teqp

Release 0.17.0

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CHAPTER

ONE

GETTING STARTED

1.1 Introduction

teqp (phonetically: tɛk pi) is a C++-based library with wrappers. It was written because implementing EOS (particularly working out the derivatives) is a painful, error-prone, and slow process. The advent of open-source automatic differentiation libraries makes the implementation of EOS as fast as hand-written derivatives, and much easier to implement without errors.

There is a paper about teqp: https://doi.org/10.1021/acs.iecr.2c00237

The documentation is based on the Python wrapper because it can be readily integrated with the documentation tools (sphinx in this case) and can be auto-generated at documentation build time.

1.2 Installation

1.2.1 Python

The library can be installed with:

```
pip install teqp
```

because the binary wheels for all major platforms are provided on pypi.

If you desire to build teqp yourself, it is recommended to pull from github and build a binary wheel, and then subsequently install that wheel:

```
git clone --recursive https://github.com/usnistgov/teqp
cd teqp
python setup.py bdist_wheel
pip install dist/*.whl # or replace with the appropriate binary wheel
```

1.2.2 C++

The build is cmake based. There are targets available for an interface library, etc. Please see `CMakeLists.txt`

CHAPTER

TWO

C++ INTERFACE

2.1 Introduction

The abstract base class defining the public C++ interface of teqp is documented in AbstractModel. This interface was developed because re-compilation of the core of `teqp` is VERY slow, due to the heavy use of templates, which makes the code very flexible, but difficult to work with when doing development. Especially users that would like to only use the library but not be forced to pay the price of recompilation benefit from this approach.

The models that are allowed in this abstract interface are defined in AllowedModels. A new model instance can be created by passing properly formatted JSON data structure to the make_model() function.

CHAPTER

THREE

MODELS

3.1 Constructing Models

With a few exceptions, most models are constructed by describing the model in JSON format, and passing the JSON-formatted information to the `make_model` function. There are some convenience functions exposed for backwards compatibility, but as of version 0.14.0, all model construction should go via this route.

At the C++ level, the returned value from the `make_model` function is a `shared_ptr` that wraps a pointer to an `AbstractModel` class. The `AbstractModel` class is an abstract class which defines the public C++ interface.

In Python, construction is in two parts. First, the model is constructed, which only includes the common methods. Then, the model-specific attributes and methods are attached with the `attach_model_specific_methods` method.

The JSON structure is of two parts, the `kind` field is a case-sensitive string defining which model kind is being constructed, and the `model` field contains all the information needed to build the model. In the case of hard-coded models, nothing is provided in the `model` field, but it must still be provided.

Also, the argument to `make_model` must be valid JSON. So if you are working with numpy array datatypes, make sure to convert them to a list (which is convertible to JSON). Example below.

[1]:
```
import teqp, numpy as np
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
teqp.make_model({'kind': 'vdW1', 'model': {'a': 1, 'b': 2}})
```

[2]:
```
<teqp.teqp.AbstractModel at 0x7fa8ebf64830>
```

[3]:
```
# Fields are case-sensitive
teqp.make_model({'kind': 'vdW1', 'model': {'a': 1, 'B': 2}})
```

```
---------------------------------------------------------------------------
RuntimeError                              Traceback (most recent call last)
Cell In[3], line 2
      1 # Fields are case-sensitive
----> 2 teqp.make_model({'kind': 'vdW1', 'model': {'a': 1, 'B': 2}})

File /opt/conda/lib/python3.11/site-packages/teqp/__init__.py:47, in make_model(*args,
↪ **kwargs)
     42 def make_model(*args, **kwargs):
     43     """
     44     This function is in two parts; first the make_model function (renamed to _
↪make_model in the Python interface)
     45     is used to make the model and then the model-specific methods are␣
```

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```
↪attached to the instance
     46     """
---> 47     AS = _make_model(*args, **kwargs)
     48     attach_model_specific_methods(AS)
     49     return AS

RuntimeError: :{"B":2,"a":1}': required property 'b' not found in object
|/|\|:{"B":2,"a":1}': validation failed for additional property 'B': instance invalid␣
↪as per false-schema
```

[4]:
```
# A hard-coded model
teqp.make_model({
    'kind': 'AmmoniaWaterTillnerRoth',
    'model': {}
})
```

[4]:
```
<teqp.teqp.AbstractModel at 0x7fa8d48186b0>
```

[5]:
```
# Show what to do with numpy array
Tc_K = np.array([100,200])
pc_Pa = np.array([3e6, 4e6])
teqp.make_model({
    "kind": "vdW",
    "model": {
        "Tcrit / K": Tc_K.tolist(),
        "pcrit / Pa": pc_Pa.tolist()
    }
})
```

[5]:
```
<teqp.teqp.AbstractModel at 0x7fa8d4818890>
```

[6]:
```
# methane with conventional PC-SAFT
j = {
    'kind': 'PCSAFT',
    'model': {
        'coeffs': [{
            'name': 'methane',
             'BibTeXKey': 'Gross-IECR-2001',
             'm': 1.00,
             'sigma_Angstrom': 3.7039,
             'epsilon_over_k': 150.03,
        }]
    }
}
model = teqp.make_model(j)
```

3.2 General cubics

The reduced residual Helmholtz energy for the main cubic EOS (van der Waals, Peng-Robinson, and Soave-Redlich-Kwong) can be written in a common form (see https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7365965/)

$$\alpha^r = \psi^{(-)} - \frac{\tau a_m}{RT_r}\psi^{(+)}$$

$$\psi^{(-)} = -\ln(1 - b_m\rho)$$

$$\psi^{(+)} = \frac{\ln\left(\frac{\Delta_1 b_m\rho + 1}{\Delta_2 b_m\rho + 1}\right)}{b_m(\Delta_1 - \Delta_2)}$$

with the constants given by:

- vdW: $\Delta_1 = 0, \Delta_2 = 0$
- SRK: $\Delta_1 = 1, \Delta_2 = 0$
- PR: $\Delta_1 = 1 + \sqrt{2}, \Delta_2 = 1 - \sqrt{2}$

The quantities a_m and b_m are described (with exact solutions for the numerical coefficients) for each of these EOS in https://pubs.acs.org/doi/abs/10.1021/acs.iecr.1c00847.

The models in teqp are instantiated based on knowledge of the critical temperature, pressure, and acentric factor. Thereafter all quantities are obtained from derivatives of α^r.

The Python class is here: `GeneralizedCubic`

[1]:
```
import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
import json
import CoolProp.CoolProp as CP

# Values taken from http://dx.doi.org/10.6028/jres.121.011
Tc_K = [ 190.564, 154.581, 150.687 ]
pc_Pa = [ 4599200, 5042800, 4863000 ]
acentric = [ 0.011, 0.022, -0.002 ]

# Instantiate Peng-Robinson model
modelPR = teqp.canonical_PR(Tc_K, pc_Pa, acentric)

# Instantiate Soave-Redlich-Kwong model
modelSRK = teqp.canonical_SRK(Tc_K, pc_Pa, acentric)
```

[3]:
```
# And you can get information about the model in JSON format
# from the get_meta function
modelPR.get_meta()
```

[3]:
```
{'Delta1': 2.414213562373095,
 'Delta2': -0.41421356237309515,
 'OmegaA': 0.4572355289213822,
 'OmegaB': 0.07779607390388846,
 'kind': 'Peng-Robinson'}
```

3.2.1 Adjusting k_ij

Fine-tuned values of k_{ij} can be provided when instantiating the model, for Peng-Robinson and SRK. A complete matrix of all the k_{ij} values must be provided. This allows for asymmetric mixing models in which $k_{ij} \neq k_{ji}$.

[4]:
```
k_12 = 0.01
kmat = [[0,k_12,0],[k_12,0,0],[0,0,0]]
teqp.canonical_PR(Tc_K, pc_Pa, acentric, kmat)
teqp.canonical_SRK(Tc_K, pc_Pa, acentric, kmat)
```

[4]:
```
<teqp.teqp.AbstractModel at 0x7fc4946de030>
```

3.2.2 Superancillary

The superancillary equation gives the co-existing liquid and vapor (orthobaric) densities as a function of temperature. The set of Chebyshev expansions was developed in https://pubs.acs.org/doi/abs/10.1021/acs.iecr.1c00847 . These superancillary equations are more accurate than iterative calculations in double precision arithmetic and also at least 10 times faster to calculate, and cannot fail in iterative routines, even extremely close to the critical point.

The superancillary equation is only exposed for pure fluids to remove ambiguity when considering mixtures. The returned tuple is the liquid and vapor densities

[5]:
```
teqp.canonical_PR([Tc_K[0]], [pc_Pa[0]], [acentric[0]]).superanc_rhoLV(100)
```

[5]:
```
(30846.392909514052, 42.480231719002326)
```

3.2.3 a and b

For the cubic EOS, it can be useful to obtain the a and b parameters directly. The b parameter is particularly useful because 1/b is the maximum allowed density in the EOS

[6]:
```
import numpy as np
z = np.array([0.3, 0.4, 0.3])
modelPR.get_a(140, z), modelPR.get_b(140, z)
```

[6]:
```
(0.1874177858906821, 2.1984349667726406e-05)
```

3.2.4 alpha functions

It can be advantageous to modify the alpha function to allow for more accurate handling of the attractive interactions. Coefficients are tabulated for many species in https://pubs.acs.org/doi/10.1021/acs.jced.7b00967 for the Peng-Robinson EOS with Twu alpha function and the values from the SI of that paper are in the csv file next to this file.

[7]:
```
import pandas

dfTwu = pandas.read_csv('fitted_Twu_coeffs.csv')
def get_model(INCHIKey):
    row = dfTwu.loc[dfTwu['inchikey']==INCHIKey]
    if len(row) == 1:
        row = row.iloc[0]
    Tc_K = row['Tc_K']
    pc_MPa = row['pc_MPa']
    c = [row['c0'], row['c1'], row['c2']]
```

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```
    # The JSON definition of the EOS,
    # here a generic cubic EOS to allow for
    # specification of the alpha function(s)
    j = {
        'kind': 'cubic',
        'model': {
            'type': 'PR',
            'Tcrit / K': [Tc_K],
            'pcrit / Pa': [pc_MPa*1e6],
            'acentric': [0.1],
            'alpha': [{'type': 'Twu', 'c': c}]
        }
    }
    model = teqp.make_model(j)
    return model, j

# Hexane
model, j = get_model(INCHIKey='VLKZOEOYAKHREP-UHFFFAOYSA-N')
```

[8]:
```
# And how about we calculate the pressure and s^+ = -sr/R at NBP of water
model, j = get_model(INCHIKey='XLYOFNOQVPJJNP-UHFFFAOYSA-N') # WATER

T = 373.1242958476844 # K, NBP of water
rhoL, rhoV = model.superanc_rhoLV(T)
z = np.array([1.0])
pL = rhoL*model.get_R(z)*T*(1.0 + model.get_Ar01(T, rhoL, z))
splusL = model.get_splus(T, rhoL*z)
print(pL, splusL)
```

```
102739.27983424198 6.03697343297877
```

Also implemented in version 0.17 are the alpha functions of Mathias-Copeman.

$$\alpha = (1 + c_0 x + c_1 x^2 + c_2 x^3)^2$$

with

$$x = 1 + \sqrt{\frac{T}{T_c i}}$$

Parameters are tabulated for many fluids in the paper of Horstmann (https://doi.org/10.1016/j.fluid.2004.11.002) for the SRK EOS (only)

[9]:
```
# Here is an example from Horstmann
j = {
    "kind": "cubic",
    "model": {
        "type": "SRK",
        "Tcrit / K": [647.30],
        "pcrit / Pa": [22.048321e6],
        "acentric": [0.3440],
        "alpha": [
            {"type": "Mathias-Copeman", "c": [1.07830, -0.58321, 0.54619]}
        ]
    }
}
```

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```
model = teqp.make_model(j)
T = 373.1242958476844 # K
rhoL, rhoV = model.superanc_rhoLV(T)
z = np.array([1.0])
pL = rhoL*model.get_R(z)*T*(1.0 + model.get_Ar01(T, rhoL, z))
print('And with SRK and Mathias-Copeman parameters:', pL, 'Pa')
```

```
And with SRK and Mathias-Copeman parameters: 101639.22259842217 Pa
```

3.3 Quantum PR

The quantum-corrected Peng-Robinson model of Aasen *et al.* (https://doi.org/10.1063/1.5111364) can be used to account for quantum effects by empirical fits to the Feynman-Hibbs corrections.

The conventional Peng-Robinson approach is used, with an adjusted covolume b_i given by

$$b_i = b_{i,PR}\beta_i(T)$$

with

$$\beta_i(T) = \left(\frac{1 + A_i/(T + B_i)}{1 + A_i/(T_{ci} + B_i)}\right)^3$$

and Twu alpha functions are used to correct the attractive part.

[1]:
```
import numpy as np, matplotlib.pyplot as plt, pandas
import CoolProp.CoolProp as CP

import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
kij_library = {
    ('H2','Ne'): 0.18,
    ('He','H2'): 0.17
}
lij_library = {
    ('H2','Ne'): 0.0,
    ('He','H2'): -0.16
}

def get_model(names, c_factor=0):
    param_library = {
        'H2': {
            "Ls": [156.21],
            "Ms": [-0.0062072],
            "Ns": [5.047],
            "As": [3.0696],
            "Bs": [12.682],
            "cs / m^3/mol": [c_factor*-3.8139e-6],
            "Tcrit / K": [33.19],
            "pcrit / Pa": [12.964e5]
        },
```

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```
        'Ne': {
            "Ls": [0.40453],
            "Ms": [0.95861],
            "Ns": [0.8396],
            "As": [0.4673],
            "Bs": [2.4634],
            "cs / m^3/mol": [c_factor*-2.4665e-6],
            "Tcrit / K": [44.492],
            "pcrit / Pa": [26.79e5]
        },
        'He': {
            "Ls": [0.48558],
            "Ms": [1.7173],
            "Ns": [0.30271],
            "As": [1.4912],
            "Bs": [3.2634],
            "cs / m^3/mol": [c_factor*-3.1791e-6],
            "Tcrit / K": [5.1953],
            "pcrit / Pa": [2.276e5]
        }
    }
    params = [param_library[name] for name in names]
    model = {k: [param[k][0] for param in params] for k in ['Ls','Ms','Ns','As','Bs',
↪'cs / m^3/mol','Tcrit / K','pcrit / Pa']}

    if len(names) == 1:
        model['kmat'] = [[0]]
        model['lmat'] = [[0]]
    else:
        kij = kij_library[names]
        model['kmat'] = [[0,kij],[kij,0]]
        lij = lij_library[names]
        model['lmat'] = [[0,lij],[lij,0]]

    j = {
        "kind": "QCPRAasen",
        "model": model
    }
    return teqp.make_model(j), j

model = get_model(('H2','Ne'))[0]
modelH2 = get_model(('H2',))[0]
modelNe = get_model(('Ne',))[0]

def get_traces(T, ipures):
    traces = []
    for ipure in ipures:
        rhovecL0 = np.array([0.0, 0.0])
        rhovecV0 = np.array([0.0, 0.0])
        if ipure == 1:
            rhoL, rhoV = modelNe.superanc_rhoLV(T)
        else:
            rhoL, rhoV = modelH2.superanc_rhoLV(T)
        rhovecL0[ipure] = rhoL
        rhovecV0[ipure] = rhoV

        opt = teqp.TVLEOptions();
```

