Thermodynamics of phase transitions in flowcharts

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Abstract
This paper presents in form of flowcharts the mathematical models and experimental data of phase transitions of pure substances and solutions with new ansatz and calculation methods.

It is based on two preprints about thermodynamics of phase transitions [1], [2].

Introduction

In statistical mechanics, the key entity is the partition function Z, from which all important entities of a thermal solid-fluid-gas (fgs) system can be derived: free energy *F*, Gibbs energy *G*, entropy *S*, and pressure *p* in dependence of the thermal basic variables *N, V, T*, where the pressure determines the equation-of-state (eos).
In magnetic systems, the magnetization M plays the role of pressure, and the basic variables are *N, B, T*, where *B* is the magnetic field flux.
The phase transitions in fgs systems are described by saturation curves (e.g. fluid-gas saturation curve) characterized by derivatives of pressure ($\frac{\partial p}{\partial V}=0$) significant points are critical point ($\frac{\partial^2 p}{\partial V^2}=0$) and multiple points (e.g. triple point solid-fluid-gas) i.e. branching points. Here, phase transitions are first-order transitions, i.e. first derivative of Gibbs energy, volume $V=\left(\frac{\partial G}{\partial p}\right)_T$, is discontinuous at phase transitions.

The phase transitions in magnetic systems are characterized by derivatives of magnetization ($\frac{\partial M}{\partial B}=0$).
Here, phase transitions are second-order transitions, i.e. second derivative of free (or Gibbs) energy, susceptibility $\chi_T=\left(\frac{\partial^2 F}{\partial B^2}\right)_T$, is discontinuous.
It is generally accepted that the behavior of a thermal fgs system is solely determined by its inter-molecular potential (e.g. Lennard-Jones potential in fluid argon, dipole-dipole OH-binding in ethanol),
$Z=\int \varphi_{rdf}\; dV \exp\left(-\beta\, u\left(\vec{r}\right)\right)$
The behavior of a thermal magnetic system is determined by its Landau function $\varphi=M$ magnetization, and its Landau energy $E\left(\varphi,\beta\right)=\frac{\mu\left(\beta\right)}{2}\varphi^2+\frac{\lambda\left(\beta\right)}{4!}\varphi^4-\beta\varphi B$.
In generalized form, the partition function *Z* is described by the functional integral $Z=\int D\varphi\; dV \exp\left(-H\left(\vec{r},\varphi,\beta\right)\right)$, where $H\left(\vec{r},\varphi,\beta\right)$ is the thermodynamic Hamiltonian $H\left(\vec{r},\varphi,\beta\right)=E(\varphi)+\beta\, u\left(\vec{r},\varphi\right)$,
$D\varphi=\sum_i \frac{\partial\varphi}{\partial c_i}dc_i$ for Landau function with parameters $\varphi\left(c_i\right)=\sum_i \frac{\partial\varphi}{\partial c_i}dc_i$ (fgs systems)
$Z=\int D\varphi\; dV \exp\left(-\beta\, u\left(\vec{r}\right)\right)$, approximately $Z\approx\int \varphi_{rdf}\; dV \exp\left(-\beta\, u\left(\vec{r}\right)\right)$
$D\varphi=d\varphi$ for simple Landau function without parameters (magnetic systems)
$Z=\int d\varphi\, dV \exp\left(-E(\varphi)\right)$
The goal in statistical mechanics is to calculate the phase transitions and their significant points analytically from the partition function, and to express thermal functions behavior at critical points T_C in asymptotic form
$f\left(T-T_C\right)=\left(T-T_C\right)^{\kappa}$, where κ is a critical exponent, e.g.
$M\sim\left(T_C-T\right)^{\beta}, T\to T_C-, B=0$
$p\sim\left(T_C-T\right)^{\beta}, T\to T_C-$
This is at present possible only for
- magnetic systems

with Landau energy $E\left(\varphi,\beta\right)=\frac{\mu\left(\beta\right)}{2}\varphi^2+\frac{\lambda\left(\beta\right)}{4!}\varphi^4-\beta\varphi B$
- vdWaals eos of a real gas

with eos $p\left(v-v_0\right)\beta=\left(1-\frac{\beta}{2\left(v-v_0\right)}\int\limits_{r=\sigma}^{\infty}\left|u\left(r\right)\right|d^3r\right)$, where $v_0=\frac{2\pi}{3}\sigma^3$ is the hard-core volume= vdWaals b-parameter, σ is the hard-core radius.

In this paper, we formulate a general Landau theory for thermal systems, where the original Landau ansatz for magnetic systems and an ansatz with rdf function for fgs systems are special cases. The fgs ansatz is applied to two intermolecular potentials : Lennard-Jones and dipole-dipole.
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 the second part of this paper, the Maxwell-Gibbs equation is solved for both fluid-gas and the solid phase in the form $p(E_{th})$, based on Peng-Robinson and Mie-Grueneisen eos, 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.

Flowcharts

From the microscopic to the macroscopic world: static systems in equilibrium

Intermolecular potential

$u(\vec{r}) = \varepsilon_0 u_0(\vec{r}/\sigma_0)$

Molecular params: $m_k = (m, \sigma_0, d_0, m_0,)$

radius σ_0 , e-dipole mom. d_0, mag.mom. m_0, potential min. radius r_0

Statistical variables

N, V, T

$\beta = 1/k_B T$, $\lambda = v^{1/3}$,

$v = V/N$

Solid-fluid-gas-solid system

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

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

$$\varphi_{rdf} = \varphi_{rdf}(r,\theta;m_k,c_k)$$

Landau minimal principle

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

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

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

$$c_{0.k} = c_{0.k}(\lambda,\beta;m_k)$$

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

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

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

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

$\rightarrow$solution $\varphi_{rdf}(r,\theta;c_{1,k})$

$c_{1,k} = c_{1,k}(\lambda,\beta;m_k)$, $c_{1,k} \approx c_{0,k}$

Thermodynamic functions

eos $p = p(\lambda,\beta;c_k(\lambda,\beta;m_k)) = -\dfrac{\partial F}{\partial v} = \dfrac{1}{\beta}\dfrac{\partial \log Z}{\partial v} = \dfrac{1}{\beta Z}\dfrac{1}{3\lambda^2}\dfrac{\partial Z}{\partial \lambda}$

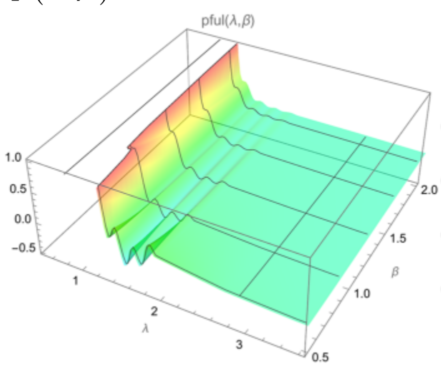
saturation curves

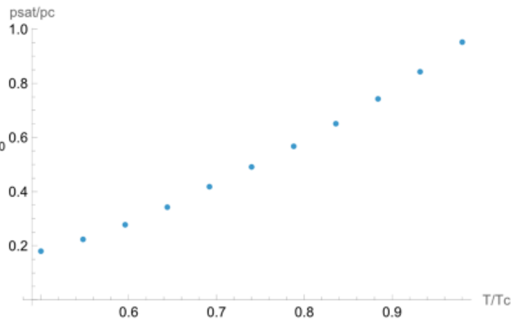
$\lambda_{sat} = \lambda(\beta;m_k)$, $\beta_{cr} \le \beta \le \beta_{tr}$

triple pt. $\lambda_{tr} = \lambda(\beta_{tr};m_k)$, $\beta_{tr} = \beta_{tr}(m_k)$, $p_{tr} = p(\lambda_{tr},\beta_{tr};c_k(\lambda_{tr},\beta_{tr};m_k))$

critical pt. $\lambda_{cr} = \lambda(\beta_{cr};m_k)$, $\beta_{cr} = \beta_{cr}(m_k)$, $p_{cr} = p(\lambda_{cr},\beta_{cr};c_k(\lambda_{cr},\beta_{cr};m_k))$

$p(\lambda,\beta)$ saturation curve $p_{sat}(\beta)$





$$\lambda_c = \lambda(m_k)\ ,\ \beta_c = \beta(m_k),\ p_c = p\left(\lambda_c, \beta_c; c_k(\lambda_c, \beta_c; m_k)\right), \omega = \omega(m_k)$$

vdWaals eos gas-fluid (rel. coord. $\lambda/\lambda_c, \beta/\beta_c$)

$$p(v,\beta) = \frac{8}{3}\frac{1}{\beta(v-1/3)} - \frac{3}{v^2}$$

Peng-Robinson eos gas-fluid (rel. coord. $\lambda/\lambda_c, \beta/\beta_c$)

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

$a = 0.45723\ ,\ b = 0.077796$

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

ω = acentric factor $\omega = -\log_{10}\left(p_{sat}\left(\frac{10}{7}\right)\right)$

eos depending on molecular params m_k

$$p = p(\beta, v; m_k) = p\left(\beta, v, p_c = p\left(\lambda_c, \beta_c; c_k(\lambda_c, \beta_c; m_k)\right), \beta_c = \beta_c(m_k), \omega(m_k)\right)$$

Young modulus $Y = \frac{1}{r_0}\frac{\partial^2 u(r=r_0)}{\partial r^2}$, $n_{dof} \approx 6$ for solids

potential min. radius r_0 , $u(\vec{r}_0, \sigma, \varepsilon) = \min\left(\vec{r}; u(\vec{r}, \sigma, \varepsilon)\right)$

$\Gamma_0 \approx 2$, $s \approx 3/2$, lattice const. $a = 2r_0$ (fcc lattice)

$(\beta_0, v_0, p_0) = (\beta_t, v_{ts}, p_t)$ values at triple point

First-order Mie-Grüneisen eos solid

reference point (ρ_0, β_0), Young modulus $Y(\eta) = y_1\eta - y_2$

$$p(\rho,\beta) = \frac{Y(\eta-1)\left(\eta - \frac{\Gamma_0}{2}(\eta-1)\right)}{\left(\eta - s(\eta-1)\right)^2} + \Gamma_0 \frac{n_{dof}}{2}\left(\frac{1}{\beta} - \frac{1}{\beta_0}\right) + p_0\ ,\ \eta = \frac{\rho}{\rho_0}$$

From the microscopic to the macroscopic world: dynamic (time-dep.) systems

Intermolecular potential

$u(\vec{r}) = \varepsilon_0 u_0(\vec{r}/\sigma_0)$

Molecular params: $m_k = (m, \sigma_0, d_0, m_0,)$

radius σ_0 , e-dipole mom. d_0, mag.mom. m_0, mass m

Statistical variables

N, V, T

$\beta = 1/k_B T$, $\lambda = v^{1/3}$,

$v = V/N$

Solid-fluid-gas-solid system

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

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

$$\varphi_{rdf} = \varphi_{rdf}(r,\theta;m_k,c_k)$$

Boltzmann transport equation

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m}\cdot\nabla f + \vec{F}\cdot\frac{\partial f}{\partial \vec{p}} = \left(\frac{\partial f}{\partial t}\right)_{coll}$$

$\vec{F}(\vec{r},t)$ = the force field, $f(\vec{r},\vec{p},t)$ = probability density function ,

$$dN = f(\vec{r},\vec{p},t)\,d^3r\,d^3p\,,\ \left(\frac{\partial f(\vec{r},\vec{p},t)}{\partial t}\right)_{coll} = \alpha\, Q_{n,n}\left(\frac{p}{m},r\right)\,,\ \alpha = 4N\sigma_0^{\,2}$$

Chapman-Eskog method applied to Boltzmann eq.

