

bW=0.0427 L/mol = 70.9 A^3

p0=aW/bW^2= 2.05 meV/ A^3

where $a=\frac{0.45723}{p_c\beta_c{}^2}=1.083a_W$, $b=0.077796\frac{1}{p_c\beta_c}=0.62223b_W$

$\epsilon/k = 125.317$ K, $\sigma = 3.0354$ Å,

ε σ parameters

$\sigma(CO2)=3.03\dot{A}$, $\varepsilon(CO2)=k_B125K=(1.25/3)0.0259=0.0108eV$

crit. T_c=304.1K, p_c=7.38MPa, v_c=93.9cm^3/mol=156A^3, ρ_c =0.0106 mol/cm^3 =0.00642 A^{-3}, λ_c=5.38A

crit. $\beta_c=1/0.0262eV=38.1eV^{-1}$, $\lambda_c=5.38A$, $p_c=46\mu eV\ A^{-3}=0.0224p_0$

triple T_{tr}=216.6K, p_{tr}=0.52MPa, ρ_{str} =1.562g/cm3=0.0353 mol/cm3, ρ_{ftr} =1.178g/cm3=0.0266 mol/cm3, ρ_{gtr}=0.00198g/cm3= 0.0000447mol/cm3

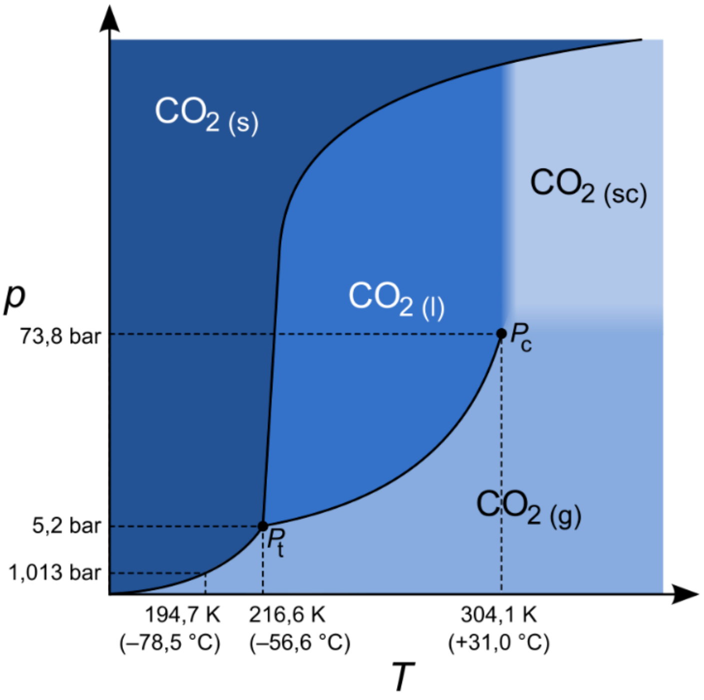
$\beta_t = 1/0.0186eV = 53.5eV^{-1}$, $p_c = 3.2\mu eV\ A^{-3}$, $\lambda_{tf} = 4.0A$, $\lambda_{tg} = 33.6A$, $\lambda_{ts} = 3.6A$, $v_{tf} = 64A^3$

ω=0.152

Y=y1/(v/vc)-y2

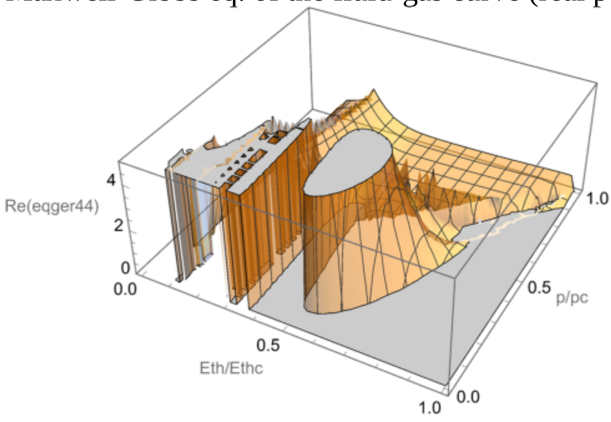
y1=8.439, y2=17.38

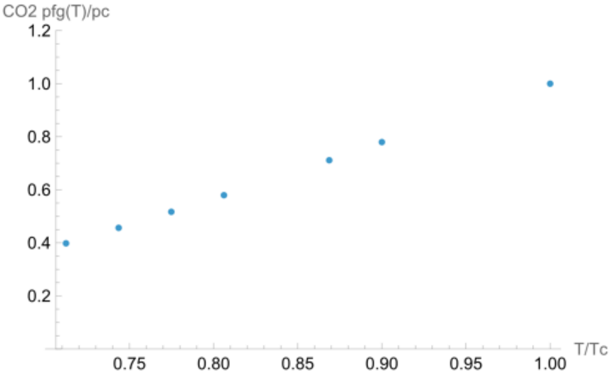
Ymax≈790MPa=4.93 meV/ A^3



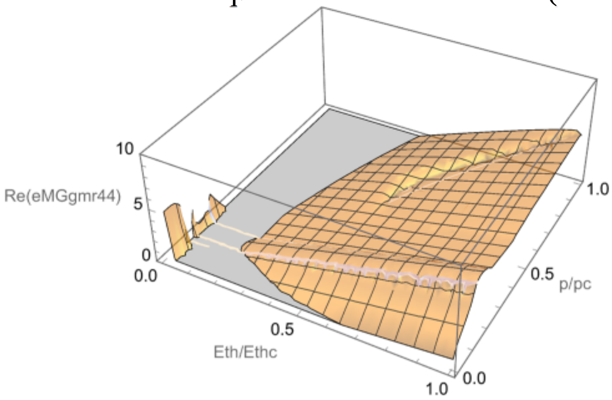
4.4.2 Equation-of-state and phase diagram carbon dioxide

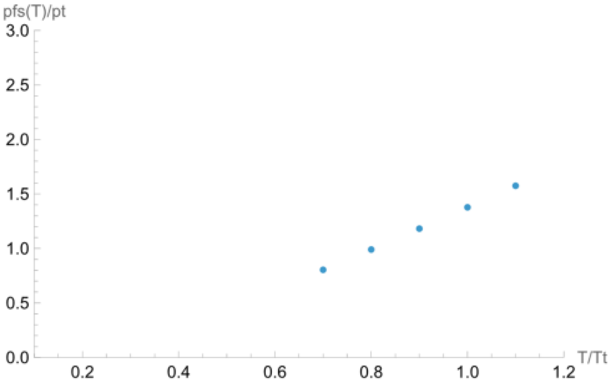
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



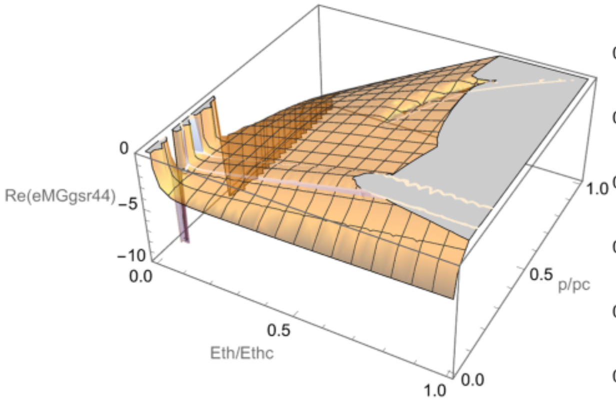


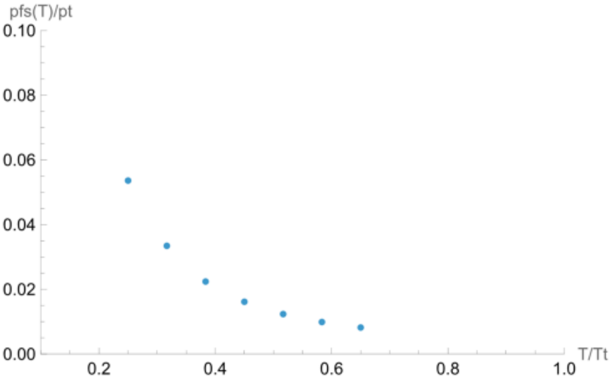
Maxwell-Gibbs eq. of the solid-fluid curve (real part)



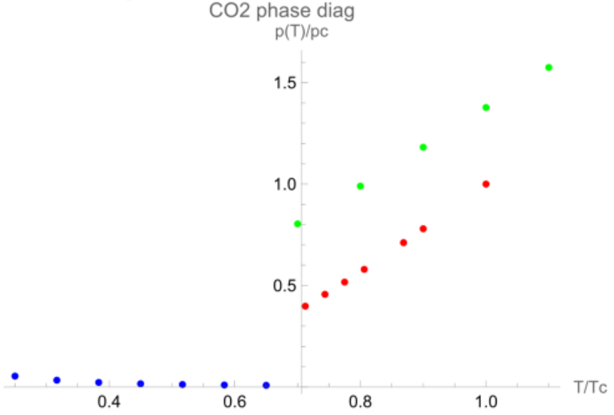


Maxwell-Gibbs eq. of the solid-gas curve (real part)





Phase diagram



5. Solutions

5.1 Equation-of-state for mixtures and solutions

A simple and reliable ansatz for the eos of mixtures/solutions is the *summing-up of partial pressures* arising from pairwise interaction of the components

$$p=\sum_{i,j}x_i x_j p_{ij}$$

where x_i is the relative concentration of component *i* , and $p_{ij}=p\left(v,T,\sigma_{ij},\varepsilon_{ij},...\right)$ is the eos of the (i,j) components. This ansatz is theoretically well-founded and yields results in agreement with measurement within the precision margin of the Peng-Robinson eos (10%).

The molecular parameters $\left(\sigma_{ij},\varepsilon_{ij},...\right)$ are calculated from individual parameters $\left(\sigma_i,\varepsilon_i,...\right)$, $\left(\sigma_j,\varepsilon_j,...\right)$ using molecular mixing rules.

For (σ,ε) we use Lorentz-Berthelot

$$\sigma_{ij}=\left(\sigma_i+\sigma_j\right)/2\ ,\ \varepsilon_{ij}=\sqrt{\varepsilon_i\varepsilon_j}\ ,$$

for volume *v* we apply the σ-rule and we obtain $v_{ij}=\left(\frac{\left(v_i\right)^{1/3}+\left(v_j\right)^{1/3}}{2}\right)^3$

- vdWaals eos

We formulate the dimensionless eos in the form in molecular parameters

$$p_{ij}=\frac{1}{\left(v-2\pi\sigma_{ij}^{\ 3}/3\right)\beta}-\frac{a_{W0}\varepsilon_{ij}\sigma_{ij}^{\ 3}}{v^2}$$

and obtain the total eos $p=\sum_{i,j}x_i x_j p_{ij}$

- Peng-Robinson eos parameter mixing

The dimensionless eos has the form in molecular parameters

$$p=p\left(\beta,v,\omega,a,b\right)=\frac{1}{\beta\left(v-b\right)}-\frac{\alpha\, a}{v\left(v+b\right)+b\left(v-b\right)}$$

where $a=\frac{0.45723}{p_c\beta_c^{\ 2}}=1.083a_W$, $b=0.077796\frac{1}{p_c\beta_c}=0.62223b_W$

$$\alpha=\left(1+\left(0.480+1.574\omega-0.176\omega^2\right)\left(1-\sqrt{0.141\frac{a}{b}\beta}\right)\right)^2$$

and $\beta_c=\frac{b}{a}\frac{0.45723}{0.077796}=5.8773\frac{b}{a}$, $p_c=\frac{0.077796}{b\beta_c}=\frac{0.077796}{5.8773}\frac{a}{b^2}=0.013236\frac{a}{b^2}$,

$v_c=3b_W=b3/0.622223=4.8214b$

and $b=0.62223*2\pi\sigma^3/3=1.3032\sigma^3$, $a=1.083a_{W0}\varepsilon\sigma^3$,

For ω , we use its definition in the form $\omega=-\log_{10}\left(p_r\right)$, $p_r=\frac{p_{sat}\left(0.7T_c\right)}{p_c}$.