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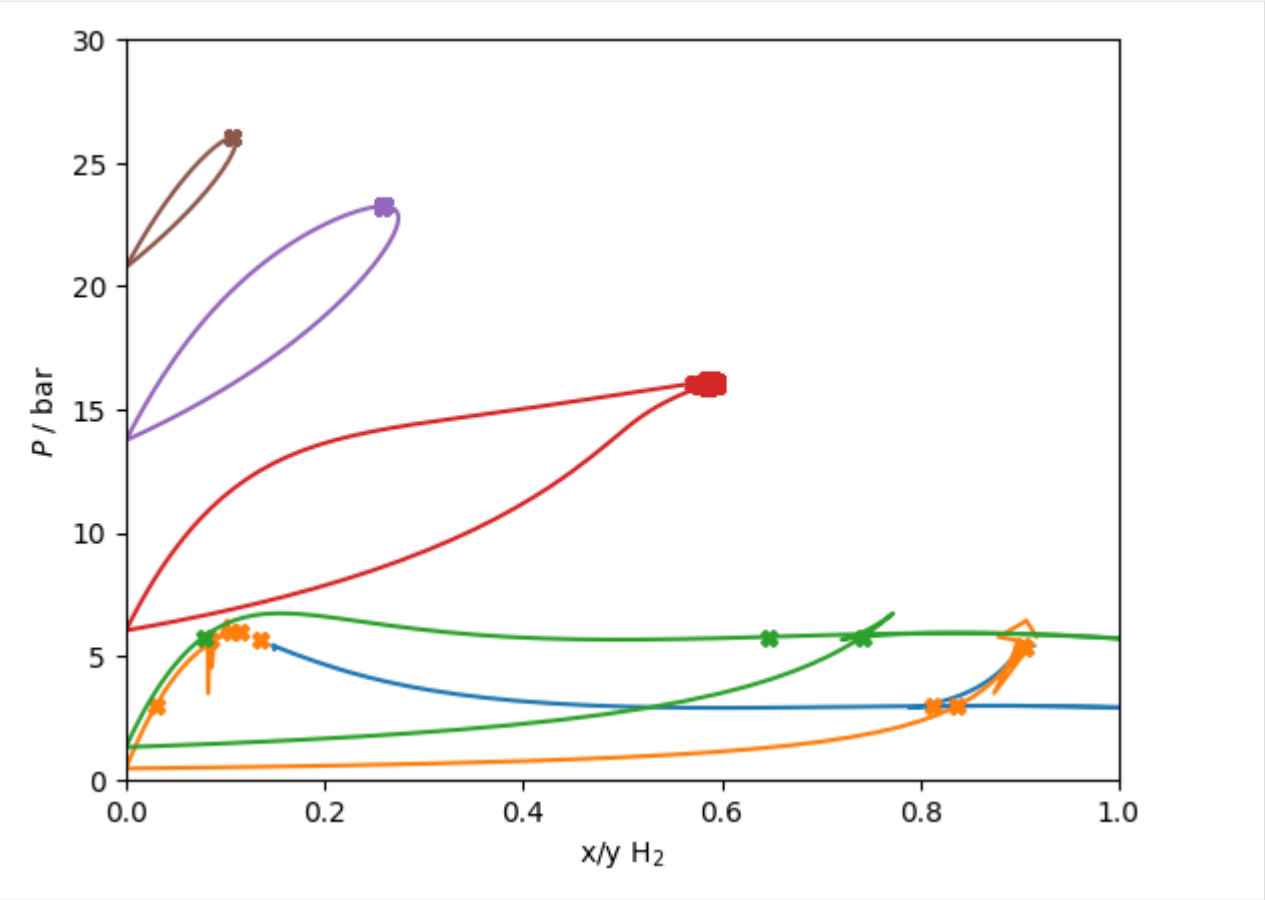
```
#         opt.polish=True;
#         opt.integration_order=5; opt.rel_err=1e-10;
#         opt.calc_criticality = True;
        opt.crit_termination=1e-10
        trace = model.trace_VLE_isotherm_binary(T, rhovecL0, rhovecV0, opt)
        traces.append(trace)
    return traces

for T in [24.59, 28.0, 34.66, 39.57, 42.50]:
    if T < 26.0:
        traces = get_traces(T, [0, 1])
    else:
        traces = get_traces(T, [1])

    for trace in traces:
        df = pandas.DataFrame(trace)

        # Plot the VLE solution
        line, = plt.plot(df['xL_0 / mole frac.'], df['pL / Pa']/1e5)
        plt.plot(df['xV_0 / mole frac.'], df['pL / Pa']/1e5, color=line.get_color())

    # Plot the VLLE solution if found
    for soln in model.find_VLLE_T_binary(traces):
        for rhovec in soln['polished']:
            rhovec = np.array(rhovec)
            rhotot = sum(rhovec)
            x = rhovec/rhotot
            p = rhotot*model.get_R(x)*T*(1+model.get_Ar01(T, rhotot, x))
            plt.plot(x[0], p/1e5, 'X', color=line.get_color())
            # print(T, rhovec, x[0], p/1e5, 'bar')

plt.gca().set(xlabel='x/y H$_2$', ylabel='$P$ / bar', xlim=(0,1), ylim=(0,30));
```



3.4 Model Potentials

These EOS for model potentials are useful for understanding theory, and capture some (but perhaps not all) of the physics of "real" fluids.

[1]:
```
import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

3.4.1 Square-well

The potential is defined by

$$V(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

from which an EOS can be developed by correlating results from molecular simulation. The EOS is from:

Rodolfo Espíndola-Heredia, Fernando del Río and Anatol Malijevsky Optimized equation of the state of the square-well fluid of variable range based on a fourth-order free-energy expansion J. Chem. Phys. 130, 024509 (2009); https://doi.org/10.1063/1.3054361

[2]:
```
model = teqp.make_model({
  "kind": "SW_EspindolaHeredia2009",
  "model": {
      "lambda": 1.3
  }
})
```

3.4.2 EXP-6

[3]:
```
model = teqp.make_model({
  "kind": "EXP6_Kataoka1992",
  "model": {
      "alpha": 12
  }
})
```

3.4.3 Lennard-Jones Fluid

The Lennard-Jones potential is given by

$$V(r) = 4\varepsilon\left((\sigma/r)^{12} - (\sigma/r)^{6}\right)$$

and EOS are available from many authors. teqp includes the EOS from Thol, Kolafa-Nezbeda, and Johnson.

[4]:
```
for kind, crit in [
    ["LJ126_TholJPCRD2016", (1.32, 0.31)], # Note the true critical point was not used
    ["LJ126_KolafaNezbeda1994", (1.3396, 0.3108)],
    ["LJ126_Johnson1993", (1.313, 0.310)]]:

    j = { "kind": kind, "model": {} }
    model = teqp.make_model(j)
    print(kind, model.solve_pure_critical(1.3, 0.3), crit)
```

```
LJ126_TholJPCRD2016 (1.3035125549100017, 0.3103860327864468) (1.32, 0.31)
LJ126_KolafaNezbeda1994 (1.3396478193468193, 0.3108038977722935) (1.3396, 0.3108)
LJ126_Johnson1993 (1.3130000571792173, 0.3099999768607838) (1.313, 0.31)
```

3.4.4 Two-Center Lennard-Jones Fluid

[5]:
```
model = teqp.make_model({
  'kind': '2CLJF-Dipole',
  'model': {
      "author": "2CLJF_Lisal",
      'L^*': 0.5,
      '(mu^*)^2': 0.1
  }
})
print(model.solve_pure_critical(1.3, 0.3))

model = teqp.make_model({
  'kind': '2CLJF-Quadrupole',
  'model': {
```

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```
      "author": "2CLJF_Lisal",
      'L^*': 0.5,
      '(Q^*)^2': 0.1
  }
})
print(model.solve_pure_critical(1.3, 0.3))
```

```
(2.8282972062188056, 0.2005046666634018)
(2.832574303561834, 0.2003194655463274)
```

3.5 Cubic Plus Association (CPA)

The combination of a cubic EOS with association

3.6 PC-SAFT

The PC-SAFT implementation in teqp is based on the implementation of Gross and Sadowski (https://doi.org/10.1021/ie0003887), with the typo from their paper fixed. It does NOT include the association contribution, only the dispersive contributions.

The model in teqp requires the user to specify the values of `sigma`, `epsilon/kB`, and `m` for each substance. A very few substances are hardcoded in teqp, for testing purposes.

The Python class is here: `PCSAFTEOS`

[1]:
```
import teqp
import numpy as np
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
TeXkey = 'Gross-IECR-2001'
ms = [1.0, 1.6069, 2.0020]
eoverk = [150.03, 191.42, 208.11]
sigmas = [3.7039, 3.5206, 3.6184]

coeffs = []
for i in range(len(ms)):
    c = teqp.SAFTCoeffs()
    c.m = ms[i]
    c.epsilon_over_k = eoverk[i]
    c.sigma_Angstrom = sigmas[i]
    coeffs.append(c)

model = teqp.PCSAFTEOS(coeffs)
```

[3]:
```
# Here are some rudimentary timing results
T = 300.0
rhovec = np.array([3.0, 4.0, 5.0])
rho = rhovec.sum()
x = rhovec/np.sum(rhovec)
%timeit model.get_fugacity_coefficients(T,rhovec)
```

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```
%timeit (-1.0)*model.get_Ar20(T, rho, x)
%timeit model.get_partial_molar_volumes(T, rhovec)
```

```
4.55 µs ± 13.3 ns per loop (mean ± std. dev. of 7 runs, 100,000 loops each)
4.33 µs ± 38.1 ns per loop (mean ± std. dev. of 7 runs, 100,000 loops each)
22.6 µs ± 2.28 µs per loop (mean ± std. dev. of 7 runs, 10,000 loops each)
```

The model parameters can be queried:

[4]:
```
model.get_m(), model.get_epsilon_over_k_K(), model.get_sigma_Angstrom()
```

[4]:
```
(array([1.    , 1.6069, 2.002 ]),
 array([150.03, 191.42, 208.11]),
 array([3.7039, 3.5206, 3.6184]))
```

3.6.1 Adjusting k_ij

Fine-tuned values of k_{ij} can be provided when instantiating the model. A complete matrix of all the k_{ij} values must be provided. This allows for asymmetric mixing models in which $k_{ij} \neq k_{ji}$.

[5]:
```
k_01 = 0.01; k_10 = k_01
kmat = [[0,k_01,0],[k_10,0,0],[0,0,0]]
model = teqp.PCSAFTEOS(coeffs, kmat)
```

[6]:
```
# and the matrix of parameters can be printed back out
model.get_kmat()
```

[6]:
```
array([[0.  , 0.01, 0.  ],
       [0.01, 0.  , 0.  ],
       [0.  , 0.  , 0.  ]])
```

3.6.2 Superancillary

The superancillary equation for PC-SAFT has been developed, and is much more involved than that of the cubic EOS. As a consequence, the superancillary equation has been provided as a separate package rather than integrating it into to teqp to minimize the binary size of teqp. It can be installed from PYPI with: `pip install PCSAFTsuperanc`

The scaling in the superancillaries uses reduced variables:

$$\tilde{T} = T/(\epsilon/k_{\mathrm{B}})$$

$$\tilde{\rho} = \rho_{\mathrm{N}}\sigma^3$$

where ρ_{N} is the number density, and the other parameters are from the PC-SAFT model

[7]:
```
import PCSAFTsuperanc

sigma_m = 3e-10 # [meter]
e_over_k = 150.0 # [K]
m = 5

# The saturation temperature
T = 300
```

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```
[Ttilde_crit, Ttilde_min] = PCSAFTsuperanc.get_Ttilde_crit_min(m=m)
print('Ttilde crit:', Ttilde_crit)

# Get the scaled densities for liquid and vapor phases
[tilderhoL, tilderhoV] = PCSAFTsuperanc.PCSAFTsuperanc_rhoLV(Ttilde=T/e_over_k, m=m)
# Convert back to molar densities
N_A = PCSAFTsuperanc.N_A # The value of Avogadro's constant used in superancillaries
rhoL, rhoV = [tilderho/(N_A*sigma_m**3) for tilderho in [tilderhoL, tilderhoV]]

# As a sanity check, confirm that we got the same pressure in both phases
c = teqp.SAFTCoeffs()
c.sigma_Angstrom = sigma_m*1e10
c.epsilon_over_k = e_over_k
c.m = m
model = teqp.PCSAFTEOS([c])
z = np.array([1.0])
pL = rhoL*model.get_R(z)*T*(1+model.get_Ar01(T, rhoL, z))
pV = rhoV*model.get_R(z)*T*(1+model.get_Ar01(T, rhoV, z))
print('Pressures are:', pL, pV, 'Pa')
```

```
Ttilde crit: 2.648680568587752
Pressures are: 227809.12314460654 227809.12314409122 Pa
```

3.6.3 Maximum density

The maximum number density allowed by the EOS is defined based on the packing fraction. To get a molar density, divide by Avogadro's number. The function is conveniently exposed in Python:

[8]:
```
max_rhoN = teqp.PCSAFTEOS(coeffs).max_rhoN(130.0, np.array([0.3, 0.3, 0.4]))
display(max_rhoN)
max_rhoN/6.022e23 # the maximum molar density in mol/m^3
```

```
1.9139171771761775e+28
```

[8]:
```
31782.085306811314
```

3.6.4 Polar contributions

As of teqp version 0.15, quadrupolar and dipolar contributions have been added to the hard chain plus dispersion model which is referred to conventionally as PC-SAFT. The definitions of the reduced dipolar and quadrupolar parameters are not well documented, so they are given here. The work of Stoll, Vrabec, and Hasse (https://doi.org/10.1063/1.1623475) clearly describes the formulation of the star-scaling.