$f(\vec{r},\vec{p},t)$ in powers of Knudsen number $K_n = \lambda_f/\sigma_0$, condition $K_n \gg 1$

$f = f^{(0)} + K_n^{-1} f^{(1)} + K_n^{-2} f^{(2)} + \ldots$, λ_f = mean free path length

Boltzmann-Chapman-Eskog equations (first order)

$$\frac{\partial n}{\partial t} + \nabla\cdot(n\vec{v}_0) = 0$$

$$\frac{\partial \vec{v}_0}{\partial t} + \vec{v}_0\cdot(\nabla\circ\vec{v}_0) - \frac{\vec{F}}{m} + \frac{1}{n}\nabla\cdot\sigma = 0$$

$$\frac{\partial T}{\partial t} + \vec{v}_0\cdot(\nabla T) + \frac{2}{3k_B n}\left(tr\left(\sigma\cdot(\nabla\circ\vec{v}_0)\right) + \nabla\cdot\vec{q}\right) = 0$$

momentum-flux tensor $\sigma = pI - \mu\left(\nabla\circ\vec{v}_0 + (\nabla\circ\vec{v}_0)^T\right) + \frac{2}{3}\mu(\nabla\cdot\vec{v}_0)I$

Heat equation
heat flux $\vec{q} = -\lambda_q \nabla T$,

Navier-Stokes equation
velocity distribution $\vec{v}(\vec{r},t)$ of fluid-gas
dynamic viscosity $\mu = \mu(m_k)$,
second coefficient of viscosity $\lambda_\mu = \lambda_\mu(m_k)$,

$$\rho \frac{D\vec{v}}{Dt} = \rho\left(\frac{\partial \vec{v}}{\partial t} + (\vec{v} \bullet \nabla)\vec{v}\right) = -\nabla p + \mu \nabla^2 \vec{v} + (\lambda_\mu + \mu)\nabla(\nabla \cdot \vec{v}) + \vec{f}$$

external force density $\vec{f} = \vec{F}\, n$, density $\rho = m\, n$, $\vec{v}(\vec{r},t) = \vec{v}_0$

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 $Z=\sum_k exp\left(-\frac{E_k-\mu N_k}{k_B T}\right)$ $Z\left(\beta,\mu_1,\mu_2,...\right)=Tr\left(exp\left(\beta\left(\sum_k \mu_k N_k-H\right)\right)\right)$
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 $\Omega=-k_B T\log Z=\min$

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 $f_{rdf}\left(r,\theta,\sigma;c_k\right)$

(second-order) magnetic systems: $\varphi=M$ magnetization

Solid-fluid-gas-solid system

$$\left(Z\right)^{1/N}=z\left(\beta\right)=\int dV\, g\left(\vec r\right)\exp\left(-\beta\, u\left(\vec r\right)\right)$$

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

magnetic system

φ-induced Landau energy=

$$E\left(\varphi,\beta,B\right)=\frac{\mu\left(\beta\right)}{2}\varphi^2+\frac{\lambda\left(\beta\right)}{4!}\varphi^4-\beta\varphi B$$

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

Magnetic, second order transition

(zero latent heat)

basic variables T, M, N

$\left(\frac{\partial^2 F}{\partial\varphi^2}\right)$ discontinuous, $\Delta C=0$

$$Z=\int D\varphi\, dV\exp\left(-E(\varphi)\right), D\varphi=d\varphi, \left(c_k\right)=\{\ \},$$

$$H\left(\vec r,\varphi,\beta\right)=E(\varphi)$$

$\varphi=M_s=\frac{M}{N}$ spec.magnetization, $\rightarrow v$ fgs

φ-induced Landau energy=

$$E\left(\varphi,\beta,B\right)=\frac{\mu\left(\beta\right)}{2}\varphi^2+\frac{\lambda\left(\beta\right)}{4!}\varphi^4-\beta\varphi B$$

Magnetic, second order $Z\left(\lambda,\beta;c_k\right)$

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

$$=V\left(\frac{const}{\beta}+\frac{1}{2\beta}\mu^2\varphi^2+\frac{1}{4!\beta}\lambda^2\varphi^4-B\varphi\right)$$

T_c=crit. temp. , $\beta_c=\frac{1}{k_BT_c}$, $\mu^2\left(\beta_c\right)=2\mu'\left(\beta_c\right)\left(\beta-\beta_c\right)$

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

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

Solid-fluid-gas $Z(\lambda, \beta; c_k)$

F-minimization Landau principle

Rescaling

radius $\sigma = 1$, energy $\varepsilon = 1$ in $u(\vec{r})$

$\lambda \to \lambda / \sigma$, $r \to r / \sigma$

$u \to u / \varepsilon$, $p \to p\sigma^2 / \varepsilon$

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

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

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

Solid-fluid-gas $Z(\lambda, \beta; c_k)$

Calculation of correlation function $\varphi_{rdf}(r, \theta; c_k)$

Rescaling

radius $\sigma = 1$, energy $\varepsilon = 1$ in $u(\vec{r})$

$\lambda \to \lambda / \sigma$, $r \to r / \sigma$

$u \to u / \varepsilon$, $p \to p\sigma^2 / \varepsilon$

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

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

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

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

$\to$solution $g(r, \theta; c_{1,k})$

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

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

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

Magnetic phase transition
Critical temperature T=T$_c$,

Fundamental variables β , spec. magnetization $\varphi_0 = M_s = \frac{M}{N}$

$$F(T,V,N) = \min \rightarrow \frac{\partial F}{\partial \varphi} = 0$$

$$\mu^2 \varphi_0 + \frac{1}{3!}\lambda^2 \varphi_0{}^3 - \beta B = 0$$

solution $\varphi_0 = u + v$

$$u = \sqrt[3]{\frac{3B}{\lambda} + \sqrt{\frac{9B^2}{\lambda^2} + \frac{8\mu^6}{\lambda^3}}} \ , \ v = \sqrt[3]{\frac{3B}{\lambda} - \sqrt{\frac{9B^2}{\lambda^2} + \frac{8\mu^6}{\lambda^3}}}$$

$$B = 0: \ \varphi_0{}^2 = \begin{cases} 0 & \mu^2 \geq 0 \\ -\frac{6\mu^2}{\lambda} & \mu^2 < 0 \end{cases}, \ \varphi_0 \propto |T - T_c|^{1/2} \ .$$

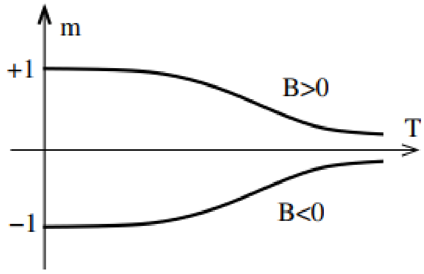
$$B \neq 0 \ : \mathrm{T{=}T_c}\ , \mu^2 = 0, \ \ \varphi_0{}^3 = \frac{6\beta}{\lambda} B$$

magnetization $M = \varphi_0(\beta)$ continuous at T=T$_C$

latent heat $\Delta C = 0$

magnetic susceptibility $\chi_T = \frac{\partial \varphi_0}{\partial B}$ is discontinuous at T=T$_C$,

$$\chi_T\big|_{B=0} = \begin{cases} \frac{\beta}{\mu^2} & T > T_c \\ \frac{\beta}{2|\mu|^2} & T < T_c \end{cases}$$



Superconductivity

Critical temperature T=T_c ,

Fundamental variables β , superconducting electron density $n_s = |\varphi_0|^2$

$$F(T,V,N) = \min \to \frac{\partial F}{\partial \varphi} = 0$$

$$\mu^2 \varphi_0 + \frac{1}{3!} \lambda^2 \varphi_0{}^3 - \beta B = 0$$

superconductive fraction φ^2 is zero at T=T_C

$$|\varphi_0|^2 = \begin{cases} 0 & T \geq T_c \\ -\dfrac{6\mu^2}{\lambda} & T < T_c \end{cases} = \begin{cases} 0 & T \geq T_c \\ \dfrac{6\mu_1{}^2 (T_c - T)}{\lambda} & T < T_c \end{cases}$$

coherence length at small perturbations

$$\xi_{LG} = \begin{cases} \sqrt{\dfrac{\hbar^2}{2m_e \mu_1{}^2 |T_c - T|}} & T > T_c \\ \sqrt{\dfrac{\hbar^2}{4m_e \mu_1{}^2 |T_c - T|}} & T < T_c \end{cases}$$

penetration length of magnetic field

$$\lambda_{LG} = \sqrt{\frac{m_e c^2}{8\pi e^2 |\varphi_0|^2}}$$

Solid-fluid-gas

Partition function $Z(\lambda,\beta)=Z(\lambda,\beta;c_{0,k})$

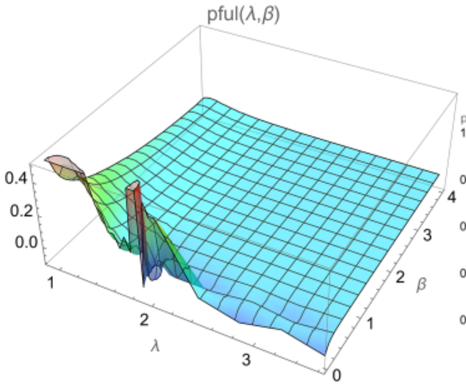
Free energy $F(\lambda,\beta)=-\frac{1}{\beta}\log Z(\lambda,\beta)$

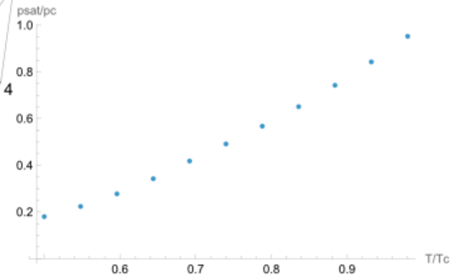
Pressure $p(\lambda,\beta)=-\frac{\partial F}{\partial v}=-\frac{1}{3\lambda^2}\frac{\partial F}{\partial \lambda}$

Equation-of state

Ideal gas $p=\frac{1}{v\beta}$, $v=\lambda^3$, vdWaals (rel.coord.) $p(v,\beta)=\frac{8}{3}\frac{1}{\beta(v-1/3)}-\frac{3}{v^2}$

general $p=p(\lambda,\beta)$ saturation curve $p_{sat}(\beta)$





Extremal curve $\frac{\partial^2 p(\lambda,\beta)}{\partial v^2}=0 \quad \rightarrow \quad \lambda=\lambda_{ext}(\beta)$

Saturation eq.: Maxwell-area-rule $p=p(\lambda_1,\beta)$, $p=p(\lambda_2,\beta)$, $G(\lambda_1,\beta)=G(\lambda_2,\beta)$, $\lambda_{sat}(\beta)=\lambda_1$

critical point

- Maxwell-eq.
- $\frac{\partial^2 p(\lambda,\beta)}{\partial v^2}=0$ →trigonometric equation $\left(\sum_k \alpha_k(\lambda,\beta)\cos\left(2\pi\frac{\lambda-\sigma}{l_{a,k}}\right)+\beta_k(\lambda,\beta)\sin\left(2\pi\frac{\lambda-\sigma}{l_{a,k}}\right)\right)=0$

$\alpha_k(\lambda,\beta)=\sum_{k_1,k_2} a_{k,k_1,k_2}\lambda^{k_1}\beta^{-k_2}$, $\beta_k(\lambda,\beta)=\sum_{k_1,k_2} b_{k,k_1,k_2}\lambda^{k_1}\beta^{-k_2}$

triple point

- eos $p=p(\lambda,\beta)$ order >=3 (cubic) in λ

solution $\lambda=\lambda(p,\beta)$ has three branches at triple point: fluid-gas, solid-fluid, solid-gas

$\lambda_{fg}(p,\beta)$, $\lambda_{sf}(p,\beta)$, $\lambda_{sg}(p,\beta)$

Solid-fluid-gas phase transition

Fundamental variables β , specific volume $v=\frac{V}{N}$

Critical point T=T$_c$,

v , specific heat c_v are discontinuous, latent heat $\Delta C>0$

T=T$_c$: $\frac{\partial p}{\partial v}=0$, $\frac{\partial^2 p}{\partial v^2}=0$, end point of $p_{sat}(T)$

Saturation curve fluid-gas $p_{sat}(T)$:

Maxwell-area-rule $p=p(v_f,T)$, $p=p(v_g,T)$, $G(v_f,T)=G(v_g,T)$

second Cardano's root $v_f=v_2(p,\beta)$, third Cardano's root $v_g=v_3(p,\beta)$

follows Maxwell-Gibbs equation $eqgr(v_f,v_g,\beta)=0$

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

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

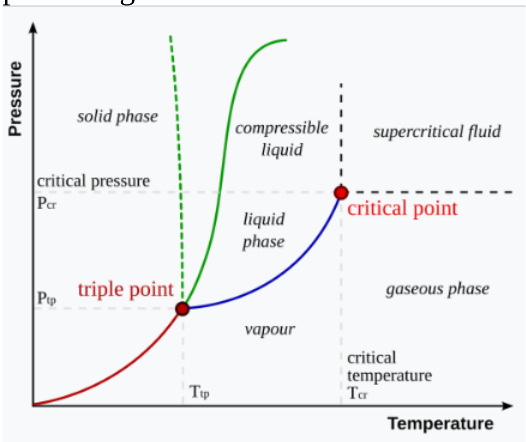
yields $p_{sat}(T)$, $T_{tr}\le T\le T_c$