The energy ratio in p_r is constant $\frac{T}{T_c}=0.7$, so p_r transforms like 1/v ,

$$p_{r,ij}=\left(\frac{2}{\left(1/p_{r,i}\right)^{1/3}+\left(1/p_{r,j}\right)^{1/3}}\right)^{3},$$

$$\omega_{ij}=-\log_{10}\left(p_{r,ij}\right)=3\left(\log_{10}\left(\left(1/p_{r,i}\right)^{1/3}+\left(1/p_{r,j}\right)^{1/3}\right)-\log_{10}2\right)=3\left(\log_{10}\left(\frac{10^{\omega_i/3}+10^{\omega_j/3}}{2}\right)\right)$$

We apply the v-rule to b : $b_{ij}=\left(\frac{\left(b_i\right)^{1/3}+\left(b_j\right)^{1/3}}{2}\right)^{3}$

As for a , we see that $\tilde{a}=\frac{a}{b}$ is an energy, so we can apply the ε-rule

$$\tilde{a}_{ij}=\sqrt{\tilde{a}_i\tilde{a}_j}\ ,\ a_{ij}=\sqrt{\tilde{a}_i\tilde{a}_j}b_{ij}=\sqrt{\tilde{a}_i\tilde{a}_j}\frac{\left(\left(b_i\right)^{1/3}+\left(b_j\right)^{1/3}\right)^{3}}{8}=\sqrt{\frac{a_i}{b_i}\frac{a_j}{b_j}}\frac{\left(\left(b_i\right)^{1/3}+\left(b_j\right)^{1/3}\right)^{3}}{8}$$

- Mie-Grueneisen eos parameter mixing

$$p\left(\eta,\beta\right)=p_0+\frac{Y\left(\eta-1\right)\left(\eta-\frac{\Gamma_0}{2}\left(\eta-1\right)\right)}{\eta\left(\eta-s\left(\eta-1\right)\right)^{2}}+3\frac{\Gamma_0}{v_0}\left(\frac{1}{\beta}-\frac{1}{\beta_0}\right)\text{ per particle}$$

$$\frac{p\left(\eta,\beta\right)}{p_0}=1+\frac{\frac{Y}{p_0}\left(\eta-1\right)\left(\eta-\frac{\Gamma_0}{2}\left(\eta-1\right)\right)}{\eta\left(\eta-s\left(\eta-1\right)\right)^{2}}-\frac{3\Gamma_0}{p_0v_0\beta_0}\left(1-\frac{\beta_0}{\beta}\right),\ \eta=\frac{v_0}{v}$$

The reference point $\left(p_0,\beta_0,v_0\right)$ becomes the triple point $\left(p_t,\beta_t,v_t\right)$ in the phase diagram, so it must be calculated for the mixture/solution.
We apply the σ mixing rule for length to v

$$v_{t,ij}=\left(\lambda_{t,ij}\right)^{3}=\left(\frac{\lambda_{t,i}+\lambda_{t,j}}{2}\right)^{3}=\left(\frac{\left(v_{t,i}\right)^{1/3}+\left(v_{t,j}\right)^{1/3}}{2}\right)^{3}$$

We apply the ε mixing rule for energy to β , T , pv and Yv

$$\beta_{t,ij}=\sqrt{\beta_{t,i}\beta_{t,j}}\ ,\ T_{t,ij}=\sqrt{T_{t,i}T_{t,j}}$$

$$p_{t,ij}v_{t,ij}=\sqrt{p_{t,i}v_{t,i}p_{t,j}v_{t,j}}\ \text{, so }\ p_{t,ij}=\frac{\sqrt{p_{t,i}v_{t,i}p_{t,j}v_{t,j}}}{v_{t,ij}}=\frac{\sqrt{p_{t,i}v_{t,i}p_{t,j}v_{t,j}}}{\left(\frac{\left(v_{t,i}\right)^{1/3}+\left(v_{t,j}\right)^{1/3}}{2}\right)^{3}}$$

$$Y_{ij}=\frac{\sqrt{Y_iY_jv_{t,i}v_{t,j}}}{v_{t,ij}}$$

5.2 Example solutions

- benzene-ethanol solution

Ethanol dissolves in benzene because of a balance of intermolecular interactions and favorable mixing entropy that allows the two liquids—polar protic ethanol and nonpolar aromatic benzene—to form a stable homogeneous solution at common concentrations.
-Dispersion forces dominate benzene: Benzene is nonpolar; its primary attractive forces are London (induced-dipole) dispersion forces between aromatic rings.

-Ethanol is amphiphilic: Ethanol (CH3CH2OH) has a small nonpolar ethyl group (CH3CH2–) and a polar hydroxyl group (–OH). The ethyl portion is compatible with benzene’s nonpolar environment; the hydroxyl can form weaker interactions with benzene than with water, but does not prohibit mixing.

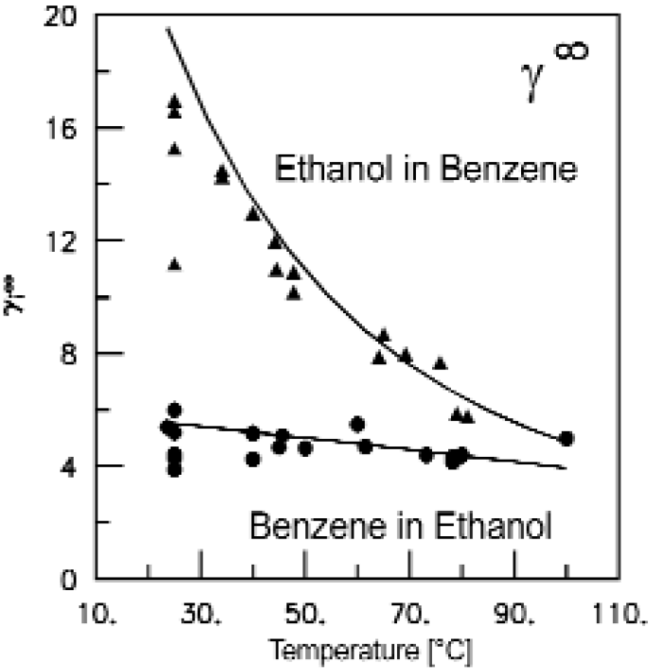
-Dispersion interactions between ethanol’s alkyl portion and benzene are favorable: The ethyl group can engage in London dispersion with benzene, lowering the energy cost of breaking ethanol–ethanol and benzene–benzene contacts.

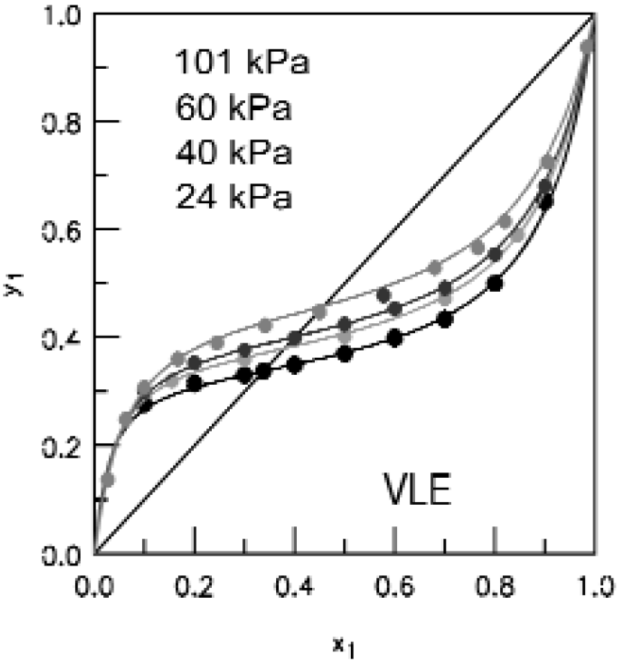
-Hydrogen bonding is not an absolute barrier: While ethanol forms hydrogen bonds with itself, those bonds are not so strong that they prevent disruption. In a benzene solution, some ethanol molecules retain hydrogen bonding clusters; many simply lose some H-bonds while gaining stabilizing dispersion contacts with benzene. The net energetic change can be small or slightly favorable.

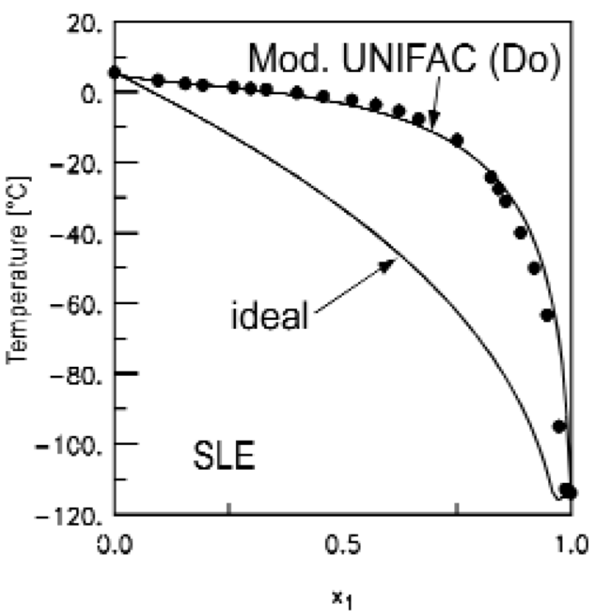
-Entropy of mixing helps: Mixing increases configurational entropy, which favors solution formation even when enthalpic changes are modestly unfavorable. For small organic molecules like ethanol and benzene, the entropy term often offsets small positive enthalpy changes.

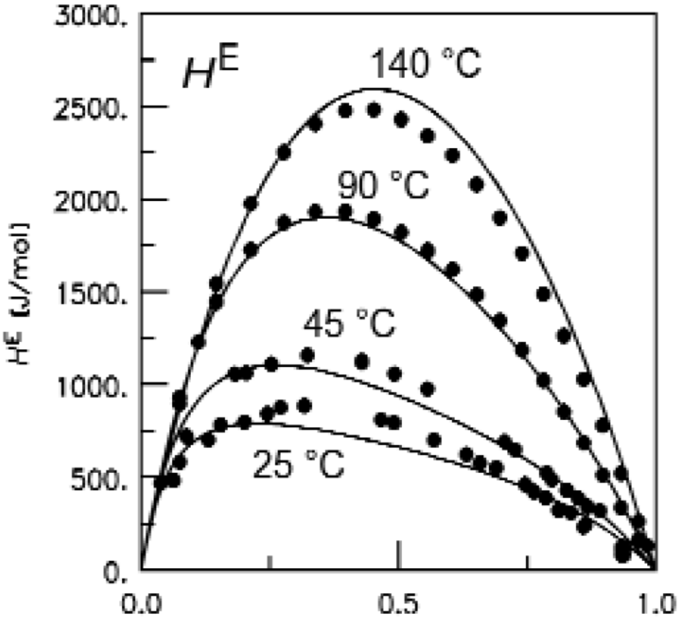
-Concentration dependence and limits: Ethanol is fully miscible with many organic solvents including benzene over a wide range, but its solubility in purely nonpolar solvents decreases as the solvent becomes less able to accommodate the hydroxyl group. Benzene can solvate moderate amounts of ethanol because ethanol’s nonpolar tail is sufficient to integrate into the benzene network; at very high ethanol fractions the system tends toward ethanol-like behavior with retained hydrogen bonding.

Measured values for the benzene-ethanol solution [6] are shown for
γ^{∞} activity coefficient at infinite dilution, y_i component concentration in vapor, T_m melting temperature at normal pressure, H_E excess enthalpy

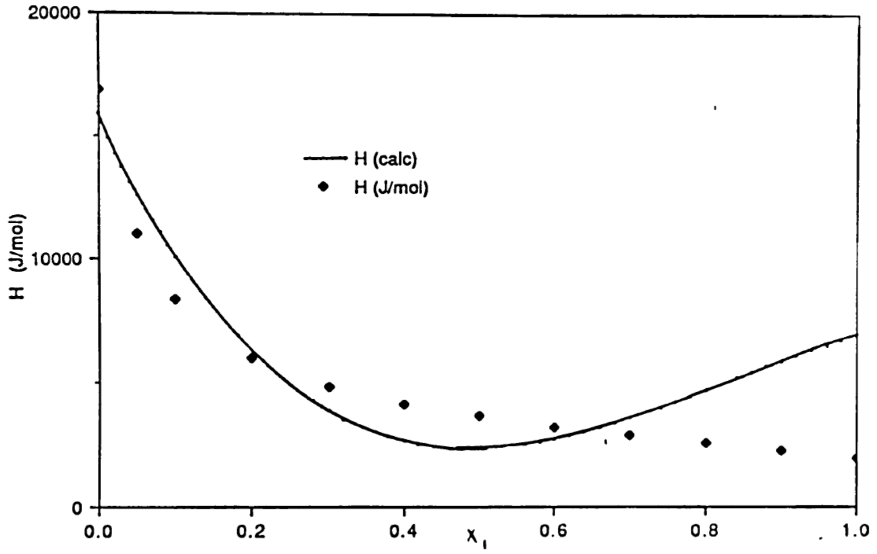








and [28] vaporization enthalpy H_v at 35°C

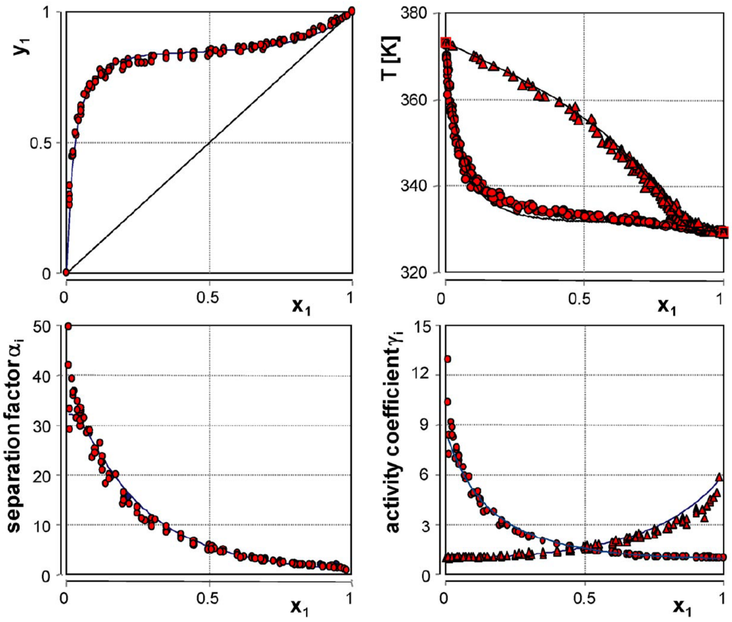


- acetone-water

Acetone-water mixtures are miscible in all proportions and do not form a binary azeotrope. The boiling point depends on the mixture's composition, ranging between the boiling points of pure acetone (56°C ..56.5°C) and pure water (100°C).