In SI units, the reduced squared dipole moment is defined by

$$(\mu^*)^2_{\text{conventional}} = \frac{(\mu[Cm])^2}{4\pi\epsilon_0(\varepsilon[J])(\sigma[m])^3}$$

$$(Q^*)^2_{\text{conventional}} = \frac{(\mu[Cm])^2}{4\pi\epsilon_0(\varepsilon[J])(\sigma[m])^5}$$

In the PC-SAFT formulation, the only difference is the addition of dividing the denominator by the number of segments m

$$(\mu^*)^2 = \frac{(\mu[Cm])^2}{4\pi\epsilon_0 m(\varepsilon/k_B[K])k_B(\sigma[m])^3}$$

$$(Q^*)^2 = \frac{(Q[Cm^2])^2}{4\pi\epsilon_0 m(\varepsilon/k_B[K])k_B(\sigma[m])^5}$$

The unit conversions are obtained from

$$(\sigma[m]) = (10^{-10}m/A)(\sigma[A])$$

$$(\mu[Cm]) = (3.33564 \times 10^{-30}Cm/D)(\mu[D])$$

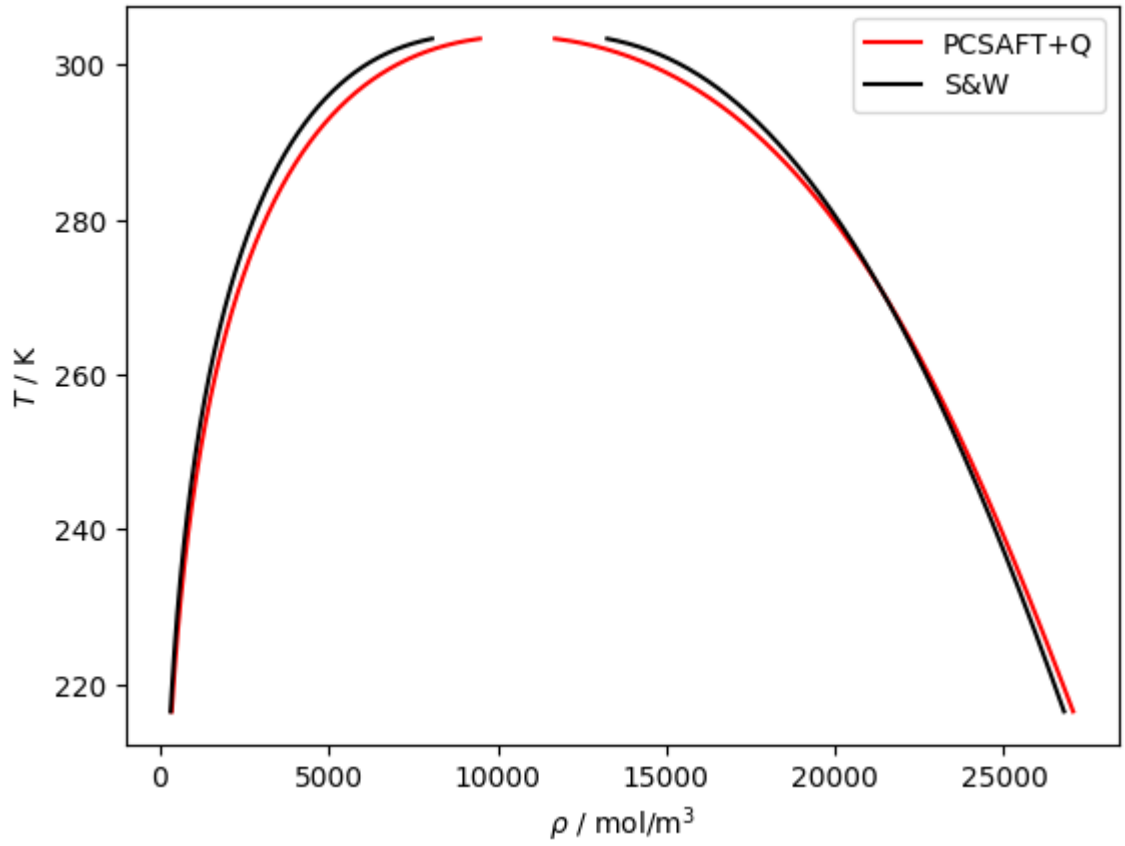
and $\epsilon_0 = 8.85419e-12$ C^2 N^{-1} m^{-2} is the permittivity of vacuum.

[9]:
```
# CO2 with quadrupolar contributions
j = {
    'kind': 'PCSAFT',
    'model': {
        'coeffs': [{
            'name': 'CO2',
             'BibTeXKey': 'Gross-AICHEJ',
             'm': 1.5131,
             'sigma_Angstrom': 3.1869,
             'epsilon_over_k': 169.33,
             '(Q^*)^2': 1.26, # modified from the values in Gross and Vrabec since the base model is different
             'nQ': 1
        }]
    }
}

model = teqp.make_model(j)
Tc, rhoc = model.solve_pure_critical(300, 11000)

T = Tc*0.999
rhoL_, rhoV_ = model.extrapolate_from_critical(Tc, rhoc, T)
rhoL, rhoV = model.pure_VLE_T(T, rhoL_, rhoV_, 10)

import CoolProp.CoolProp as CP
import matplotlib.pyplot as plt
import pandas
o = []
for T_ in np.linspace(T, 215, 1000):
    rhoL, rhoV = model.pure_VLE_T(T_, rhoL, rhoV, 10)
    try:
        o.append({
          'T': T_, 'rhoL': rhoL, 'rhoV': rhoV,
          'rhoLSW': CP.PropsSI('Dmolar','T',T_,'Q',0,'CO2'),
          'rhoVSW': CP.PropsSI('Dmolar','T',T_,'Q',1,'CO2')
        })
    except:
        pass
df = pandas.DataFrame(o)
plt.plot(df['rhoL'], df['T'], 'r', label='PCSAFT+Q')
plt.plot(df['rhoV'], df['T'], 'r')
plt.plot(df['rhoLSW'], df['T'], 'k', label='S&W')
plt.plot(df['rhoVSW'], df['T'], 'k')
plt.legend()
plt.gca().set(xlabel=r'$\rho$ / mol/m$^3$', ylabel='$T$ / K')
plt.show()
```



[10]:
```
# Acetone with dipolar contributions
j = {
    'kind': 'PCSAFT',
    'model': {
        'coeffs': [{
            'name': 'acetone',
             'BibTeXKey': 'Gross-IECR',
             'm': 2.7447,
             'sigma_Angstrom': 3.2742,
             'epsilon_over_k': 232.99,
             '(mu^*)^2': 1.9, # modified from the values in Gross and Vrabec since␣
↪the base model is different
             'nmu': 1
        }]
    }
}

model = teqp.make_model(j)
Tc, rhoc = model.solve_pure_critical(300, 11000)

T = Tc*0.999
rhoL_, rhoV_ = model.extrapolate_from_critical(Tc, rhoc, T)
rhoL, rhoV = model.pure_VLE_T(T, rhoL_, rhoV_, 10)

import CoolProp.CoolProp as CP
import matplotlib.pyplot as plt
```

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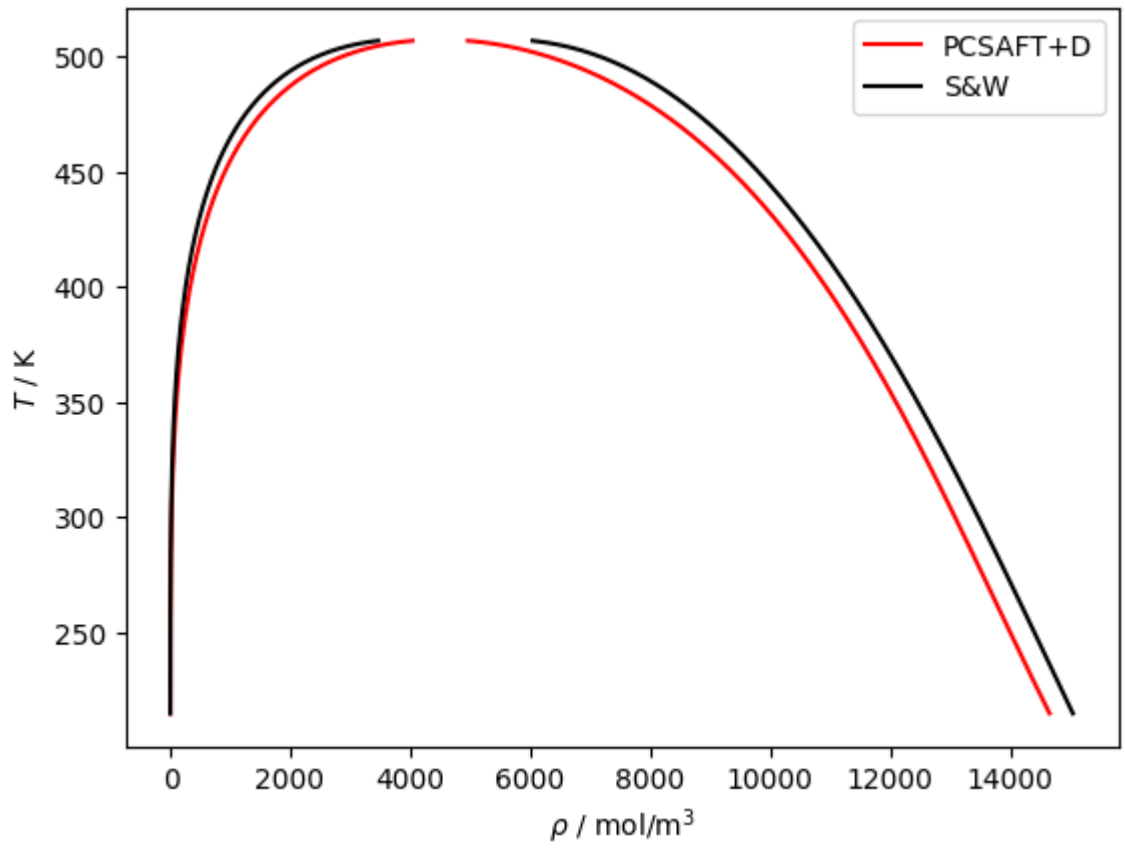
```
import pandas
o = []
for T_ in np.linspace(T, 215, 1000):
    rhoL, rhoV = model.pure_VLE_T(T_, rhoL, rhoV, 10)
    try:
        o.append({
          'T': T_, 'rhoL': rhoL, 'rhoV': rhoV,
          'rhoLSW': CP.PropsSI('Dmolar','T',T_,'Q',0,'acetone'),
          'rhoVSW': CP.PropsSI('Dmolar','T',T_,'Q',1,'acetone')
        })
    except:
        pass
df = pandas.DataFrame(o)
plt.plot(df['rhoL'], df['T'], 'r', label='PCSAFT+D')
plt.plot(df['rhoV'], df['T'], 'r')
plt.plot(df['rhoLSW'], df['T'], 'k', label='S&W')
plt.plot(df['rhoVSW'], df['T'], 'k')
plt.legend()
plt.gca().set(xlabel=r'$\rho$ / mol/m$^3$', ylabel='$T$ / K')
plt.show()
```



3.7 Multi-fluid EOS

Peering into the innards of teqp

[1]:
```
import timeit, json
import pandas
import numpy as np
import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

3.7.1 Ancillary Equations

Ancillary equations are provided along with multiparameter equations of state. The give a good *approximation* to the phase equilibrium densities. There are routines in teqp to use the ancillary equations provided with the EOS. First a class containing the ancillary equations is obtained, then methods on that class are called

[2]:
```
model = teqp.build_multifluid_model(["Methane"], teqp.get_datapath())
anc = model.build_ancillaries()
T = 100.0 # [K]
rhoL, rhoV = anc.rhoL(T), anc.rhoV(T)
print('Densities are:', rhoL, rhoV, 'mol/m^3')
```

```
Densities are: 27357.335621492966 42.04100696197727 mol/m^3
```

But those densities do not correspond to the *true* phase equilibrium solution, so we need to polish the solution:

[3]:
```
Niter = 10
rhoLtrue, rhoVtrue = model.pure_VLE_T(T, rhoL, rhoV, Niter)
print('VLE densities are:', rhoLtrue, rhoVtrue, 'mol/m^3')
```

```
VLE densities are: 27357.147019094467 42.047982278351704 mol/m^3
```

And looking the densities, they are slightly different after the phase equilibrium calculation

3.7.2 Ammonia-Water

Tillner-Roth and Friend provided a hard-coded model that is in a form not compatible with the other multi-fluid models. It is available via the high-level factory function

[4]:
```
AW = teqp.AmmoniaWaterTillnerRoth()
AW.get_Ar01(300, 300, np.array([0.9, 0.0]))
```

[4]:
```
-0.09731055757504622
```

3.7.3 Pure fluid loading

[5]:
```
# By default teqp looks for fluids relative to the set of fluids in ROOT/dev/fluids
# The name (case-sensitive) should match the .json file, without the json extension.
%timeit model = teqp.build_multifluid_model(["Methane"], teqp.get_datapath())
```

```
626 µs ± 4.21 µs per loop (mean ± std. dev. of 7 runs, 1,000 loops each)
```

[6]:
```
# And if you provide valid aliases, alias lookup will be used to resolve the name
# But beware, this is rather a lot slower than the above because all fluid files need␣
↪to be read
# in to build the alias map
%timeit model = teqp.build_multifluid_model(["n-C1H4"], teqp.get_datapath())
```

```
38.3 ms ± 108 µs per loop (mean ± std. dev. of 7 runs, 10 loops each)
```

So, how to make it faster? Only do it once and cache

[7]:
```
# Here is the set of possible aliases to absolute paths of files
# Building this map takes a little while (somewhat faster in C++) due to all the file␣
↪reads
# If you know your files will not change, good idea to build this alias map yourself.
%timeit aliasmap = teqp.build_alias_map(teqp.get_datapath())
aliasmap = teqp.build_alias_map(teqp.get_datapath())
list(aliasmap.keys())[0:10] # the first 10 aliases in the dict
```

```
37.8 ms ± 371 µs per loop (mean ± std. dev. of 7 runs, 10 loops each)
```

[7]:
```
['1,2-DICHLOROETHANE',
 '1,2-dichloroethane',
 '1-BUTENE',
 '1-Butene',
 '100-41-4',
 '10024-97-2',
 '102687-65-0',
 '106-42-3',
 '106-97-8',
 '106-98-9']
```

[8]:
```
# Then load the absolute paths from the alias map,
# which will guarantee that you hit exactly what you were looking for,
# resolving aliases as needed
identifiers = [aliasmap[n] for n in ["n-C1H4"]]
%timeit model = teqp.build_multifluid_model(identifiers, teqp.get_datapath())
```

```
625 µs ± 2.35 µs per loop (mean ± std. dev. of 7 runs, 1,000 loops each)
```

At some point soon teqp will support in-memory loading of JSON data for the pure components, without requiring reads from the operating system

[9]:
```
# And you can also load the JSON that teqp is loading for the pure fluids
pureJSON = teqp.collect_component_json(['Neon','Hydrogen'], teqp.get_datapath())
```

3.7.4 Mixture model loading

[10]:
```
# Load the default JSON for the binary interaction parameters
BIP = json.load(open(teqp.get_datapath()+'/dev/mixtures/mixture_binary_pairs.json'))
```

[11]:
```
# You can obtain interaction parameters either by pairs of names, where name is the␣
↪name that teqp uses, the ["INFO"]["NAME"] field
params, swap_needed = teqp.get_BIPdep(BIP, ['Methane','Ethane'])
params
```

[11]:
```
{'BibTeX': 'Kunz-JCED-2012',
 'CAS1': '74-82-8',
 'CAS2': '74-84-0',
 'F': 1.0,
 'Name1': 'Methane',
 'Name2': 'Ethane',
 'betaT': 0.996336508,
 'betaV': 0.997547866,
 'function': 'Methane-Ethane',
 'gammaT': 1.049707697,
 'gammaV': 1.006617867}
```

[12]:
```
# Or also by CAS#
params, swap_needed = teqp.get_BIPdep(BIP, ['74-82-8','74-84-0'])
params
```

[12]:
```
{'BibTeX': 'Kunz-JCED-2012',
 'CAS1': '74-82-8',
 'CAS2': '74-84-0',
 'F': 1.0,
 'Name1': 'Methane',
 'Name2': 'Ethane',
 'betaT': 0.996336508,
 'betaV': 0.997547866,
 'function': 'Methane-Ethane',
 'gammaT': 1.049707697,
 'gammaV': 1.006617867}
```

[13]:
```
# But mixing is not allowed
params, swap_needed = teqp.get_BIPdep(BIP, ['74-82-8','Ethane'])
params
```

```
---------------------------------------------------------------------------
ValueError                                Traceback (most recent call last)
Cell In[13], line 2
      1 # But mixing is not allowed
----> 2 params, swap_needed = teqp.get_BIPdep(BIP, ['74-82-8','Ethane'])
      3 params