Latent heat $\Delta C=\frac{\left(S(v_g,T)-S(v_f,T)\right)T}{(v_g-v_f)}$

Triple point T=T$_{tr}$:branching curve fluid-gas, solid-fluid, solid-gas $p(v_g,T)=p(v_f,T)=p(v_s,T)$

starting point of $p_{sat}(T)$

phase diagram



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),

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

Redlich–Kwong equation fluid-gas

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

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

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 fluid-gas

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

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

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

mixing rules PSRK

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

Mie-Grueneisen equation solid

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

where $\eta = \frac{v_0}{v}$, $\Gamma_0 \approx 2$, $s \approx 3/2$

$\beta_0 = \beta_t$, $p_0 = p_t$, $v_0 = v_t$ triple-point values

Saturation curve fluid-gas $p_{fg}(T)$:

Maxwell-area-rule $p = p_{PR}(v_f, T)$,

$p = p_{PR}(v_g, T)$, $G_{PR}(v_f, T) = G_{PR}(v_g, T)$

Melting curve solid-fluid $p_{sf}(T)$:

Maxwell-area-rule $p_{PR} = p(v_f, T)$,

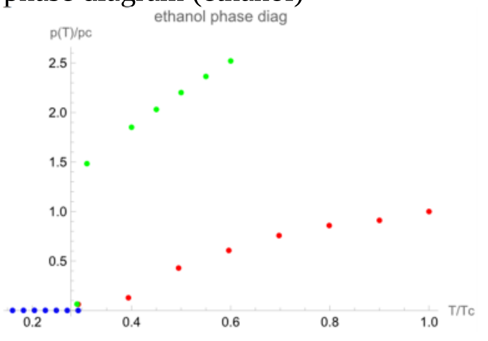
$p = p_{MG}(v_s, T)$, $G_{PR}(v_f, T) = G_{MG}(v_s, T)$

Sublimation curve solid-gas $p_{sg}(T)$:

Maxwell-area-rule $p_{PR} = p(v_g, T)$,

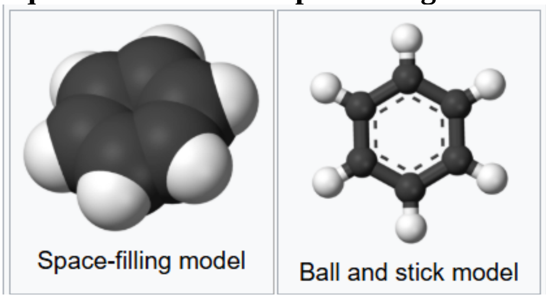
$p = p_{MG}(v_s, T)$, $G_{PR}(v_g, T) = G_{MG}(v_s, T)$

phase diagram (ethanol)

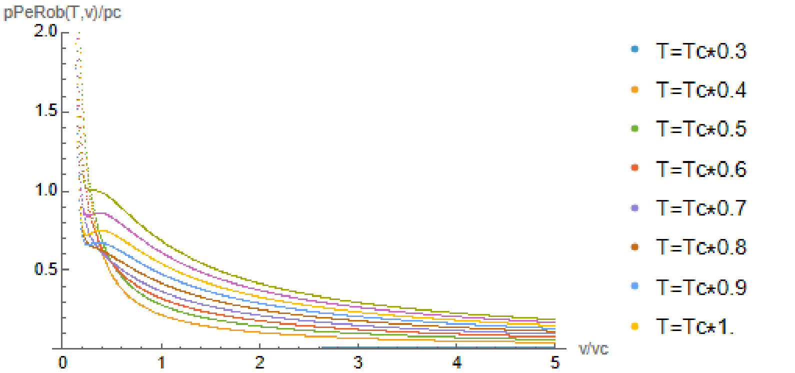


phase diagram measured

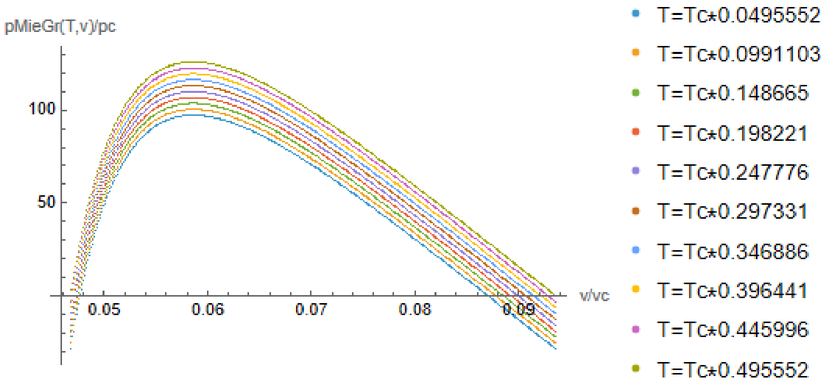
Equation-of-state and phase diagram benzene



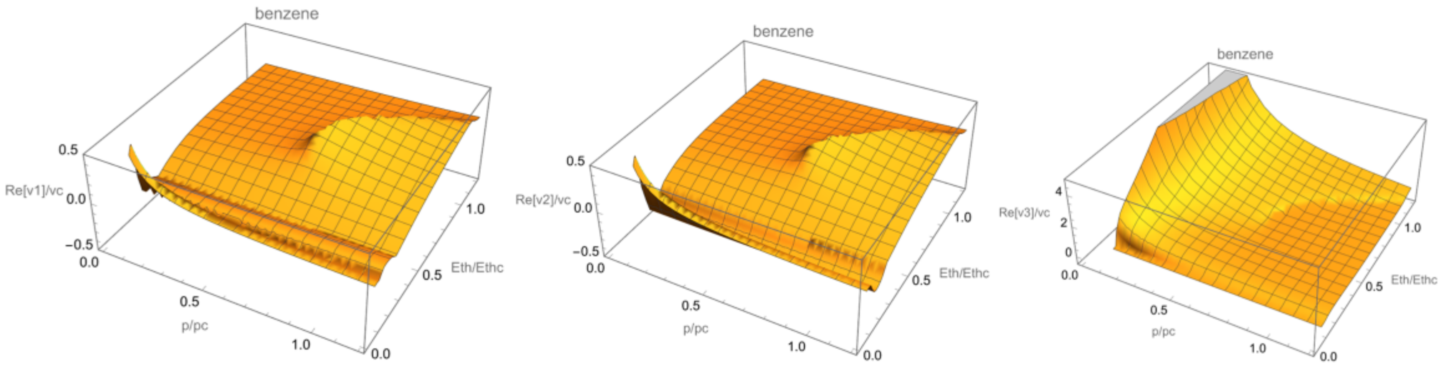
Peng-Robinson fluid-gas eos in relative coordinates



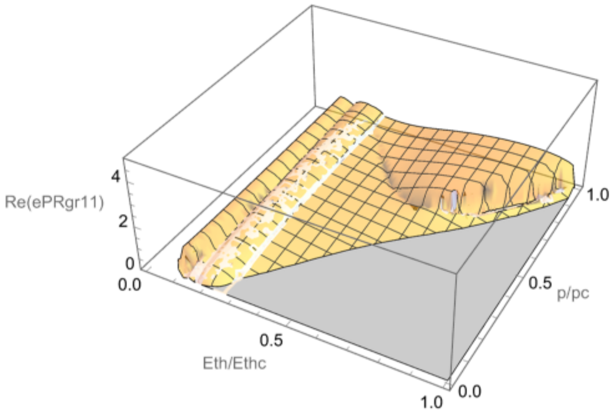
Mie-Grueneisen solid eos

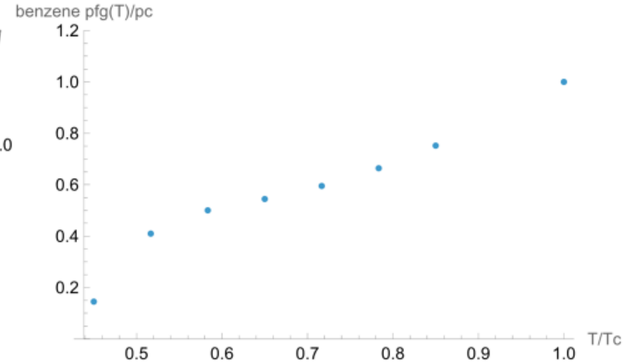


The three branches (real part) of the volume function $v = v(p, \beta)$ Peng-Robinson eos

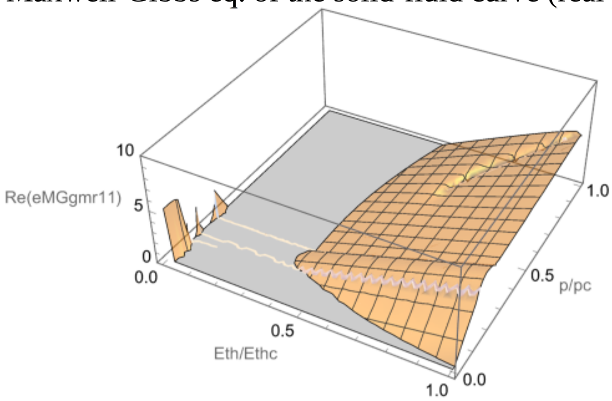


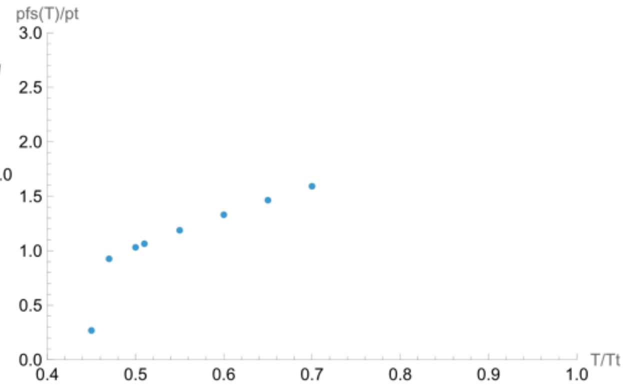
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



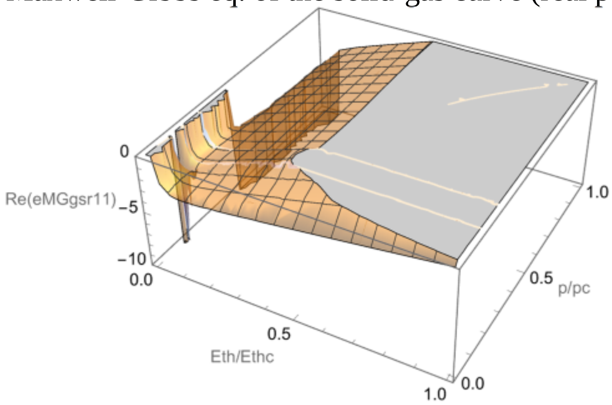


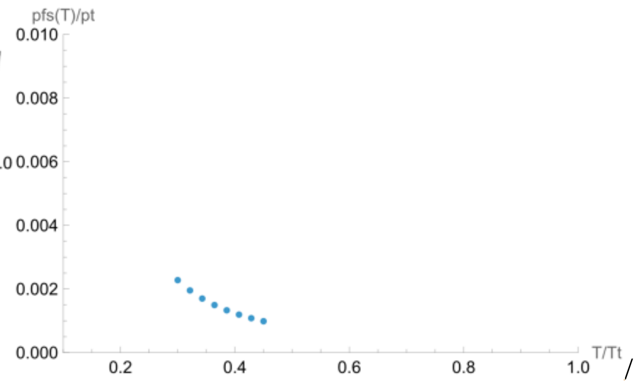
Maxwell-Gibbs eq. of the solid-fluid curve (real part)



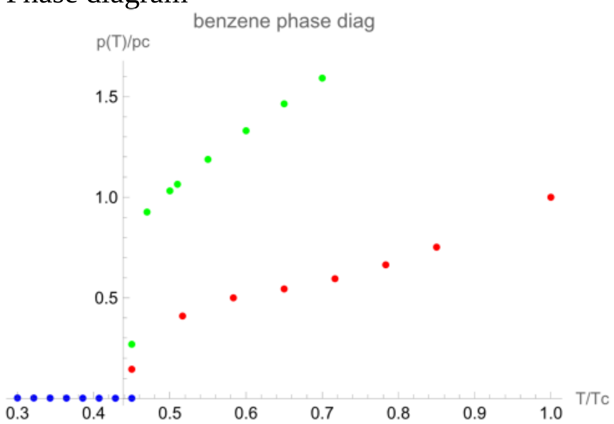


Maxwell-Gibbs eq. of the solid-gas curve (real part)