For instance, a liquid mixture with 80% mole acetone boils at approximately 57.65°C, producing a vapor of 89.4% acetone.

Measured values for the benzene-ethanol solution [8] are shown for y_i component concentration in vapor, α_i component separation factor, γ activity coefficient , T_b boiling temperature at normal pressure . The double curves on the right refer to heated liquid, resp. cooled vapor, which show a hysteresis effect. The continuous line is the calculated value using the NRTL model.


y1
1
0.5
0
0
0.5
1
x1
T [K]
380
360
340
320
0
0.5
1
x1
separation factor αi
50
40
30
20
10
0
0
0.5
1
x1
activity coefficient γi
15
12
9
6
3
0
0
0.5
1
x1

5.3 Saturation curves of solutions benzene-ethanol

$\left(E_{th}, p, v\right)$ are in relative coordinates (critical values $\left(E_{th,c}, p_c, v_c\right)$) rel. benzene-ethanol-50 (i.e. 50%).

The concentration parameter *x* is the relative benzene concentration x_0=(1, 0.75, 0.5, 0.4, 0.25, 0.1, 0.)

For the eos we use here the ansatz $p = \sum_{i,j} x_i x_j p_{ij}$. This ansatz is theoretically well-founded and yields results in agreement with measurement within the precision margin of the Peng-Robinson eos (10%).

Specifically, for the Peng-Robinson eos we have

$$p_{PR}\left(E_{th}, v, x_0\right) = x_0^{\ 2} p_{PR}\left(E_{th}, v; E_{thc1}, p_{c1}, \omega_1\right) + \left(1 - x_0\right)^2 p_{PR}\left(E_{th}, v; E_{thc2}, p_{c2}, \omega_2\right) + 2x_0\left(1 - x_0\right) p_{PR}\left(E_{th}, v; E_{thc12}, p_{c12}, \omega_{12}\right)$$

where indices 1=benzene, 2=ethanol, 12=benzene-ethanol-50 .

Peng-Robinson eos is calculated in the individual relative coordinates, scaled from benzene-ethanol-50 .

The parameters $E_{thc12}, p_{c12}, \omega_{12}$ of benzene-ethanol-50 are calculated according to the mixing rules (see above).

Specifically, for the Mie-Grueneisen eos we have

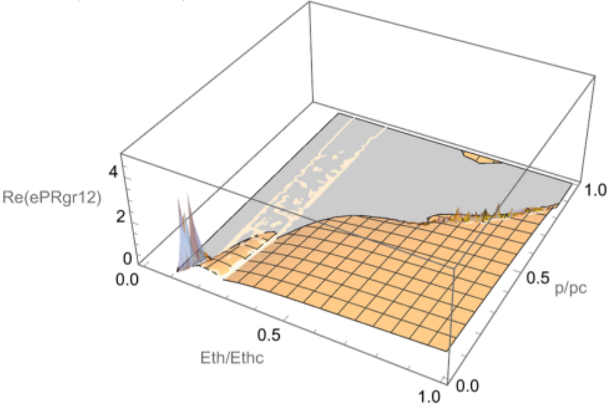
$$p_{MG}\left(E_{th}, v, x_0\right) = x_0^{\ 2} p_{MG}\left(E_{th}, v; Y_1, E_{th0}, v_0, p_0\right) + \left(1 - x_0\right)^2 p_{MG}\left(E_{th}, v; Y_2, E_{th0}, v_0, p_0\right) + 2x_0\left(1 - x_0\right) p_{MG}\left(E_{th}, v; Y_{12}, E_{th0}, v_0, p_0\right)$$

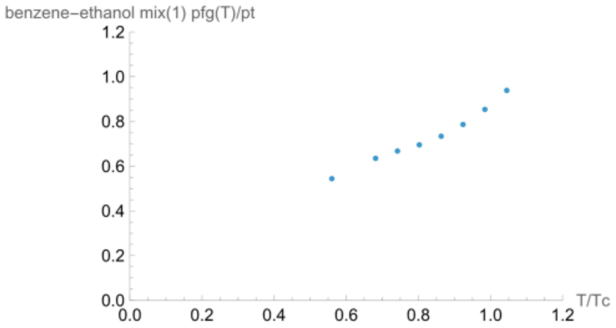
The parameter Y_{12} of benzene-ethanol-50 is calculated according to the mixing rules.

The parameters E_{th0}, v_0, p_0 are set to the triple point E_{tht}, v_t, p_t for the given x_0 , calculated from the fluid-gas curve for this x_0 .

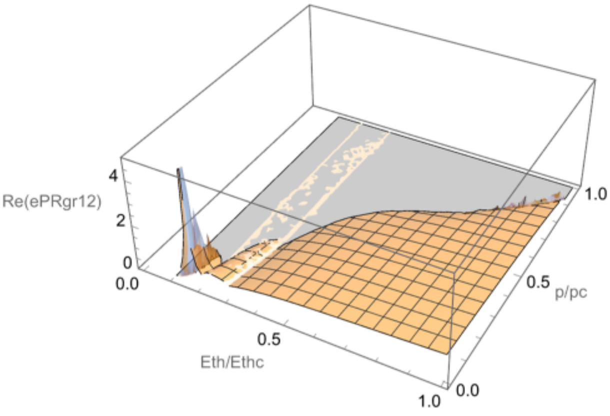
Maxwell-Gibbs eq. of the fluid-gas curve (real part)

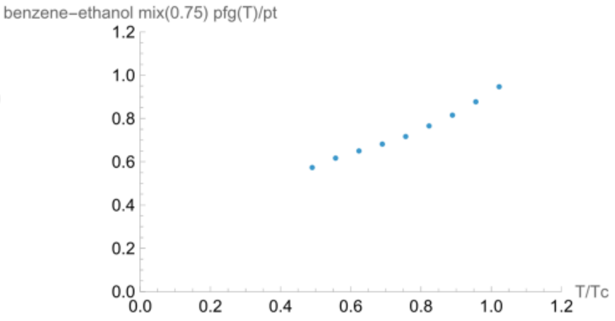
x_0=1 (benzene)