ValueError: Can't match the binary pair for: 74-82-8/Ethane
```

3.7.5 Estimation of interaction parameters

Estimation of interaction parameters can be used when no mixture model is present. The `flags` keyword argument allows the user to control how estimation is applied. The `flags` keyword argument should be a dictionary, with keys of `"estimate"` to provide the desired estimation scheme as-needed. For now, the only allowed estimation scheme is `Lorentz-Berthelot`.

If it is desired to force the estimation, the `"force-estimate"` to force the use of the provided estimation scheme for all binaries, even when a proper mixture model is available. The value associated with `"force-estimate"` is ignored.

[14]:
```
params, swap_needed = teqp.get_BIPdep(BIP, ['74-82-8','74-84-0'], flags={'force-
↪estimate':'yes', 'estimate': 'Lorentz-Berthelot'})
params
```

[14]:
```
{'F': 0.0, 'betaT': 1.0, 'betaV': 1.0, 'gammaT': 1.0, 'gammaV': 1.0}
```

[15]:
```
# And without the force, the forcing is ignored
params, swap_needed = teqp.get_BIPdep(BIP, ['74-82-8','74-84-0'], flags={'estimate':
↪'Lorentz-Berthelot'})
params
```

[15]:
```
{'BibTeX': 'Kunz-JCED-2012',
 'CAS1': '74-82-8',
 'CAS2': '74-84-0',
 'F': 1.0,
 'Name1': 'Methane',
 'Name2': 'Ethane',
 'betaT': 0.996336508,
 'betaV': 0.997547866,
 'function': 'Methane-Ethane',
 'gammaT': 1.049707697,
 'gammaV': 1.006617867}
```

[16]:
```
# And the same flags can be passed to the multifluid model constructor
model = teqp.build_multifluid_model(
    ['74-82-8','74-84-0'],
    teqp.get_datapath(),
    flags={'force-estimate':'yes', 'estimate': 'Lorentz-Berthelot'})
```

3.8 Multfluid mutant

These adapted multifluid models are used for fitting departure functions. The pure fluids remain fixed while you can adjust the mixture model, both the interaction parameters as well as the departure function terms

[1]:
```
import teqp, numpy as np
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
basemodel = teqp.build_multifluid_model(['Nitrogen','Ethane'], teqp.get_datapath())
s = {
    "0": {
        "1": {
            "BIP": {
```

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```
                "betaT": 1.1,
                "gammaT": 0.9,
                "betaV": 1.05,
                "gammaV": 1.3,
                "Fij": 1.0
            },
            "departure":{
                "type": "none"
            }
        }
    }
}
mutant = teqp.build_multifluid_mutant(basemodel, s)
```

[3]:
```
%timeit teqp.build_multifluid_mutant(basemodel, s)
```

```
29 µs ± 2.48 µs per loop (mean ± std. dev. of 7 runs, 10,000 loops each)
```

[4]:
```
mutant.get_Ar01(300, 3.0, np.array([0.5, 0.5]))
```

[4]:
```
-0.00017517184039893556
```

3.9 SAFT-VR-Mie

The SAFT-VR-Mie EOS of Lafitte et al. (https://doi.org/10.1063/1.4819786) is based on the use of a Mie potential of the form

$$u(r) = C\epsilon\left((\sigma/r)^{\lambda_r} - (\sigma/r)^{\lambda_a}\right)$$

with

$$C = \frac{\lambda_r}{\lambda_r - \lambda_a}\left(\frac{\lambda_r}{\lambda_a}\right)^{\lambda_a/(\lambda_r-\lambda_a)}$$

which allows for a better representation of thermodynamic properties in general, but not always.

[1]:
```
import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
import numpy as np
import pandas
import matplotlib.pyplot as plt
import CoolProp.CoolProp as CP
import scipy.integrate
```

[3]:
```
# Show two ways to instantiate a SAFT-VR-Mie model, the
# first by providing the coefficients, and the second
# by providing the name of the species. Only a very small
# number of molecules are provided for testing, you should
# plan on providing your own parameters.
#
```

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```
# Show that both give the same result for the residual pressure

z = np.array([1.0])
model = teqp.make_model({
    "kind": 'SAFT-VR-Mie',
    "model": {
        "coeffs": [{
            "name": "Ethane",
            "BibTeXKey": "Lafitte",
            "m": 1.4373,
            "epsilon_over_k": 206.12, # [K]
            "sigma_m": 3.7257e-10,
            "lambda_r": 12.4,
            "lambda_a": 6.0
        }]
    }
})
display(model.get_Ar01(300, 300, z))

model = teqp.make_model({
    "kind": 'SAFT-VR-Mie',
    "model": {
        "names": ["Ethane"]
    }
})
display(model.get_Ar01(300, 300, z))
```

```
-0.04926724350863724
```

```
-0.04926724350863724
```

[4]:
```
# Here is an example of using teqp to trace VLE for propane
# with the default parameters of PC-SAFT and SAFT-VR-Mie
# models
for kind in ['SAFT-VR-Mie', 'PCSAFT']:
    j = {
        "kind": kind,
        "model": {
            "names": ["Propane"]
        }
    }
    model = teqp.make_model(j)

    z = np.array([1.0])
    Tc, rhoc = model.solve_pure_critical(300, 10000)

    # Extrapolate away from the critical point
    Ti = Tc*0.9997
    rhoL, rhoV = model.extrapolate_from_critical(Tc, rhoc, Ti)

    o = []
    T = Ti
    while T > 88:
        rhoL, rhoV = model.pure_VLE_T(T, rhoL, rhoV, 10)
        T -= 0.1
        o.append({'rhoL': rhoL, 'rhoV': rhoV, 'T': T})
```

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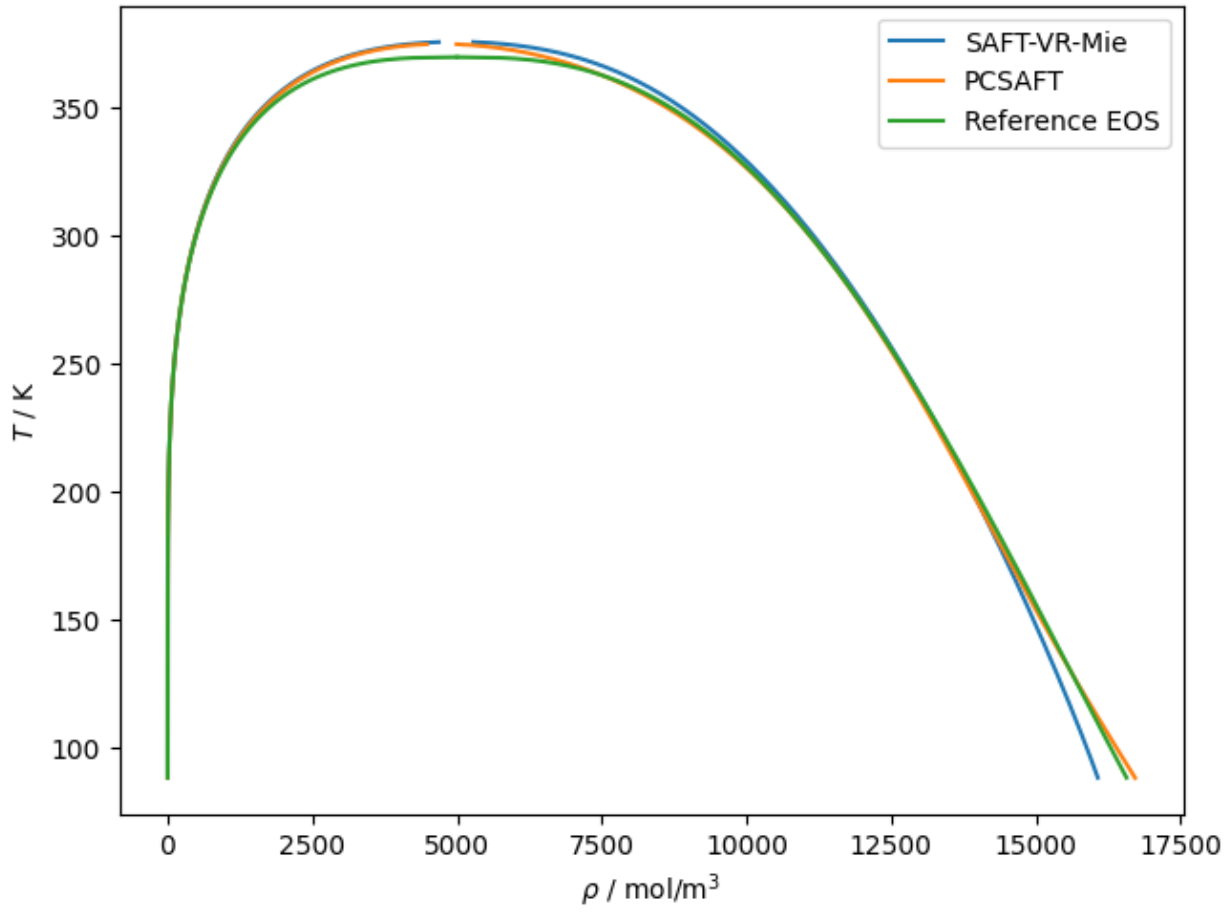
```
    df = pandas.DataFrame(o)
    line, = plt.plot(df['rhoL'], df['T'], label=kind)
    plt.plot(df['rhoV'], df['T'], color=line.get_color())

# From the reference EOS of Lemmon et al. via CoolProp
name = 'Propane'
Tc = CP.PropsSI(name, 'Tcrit')
Ts = np.linspace(88, Tc, 1000)
rhoL = CP.PropsSI('Dmolar','T',Ts,'Q',0,name)
rhoV = CP.PropsSI('Dmolar','T',Ts,'Q',1,name)
line, = plt.plot(rhoL, Ts, label='Reference EOS')
plt.plot(rhoV, Ts, line.get_color())

plt.gca().set(xlabel=r'$\rho$ / mol/m$^3$', ylabel=r'$T$ / K')
plt.legend()
plt.tight_layout(pad=0.2)
plt.savefig('SAFTVRMIE_PCSAFT.pdf')
plt.show()
```



[5]:
```
# Time calculation of critical points
for kind in ['SAFT-VR-Mie', 'PCSAFT']:
    j = {
        "kind": kind,
```

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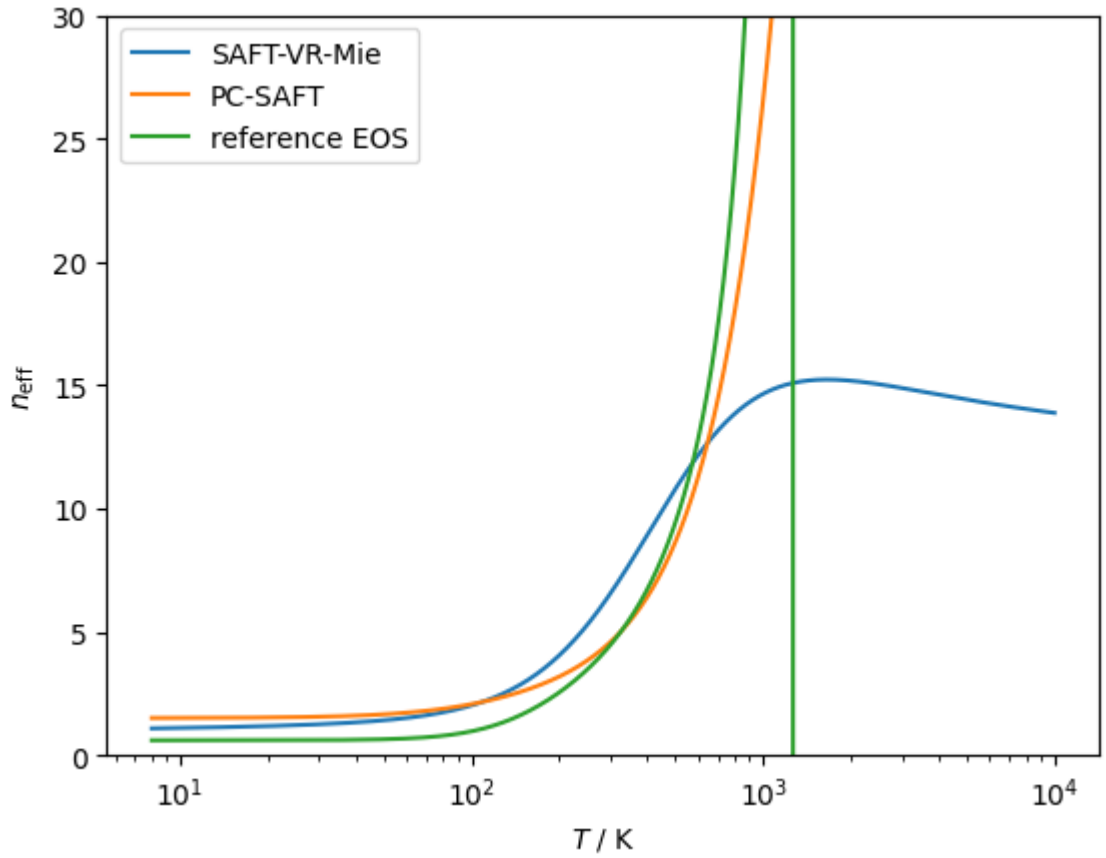
```
        "model": {
            "names": ["Propane"]
        }
    }
    model = teqp.make_model(j)

    z = np.array([1.0])
    %timeit model.solve_pure_critical(300, 10000)
```

```
1.41 ms ± 3.54 µs per loop (mean ± std. dev. of 7 runs, 1,000 loops each)
250 µs ± 668 ns per loop (mean ± std. dev. of 7 runs, 1,000 loops each)
```

[6]:
```
# Checking the effective hardness of interaction,
# the neff parameter defined in https://doi.org/10.1063/5.0007583
# SAFT-VR-Mie comes closest to the right behavior
modelVR = teqp.make_model({
        "kind": 'SAFT-VR-Mie',
        "model": { "names": ["Methane"] }
})
modelPCSAFT = teqp.make_model({
        "kind": 'PCSAFT',
        "model": { "names": ["Methane"] }
})
modelMF = teqp.build_multifluid_model(["Methane"], teqp.get_datapath())

for model, label in [(modelVR, 'SAFT-VR-Mie'),
                     (modelPCSAFT, 'PC-SAFT'),
                     (modelMF, 'reference EOS')]:
    z = np.array([1.0])
    rho = 1e-5
    T = np.geomspace(8, 10000, 10000)
    neff = []
    for T_ in T:
        neff.append(model.get_neff(T_, rho, z))
    plt.plot(T, neff, label=label)
plt.xscale('log')
plt.ylim(0, 30)
plt.gca().set(xlabel=r'$T$ / K', ylabel=r'$n_{\rm eff}$')
plt.legend()
plt.show()
```



[7]:
```
# Checking the temperature derivative of the virial coefficient
name = 'Methane'
modelVR = teqp.make_model({
        "kind": 'SAFT-VR-Mie',
        "model": { "names": [name] }
})
modelPCSAFT = teqp.make_model({
        "kind": 'PCSAFT',
        "model": { "names": [name] }
})
modelMF = teqp.build_multifluid_model([name], teqp.get_datapath())