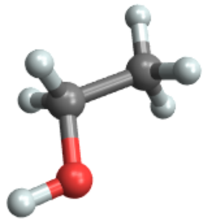




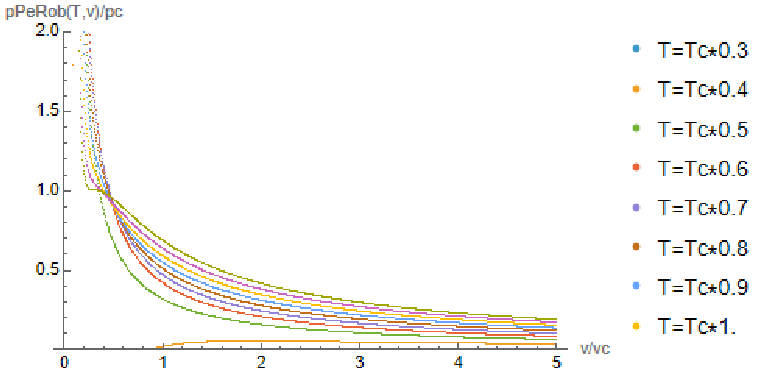
Phase diagram



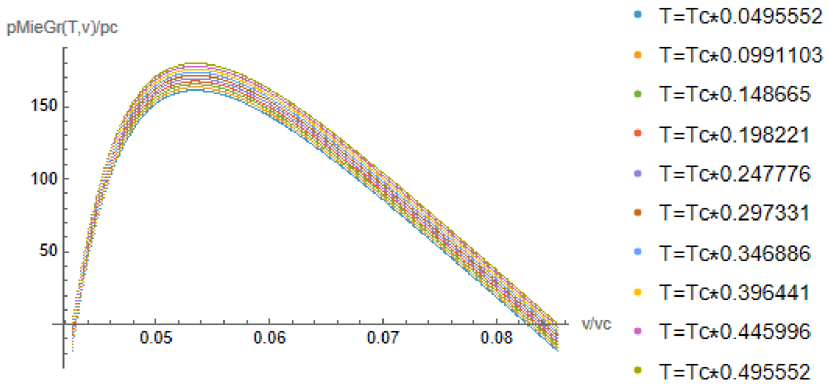
Equation-of-state and phase diagram ethanol



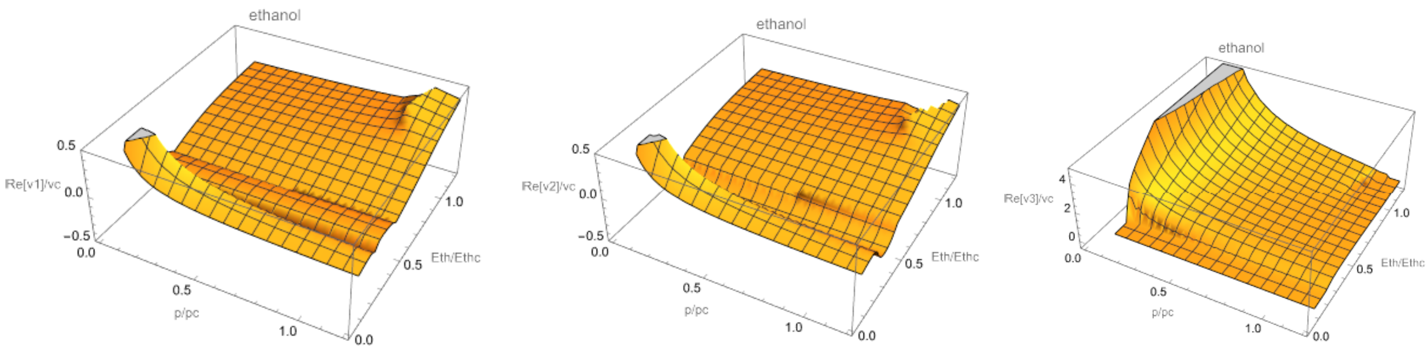
Peng-Robinson fluid-gas eos in relative coordinates



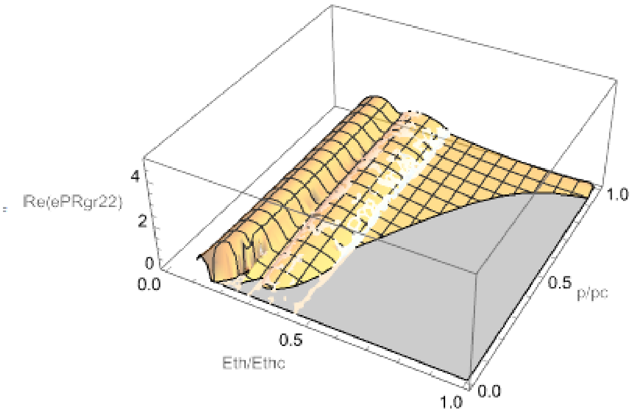
Mie-Grueneisen solid eos

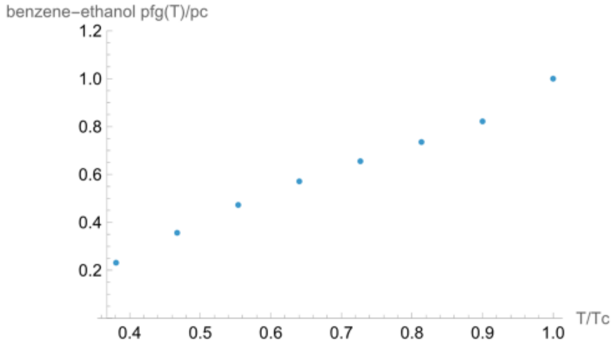


The three branches (real part) of the volume function $v = v(p, \beta)$ Peng-Robinson eos

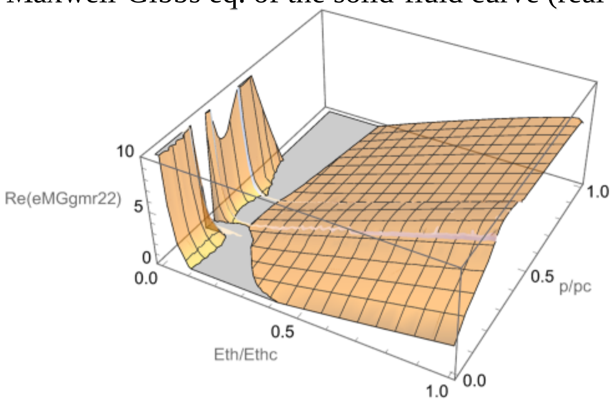


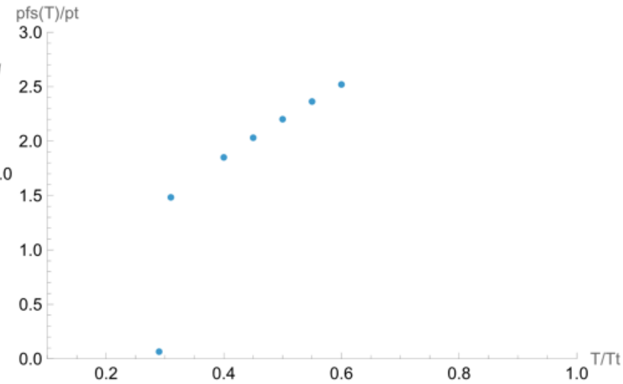
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



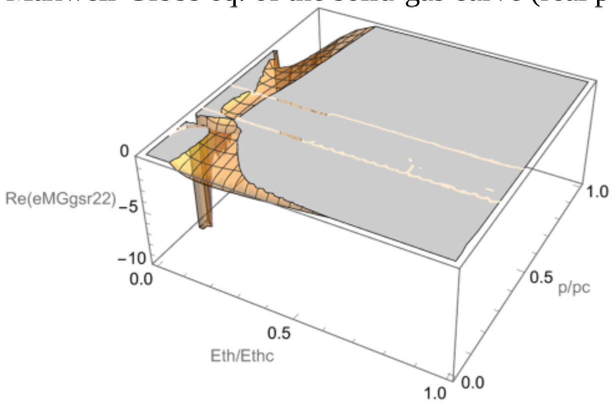


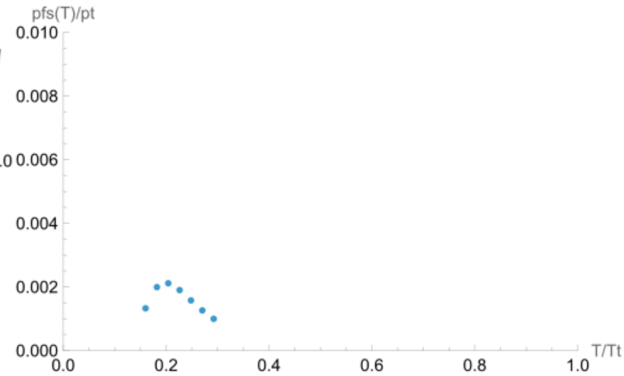
Maxwell-Gibbs eq. of the solid-fluid curve (real part)



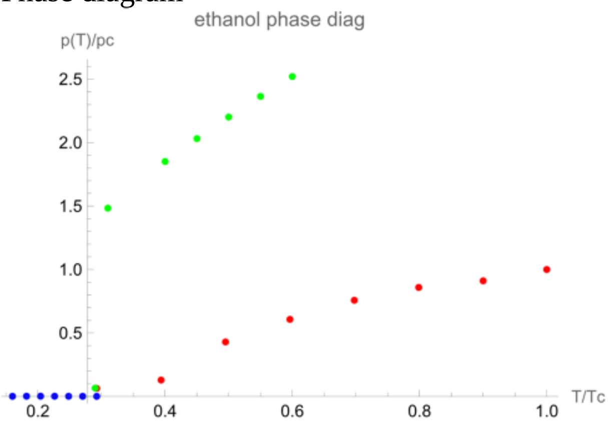


Maxwell-Gibbs eq. of the solid-gas curve (real part)

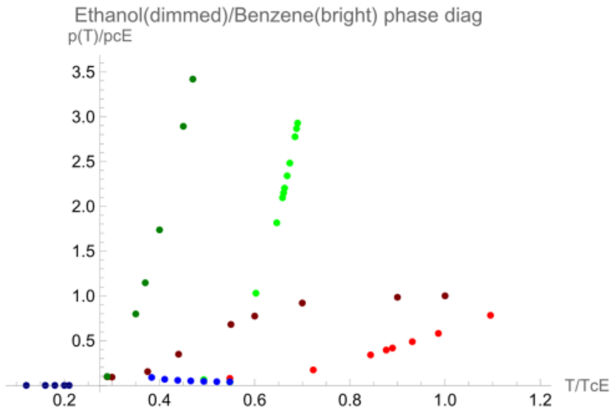




Phase diagram



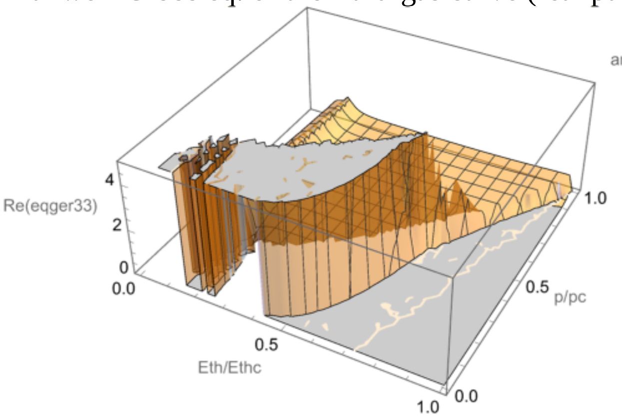
Phase diagram ethanol and benzene, rel. ethanol

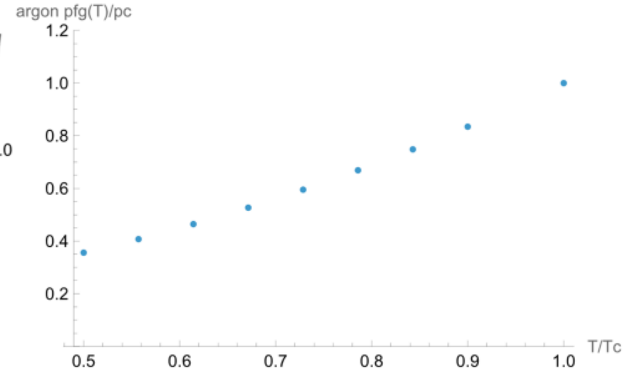


Ethanol(dimmed)/Benzene(bright) phase diag
p(T)/pcE
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.2
0.4
0.6
0.8
1.0
1.2
T/TcE