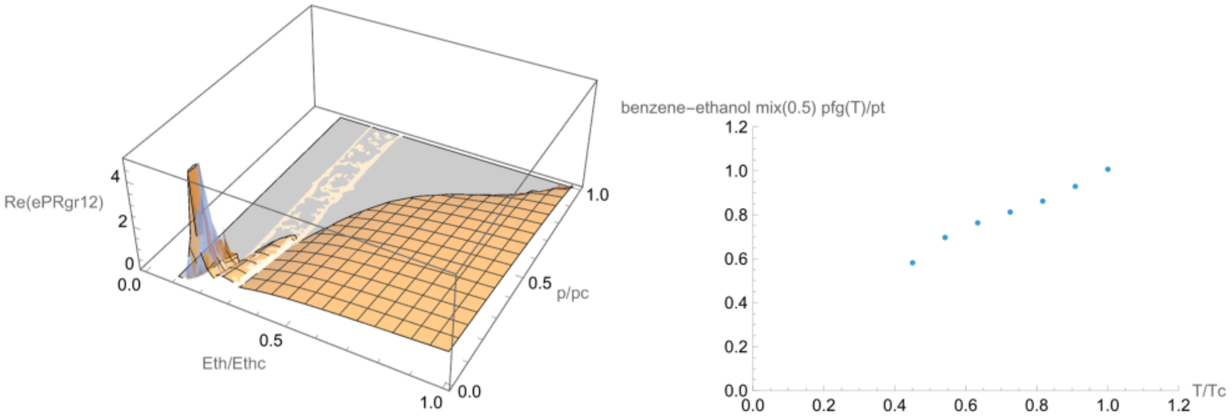


x_0=0.75

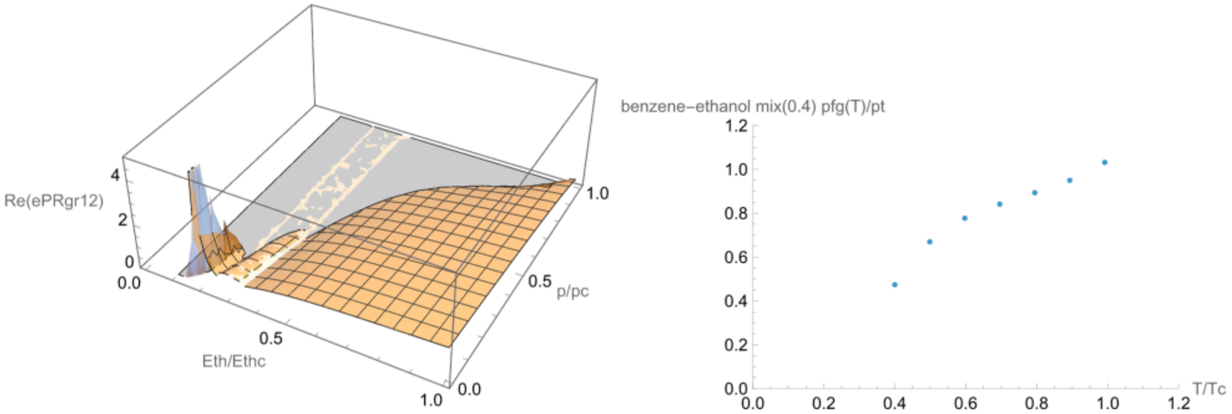




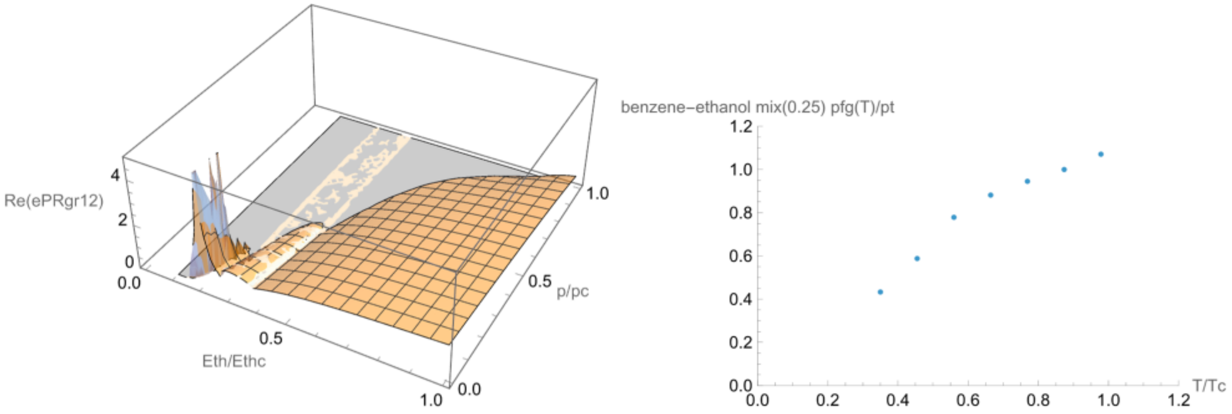
x_0=0.5



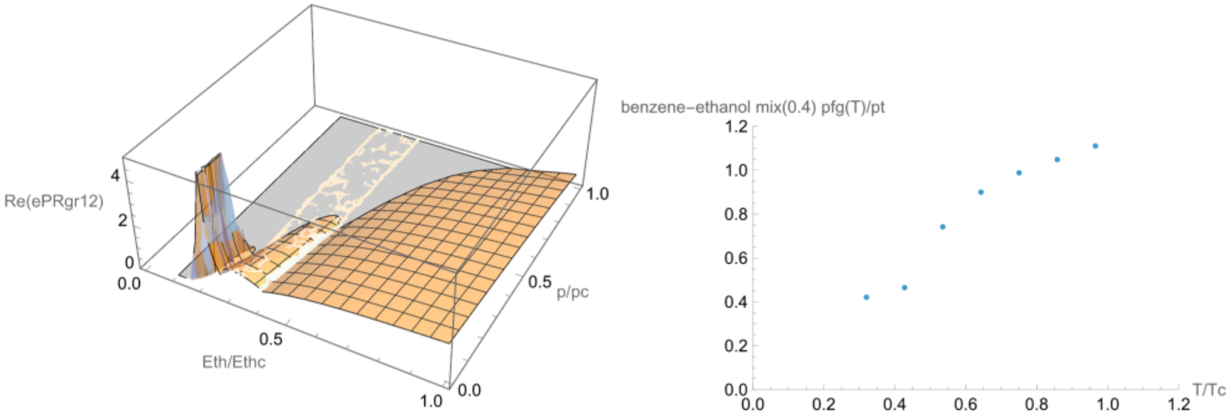
x_0=0.40



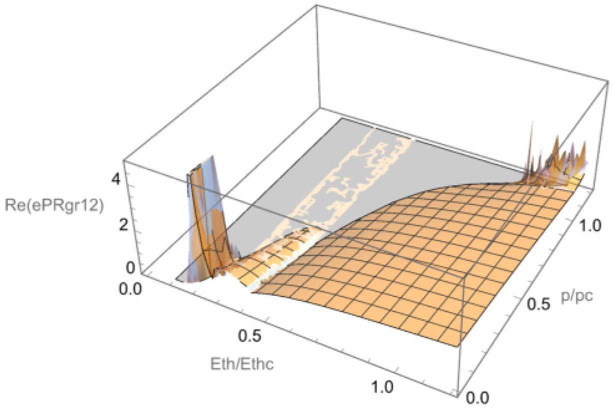
x_0=0.25

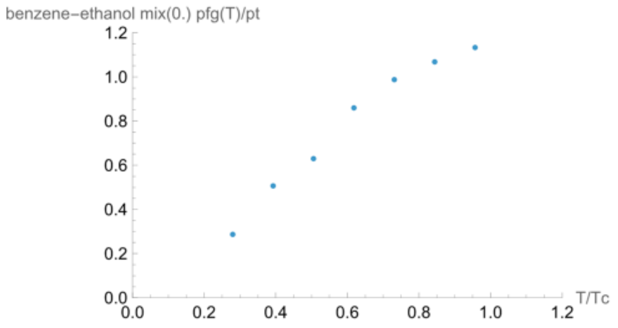


x_0=0.1

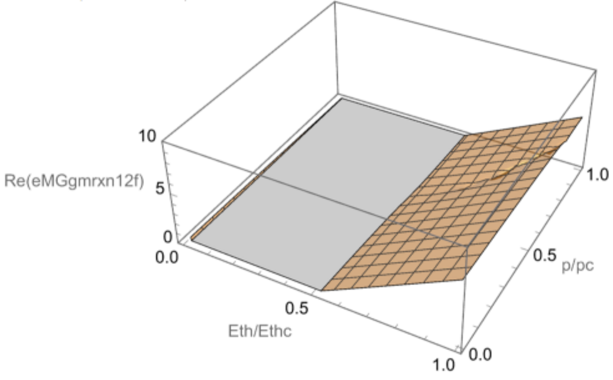


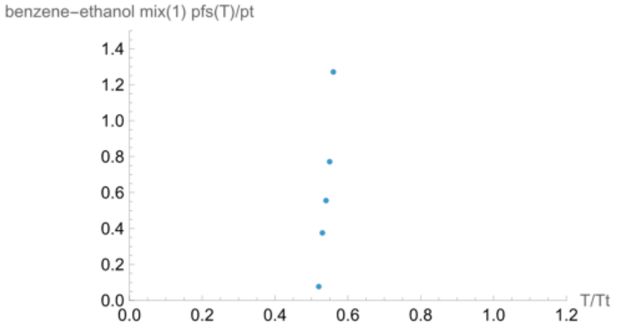
x_0=0 (ethanol)



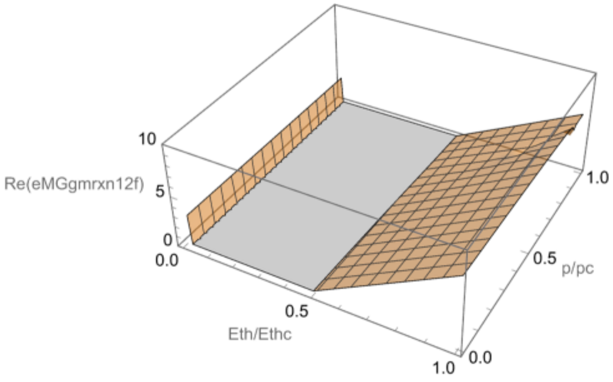


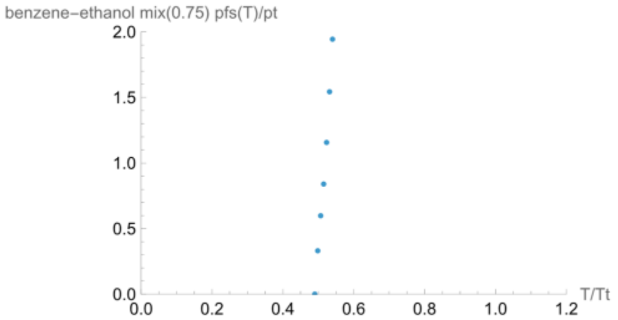
Maxwell-Gibbs eq. of the solid-fluid curve (real part)
x_0=1 (benzene)



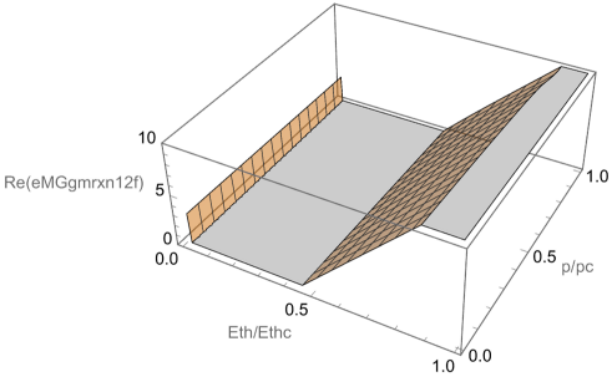


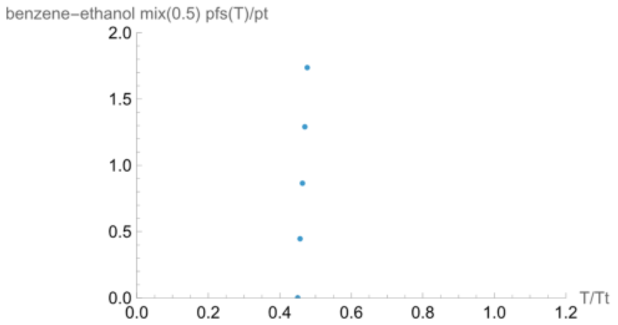
x_0=0.75



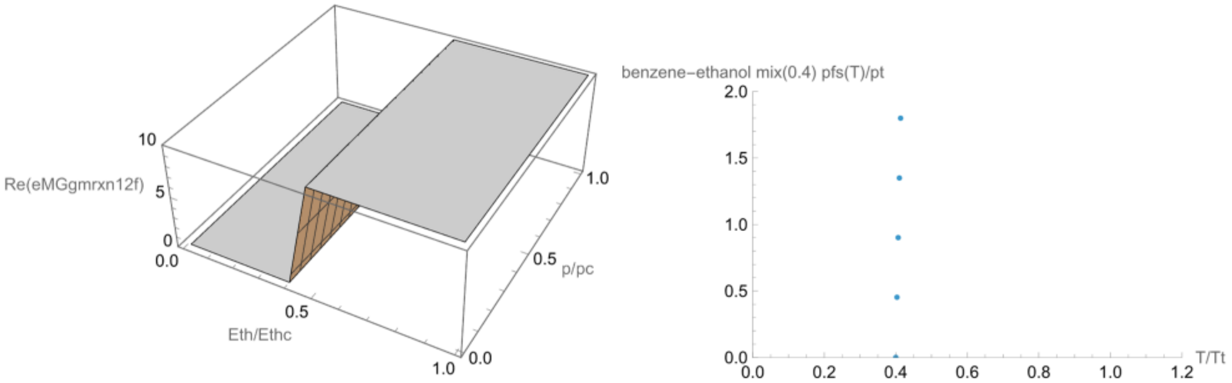


x_0=0.5

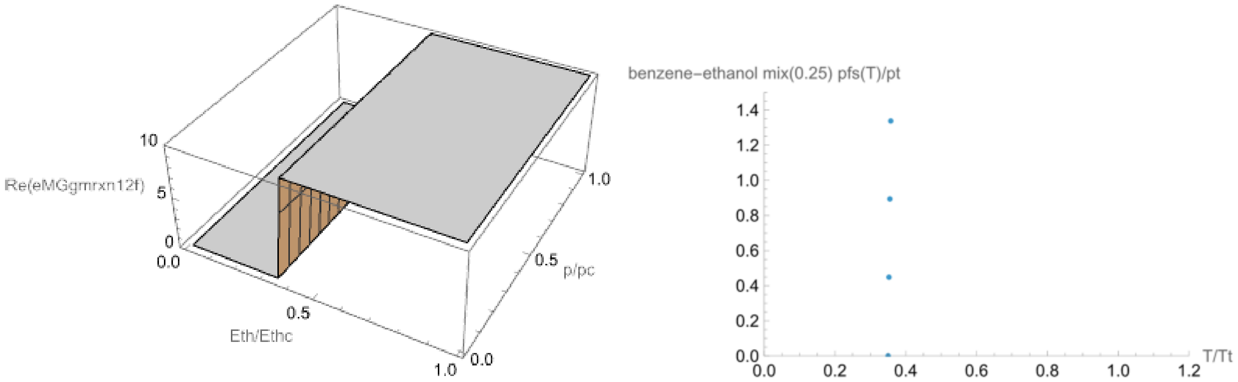




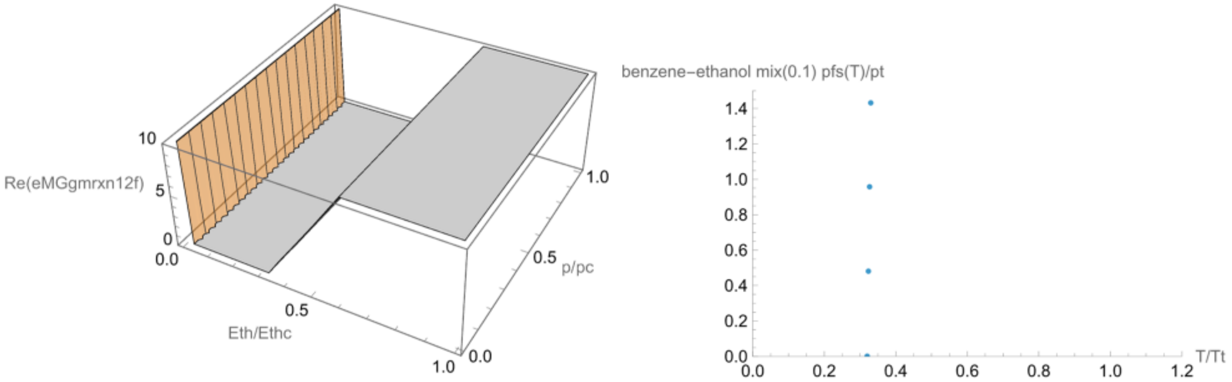
x_0=0.4



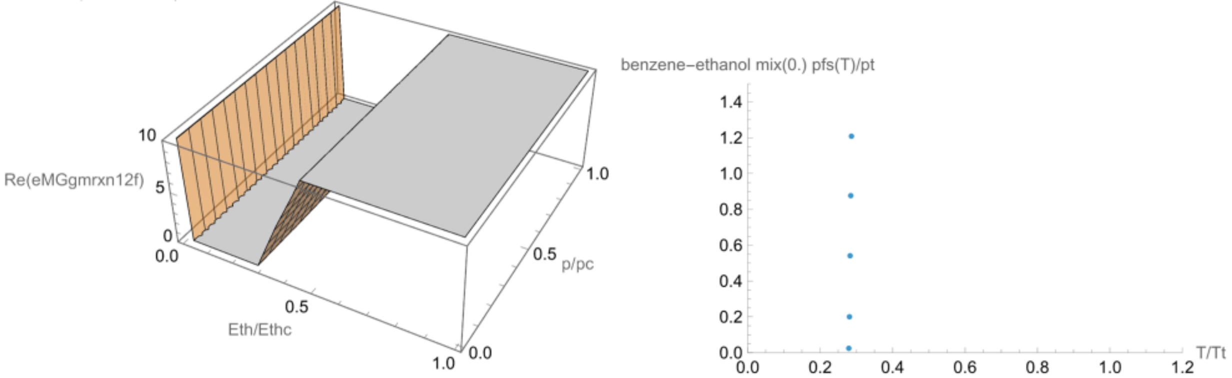
x_0=0.25



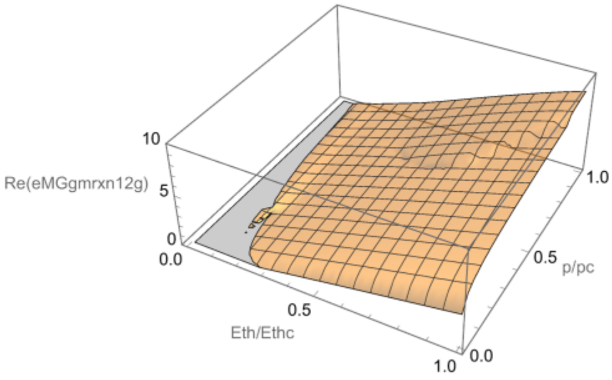
x_0=0.1

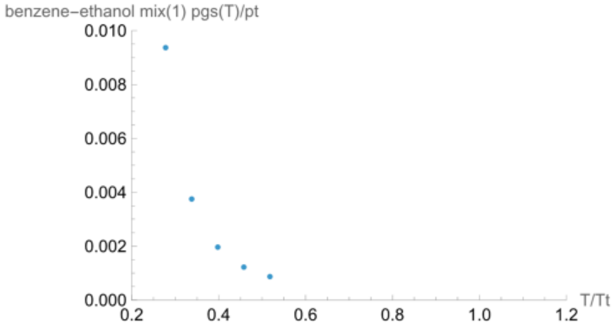


x_0=0 (ethanol)