for model, label in [(modelVR, 'SAFT-VR-Mie'),
                     (modelPCSAFT, 'PC-SAFT'),
                     (modelMF, 'reference EOS')]:
    z = np.array([1.0])
    T = np.geomspace(8, 10000, 10000)
    n = 2
    B, TdBdT, thetan = [],[],[]
    for T_ in T:
        TdBdT.append(model.get_dmBnvirdTm(n, 1, T_, z)*T_)
        B.append(model.get_dmBnvirdTm(n, 0, T_, z))
        thetan.append(B[-1]+TdBdT[-1])
    plt.plot(T, thetan, label=label)
plt.xscale('log')
plt.yscale('log')
```

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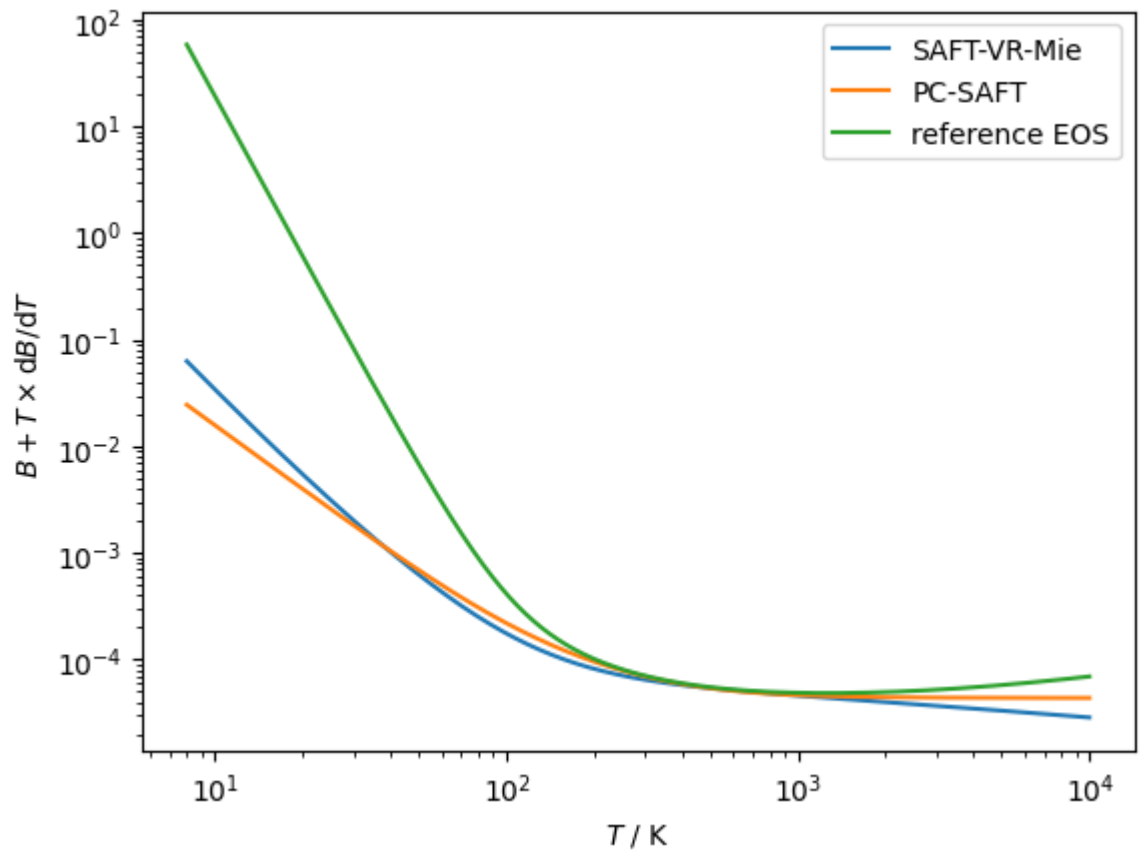
```
plt.gca().set(xlabel=r'$T$ / K', ylabel=r'$B+T\times$d$B$/d$T$')
plt.legend()
plt.show()
```



[8]:
```
# Time model instantiation
for kind in ['SAFT-VR-Mie', 'PCSAFT']:
    j = {
        "kind": kind,
        "model": {
            "names": ["Propane"]
        }
    }
    %timeit teqp.make_model(j)
```

```
1.03 ms ± 2.5 µs per loop (mean ± std. dev. of 7 runs, 1,000 loops each)
431 µs ± 3.51 µs per loop (mean ± std. dev. of 7 runs, 1,000 loops each)
```

3.9.1 Calculation of diameter

The calculation of the diameter is based upon

$$d_{ii} = \int_0^{\sigma_{ii}} (1 - \exp(-\beta u_{ii}^{\text{Mie}}(r))\mathrm{d}r$$

but the integrand is basically constant from 0 to some cutoff value of r, which we'll call r_{cut}. So first we need to find the value of r_{cut} that makes the integrand take its constant value, which is explained well in the paper from Aasen (https://github.com/ClapeyronThermo/Clapeyron.jl/issues/152#issuecomment-1480324192). Finding the cutoff value is obtained when

$$\exp(-\beta u_{ii}^{\text{Mie}}(r)) = EPS$$

where EPS is the numerical precision of the floating point type. Taking the logs of both sides,

$$-\beta u_{ii}^{\text{Mie}} = \ln(EPS)$$

To get a starting value, it is first assumed that only the repulsive contribution contributes to the potential, yielding $u^{\text{rep}} = C\epsilon(\sigma/r)^{\lambda_r}$ which yields

$$-\beta C\epsilon(\sigma/r)^{\lambda_r} = \ln(EPS)$$

and

$$(\sigma/r)_{\text{guess}} = (-\ln(EPS)/(\beta C\epsilon))^{1/\lambda_r}$$

Then we solve for the residual $R(r) = 0$, where $R_0 = \exp(-u/T) - EPS$. Equivalently we can write the residual in logarithmic terms as $R = -u/T - \ln(EPS)$. This simplifies the rootfinding as you need R, R' and R'' to apply Halley's method, which are themselves quite straightforward to obtain because $R' = -u'/T$, $R'' = -u''/T$, where the primes are derivatives taken with respect to σ/r.

[9]:
```
# Calculation of the residual function (needed for Halley's method)
import sympy as sy
kappa, j, lambda_r, lambda_a = sy.symbols('kappa, j, lambda_r, lambda_a')
u = kappa*(j**lambda_r - j**lambda_a)
display(sy.diff(u, j))
display(sy.simplify(sy.diff(u, j, 2)))
```

$$\kappa\left(-\frac{j^{\lambda_a}\lambda_a}{j} + \frac{j^{\lambda_r}\lambda_r}{j}\right)$$

$$\frac{\kappa\left(-j^{\lambda_a}\lambda_a^2 + j^{\lambda_a}\lambda_a + j^{\lambda_r}\lambda_r^2 - j^{\lambda_r}\lambda_r\right)}{j^2}$$

[10]:
```
# Here is a small example of using adaptive quadrature
# to obtain the quasi-exact value of d for ethane
# according to the pure-fluid parameters given in
# Lafitte et al.

epskB = 206.12 # [K]
sigma_m = 3.7257e-10 # [m]
lambda_r = 12.4
lambda_a = 6.0
C = lambda_r/(lambda_r-lambda_a)*(lambda_r/lambda_a)**(lambda_a/(lambda_r-lambda_a))
T = 300.0 # [K]
```

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```
# The classical method based on adaptive quadrature
def integrand(r_m):
    u = C*epskB*((sigma_m/r_m)**(lambda_r) - (sigma_m/r_m)**(lambda_a))
    return 1.0 - np.exp(-u/T)

print('quasi-exact; (value, error estimate):')
exact, exact_error = scipy.integrate.quad(integrand, 0.0, sigma_m, epsrel=1e-16,␣
↪epsabs=1e-16)
print(exact*1e10, exact_error*1e10)

j = {"kind": 'SAFT-VR-Mie', "model": {"names": ["Ethane"]}}
model = teqp.make_model(j)
d = model.get_core_calcs(T, -1, z)["dmat"][0][0]
print('teqp; (value, error from quasi-exact in %)')
print(d, abs(d/(exact*1e10)-1)*100)
```

```
quasi-exact; (value, error estimate):
3.597838592720949 3.228005612223332e-12
teqp; (value, error from quasi-exact in %)
3.597838640613809 1.331156429529301e-06
```

3.10 SAFT-VR-Mie with polar contributions

[1]:
```
import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
import numpy as np
import matplotlib.pyplot as plt
import math
```

[3]:
```
ek = 100 # [K]
sigma_m = 3e-10

N_A = 6.022e23
fig, (ax1, ax2) = plt.subplots(2, 1)

# # From https://arxiv.org/pdf/mtrl-th/9501001.pdf which pulled from M. van Leeuwen␣
↪and B. Smit, Phys. Rev. Lett. 71, 3991 (1993)
# These data need to be rescaled according to Hentschke et al. (DOI: https://doi.org/
↪10.1103/physreve.75.011506)
# mustar2 = [2.5, 3.0, 3.5, 4.0]
# T = [2.63, 3.35, 4.20, 5.07]
# rho = [0.29, 0.25, 0.24, 0.24]
# ax1.plot(mustar2, T, 'd')
# ax2.plot(mustar2, rho, 'd')

# Comparing with Hentschke, DOI: https://doi.org/10.1103/physreve.75.011506
mustar2 = [1, 2, 3, 4]
T = [1.41, 1.60, 1.82, 2.06]
rho = [0.30, 0.31, 0.312, 0.289]
ax1.plot(mustar2, T, 's')
ax2.plot(mustar2, rho, 's')
```

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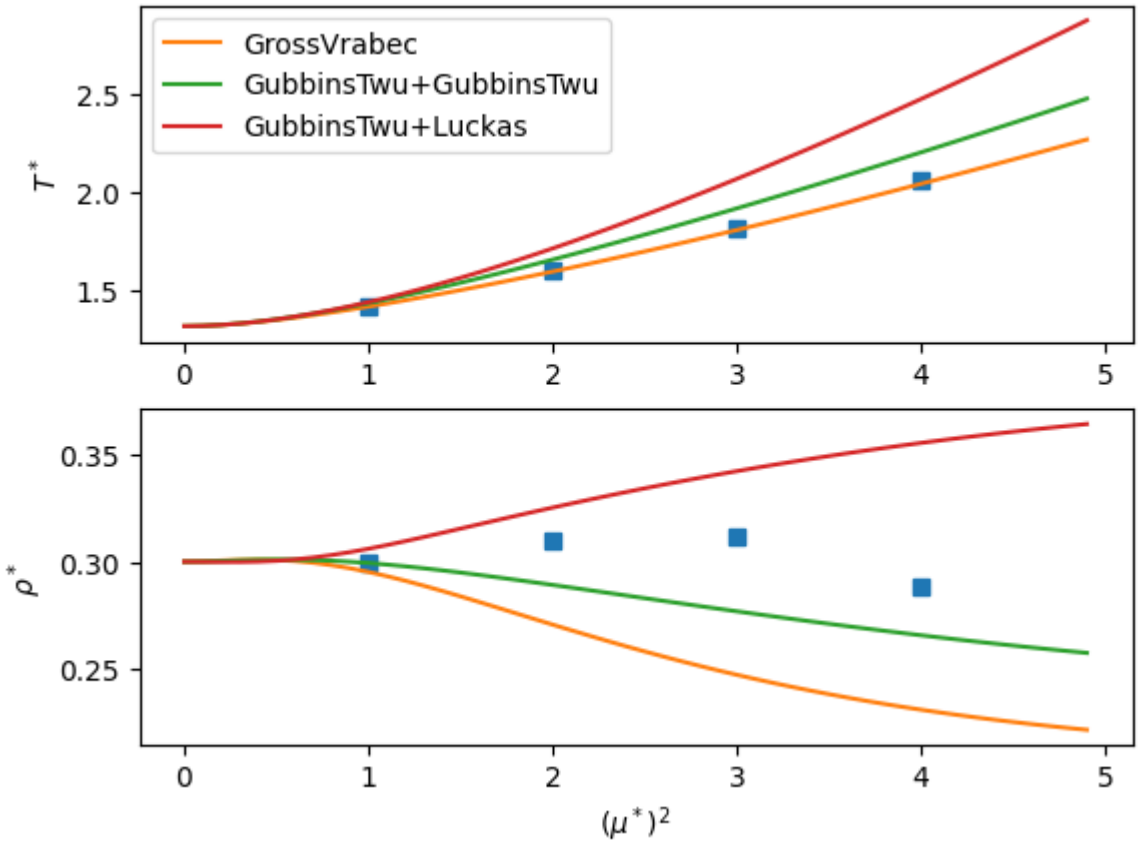
```
kB = 1.380649e-23 # Boltzmann's constant, J/K
epsilon_0 = 8.8541878128e-12 # Vacuum permittivity

for polar_model in ['GrossVrabec','GubbinsTwu+GubbinsTwu','GubbinsTwu+Luckas']:

    x = []; y = []; TT = []; DD = []
    rhostar_guess = 0.27
    Tstar_guess = 1.5
    for mustar2 in np.arange(0.001, 5, 0.1):
        z = np.array([1.0])
        mu2_C2m2 = 4.0*np.pi*epsilon_0*sigma_m**3*ek*kB*mustar2
        mu_Cm = mu2_C2m2**0.5
        model = teqp.make_model({
            "kind": 'SAFT-VR-Mie',
            "model": {
                "polar_model": polar_model,
                "coeffs": [{
                    "name": "Stockmayer",
                    "BibTeXKey": "me",
                    "m": 1.0,
                    "epsilon_over_k": ek, # [K]
                    "sigma_m": sigma_m,
                    "lambda_r": 12.0,
                    "lambda_a": 6.0,
                    "mu_Cm": mu_Cm,
                    "nmu": 1.0
                }]
            }
        })

        T, rho = model.solve_pure_critical(Tstar_guess*ek, rhostar_guess/(N_A*sigma_
↪m**3))
        # Store the values
        x.append(mustar2)
        TT.append(T/ek)
        DD.append(rho*N_A*sigma_m**3)
        # Update the guess for the next calculation
        Tstar_guess = TT[-1]
        rhostar_guess = DD[-1]

    ax1.plot(x, TT, label=polar_model)
    ax2.plot(x, DD)

ax1.legend(loc='best')
ax1.set(ylabel=r'$T^*$')
ax2.set(ylabel=r'$\rho^*$', xlabel=r'$(\mu^*)^2$')
plt.show()
```



3.11 Extended Corresponding States

This implements the method of Huber and Ely: https://doi.org/10.1016/0140-7007(94)90083-3

It does not include the undocumented temperature and density terms that are included in REFPROP

[1]:
```
import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
import numpy as np
import CoolProp.CoolProp as CP
```

[3]:
```
# These parameters are from Huber & Ely
j = {
    "kind": "multifluid-ECS-HuberEly1994",
    "model": {
      "reference_fluid": {
            "name": teqp.get_datapath() + "/dev/fluids/R134a.json",
            "acentric": 0.326680,
            "Z_crit": 4.056e6/(5030.8*8.314471*374.179),
            "T_crit / K": 374.179,
            "rhomolar_crit / mol/m^3": 5030.8
```