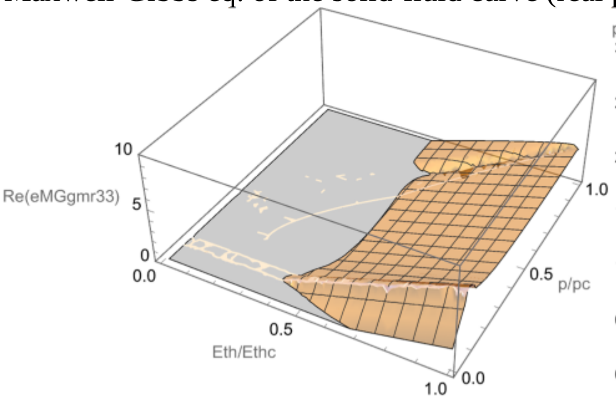
Equation-of-state and phase diagram argon

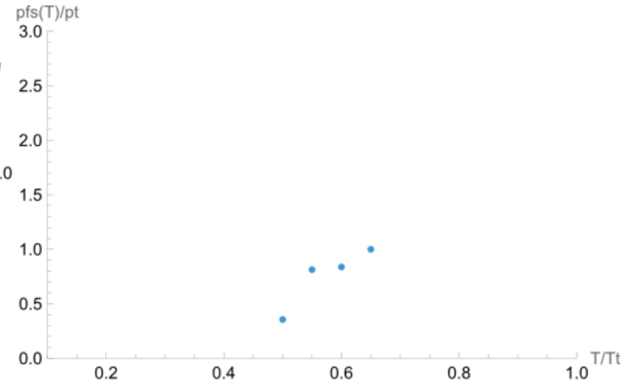
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



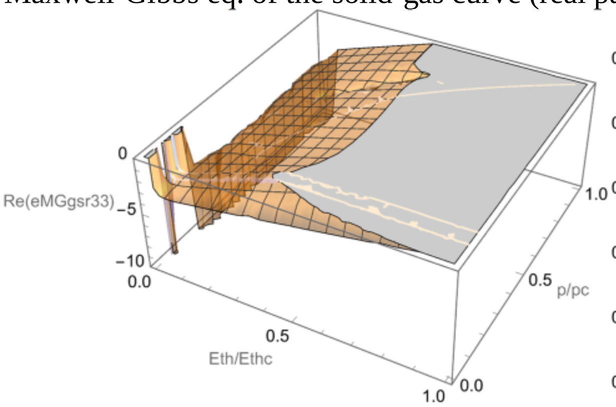


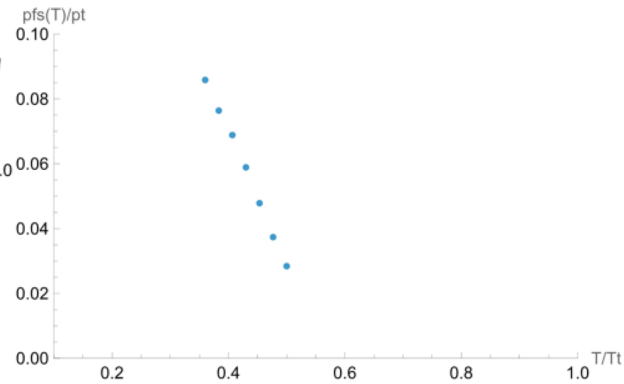
Maxwell-Gibbs eq. of the solid-fluid curve (real part)



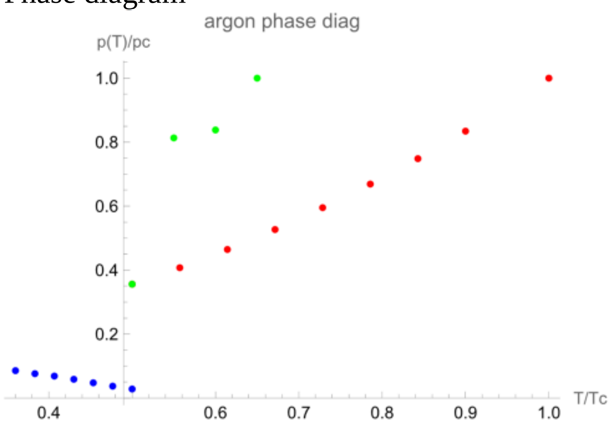


Maxwell-Gibbs eq. of the solid-gas curve (real part)

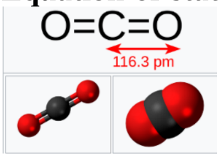




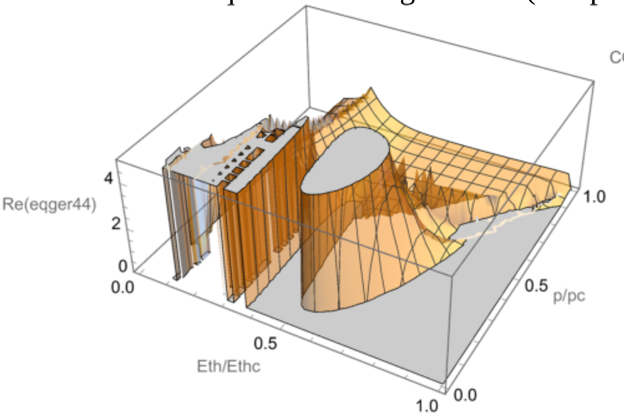
Phase diagram

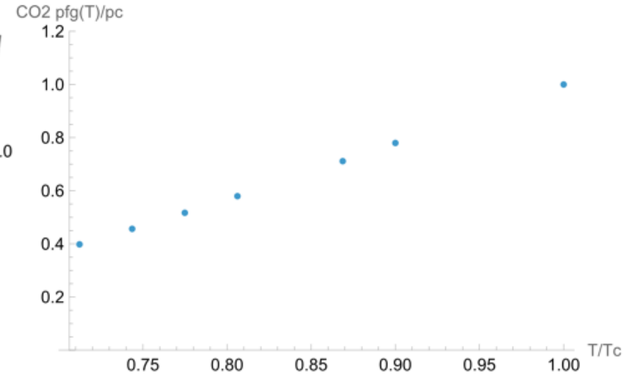


Equation-of-state and phase diagram carbon dioxide

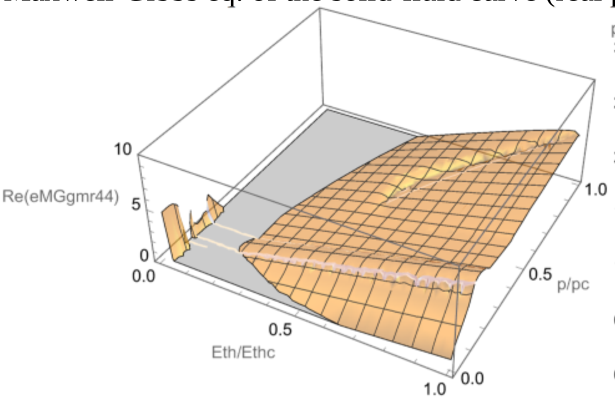


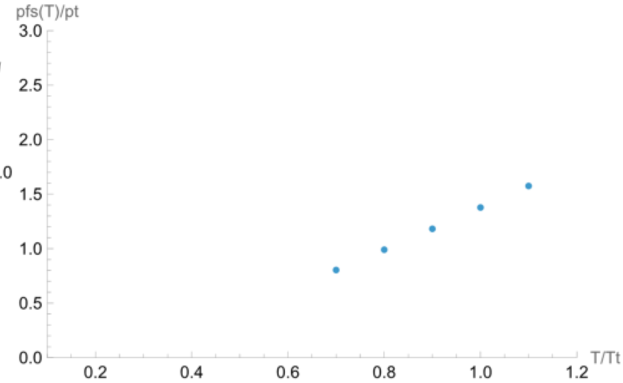
Maxwell-Gibbs eq. of the fluid-gas curve (real part)



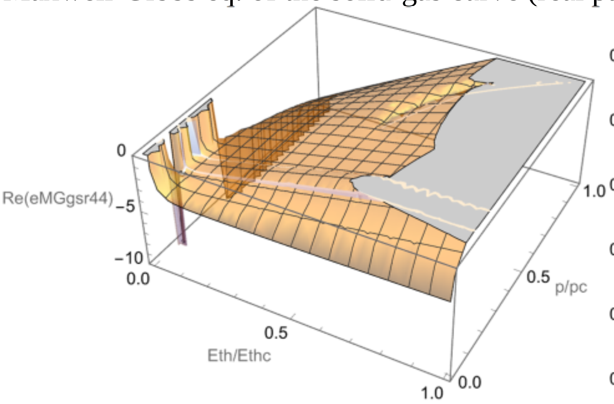


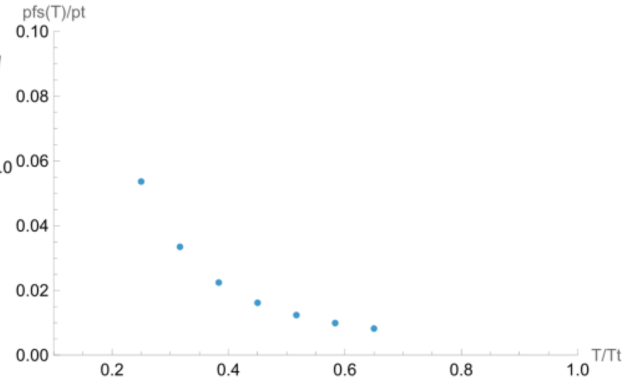
Maxwell-Gibbs eq. of the solid-fluid curve (real part)



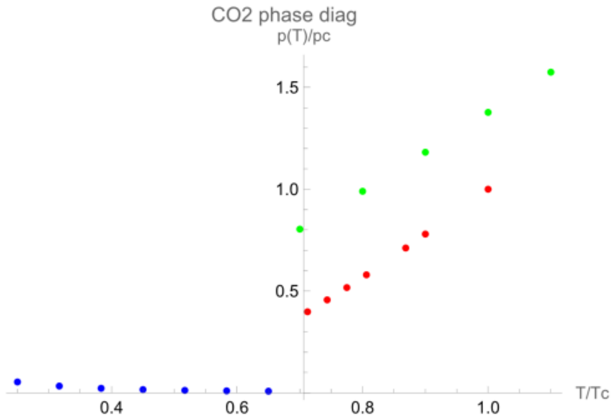


Maxwell-Gibbs eq. of the solid-gas curve (real part)





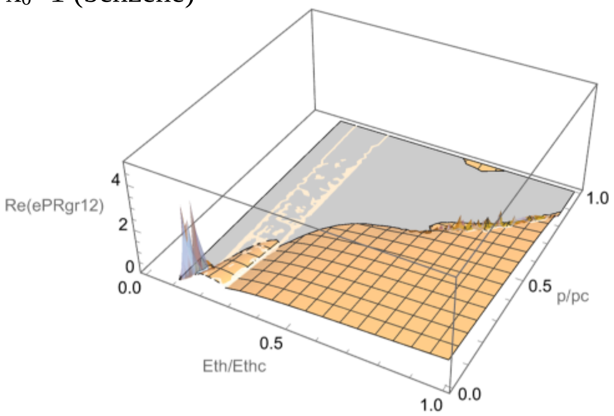
Phase diagram

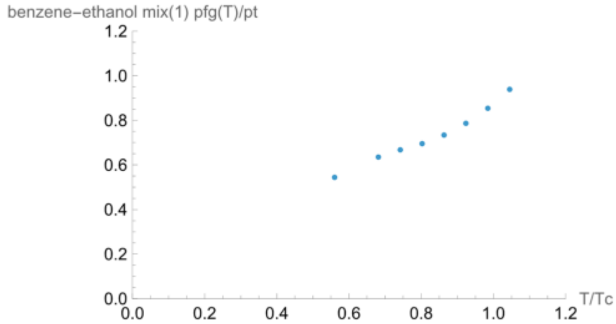


CO2 phase diag
p(T)/pc
1.5
1.0
0.5
0.4
0.6
0.8
1.0
T/Tc

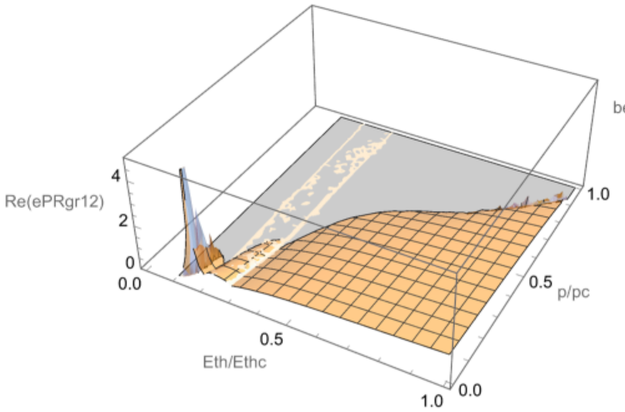
Saturation curves for benzene-ethanol solutions
in relative coordinates rel. benzene-ethanol-1:1
rel. benzene concentration x_0=(1, 0.75, 0.5, 0.4, 0.25, 0.1, 0.)