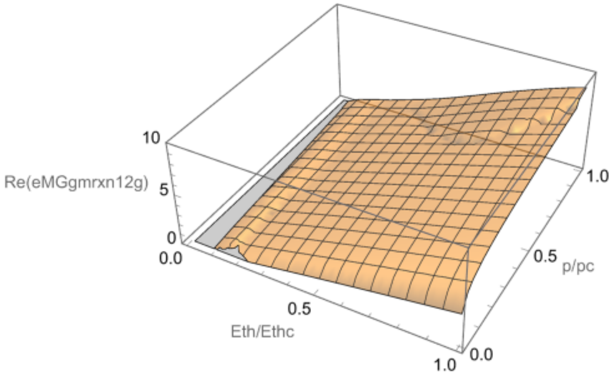


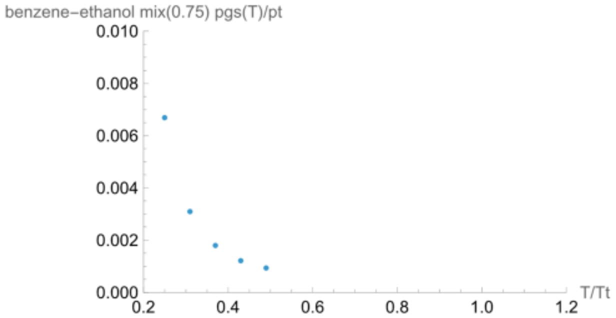
Maxwell-Gibbs eq. of the solid-gas curve (real part)
x_0=1 (benzene)



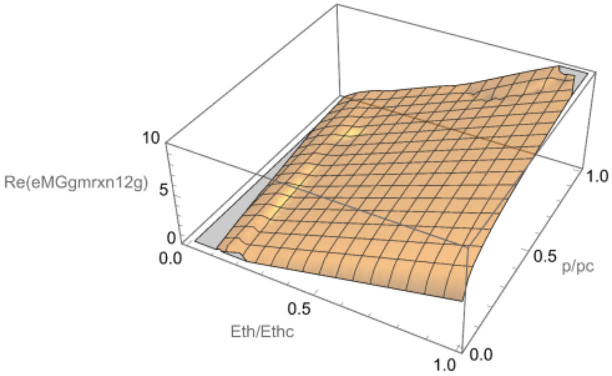


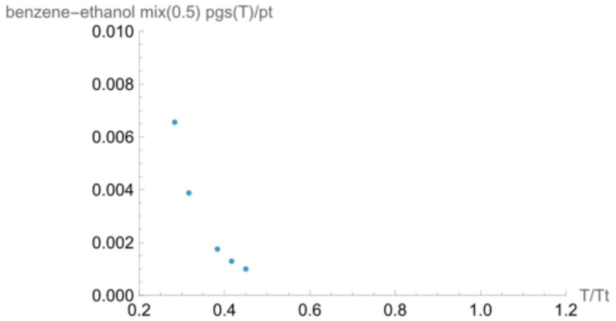
x_0=0.75



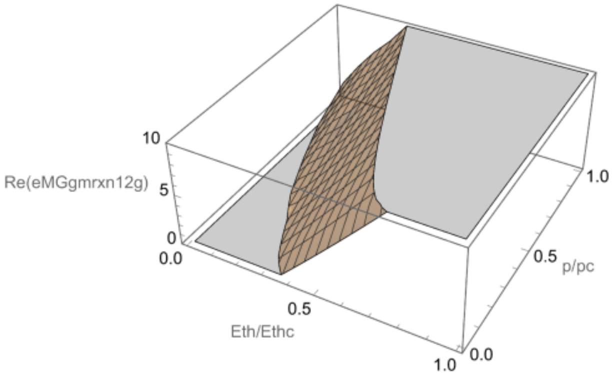


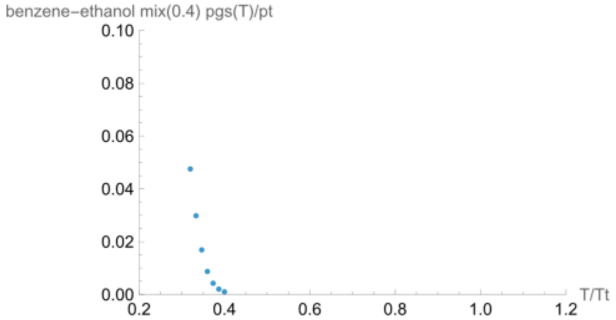
x_0=0.5



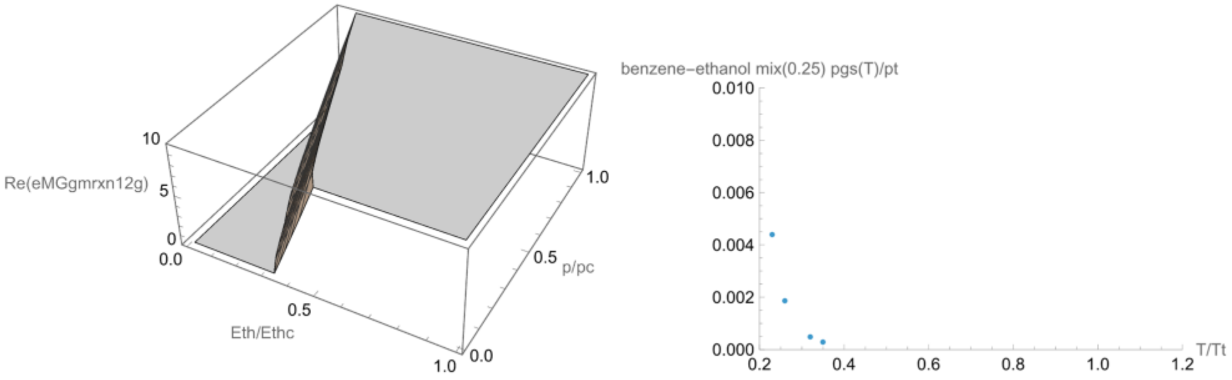


x_0=0.4

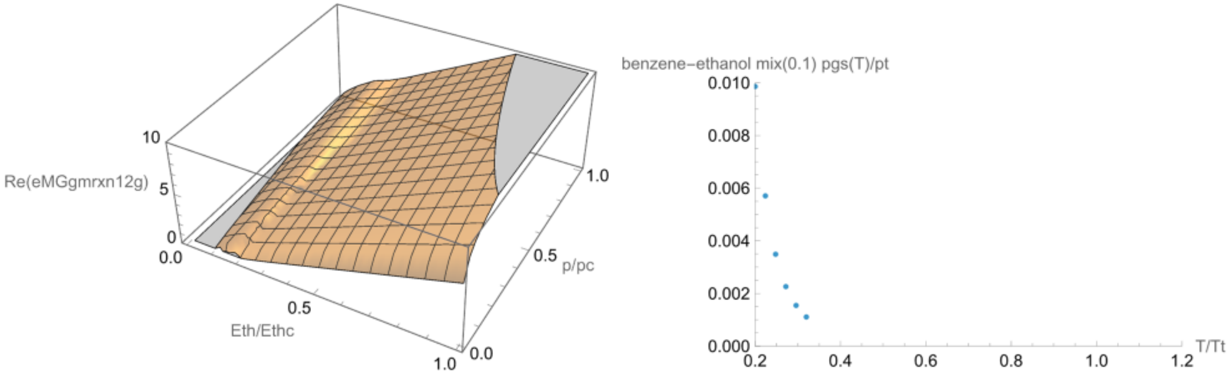




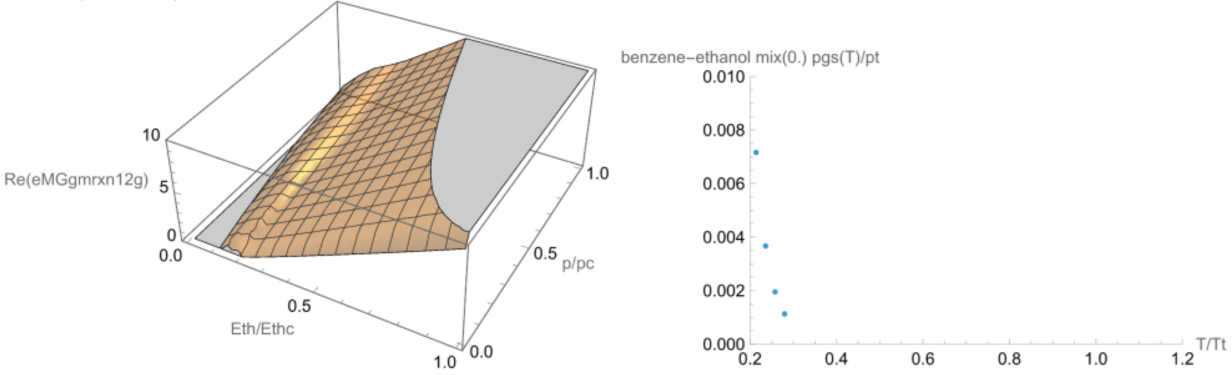
x_0=0.25



x_0=0.1



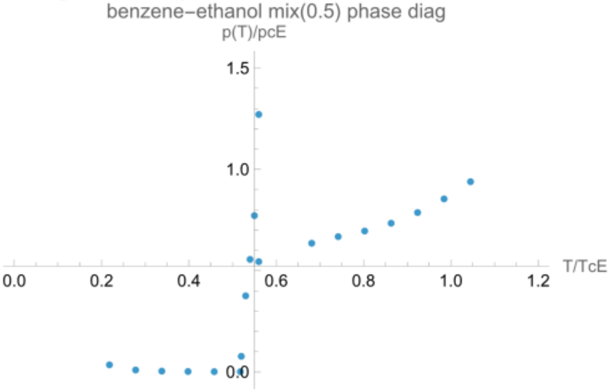
x_0=0 (ethanol)



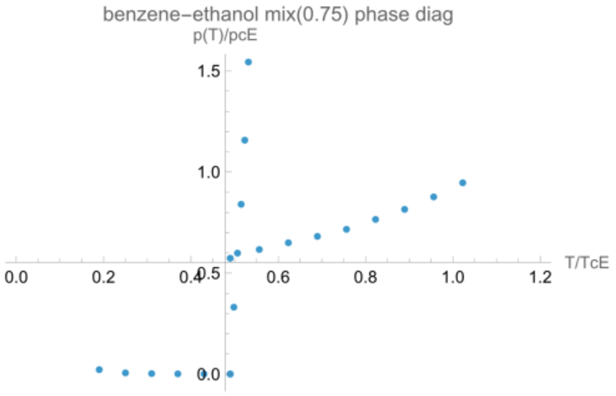
5.4 Phase diagrams, enthalpy, characteristic points of solutions benzene-ethanol

Phase diagrams

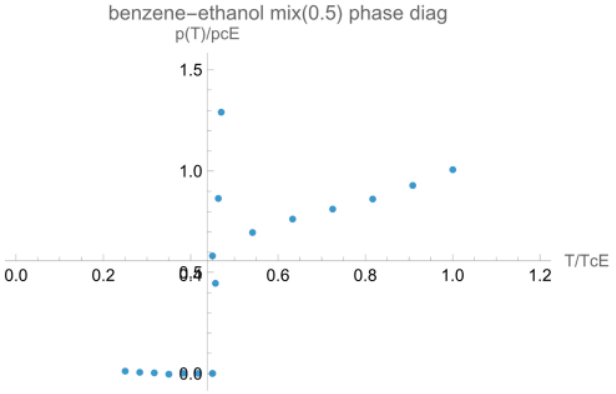
The phase diagrams of the solutions are shown below



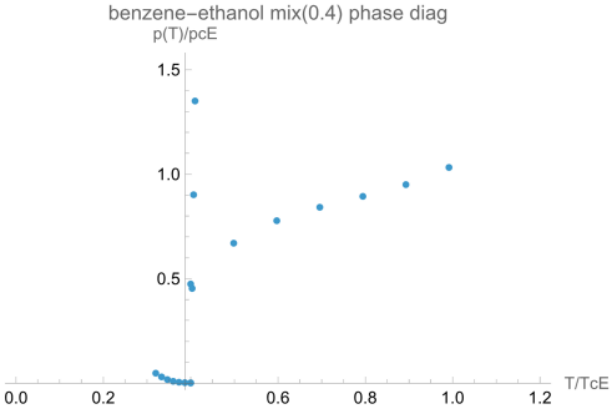
x_0=1.