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```
      },
      "fluid": {
            "name": "R143a",
            "f_T_coeffs": [ -0.22807e-1, -0.64746],
            "h_T_coeffs": [ 0.36563, -0.26004e-1],
            "acentric": 0.25540,
            "T_crit / K": 346.3,
            "rhomolar_crit / mol/m^3": (1/0.194*1000),
            "Z_crit": 3.76e6/(346.3*8.314471*(1/0.194*1000))
      }
    }
}

model = teqp.make_model(j)
z = np.array([1.0])
R = model.get_R(z)
T, rho = 400, 2600
p = rho*R*T*(1+model.get_Ar01(T, rho, z))
display('pressure from ECS:', p)

display('pressure from EOS:', CP.PropsSI('P','T',T,'Dmolar',rho,'R143a'))
```

```
'pressure from ECS:'
```

```
5556329.442047298
```

```
'pressure from EOS:'
```

```
5478978.746656995
```

CHAPTER

FOUR

DERIVATIVES

4.1 Thermodynamic Derivatives

4.1.1 Helmholtz energy derivatives

Thermodynamic derivatives are at the very heart of teqp. All models are defined in the form $\alpha^r(T, \rho, z)$, where ρ is the molar density, and z are mole fractions. There are exceptions for models for which the independent variables are in simulation units (Lennard-Jones and its ilk).

Thereofore, to obtain the residual pressure, it is obtained as a derivative:

$$p^r = \rho RT\left(\rho\left(\frac{\partial \alpha^r}{\partial \rho}\right)_T\right)$$

and other residual thermodynamic properties are defined likewise.

We can define the concise derivative

$$\Lambda^r_{xy} = (1/T)^x(\rho)^y\left(\frac{\partial^{x+y}(\alpha^r)}{\partial(1/T)^x\partial\rho^y}\right)$$

so we can re-write the derivative above as

$$p^r = \rho RT\Lambda^r_{01}$$

Similar definitions apply for all the other thermodynamic properties, with the tot superscript indicating it is the sum of the residual and ideal-gas (not included in teqp) contributions:

$$\frac{p}{\rho RT} = 1 + \Lambda^r_{01}$$

Internal energy ($u = a + Ts$):

$$\frac{u}{RT} = \Lambda^{\mathrm{tot}}_{10}$$

Enthalpy ($h = u + p/\rho$):

$$\frac{h}{RT} = 1 + \Lambda^r_{01} + \Lambda^{\mathrm{tot}}_{10}$$

Entropy ($s \equiv -(\partial a/\partial T)_v$):

$$\frac{s}{R} = \Lambda^{\mathrm{tot}}_{10} - \Lambda^{\mathrm{tot}}_{00}$$

Gibbs energy ($g = h - Ts$):

$$\frac{g}{RT} = 1 + \Lambda_{01}^r + \Lambda_{00}^{\text{tot}}$$

Derivatives of pressure:

$$\left(\frac{\partial p}{\partial \rho}\right)_T = RT\left(1 + 2\Lambda_{01}^r + \Lambda_{02}^r\right)$$

$$\left(\frac{\partial p}{\partial T}\right)_\rho = R\rho\left(1 + \Lambda_{01}^r - \Lambda_{11}^r\right)$$

Isochoric specific heat ($c_v \equiv (\partial u/\partial T)_v$):

$$\frac{c_v}{R} = -\Lambda_{20}^{\text{tot}}$$

Isobaric specific heat ($c_p \equiv (\partial h/\partial T)_p$; see Eq. 3.56 from Span [**?**] for the derivation):

$$\frac{c_p}{R} = -\Lambda_{20}^{\text{tot}} + \frac{(1 + \Lambda_{01}^r - \Lambda_{11}^r)^2}{1 + 2\Lambda_{01}^r + \Lambda_{02}^r}$$

[1]:
```
import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
import numpy as np
```

[3]:
```
Tc_K = [300]
pc_Pa = [4e6]
acentric = [0.01]
model = teqp.canonical_PR(Tc_K, pc_Pa, acentric)
```

[4]:
```
z = np.array([1.0])
model.get_Ar01(300,300,z)
```

[4]:
```
-0.06836660379313926
```

And there are additional methods to obtain all the derivatives up to a given order:

[5]:
```
model.get_Ar06n(300,300,z) # derivatives 00, 01, 02, ... 06
```

[5]:
```
array([-6.96613834e-02, -6.83666038e-02,  2.53578225e-03, -1.57011622e-04,
        1.68186288e-05, -2.23059409e-06,  3.82592585e-07])
```

But more derivatives are slower than fewer:

[6]:
```
%timeit model.get_Ar01(300,300,z)
%timeit model.get_Ar04n(300,300,z)
```

```
593 ns ± 2.24 ns per loop (mean ± std. dev. of 7 runs, 1,000,000 loops each)
1.19 µs ± 2.88 ns per loop (mean ± std. dev. of 7 runs, 1,000,000 loops each)
```

Note: calling overhead is usually on the order of 1 microsecond

4.1.2 Virial coefficients

Virial coefficients represent the thermodynamics of the interaction of two-, three-, … bodies interacting with each other. They can be obtained rigorously if the potential energy surface of interaction is fully known. In general, such a surface can only be constructed for small rigid molecules. Many simple thermodynamic models do a poor job of predicting the thermodynamics captured by the virial coefficients.

The i-th virial coefficient is defined by

$$B_i = \frac{(\alpha^r)^{(i-1)}}{(i-2)!}$$

with the concise derivative term

$$(\alpha^r)^{(i)} = \lim_{\rho \to 0} \left(\frac{\partial^i \alpha^r}{\partial \rho^i} \right)_{T,\vec{x}}$$

teqp supports the virial coefficient directly, there is the `get_B2vir` method for the second virial coefficient:

```
[7]: model.get_B2vir(300, z)
```

```
[7]: -0.00023661263734465424
```

And the `get_Bnvir` method that allows for the calculation of higher virial coefficients:

```
[8]: model.get_Bnvir(7, 300, z)
```

```
[8]: {2: -0.0002366126373446542,
 3: 3.001768410777936e-08,
 4: -3.2409760373816364e-12,
 5: 3.961781646633723e-16,
 6: -4.5529239838367004e-20,
 7: 5.375927851118494e-24}
```

The `get_Bnvir` method was implemented because when doing automatic differentiation, all the intermediate derivatives are also retained.

There is also a method to calculate temperature derivatives of a given virial coefficient

```
[9]: model.get_dmBnvirdTm(2, 3, 300, z) # third temperature derivative of the second␣
↪virial coefficient
```

```
[9]: 1.0095625628421257e-10
```

4.1.3 Isochoric Thermodynamics Derivatives

In the isochoric thermodynamics formalism, the EOS is expressed in the Helmholtz energy density Ψ as a function of temperature and molar densities $\vec{\rho}$. This formalism is handy because it allows for a concise mathematical structure, well suited to implementation in teqp. For instance the pressure is obtained from (see https://doi.org/10.1002/aic.16074):

$$p = -\Psi + \sum_{i=1}^{N} \rho_i \mu_i$$

with the chemical potential μ_i obtained from

$$\mu_i = \left(\frac{\partial \Psi}{\partial \rho_i} \right)_{T,\rho_{j \neq i}}$$

The molar densities ρ_i are related to the total density and the mole fractions:

$$\rho_i = x_i \rho$$

In teqp, the isochoric derivative functions like `get_fugacity_coefficients`, `get_partial_molar_volumes` take as arguments the temperature `T` and the vector of molar concentrations `rhovec`=$\vec{\rho}$, which are obtained by multiplying the mole fractions by the total density.

Example:

[10]:
```
model = teqp.build_multifluid_model(["CO2","Argon"], teqp.get_datapath())
T, rhovec = 300, np.array([0.3,0.4])*300 # K, mol/m^3
display(model.get_fugacity_coefficients(T, rhovec))
display(model.get_partial_molar_volumes(T, rhovec))
```

```
array([0.97884567, 0.99866748])
```

```
array([0.00470644, 0.00480351])
```

4.2 Term conversion

$$\alpha_0 = \frac{a_0}{RT} = -1 + \ln\frac{\rho T}{\rho_0 T_0} + \frac{h_0^0}{RT} - \frac{s_0^0}{R} + \frac{1}{RT}\int_{T_0}^{T} c_p^0(T)dT - \frac{1}{R}\int_{T_0}^{T}\frac{c_p^0(T)}{T}dT$$

$$\alpha_0 = \frac{a_0}{RT} = \ln(\rho) + \ln(T) - \ln(\rho_0 T_0) - 1 + \frac{h_0^0}{RT} - \frac{s_0^0}{R} + \frac{1}{RT}\int_{T_0}^{T} c_p^0(T)dT - \frac{1}{R}\int_{T_0}^{T}\frac{c_p^0(T)}{T}dT$$

You can set the values of h_0^0 and h_0^0 to any value, including zero. So if you are converting a term from c_p^0/R, then you could do

$$\alpha_0 = \frac{a_0}{RT} = \ln(\rho) + \ln(T) - \ln(\rho_0 T_0) - 1 + \frac{1}{RT}\int_{T_0}^{T} c_p^0(T)dT - \frac{1}{R}\int_{T_0}^{T}\frac{c_p^0(T)}{T}dT$$

4.2.1 From CP0

Terms obtained in the form of contributions to c_p^0/R.

Constant term

A constant term of the form

$$c_p^0/R = c$$

yields a contribution of

$$\frac{c(T-T_0)}{T} - c\log\left(\frac{T}{T_0}\right)$$

Power term

A power term of the form

$$c_p^0/R = cT^t, t \neq 0, t \neq -1$$

yields a contribution of

$$cT^t\left(\frac{1}{t+1} - \frac{1}{t}\right) - c\frac{T_0^{t+1}}{T(t+1)} + c\frac{T_0^t}{t}$$

Planck-Einstein term

A term of the form

$$c_p^0/R = \sum_k a_k \frac{(b_k/T)^2 \exp(b_k/T)}{(\exp(b_k/T) - 1)^2}$$

yields a contribution of

$$\sum_k a_k \ln\left[1 - \exp\left(\frac{-\theta_k}{T}\right)\right]$$

[1]:
```
import teqp, os, numpy as np
teqp.__version__
```

[1]:
```
'0.17.0'
```

[2]:
```
path = teqp.get_datapath()+'/dev/fluids/n-Propane.json'
os.path.exists(path)
jig = teqp.convert_CoolProp_idealgas(path, 0)
aig = teqp.IdealHelmholtz([jig])
-aig.get_Ar20(300, 3, np.array([1.0]))
```

[2]:
```
7.863830967842212
```

CHAPTER

FIVE

ALGORITHMS

5.1 Phase equilibria

Two basic approaches are implemented in teqp:

- Iterative calculations given guess values
- Tracing along iso-curves (constant temperature, etc.) powered by the isochoric thermodynamics formalism

[1]:
```
import teqp
import numpy as np
import pandas
import matplotlib.pyplot as plt
teqp.__version__
```

[1]:
```
'0.17.0'
```

5.1.1 Iterative Phase Equilibria

Pure fluid

For a pure fluid, phase equilibrium between two phases is defined by equating the pressures and Gibbs energies in the two phases. This represents a 2D non-linear rootfinding problem. Newton's method can be used for the rootfinding, and in teqp, automatic differentiation is used to obtain the necessary Jacobian matrix so the implementation is quite efficient.

The method requires guess values, which are the densities of the liquid and vapor densities. In some cases, ancillary or superancillary equations have been developed which provide curves of guess densities as a function of temperature.

For a pure fluid, you can use the `pure_VLE_T` method to carry out the iteration.

The Python method is here: `pure_VLE_T`

[2]:
```
# Instantiate the model
model = teqp.canonical_PR([300], [4e6], [0.1])

T = 250 # [K], Temperature to be used

# Here we use the superancillary to get guess values (actually these are more
# accurate than the results we will obtain from iteration!)
rhoL0, rhoV0 = model.superanc_rhoLV(T)
display('guess:', [rhoL0, rhoV0])

# Carry out the iteration, return the liquid and vapor densities
```

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```
# The guess values are perturbed to make sure the iteration is actually
# changing the values
model.pure_VLE_T(T, rhoL0*0.98, rhoV0*1.02, 10)
```

```
'guess:'
```

```
[12735.311173407898, 752.4082303122791]
```

[2]:
```
array([12735.31117341,   752.40823031])
```

Binary Mixture

For a binary mixture, the approach is roughly similar to that of a pure fluid. The pressure is equated between phases, and the chemical potentials of each component in each phase are forced to be the same.

Again, the user is required to provide guess values, in this case molar concentrations in each phase, and a Newton method is implemented to solve for the phase equilibrium. The analytical Jacobian is obtained from automatic differentiation.

The `mix_VLE_Tx` function is the binary mixture analog to `pure_VLE_T` for pure fluids.

The Python method is here: `mix_VLE_Tx`

[3]:
```
zA = np.array([0.01, 0.99])
model = teqp.canonical_PR([300,310], [4e6,4.5e6], [0.1, 0.2])
model1 = teqp.canonical_PR([300], [4e6], [0.1])
T = 273.0 # [K]
# start off at pure of the first component
rhoL0, rhoV0 = model1.superanc_rhoLV(T)

# then we shift to the given composition in the first phase
# to get guess values
rhovecA0 = rhoL0*zA
rhovecB0 = rhoV0*zA

# carry out the iteration
code, rhovecA, rhovecB = model.mix_VLE_Tx(T, rhovecA0, rhovecB0, zA,
     1e-10, 1e-10, 1e-10, 1e-10,  # stopping conditions
     10 # maximum number of iterations
    )
code, rhovecA, rhovecB
```

[3]:
```
(<VLE_return_code.xtol_satisfied: 1>,
 array([  128.66049209, 12737.38871682]),
 array([  12.91868229, 1133.77242677]))
```

You can (and should) check the value of the return code to make sure the iteration succeeded. Do not rely on the numerical value of the enumerated return codes!

5.2 Tracing (isobars and isotherms)

When it comes to mixture thermodynamics, as soon as you add another component to a pure component to form a binary mixture, the complexity of the thermodynamics entirely changes. For that reason, mixture iterative calculations for mixtures are orders of magnitude more difficult to carry out. Asymmetric mixtures can do all sorts of interesting things that are entirely unlike those of pure fluids, and the algorithms are therefore much, much more complicated. Formulating phase equilibrium problems is not much more complicated than for pure fluids, but the most challenging aspect is to obtain good guess values from which to start an iterative routine, and the difficulty of this problem increases with the complexity of the mixture thermodynamics.

Ulrich Deiters and Ian Bell have developed a number of algorithms for tracing phase equilibrium solutions as the solution of ordinary differential equations rather than carrying out iterative routines for a given state point. The advantage of the tracing calculations is that they can often be initiated at a state point that is entirely known, for instance the pure fluid endpoint for a subcritical isotherm or isobar.