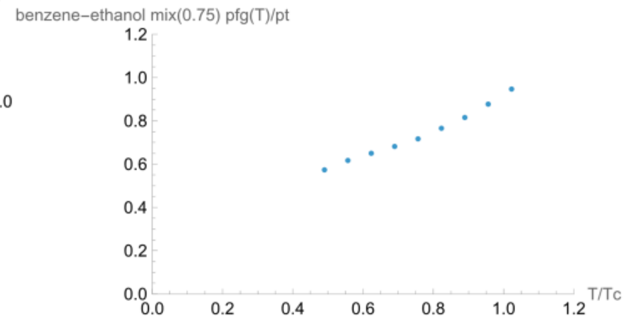
Maxwell-Gibbs eq. of the fluid-gas curve (real part)
x_0=1 (benzene)



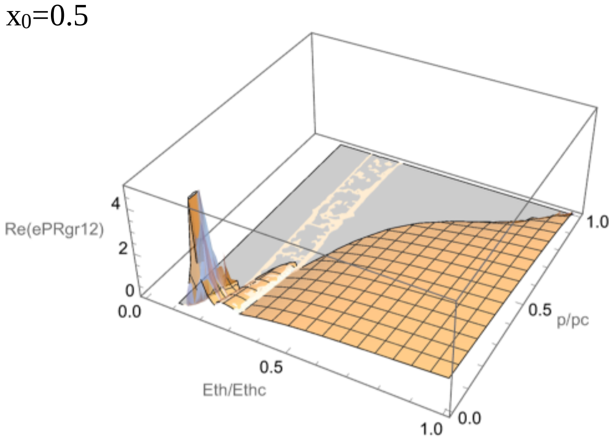


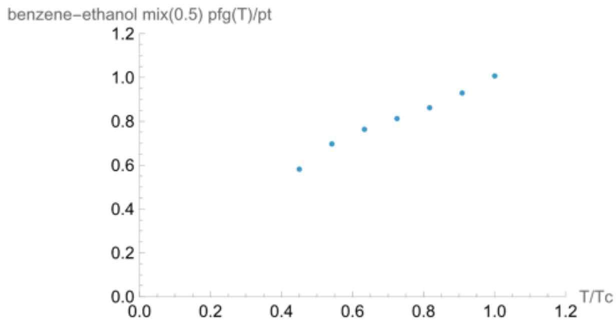
x_0=0.75



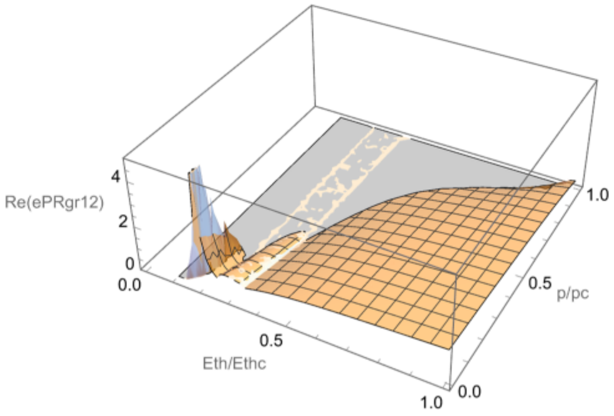


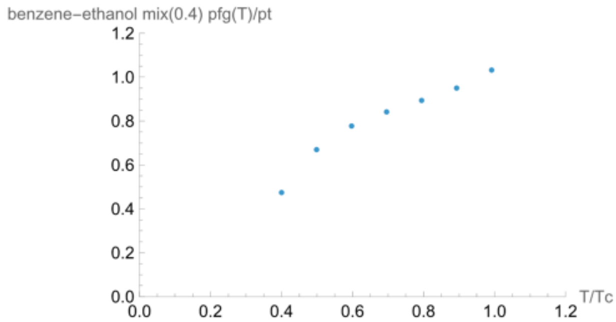
x_0=0.5



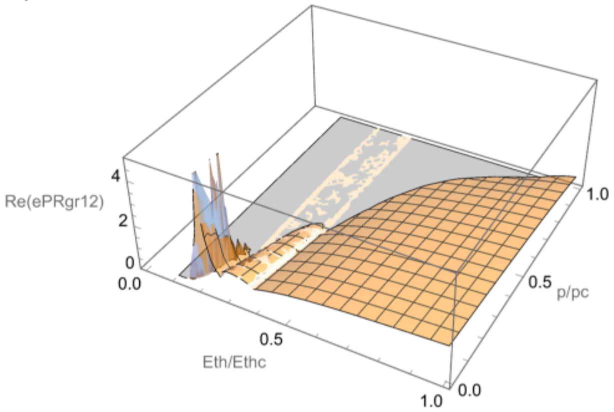


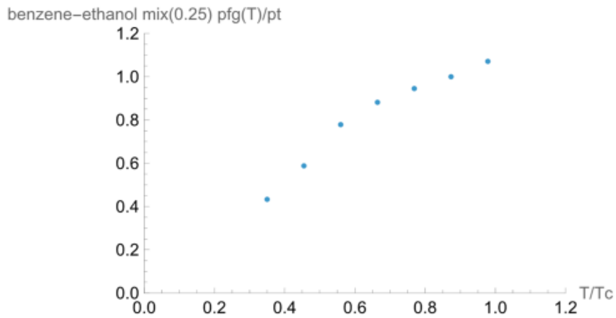
x_0=0.40



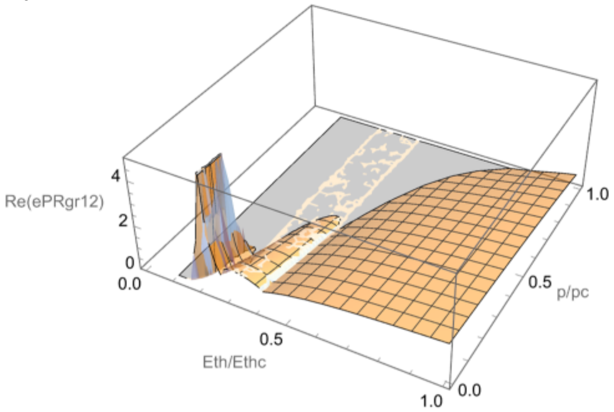


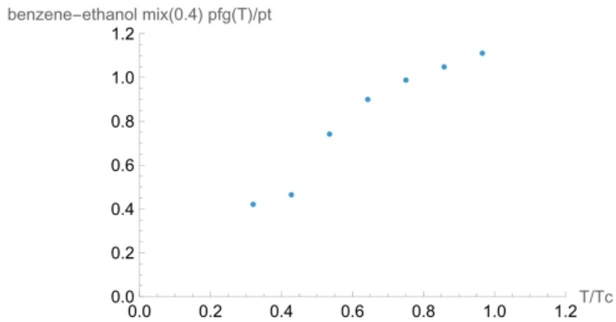
x_0=0.25



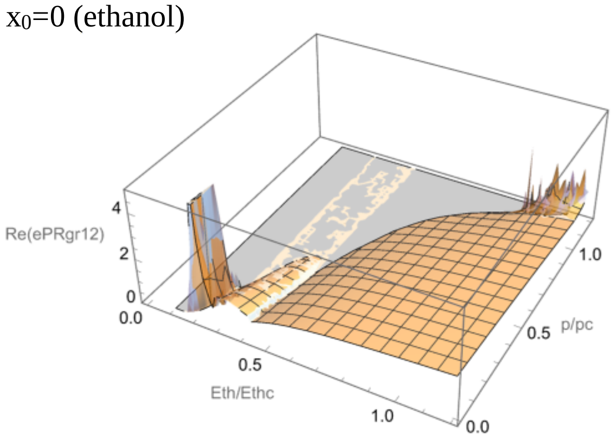


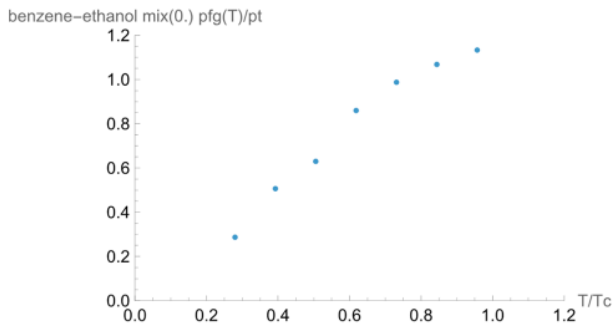
x_0=0.1



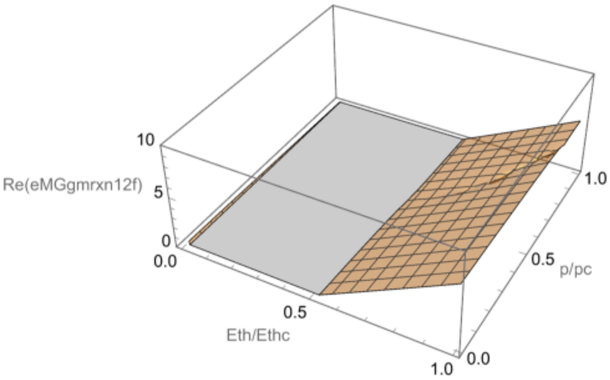


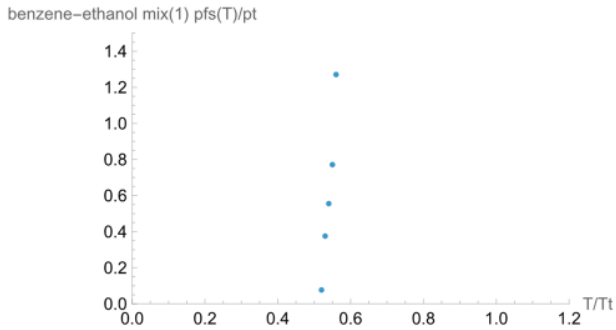
x_0=0 (ethanol)



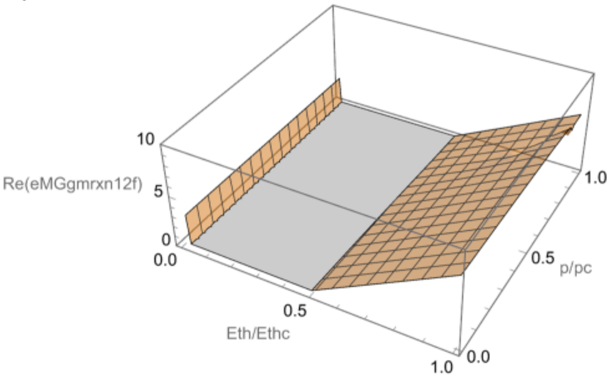


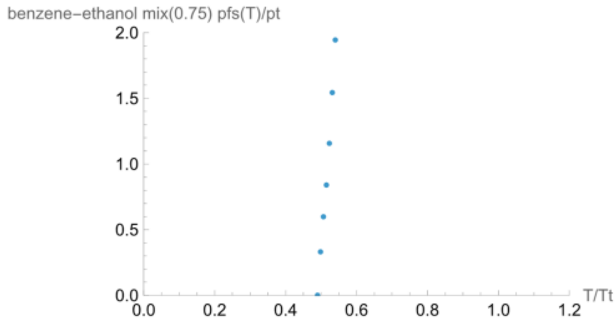
Maxwell-Gibbs eq. of the solid-fluid curve (real part)
x_0=1 (benzene)