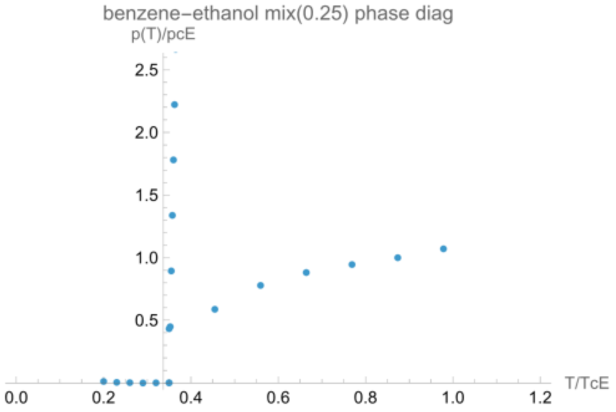
x_0=0.75



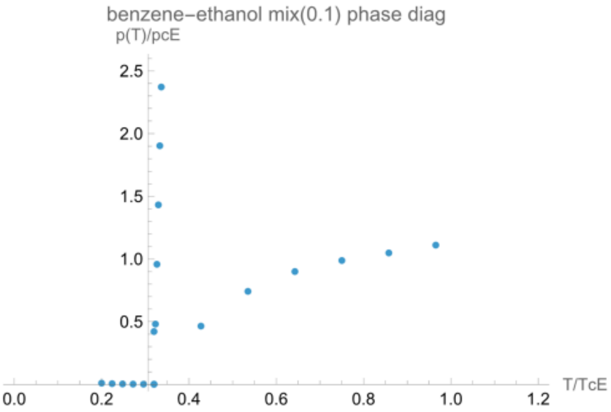
x_0=0.5



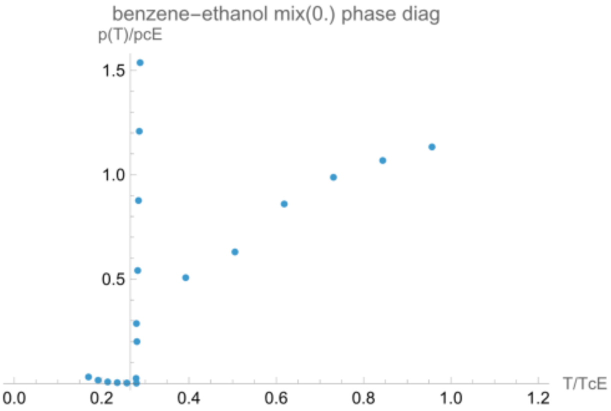
x_0=0.4



x_0=0.25

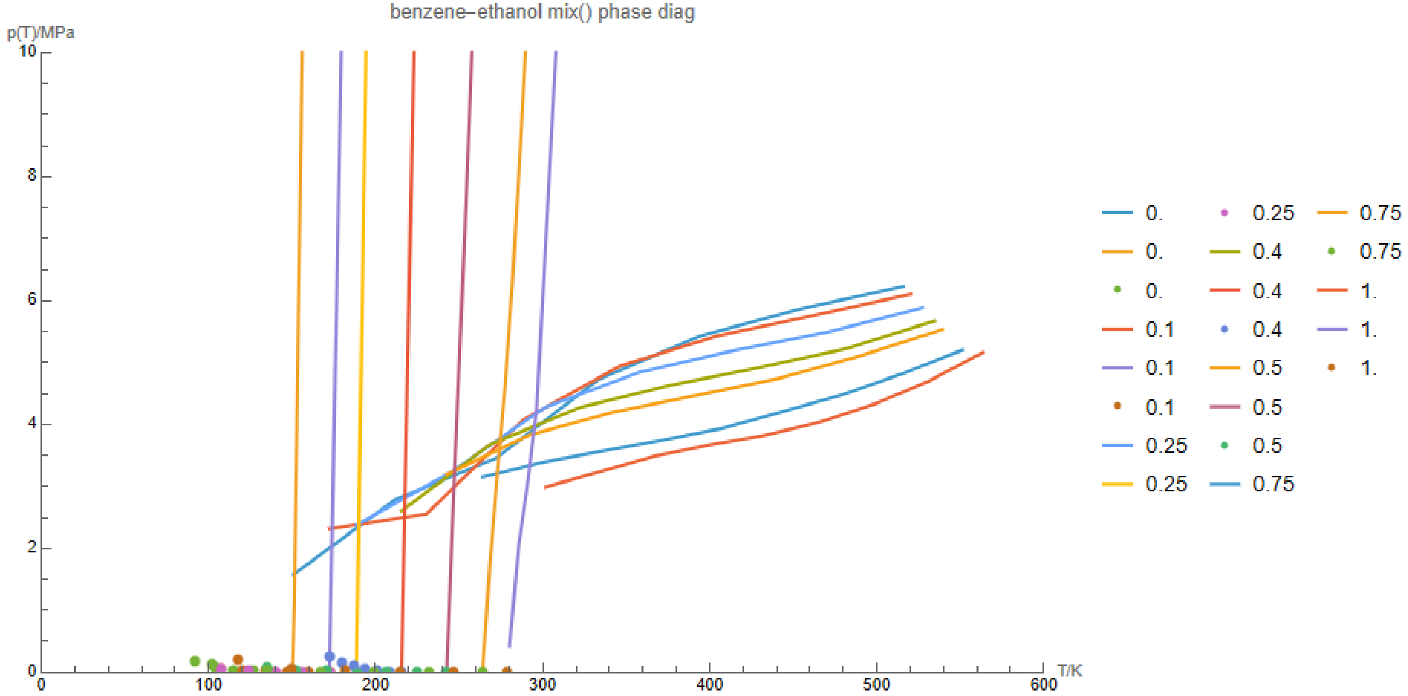


x_0=0.1



x_0=0

The combined phase diagram of all solutions is shown below.



Each fluid-gas saturation curve descends steeply to the triple point of the corresponding solid-fluid curve, the triple point is the intersection of the solid-fluid and the solid-gas curve at the low pressure p_t<0.01 .

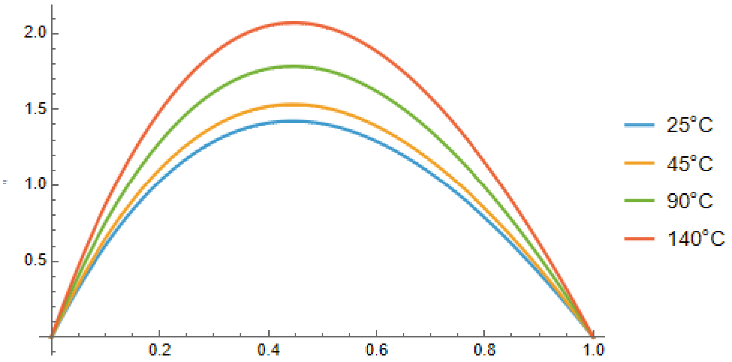
Enthalpy

The excess enthalpy of the fluid-gas transition is the difference between the two enthalpies

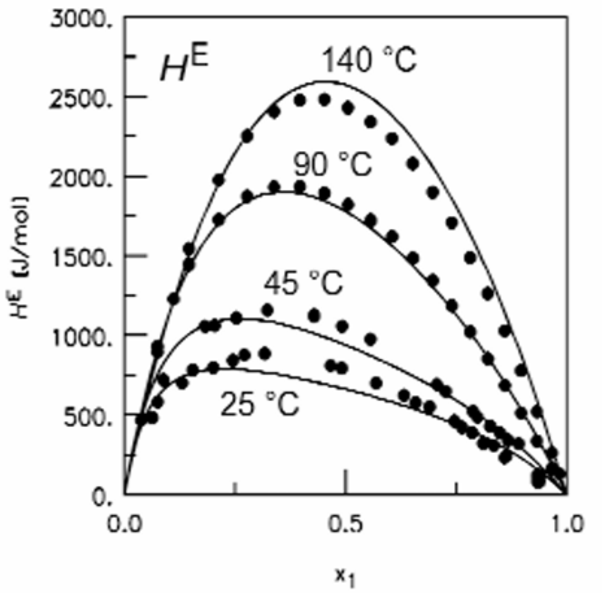
$$H_E\left(E_{th},p\right)=G\left(E_{th},v_g\left(E_{th},p\right),p\right)-G\left(E_{th},v_f\left(E_{th},p\right),p\right),$$

measured at normal pressure $H_{E,0}\left(E_{th}\right)=H_E\left(E_{th},p_0\right)$, p_0 =1bar=0.1MPa

Excess enthalpy $H_{E,0}\left(E_{th}\right)$ in kJ/mol vs. relative benzene concentration x_0 is shown below



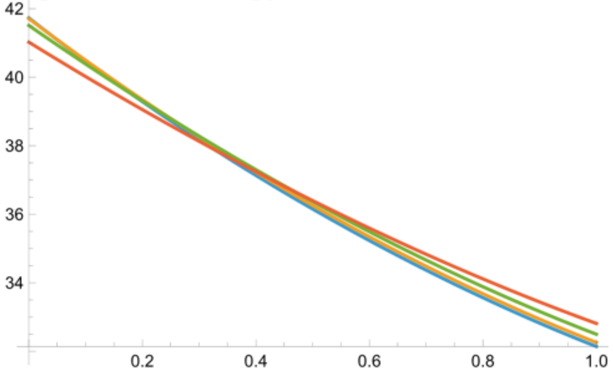
Measured excess enthalpy in J/mol is [6] roughly in agreement



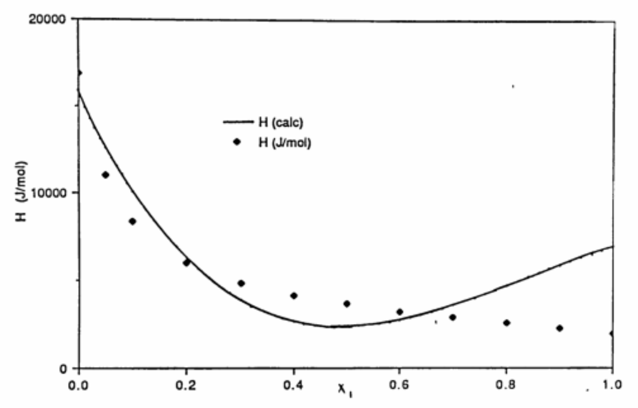
The vaporization enthalpy is the enthalpy of the gas phase at normal pressure

$$H_v\left(E_{th},p_0\right)=G\left(E_{th},v_g\left(E_{th},p_0\right),p_0\right)$$

Vaporization enthalpy in kJ/mol is shown below

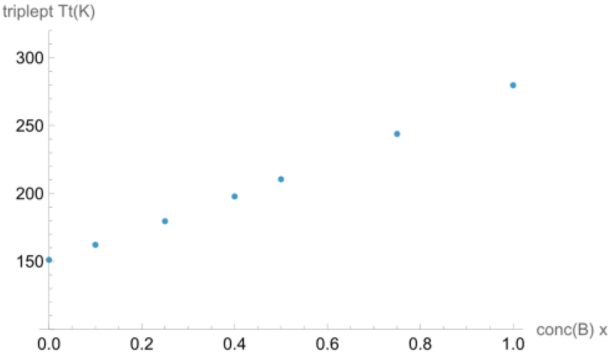


Vaporization enthalpy depends only weakly on the temperature.
Measured values agree roughly with the calculation [28]



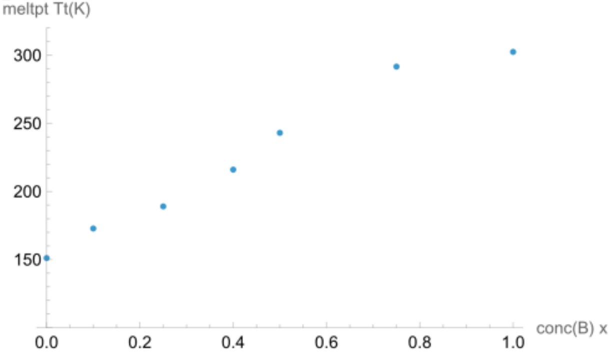
Triple point temperature

The calculated triple point temperature $E_{th,t}$ in K



The dependence on concentration is approximately linear.