The Python method is here: `trace_VLE_isotherm_binary`

The C++ implementation returns a string in JSON format, which can be conveniently operated upon, for instance after converting the returned data structure to a `pandas.DataFrame`. A simple example of plotting a subcritical isotherm for a "boring" mixture is presented here:

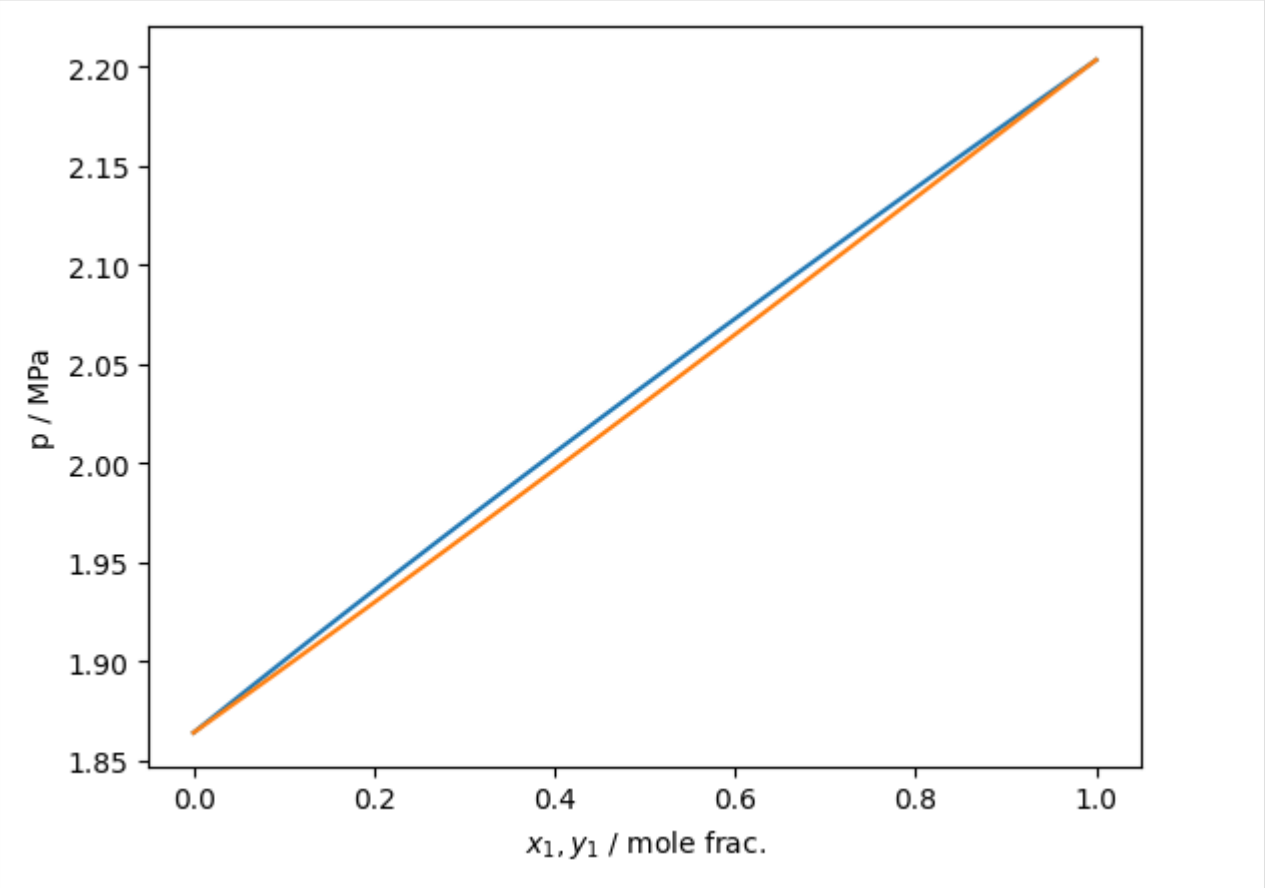
[4]:
```
model = teqp.canonical_PR([300,310], [4e6,4.5e6], [0.1, 0.2])
model1 = teqp.canonical_PR([300], [4e6], [0.1])
T = 273.0 # [K]
rhoL0, rhoV0 = model1.superanc_rhoLV(T) # start off at pure of the first component
j = model.trace_VLE_isotherm_binary(T, np.array([rhoL0, 0]), np.array([rhoV0, 0]))
display(str(j)[0:100]+'...') # The first few bits of the data
df = pandas.DataFrame(j) # Now as a data frame
df.head(3)
```

```
"[{'T / K': 273.0, 'c': -1.0, 'drho/dt': [-0.618312383229212, 0.7690760182230469, -0.
↪1277526773161415…"
```

[4]:

	T / K	c	drho/dt	dt	pL / Pa	pV / Pa	rhoL / mol/m^3	rhoV / mol/m^3	t	xL_0 / mole frac.	xV_0 / mole frac.
0	273.0	-1.0	[-0.618312383229212, 0.7690760182230469, -0.12…	0.000010	2.203397e+06	2.203397e+06	[10697.985891540735, 0.0]	[1504.6120879290752, 0.0]	0.000000	1.0	1.0
1	273.0	-1.0	[-0.6183123817120353, 0.7690760162922189, -0.1…	0.000045	2.203397e+06	2.203397e+06	[10697.985885357639, 7.690760309421386e-06]	[1504.6120866515366, 9.945415375682985e-07]	0.000010	1.0	1.0
2	273.0	-1.0	[-0.6183123827116788, 0.7690760173388914, -0.1…	0.000203	2.203397e+06	2.203397e+06	[10697.98585753358, 4.229918121248511e-05]	[1504.6120809026731, 5.469978386095445e-06]	0.000055	1.0	1.0

[5]:
```
plt.plot(df['xL_0 / mole frac.'], df['pL / Pa']/1e6)
plt.plot(df['xV_0 / mole frac.'], df['pL / Pa']/1e6)
plt.gca().set(xlabel='$x_1,y_1$ / mole frac.', ylabel='p / MPa')
plt.show()
```



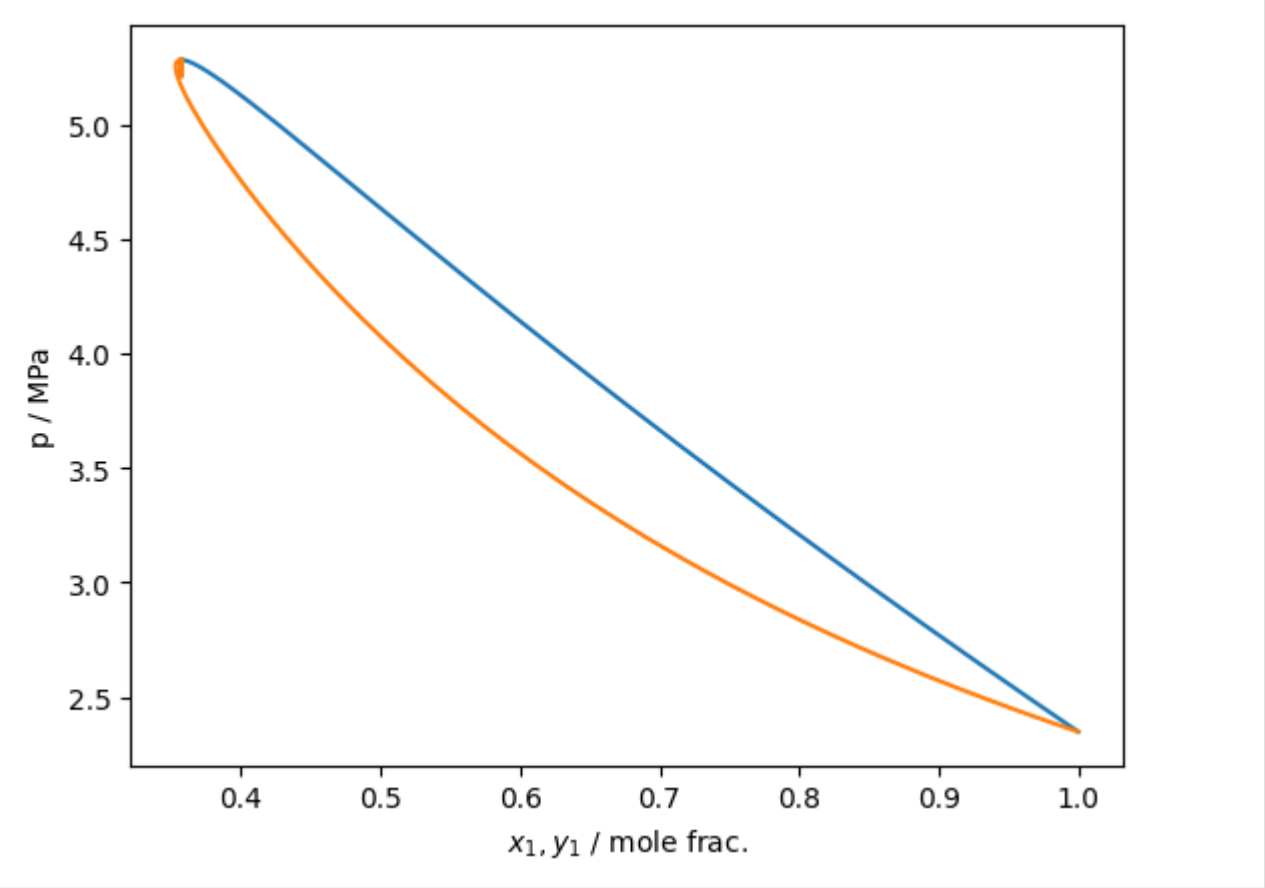
Isn't that exciting!

You can also provide an optional set of flags to the function to control other behaviors of the function, and switch between simple Euler and adaptive RK45 integration (the default)

The options class is here: *TVLEOptions*

Supercritical isotherms work approximately in the same manner

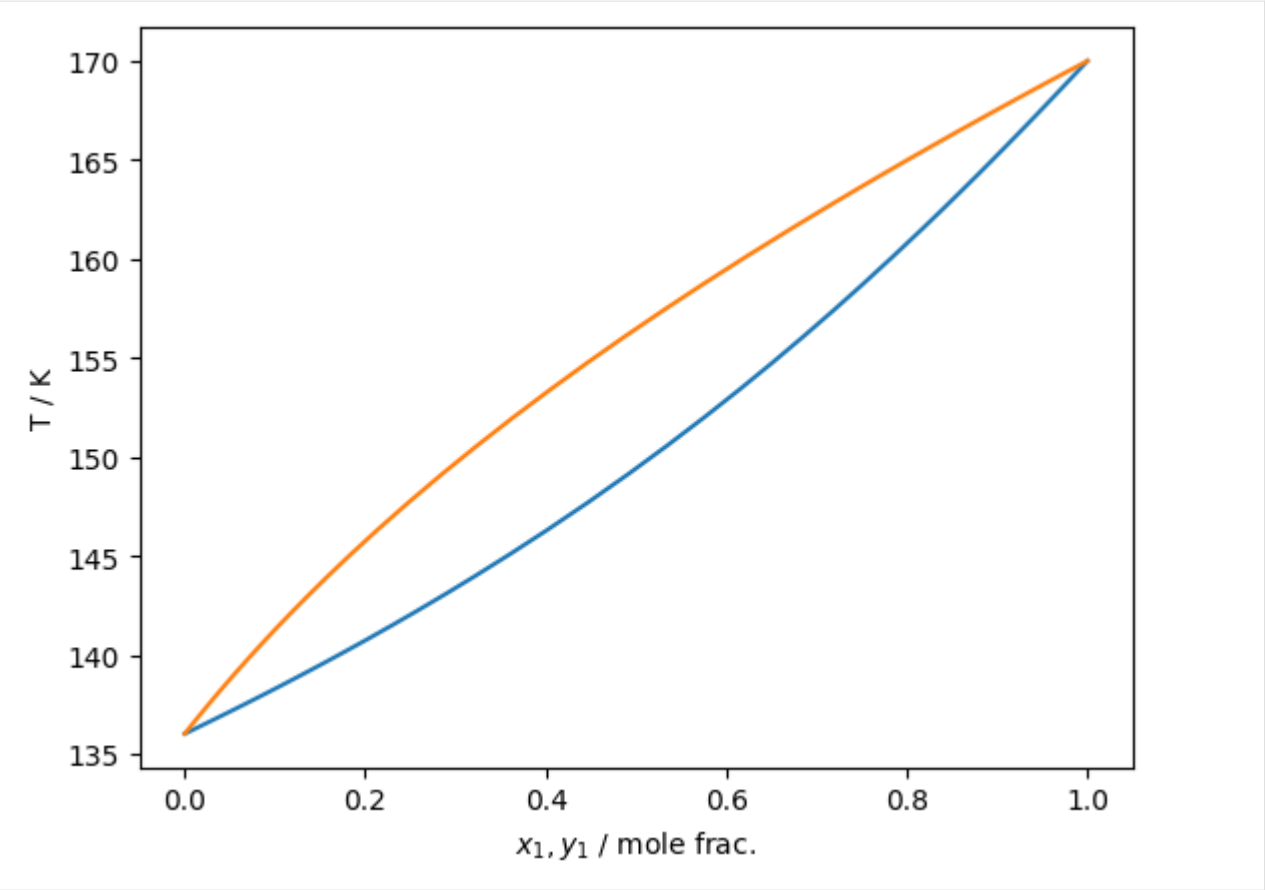
[6]:
```
Tc_K = [190.564, 154.581]
pc_Pa = [4599200, 5042800]
acentric = [0.011, 0.022]
model = teqp.canonical_PR(Tc_K, pc_Pa, acentric)
model1 = teqp.canonical_PR([Tc_K[0]], [pc_Pa[0]], [acentric[0]])
T = 170.0 # [K] # Note: above Tc of the second component
rhoL0, rhoV0 = model1.superanc_rhoLV(T) # start off at pure of the first component
j = model.trace_VLE_isotherm_binary(T, np.array([rhoL0, 0]), np.array([rhoV0, 0]))
df = pandas.DataFrame(j) # Now as a data frame
plt.plot(df['xL_0 / mole frac.'], df['pL / Pa']/1e6)
plt.plot(df['xV_0 / mole frac.'], df['pL / Pa']/1e6)
plt.gca().set(xlabel='$x_1,y_1$ / mole frac.', ylabel='p / MPa')
plt.show()
```



As of version 0.10.0, isobar tracing has been added to `teqp`. It operates in fundamentally the same fashion as the isotherm tracing and the same recommendations about starting at a pure fluid apply

The tracer function class is here: `trace_VLE_isobar_binary`

[7]:
```
Tc_K = [190.564, 154.581]
pc_Pa = [4599200, 5042800]
acentric = [0.011, 0.022]
model = teqp.canonical_PR(Tc_K, pc_Pa, acentric)
model1 = teqp.canonical_PR([Tc_K[0]], [pc_Pa[0]], [acentric[0]])
T = 170.0 # [K] # Note: above Tc of the second component
rhoL0, rhoV0 = model1.superanc_rhoLV(T) # start off at pure of the first component
p0 = rhoL0*model1.get_R(np.array([1.0]))*T*(1+model1.get_Ar01(T, rhoL0, np.array([1.
↪0])))
j = model.trace_VLE_isobar_binary(p0, T, np.array([rhoL0, 0]), np.array([rhoV0, 0]))
df = pandas.DataFrame(j) # Now as a data frame
plt.plot(df['xL_0 / mole frac.'], df['T / K'])
plt.plot(df['xV_0 / mole frac.'], df['T / K'])
plt.gca().set(xlabel='$x_1,y_1$ / mole frac.', ylabel='T / K')
plt.show()
```



5.3 VLLE

Following the approach described in Bell et al.: https://doi.org/10.1021/acs.iecr.1c04703

for the mixture of nitrogen + ethane, with the default thermodynamic model in teqp, which is the GERG-2008 mixing parameters (no departure function).

Two traces are made, and the intersection is obtained, this gives you the VLLE solution.