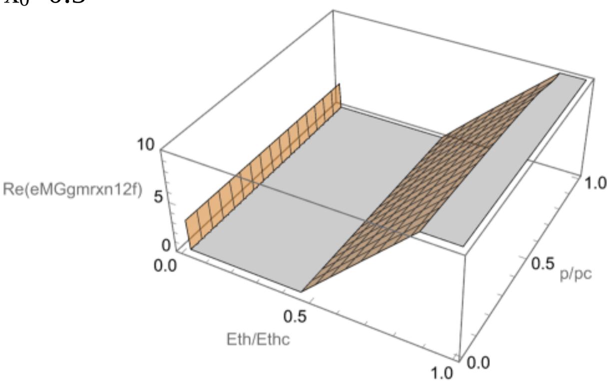


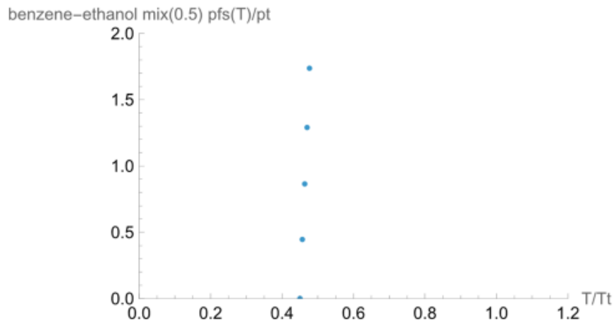
x_0=0.75



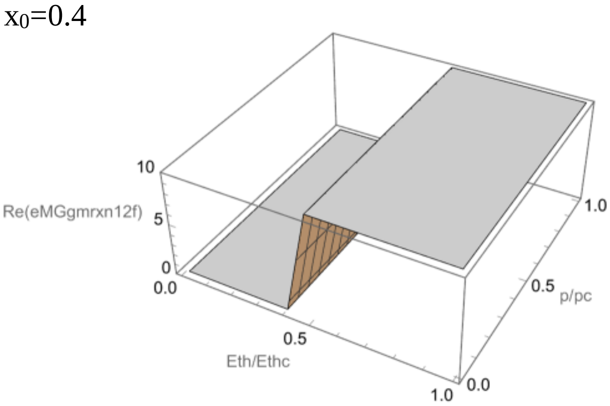


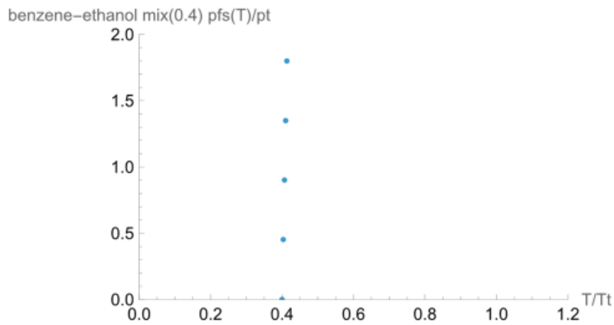
x_0=0.5



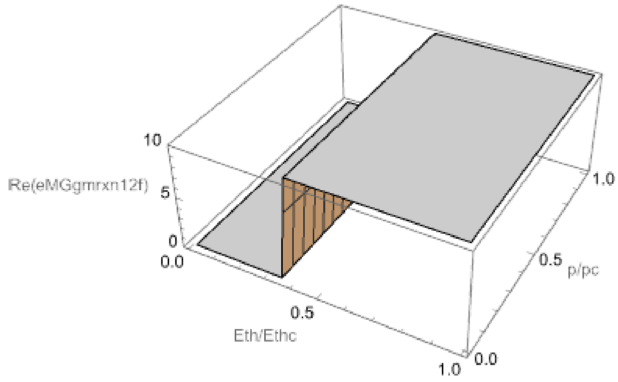


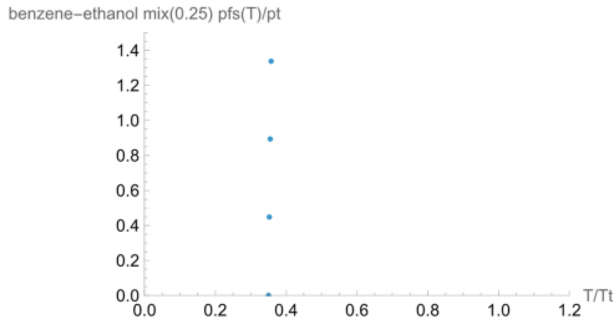
x_0=0.4



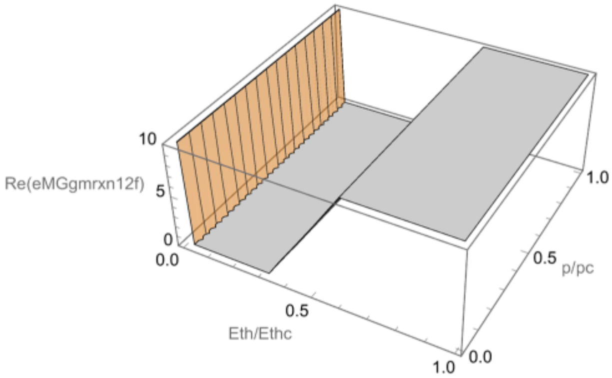


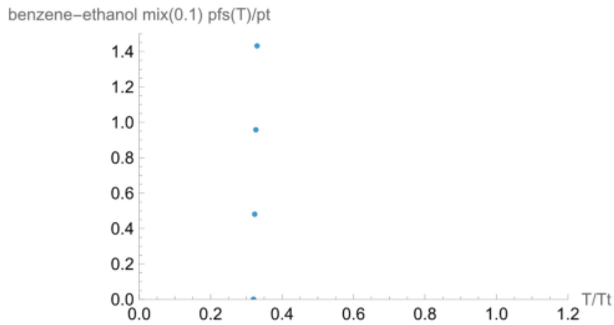
x_0=0.25



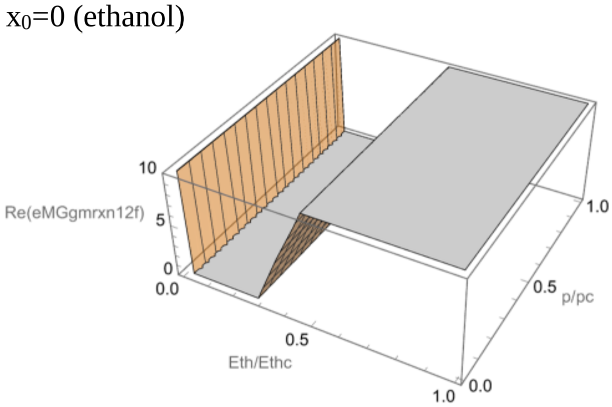


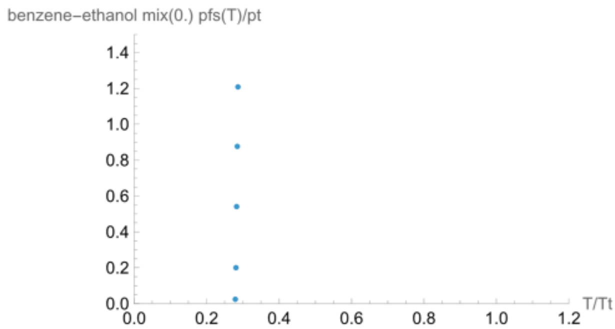
x_0=0.1



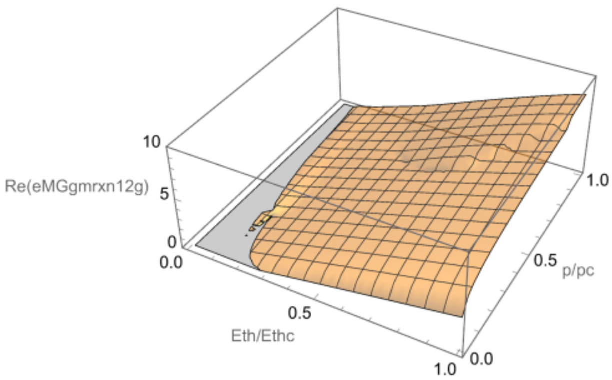


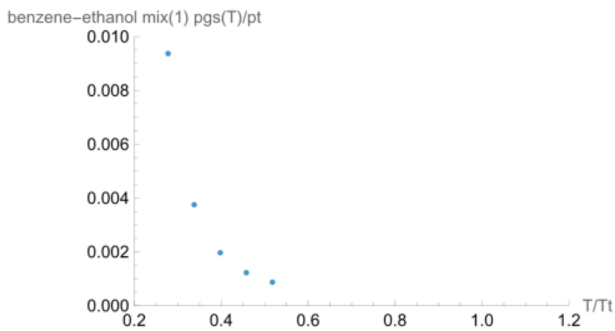
x_0=0 (ethanol)



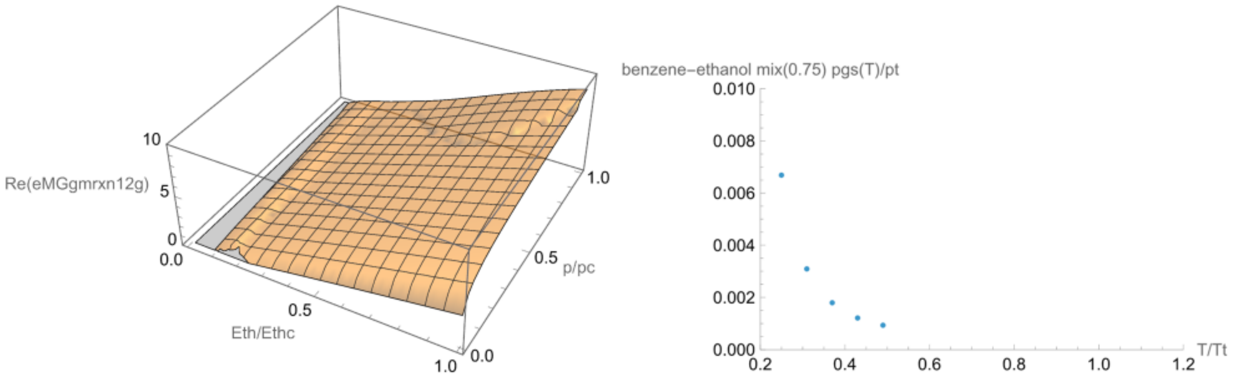


Maxwell-Gibbs eq. of the solid-gas curve (real part)
x_0=1 (benzene)