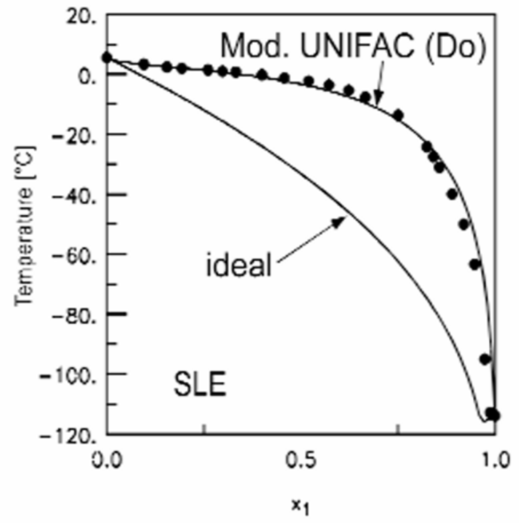
To determine the melting point, we take the point on the steep descend part of the fluid-gas curve at normal pressure



The resulting curve shows an accumulation near the benzene melting point at $x_0=1$.

Pure benzene melts (at normal pressure) at 5.53 °C (278.6K), while pure ethanol melts at -114.14 °C (159K).

The measured values of melting point [6] also show an accumulation effect near the melting point of benzene, and agree roughly with the calculated values.


Mod. UNIFAC (Do)
ideal
SLE
Temperature [°C]
20.
0.
-20.
-40.
-60.
-80.
-100.
-120.
0.0
0.5
1.0
x_1

6. Ionic solutions

6.1 Ionic solutions: solubility, hydration

In ionic solutions, the solute dissociates wholly or partially in ions ([1], [4], [2], [3]).
The solubility K_{sol} is directly related to the Gibbs energy change $\Delta_{sol}G$

$$\Delta_{sol}G = -RT\log K_{sol}$$

where K_{sol} is the product of the concentrations $K_{sol} = c_+c_-$, e.g. for AgCl , $K_{sol} = \left[Ag^+\right]\left[Cl^-\right]$

Hydration energy is the energy of ion formation.

- Born continuum approximation

For Born continuum approximation the hydration energy is

$$\Delta_{hyd}G = \frac{z^2e^2}{8\pi\varepsilon_0}\int_0^\infty\left(\frac{1}{\varepsilon(r)}-1\right)\frac{dr}{r^2} = \frac{z^2e^2}{8\pi\varepsilon_0}\left(\frac{1}{b\varepsilon_b}-\frac{1}{a}+\frac{1}{a}\int_a^b\left(\frac{\varepsilon_a}{\varepsilon_b}\right)^{f(r)}\frac{dr}{r^2}\right),$$

$$f(r) = 1-\left(\frac{b-r}{b-a}\right)^2$$ form factor

with radii *a*=radius(ion), *b*=radius(solvent) , z=(integer) charge of the ions, e=elementary charge,
with ε_0 =absolute vacuum permittivity, relative permittivity $\varepsilon_a = \varepsilon(r=a)$, $\varepsilon_b = \varepsilon(r=b)$, ε_r of the solvent ,

- Mean spherical approximation (MSA)

The ion is represented by a sphere with radius a and charge *ze*, while for the solvent is a sphere with radius *b* and dipole moment μ .
MSA consists of the core condition correlation function *g(r) = 0* for *r < 2a*

and the approximate concentration $c(r) = \begin{cases} -\beta\dfrac{q}{4\pi\varepsilon a} & r > 2a \\ 0 & r < 2a \end{cases}$

together with the Ornstein-Zernicke equation.
The molar hydration energy for diluted solution is

$$\Delta_{hyd}G = \frac{N_Az^2e^2f}{8\pi\varepsilon_0 a}\left(\frac{1}{\varepsilon_r}-1\right)\left(\frac{1}{1+b/\lambda a}\right)$$

where polarization parameter λ for the solvent is $\lambda^2(1+\lambda)^4 = 16\varepsilon_r$, f=dipole factor $f \approx 1$

6.2 Ionic solutions: Debye-Hückel theory

We make the assumptions: [1] [2] [4]

- ionic interaction is dominant
- solvent=dielectric continuum
- spherical ions
- dilute solution
- complete dissociation

We have the following relations:
ion Coulomb potential $\Psi_j^{ion}(r) = ez_j/4\pi\varepsilon r$, $\varepsilon = \varepsilon_0\varepsilon_r$

charge density $\rho_j(r)$ at distance *r* from ion *j* is $\rho_j = \sum_i ez_in_{ij}$

with Poisson equation $\dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial\Psi_j(r)}{\partial r}\right) = -\dfrac{\rho_j}{\varepsilon}$

we obtain the charge density $\rho_j = \sum_i ez_in_{ij} = \sum_i ez_in_i\exp\left(-\dfrac{ez_i\Psi_j}{k_BT}\right)$

with the cut-off approximation $\rho_j = \sum_i e z_i n_{ij} = \sum_i e z_i n_i \left(1 - \frac{e z_i \Psi_j}{k_B T}\right)$

$$\rho_j = \sum_i e z_i n_i - \sum_i \frac{e^2 z_i^2 n_i \Psi_j}{kT} + \sum_i \frac{e^3 z_i^3 n_i \Psi_j^2}{2k^2T^2} - \dots$$

From this approximation follows the Poisson–Boltzmann equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \Psi_j(r)}{\partial r}\right) = \kappa^2 \Psi_j \ , \ \kappa^2 = \frac{e^2}{\varepsilon k_B T}\sum_i z_i^2 n_i$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}\Psi_j}{\mathrm{d}r}\right) = \kappa^2 \Psi_j \quad \kappa^2 = \frac{e^2}{\varepsilon kT}\sum_i n_i z_i^2$$

with solution Ψj at a distance r ≥ a

$$\Psi_j(r) = \frac{e z_j}{4\pi\varepsilon}\frac{\exp(-\kappa(r-a))}{(1+\kappa a)r}$$

Activity

We obtain for the activity coefficient the Debye-Hückel equation, valid for $I_m < 0.1$ mole ,

$$\log\gamma = -\frac{A|z_+ z_-|\sqrt{I_m}}{1 + Ba\sqrt{I_m}} \ , \ A = \sqrt{2\pi\rho N_A}\left(\frac{e^2}{\varepsilon k_B T}\right)^{3/2} \ , \ B = \sqrt{\frac{2e^2\rho N_A}{\varepsilon k_B T}}$$

with ionic strength I_m and I_c, density ρ

$$I_m \equiv \frac{\sum_i z_i^2 m_i}{2} = \frac{\sum_i z_i^2 n_i}{2N_A\rho} \ , \ I_c \equiv \frac{\sum_i z_i^2 c_i}{2} = \frac{\sum_i z_i^2 n_i}{2N_A}$$

molality m_i , concentration $c_i \approx \rho m_i$

For aqueous solutions at 25 C , *A*= 0.51$\mathrm{mol}^{-1/2}\mathrm{dm}^{3/2}$ and *B* = 3.29 $\mathrm{nm}^{-1}\mathrm{mol}^{-1/2}\mathrm{dm}^{3/2}$

For values $I_m > 0.1$ mole, the extended Debye-Hückel equation is valid

$$\log\gamma = -0.509|z_+ z_-|\left(\frac{\sqrt{I_m}}{1+\sqrt{I_m}} - 0.30 I_m\right)$$

7. Landau formulation of binary solution thermodynamics

7.1 General Landau ansatz for binary solutions

For solid-fluid-gas phase transitions, the generalized Landau ansatz for the partition function is a functional integral [5].

The Landau function *depends on parameters* $\left(c_k\right)=\left(l_c,\alpha_k,l_{a,k},\alpha_{0k}\right)$, the differential is $D\varphi=\sum\frac{\partial\varphi}{\partial c_k}dc_k$.

Also, the Boltzmann-exponential contains only the intermolecular potential u, the partition function is

$$Z=\int D\varphi\, dV\exp\left(-\beta\, u\left(\vec{r}\right)\right)$$

The ansatz for the Landau function for solid-fluid-gas transition is the λ-damped rdf function (with axial symmetry)

$$\varphi\left(\vec{r},\sigma,\lambda;c_k\right)=\exp\left(-\frac{r}{\lambda}\right)\varphi_{rdf}\left(r,\theta,\sigma;c_k\right)$$

$$\varphi_{rdf}\left(r,\theta,\sigma;c_k\right)=\Theta_H\left(r,\sigma\right)\left(1+\exp\left(-r/l_c\right)\left(\sum_k\alpha_k\cos\left(2\pi\frac{r-\sigma}{l_{a,k}}\right)\right)f_\theta\left(\theta,\alpha_{0k}\right)\right)$$

with the soft-step-up function

$$\Theta_H\left(r,\sigma,\Delta r\right)=\left(1-\frac{1}{1+\exp\left(\frac{r-\sigma}{\Delta r\,\sigma}\right)}\right),$$

where $\varphi_{rdf}\left(r,\sigma;c_k\right)$ is the correlation (=radial distribution) function .

According to the Landau minimum principle, we obtain the minimal parameters $c_{0,k}=\left(l_c,\alpha_{k_1},l_{a,k_1},\alpha_{0k_2}\right)$ by minimization of free energy $F=-\frac{1}{\beta}\log Z$ or equivalently by maximization of Z.

The minimal parameters $c_{1,k}$ determine the rdf $f_{rdf}\left(r,\theta,\sigma;c_k\right)$ in the partition function.

The other method of fixing the parameters is to solve the Hypernetted-Chain-Ornstein-Zernicke equation in order to find the correlation function with effective parameters $c_{0,k}$.

Both methods yield the effective partition function in the form

$$Z\left(\lambda,\beta,\sigma,\varepsilon;c_{0,k}\right)=\int\varphi\left(r,\theta,\lambda;c_{0,k}\right)dv\exp\left(-\beta\, u\left(\vec{r}\right)\right)$$

In the general case with concentrations x_i , $\sum_i x_i=1$, we obtain the partition function

$$Z=\prod_{i,j}\left(Z_{0,ij}\right)^{x_ix_j}$$

with component -functions $Z_{ij}=\left(\int D\varphi_{ij}\; dv\exp\left(-\beta\,\varepsilon_{ij}\; f\left(\vec{r}/\sigma_{ij}\right)\right)\right)$, or formulated with rdf-function

$$Z_{ij}\left(\lambda,\beta,\sigma,\varepsilon\right)=\int\varphi\left(r,\theta,\lambda;c_{ijk}\right)\exp\left(-\beta\,\varepsilon_{ij}\; f\left(\vec{r}/\sigma_{ij}\right)\right)dv$$

$$\varphi\left(\vec{r},\sigma,\lambda;c_k\right)=\exp\left(-\frac{r}{\lambda}\right)\varphi_{rdf}\left(r,\theta,\sigma;c_k\right)$$

where

$$=\exp\left(-\frac{r}{\lambda}\right)\Theta_H\left(r,\sigma\right)\left(1+\exp\left(-r/l_c\right)\left(\sum_k\alpha_k\cos\left(2\pi\frac{r-\sigma}{l_{a,k}}\right)\right)f_\theta\left(\theta,\alpha_{0k}\right)\right)$$

free energy $F=-\frac{1}{\beta}\sum_{i,j}x_i x_j \log\left(Z_{0,ij}\right)$

and pressure $p=\frac{1}{\beta}\sum_{i,j}x_i x_j \frac{\partial\log\left(Z_{0,ij}\right)}{\partial v}=\sum_{i,j}x_i x_j p_{ij}$,

where the partial pressures are $p_{ij}=\frac{1}{\beta}\frac{\partial\log\left(Z_{0,ij}\right)}{\partial v}$.

This relation is the theoretical basis for the molecular mixing rules.

We obtain the minimal parameters $c_{0,ijk}=\left(l_c,\alpha_{k_1},l_{a,k_1},\alpha_{0k_2}\right)$ by minimization of free energy $F_{ij}=-\frac{1}{\beta}\log Z_{ij}$ in the parameters $c_k=\left(l_c,\alpha_{k_1},l_{a,k_1},\alpha_{0k_2}\right)$

or by solving the Hypernetted-Chain-Ornstein-Zernicke equation with the potential $\varepsilon_{ij}\; f\left(\vec{r}\,/\,\sigma_{ij}\right)$.

For binary molecular solutions with relative concentrations $x_1+x_2=1$, $f\left(r\,/\,\sigma\right)$, we make the usual assumption, that the intermolecular potentials of the components are of the same type (scalable potential)

$u_{11}=\varepsilon_{11}f\left(r/\sigma_{11}\right)$, $u_{12}=\varepsilon_{12}f\left(r/\sigma_{12}\right)$, $u_{22}=\varepsilon_{22}f\left(r/\sigma_{22}\right)$

$g_{11}=g\left(\vec{r}/\sigma_{11}\right)$, $g_{12}=g\left(\vec{r}/\sigma_{12}\right)$, $g_{22}=g\left(\vec{r}/\sigma_{22}\right)$, $\sigma_{12}=\left(\sigma_{11}+\sigma_{22}\right)/2$

(equal interaction $f\left(\vec{r}/\sigma\right)$, equal correlation function $g\left(\vec{r}/\sigma\right)$) ,

where σ is the molecular radius (=hardcore potential radius), and ε is the characteristic energy.