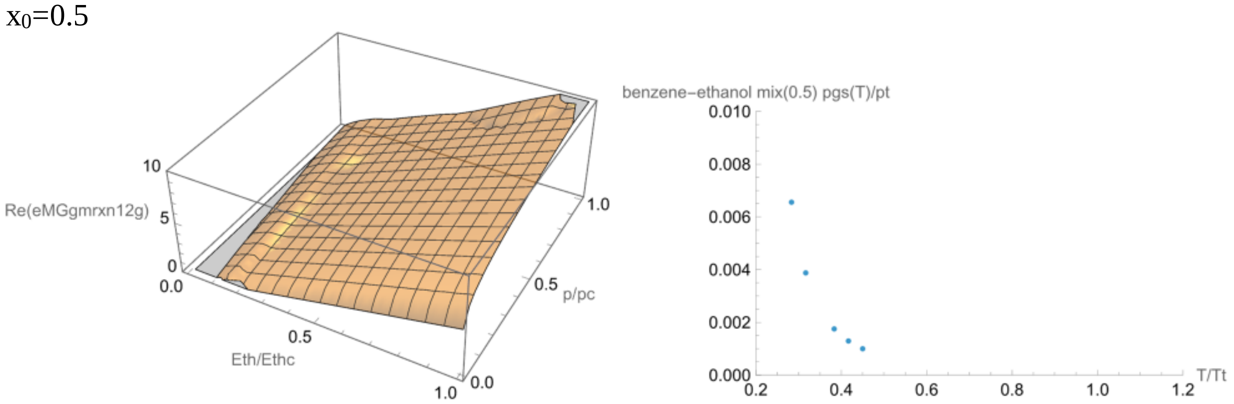




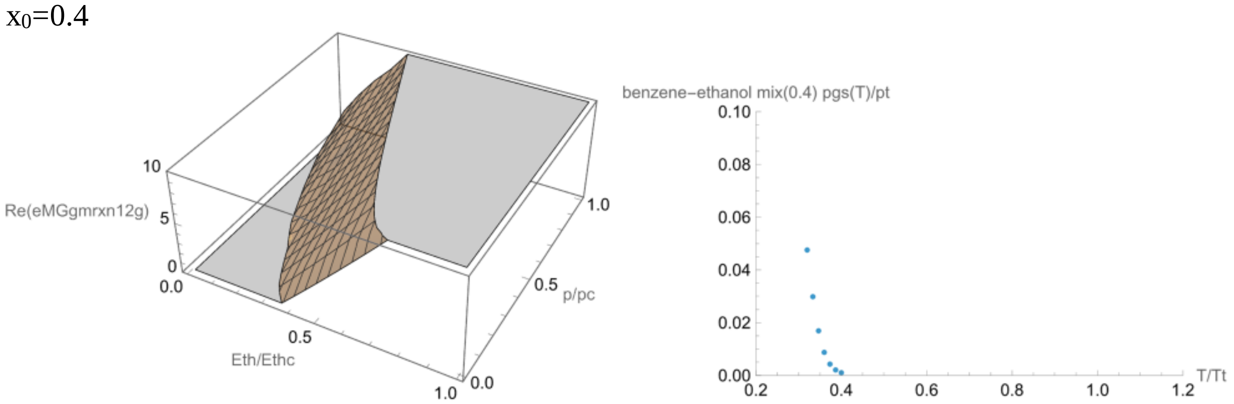
x_0=0.75



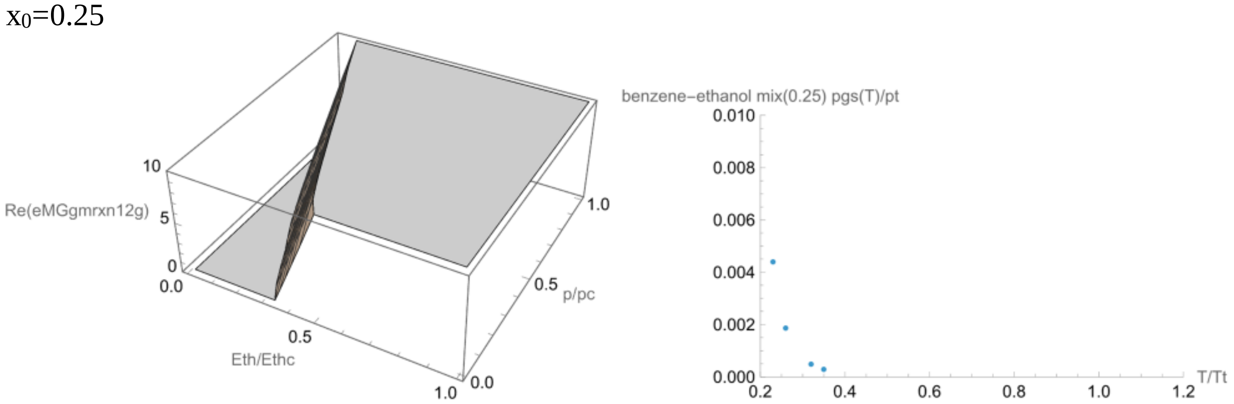
x_0=0.5



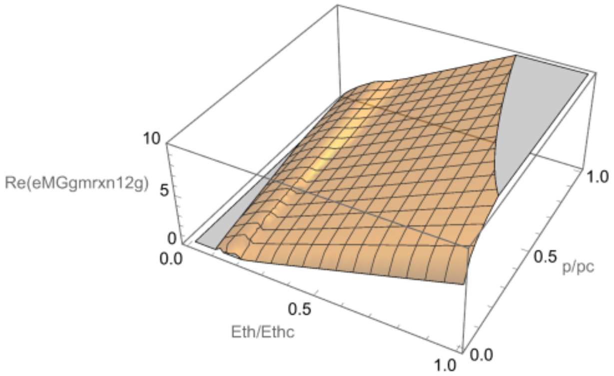
x_0=0.4

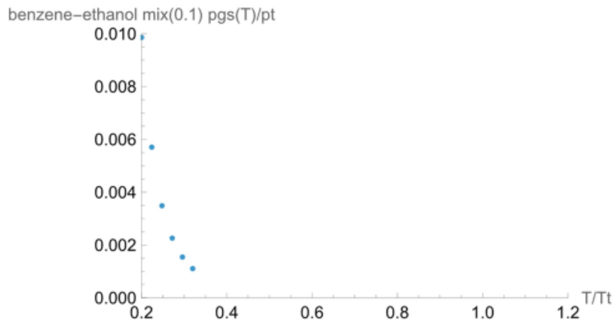


x_0=0.25

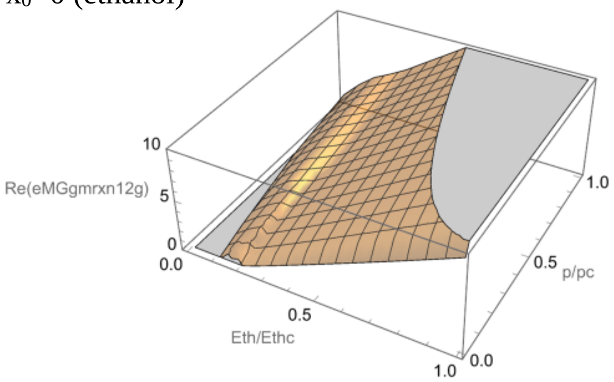


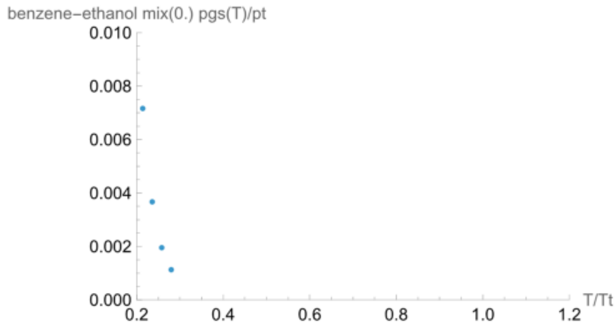
x_0=0.1


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

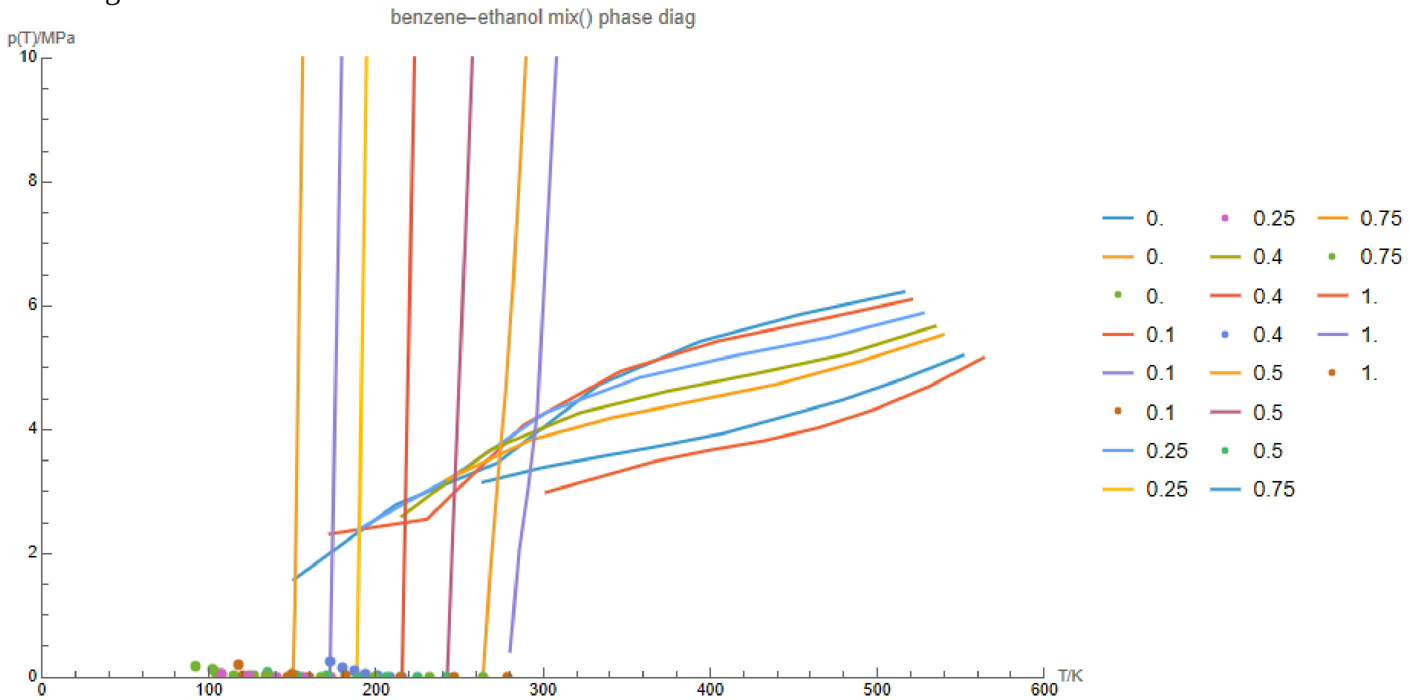
x_0=0 (ethanol)


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

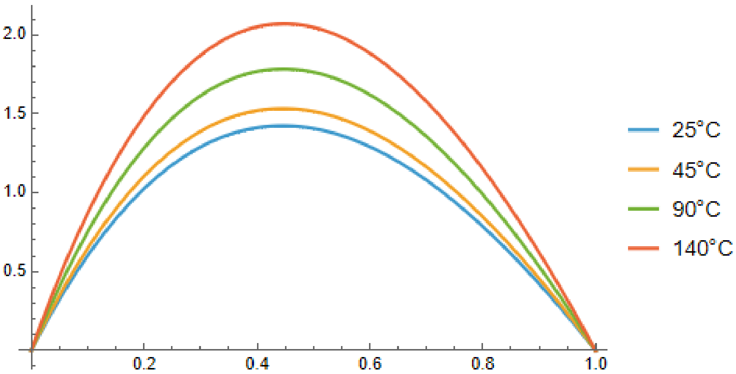

benzene-ethanol mix(0.) pgs(T)/pt
0.010
0.008
0.006
0.004
0.002
0.000
0.2
0.4
0.6
0.8
1.0
1.2
T/Tt

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

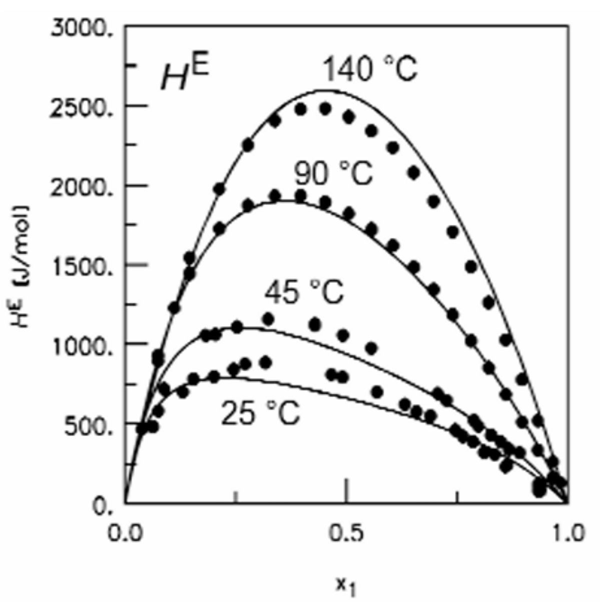
Phase diagrams



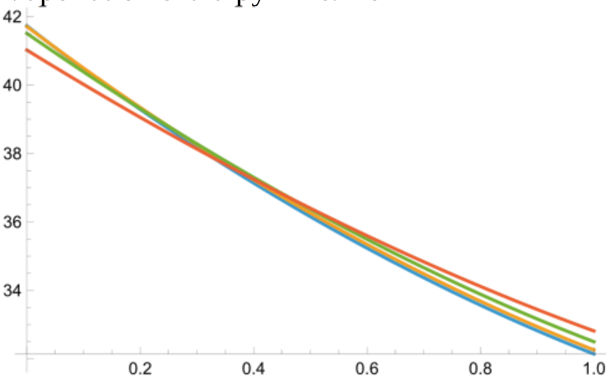
Excess enthalpy in kJ/mol vs. relative benzene concentration x_0



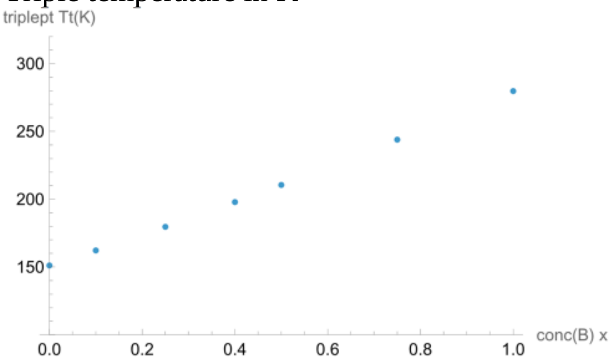
Excess enthalpy measured in J/mol



Vaporiation enthalpy in kJ/mol



Triple temperature in K



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[2] J. Helm, Thermodynamics of phase transitions for pure substances and mixtures, researchgate.net/publication/400835911, 2026
[3] J. Helm, Statistical mechanics of states of matter, Mathematica code ThermoPhaseN.nb, researchgate.net, 2025
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