We obtain the minimal parameters $c_{0,k}=\left(l_c,\alpha_{k_1},l_{a,k_1},\alpha_{0k_2}\right)$ by minimization of free energy $F=-\frac{1}{\beta}\log Z$ or by solving the Hypernetted-Chain-Ornstein-Zernicke equation .

With the above generalized Landau ansatz, the molecular solution partition function is formulated as follows. $v=V\,/\,N$ is the product of the three component partition functions (per particle, using specific volume $v=\lambda^3$

$$Z_{11}=\left(\int D\varphi_{11}\;dv\exp\left(-\beta\,\varepsilon_{11}\;f\left(\vec{r}\,/\,\sigma_{11}\right)\right)\right)^{x_1^2}\;,\;Z_{22}=\left(\int D\varphi_{22}\;dv\exp\left(-\beta\,\varepsilon_{22}\;f\left(\vec{r}\,/\,\sigma_{22}\right)\right)\right)^{x_2^2}\;,$$

$$Z_{12}=\left(\int D\varphi_{12}\;dv\exp\left(-\beta\,\varepsilon_{12}\;f\left(\vec{r}\,/\,\sigma_{12}\right)\right)\right)^{2x_1x_2},$$

with the molecular mixing rule $\sigma_{12}=\left(\sigma_1+\sigma_2\right)/2$, $\varepsilon_{12}=\sqrt{\varepsilon_1\varepsilon_2}$

$$\varphi_{11}\left(\vec{r},\sigma_{11},\lambda;c_{k,11}\right)=\exp\left(-\frac{r}{\lambda}\right)g\left(\vec{r},\sigma_{11};c_{k,11}\right)\;,\;\varphi_{22}\left(\vec{r},\sigma_{22},\lambda;c_{k,22}\right)=\exp\left(-\frac{r}{\lambda}\right)g\left(\vec{r},\sigma_{22};c_{k,22}\right)\;,$$

$$\varphi_{12}\left(\vec{r},\sigma_{12},\lambda;c_{k,12}\right)=\exp\left(-\frac{r}{\lambda}\right)g\left(\vec{r},\sigma_{12};c_{k,12}\right)$$

$$g\left(\vec{r},\sigma;c_k\right)=\Theta_H\left(r,\sigma\right)\left(1+\exp\left(-r/l_c\right)\left(\sum_k\alpha_k\cos\left(2\pi\frac{r-\sigma}{l_{a,k}}\right)\right)f_\theta\left(\theta,\alpha_{0k}\right)\right)$$

Maximizing $Z=max\left(c_{k,11},c_{k,22},c_{k,12};Z\left(\beta,\lambda^3;\sigma_{ij},\varepsilon_{ij};c_{k,11},c_{k,22},c_{k,12}\right)\right)$ according to the Landau principle yields optimal parameters $c_k^{(0)}=\left(c^{(0)}{}_{k,11},c^{(0)}{}_{k,22},c^{(0)}{}_{k,12}\right)$, and the effective partition function becomes $Z_0\left(\beta,\lambda;\sigma_{ij},\varepsilon_{ij}\right)=Z\left(\beta,\lambda^3;\sigma_{ij},\varepsilon_{ij};c_k^{(0)}\right)$.

Direct calculation of the respective correlation functions $g\left(\vec{r},\sigma_{ij};c_{k,ij}\right)$, e.g. using the Hypernet-Chain-Ornstein-Zernicke (HCOZ) equation, as in [5], yields the same result $c_k^{(0)}$ for the parameters .

The specific Gibbs energy (per particle) is then

$$G\left(\beta,v\right)=-\frac{1}{\beta}\frac{\partial}{\partial v}\left(v\log Z\right)$$

$$G\left(\beta,\lambda,x_i;\sigma_{ij},\varepsilon_{ij}\right)=-\frac{1}{\beta}\frac{\partial}{\partial\left(\lambda^3\right)}\left(\lambda^3\left(x_1{}^2\log Z_{11}\left(\beta,\lambda^3;\sigma_{ij},\varepsilon_{ij};c^{(0)}{}_{k,11}\right)+x_2{}^2\log Z_{22}\left(\beta,\lambda^3;\sigma_{ij},\varepsilon_{ij};c^{(0)}{}_{k,22}\right)+2x_1x_2\log Z_{12}\left(\beta,\lambda^3;\sigma_{ij},\varepsilon_{ij};c^{(0)}{}_{k,12}\right)\right)\right)$$

$$G\left(\beta,\lambda,x_i;\sigma_{ij},\varepsilon_{ij}\right)=-\frac{1}{\beta}\frac{\partial}{\partial\left(\lambda^3\right)}\left(\lambda^3\left(\begin{array}{l} x_1^2\log\int\sum\frac{\partial\exp\left(-\frac{r}{\lambda}\right)g\left(\vec{r},\sigma_{11};c^{(0)}{}_{k,11}\right)}{\partial c_{k,11}}dc_{k,11}\;dv\exp\left(-\beta\,\varepsilon_{11}\;f\left(\vec{r}/\sigma_{11}\right)\right)\\ +x_2^2\log\int\sum\frac{\partial\exp\left(-\frac{r}{\lambda}\right)g\left(\vec{r},\sigma_{22};c^{(0)}{}_{k,22}\right)}{\partial c_{k,22}}dc_{k,22}\;dv\exp\left(-\beta\,\varepsilon_{22}\;f\left(\vec{r}/\sigma_{22}\right)\right)\\ +\left(1-x_1{}^2-x_2{}^2\right)\log\int\sum\frac{\partial\exp\left(-\frac{r}{\lambda}\right)g\left(\vec{r},\sigma_{12};c^{(0)}{}_{k,12}\right)}{\partial c_{k,12}}dc_{k,12}\;dv\exp\left(-\beta\,\varepsilon_{12}\;f\left(\vec{r}/\sigma_{12}\right)\right)\end{array}\right)\right)$$

The Gibbs energy is a function of the inverse thermal energy $\beta=1/k_BT$, average distance $\lambda=\left(V/N\right)^{1/3}$, the relative concentrations $\left(x_1=1-x_2,x_2\right)$, and the molecular interaction parameters $\left(\sigma_{ij},\varepsilon_{ij}\right)$.

The dependence in x_i is parabolic, as is clearly visible in measurement data.

7.2 Specific Landau ansatz for ethanol-benzene solution

Ethanol is predominantly a dipole substance , its partition function reads, using the HCOZ-solution [5] [18]

$$Z_{DD,Eth}\left(\beta,\lambda\right)=Z\left(\beta,\lambda;\sigma=1,\varepsilon=1;c_{DD.k}\left(\beta,\lambda\right)\right)$$

$\left(c_{DD,k}\right)=\left(l_c,\alpha_{k1},l_{a,k1},\alpha_0\right)$, $k1=1,2,3$, 3 harmonics

with the σ,ε values [20]

$\sigma_{Eth}=2.6\dot{A}$, $\varepsilon_{Eth}=0.0542eV$

Benzene is a covalently bound Lennard-Jones substance, its partition function reads, using the HCOZ-solution [5] [18]

$$Z_{LJ,Ben}\left(\beta,\lambda\right)=Z\left(\beta,\lambda;\sigma=1,\varepsilon=1;c_{LJ.k}\left(\beta,\lambda\right)\right)$$

$\left(c_{LJ,k}\right)=\left(l_c,\alpha_{k1},l_{a,k1}\right)$, $k1=1,2$, 2 harmonics

with the σ,ε values [20]

$\sigma_{Ben}=5.27\dot{A}$, $\varepsilon_{Ben}=0.0368eV$

The ethanol-benzene interaction is covalent OH-bound Lennard-Jones, its partition function reads, using the HCOZ-solution [5] [18]

$$Z_{LJ,EB}\left(\beta,\lambda\right)=Z\left(\beta,\lambda;\sigma=1,\varepsilon=1;c_{LJ.k}\left(\beta,\lambda\right)\right)$$

$\left(c_{LJ,k}\right)=\left(l_c,\alpha_{k1},l_{a,k1}\right)$, $k1=1,2$, 2 harmonics,

where the OH-bounding has the LJ-parameters [20]

$\sigma_O=3.07\dot{A}$, $\varepsilon_O=0.074eV$

and with the σ,ε values according to the approximating mixing rule

$\sigma_{BE}=\left(\sigma_{Ben}+\sigma_O\right)/2=4.17\dot{A}$, $\varepsilon_{EB}=\sqrt{\varepsilon_{Ben}\varepsilon_O}=0.0522eV$

Now we rescale the Z-functions, taking as basic scale ethanol

$\sigma_0 = \sigma_{Eth} = 2.6\dot{A}$, $\varepsilon_0 = \varepsilon_{Eth} = 0.0542eV$,

rescaled partition function becomes $Z\left(\beta\frac{\varepsilon}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma}; c_k\left(\beta\frac{\varepsilon}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma}\right)\right)$

for mix *x* ethanol, *1-x* benzene, resulting in the partition function

$$Z_{BenEth}(\beta,\lambda) = Z_{DD}\left(\beta,\lambda;c_{DD.k}(\beta,\lambda)\right)^{x^2} Z_{LJ}\left(\beta\frac{\varepsilon_{Ben}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{Ben}}; c_{LJ.k}\left(\beta\frac{\varepsilon_{Ben}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{Ben}}\right)\right)^{(1-x)^2}$$

$$Z_{LJ}\left(\beta\frac{\varepsilon_{BE}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{BE}}; c_{LJ.k}\left(\beta\frac{\varepsilon_{BE}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{BE}}\right)\right)^{2x(1-x)}$$

free energy

$$F_{BenEth}(\beta,\lambda) = -\frac{1}{\beta}\left(\begin{array}{l} x^2\log Z_{DD}\left(\beta,\lambda;c_{DD.k}(\beta,\lambda)\right) + (1-x)^2\log Z_{LJ}\left(\beta\frac{\varepsilon_{Ben}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{Ben}}; c_{LJ.k}\left(\beta\frac{\varepsilon_{Ben}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{Ben}}\right)\right) \\ +2x(1-x)\log Z_{LJ}\left(\beta\frac{\varepsilon_{BE}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{BE}}; c_{LJ.k}\left(\beta\frac{\varepsilon_{BE}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{BE}}\right)\right) \end{array}\right)$$

and pressure

$$p_{BenEth}(\beta,\lambda) = \frac{1}{3\beta\lambda^2}\left(\begin{array}{l} x^2\frac{\partial\log Z_{DD}\left(\beta,\lambda;c_{DD.k}(\beta,\lambda)\right)}{\partial\lambda} + (1-x)^2\frac{\partial\log Z_{LJ}\left(\beta\frac{\varepsilon_{Ben}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{Ben}}; c_{LJ.k}\left(\beta\frac{\varepsilon_{Ben}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{Ben}}\right)\right)}{\partial\lambda} \\ +2x(1-x)\frac{\partial\log Z_{LJ}\left(\beta\frac{\varepsilon_{BE}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{BE}}; c_{LJ.k}\left(\beta\frac{\varepsilon_{BE}}{\varepsilon_0}, \lambda\frac{\sigma_0}{\sigma_{BE}}\right)\right)}{\partial\lambda} \end{array}\right)$$

Conclusion

In this paper, there are three important results

- Exact solution of the Maxwell-Gibbs equation and calculation of phase diagrams

The Maxwell-Gibbs equation is the equality of enthalpy for both phases along the saturation curve, the other condition is continuity of pressure. The two equations yield the Maxwell condition $eqgr\left(p,E_{th}\right)=0$ after inserting an appropriate branch $v_i(E_{th},p)$ from the three algebraic solution (i=1,2,3) of the cubic eos (vdWaals, Peng-Robinson and Mie-Grueneisen eos are all cubic in volume v) . The condition $eqgr\left(p,E_{th}\right)=0$ is an algebraic-transcendent equation for (E_{th},p) ,which yields the saturation curve in the form $p(E_{th})$, including the triple point, which is the algebraic branching point, where the three saturation curves meet.

This method is used to calculate the complete phase diagram for four selected substances (benzene, ethanol, argon, carbon dioxide), and the results are compared with measured data. The results agree with measured data within the accuracy of the Peng-Robinson eos (about 10%).

- Exact solution for the eos of binary solutions and calculation of their phase diagrams

We formulate an exact theoretical basis for binary solutions, based on the weighted sum of partial eos pressures, and including the 1-2-interaction of the components (i.e. non-ideal and irregular solutions).

Using this ansatz, we calculate the general eos in dependence on relative concentration x_0 of the first component. Furthermore, we calculate the eos for seven concentrations for the solution benzene-ethanol and compare the results with measurements. Again, the agreement is satisfactory and the deviation is within the accuracy of the Peng-Robinson eos (about 10%).

- Exact theoretical basis for binary solution eos

In chap.7 we formulate an exact theoretical basis for binary solution eos, based on the Landau theory of phase transitions.

To achieve this, we introduce two novel methods.

- Exact algebraic solution for phase diagrams based on Peng-Robinson and Mie-Grueneisen equation-of-state
- An exact theoretical ansatz for mixture phase diagrams based on the weighted sum of partial pressures

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