[1]:
```
import teqp, numpy as np, matplotlib.pyplot as plt, pandas

def get_traces(*, T, ipures):
    names = ['Nitrogen', 'Ethane']
    model = teqp.build_multifluid_model(names, teqp.get_datapath())
    pures = [teqp.build_multifluid_model([name], teqp.get_datapath()) for name in␣
↪names]
    traces = []
    for ipure in ipures:
        # Init at the pure fluid endpoint
        anc = pures[ipure].build_ancillaries()
        rhoLpure, rhoVpure = pures[ipure].pure_VLE_T(T, anc.rhoL(T), anc.rhoV(T), 10)

        rhovecL = np.array([0.0, 0.0])
        rhovecV = np.array([0.0, 0.0])
```

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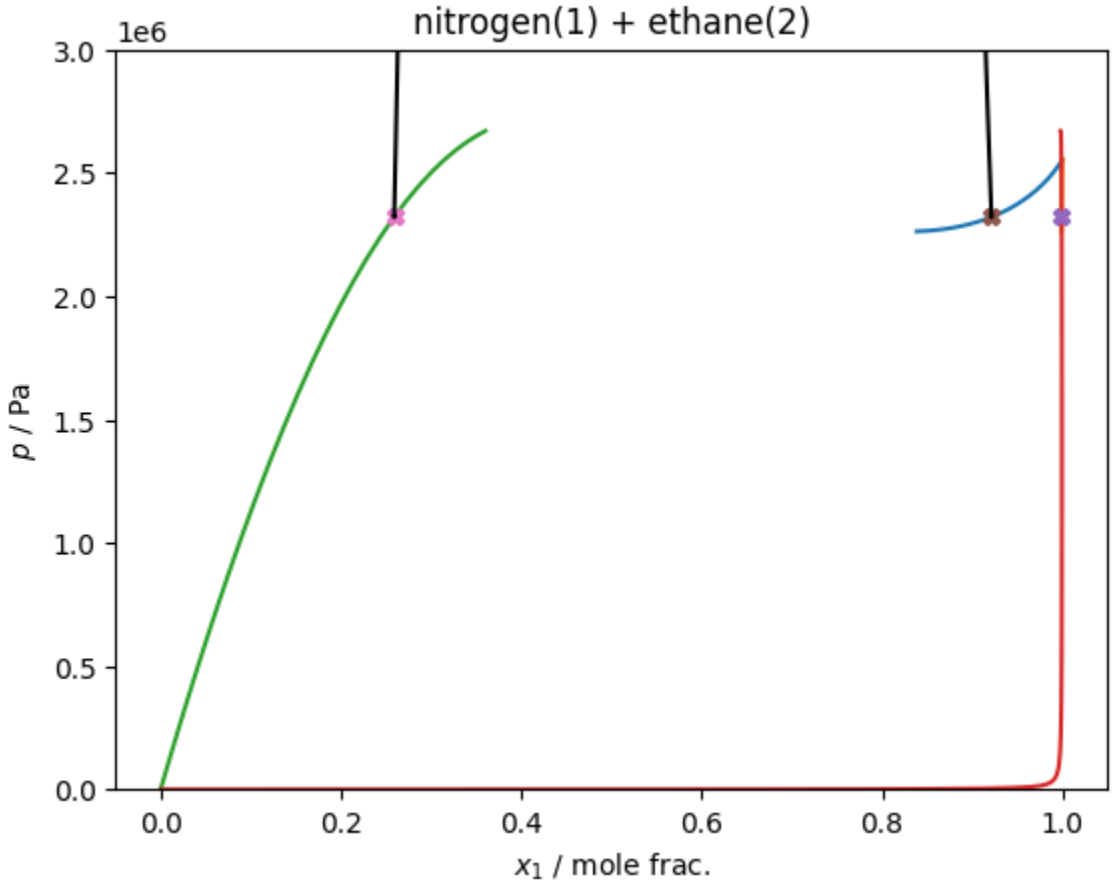
```
        rhovecL[ipure] = rhoLpure
        rhovecV[ipure] = rhoVpure
        opt = teqp.TVLEOptions()
        opt.p_termination = 1e8
        opt.crit_termination=1e-4
        opt.calc_criticality=True
        j = model.trace_VLE_isotherm_binary(T, rhovecL, rhovecV, opt)
        traces.append(j)
    return model, traces

T = 120.3420
model, traces = get_traces(T=T, ipures=[0,1])
for trace in traces:
    df = pandas.DataFrame(trace)
    plt.plot(df['xL_0 / mole frac.'], df['pL / Pa'])
    plt.plot(df['xV_0 / mole frac.'], df['pV / Pa'])

# Do the VLLE solving
for soln in model.find_VLLE_T_binary(traces):
    print('rhovec / mol/m^3 | p / Pa')
    for rhovec in soln['polished']:
        rhovec = np.array(rhovec)
        rhotot = sum(rhovec)
        x = rhovec/rhotot
        p = rhotot*model.get_R(x)*T*(1+model.get_Ar01(T, rhotot, x))
        plt.plot(x[0], p, 'X')
        print(rhovec, p)

    # And also carry out the LLE trace for the two liquid phases
    j = model.trace_VLE_isotherm_binary(T, np.array(soln['polished'][1]), np.
↪array(soln['polished'][2]))
    df = pandas.DataFrame(j)
    plt.plot(df['xL_0 / mole frac.'], df['pL / Pa'], 'k')
    plt.plot(df['xV_0 / mole frac.'], df['pV / Pa'], 'k')

# Plotting niceties
plt.ylim(top=3e6, bottom=0)
plt.gca().set(xlabel='$x_1$ / mole frac.', ylabel='$p$ / Pa', title='nitrogen(1) +␣
↪ethane(2)')
plt.show()
```

```
rhovec / mol/m^3 | p / Pa
[3.66984834e+03 3.25893958e+00] 2321103.087319132
[19890.16767481  1698.86505766] 2321103.087318946
[ 5641.24690517 16140.85769908] 2321103.0873195715
```



[2]:
```
# Trace from both pure fluid endpoints
T = 113
model, traces = get_traces(T=T, ipures = [0,1])

# Find the VLLE solution for the starting temperature
solns = model.find_VLLE_T_binary(traces)
rhovecV, rhovecL1, rhovecL2 = solns[0]['polished']

# Obtain the VLLE trace towards higher temperatures
opt = teqp.VLLETracerOptions()
a = lambda x: np.array(x)
VLLE = model.trace_VLLE_binary(T, a(rhovecV), a(rhovecL1), a(rhovecL2), opt)
df = pandas.DataFrame(VLLE)

# Add the pressure to the DataFrame
def add_ps(row, key):
    T = row['T / K']
    rhovec = np.array(row[key])
    rhotot = sum(rhovec)
    x = rhovec/rhotot
    p = rhotot*model.get_R(x)*T*(1+model.get_Ar01(T, rhotot, x))
    return p
df['p / Pa']  = df.apply(add_ps, axis=1, key='rhoV / mol/m^3')

# Plot the p-T curve
```

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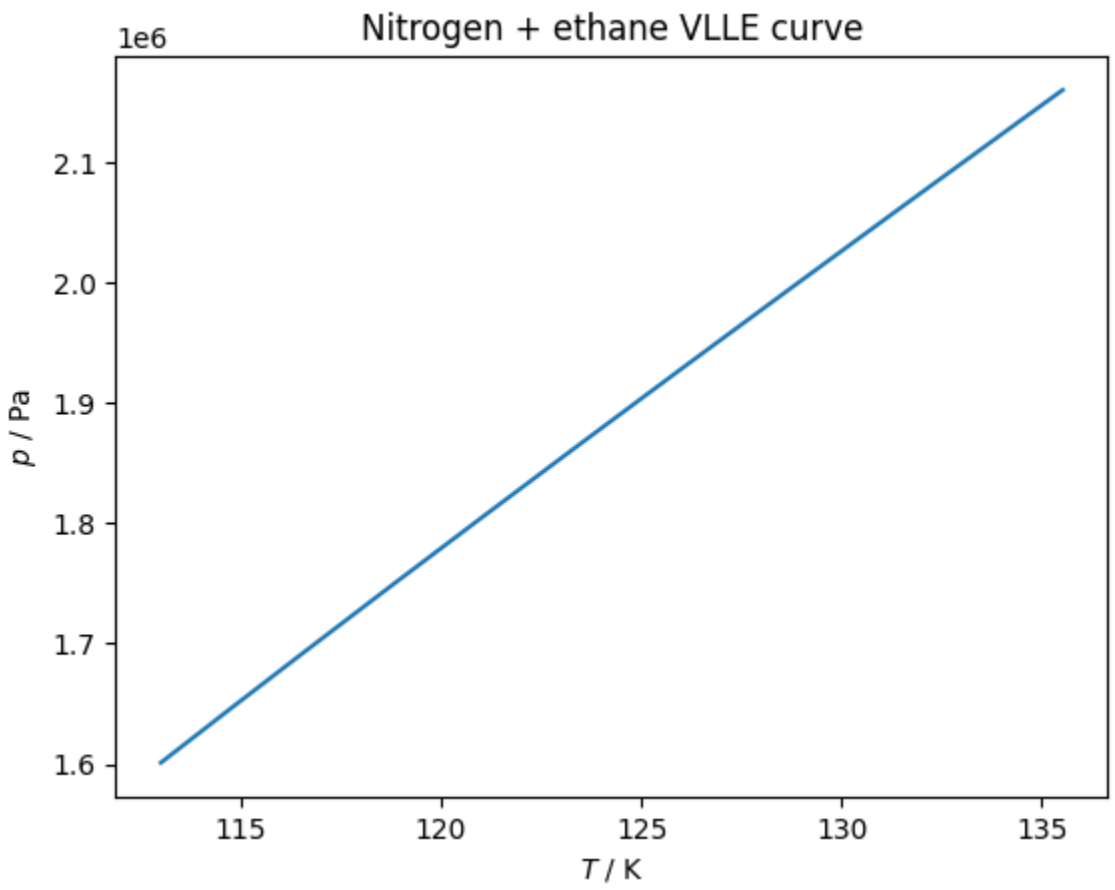
```
plt.plot(df['T / K'], df['p / Pa'])
plt.gca().set(xlabel='$T$ / K', ylabel='$p$ / Pa');
plt.title('Nitrogen + ethane VLLE curve')
```

[2]:
```
Text(0.5, 1.0, 'Nitrogen + ethane VLLE curve')
```



5.4 VLLE @ constant pressure

Following the approach described in Bell et al.: https://doi.org/10.1021/acs.iecr.1c04703, but slightly different because the pressure is fixed rather than the temperature, but the same basic principles hold

for the mixture of nitrogen + ethane, with the default thermodynamic model in teqp, which is the GERG-2008 mixing parameters (no departure function).

Two traces are made, and the intersection is obtained, this gives you the VLLE solution.

[1]:
```
import teqp, numpy as np, matplotlib.pyplot as plt, pandas
import CoolProp.CoolProp as CP

names = ['Nitrogen', 'Ethane']
model = teqp.build_multifluid_model(names, teqp.get_datapath())
pures = [teqp.build_multifluid_model([name], teqp.get_datapath()) for name in names]
p = 29e5 # Pa
```

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```
# Trace from both pure fluid endpoints
traces = []
for ipure in [1,0]:
    # Init at the pure fluid endpoint
    anc = pures[ipure].build_ancillaries()
    rhoLpure, rhoVpure = [CP.PropsSI('Dmolar','P',p,'Q',Q,names[ipure]) for Q in [0,
↪1]]
    T = CP.PropsSI('T','P',p,'Q',0,names[ipure])

    rhovecL = np.array([0.0, 0.0])
    rhovecV = np.array([0.0, 0.0])
    rhovecL[ipure] = rhoLpure
    rhovecV[ipure] = rhoVpure
    j = model.trace_VLE_isobar_binary(p, T, rhovecL, rhovecV)
    df = pandas.DataFrame(j)
    plt.plot(df['xL_0 / mole frac.'], df['T / K'])
    plt.plot(df['xV_0 / mole frac.'], df['T / K'])
    traces.append(j)

# Do the VLLE solving
for soln in model.find_VLLE_p_binary(traces):
    T = soln['polished'][-1]
    print('rhovec / mol/m^3 | T / K')
    for rhovec in soln['polished'][0:3]:
        rhovec = np.array(rhovec)
        rhotot = sum(rhovec)
        x = rhovec/rhotot
        p = rhotot*model.get_R(x)*T*(1+model.get_Ar01(T, rhotot, x))
        plt.plot(x[0], T, 'X')
        print(rhovec, T)

    # And also carry out the LLE trace for the two liquid phases
    opt = teqp.PVLEOptions()
    opt.integration_order = 5
    opt.init_dt = 1e-10
    # Or could be 1 depending on the initial integration direction, do not know the␣
↪direction
    # a priori because not starting at a pure fluid endpoint
    for init_dt in [-1]:
        opt.init_c = init_dt
        rhovecV, rhovecL1, rhovecL2, T = soln['polished']
        j = model.trace_VLE_isobar_binary(p, T, np.array(rhovecL1), np.
↪array(rhovecL2), opt)
        df = pandas.DataFrame(j)
        plt.plot(df['xL_0 / mole frac.'], df['T / K'], 'k')
        plt.plot(df['xV_0 / mole frac.'], df['T / K'], 'k')

# Plotting niceties
plt.ylim(top=280, bottom=100)
plt.gca().set(xlabel='$x_1$ / mole frac.', ylabel='$T$ / K', title='nitrogen(1) +␣
↪ethane(2)')
plt.show()
```

```
rhovec / mol/m^3 | T / K
[4921.97976373    9.6755684 ] 125.14729018874252
[ 6008.68040253 15630.22353351] 125.14729018874252
```

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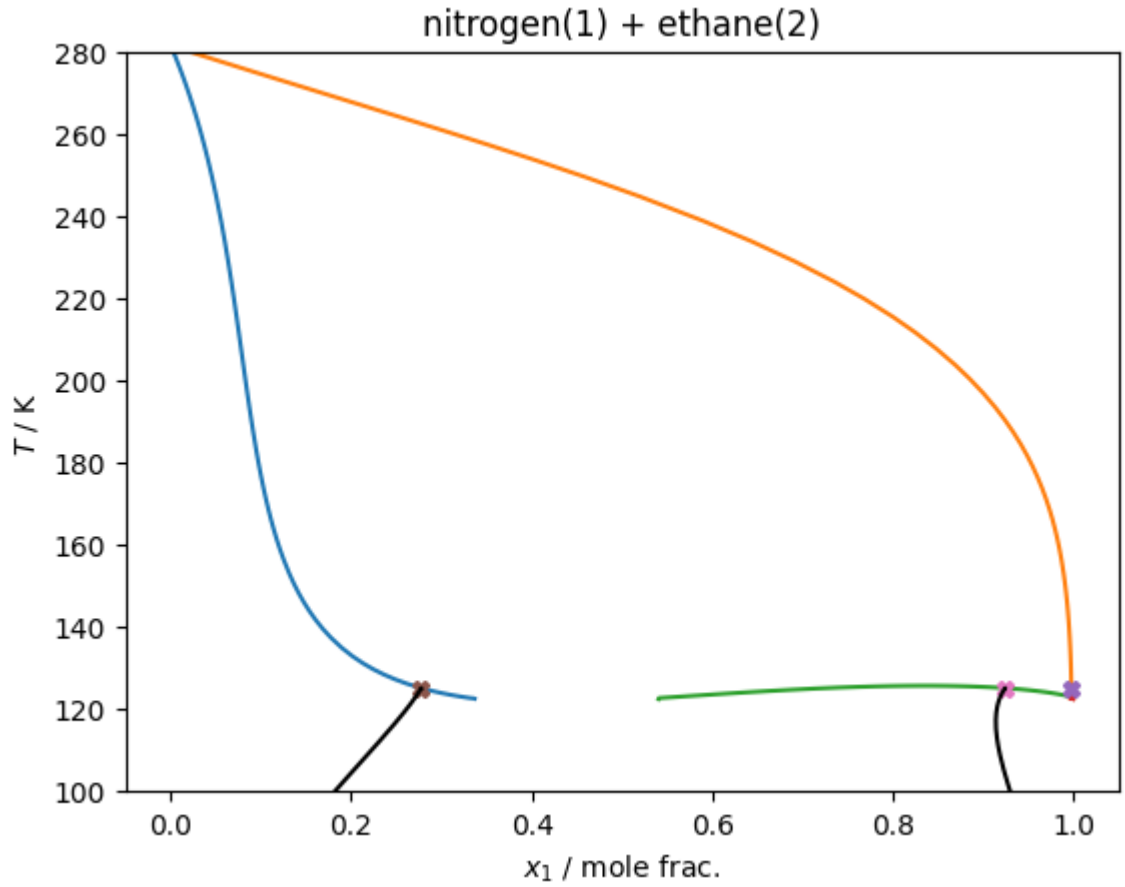
```
[18948.39537895  1540.60935171] 125.14729018874252
```



[1]:
```
import scipy.interpolate
import teqp
teqp.__version__
```

[1]:
```
'0.17.0'
```

5.5 Critical curves & points

5.5.1 Pure Fluids

Solving for the critical point involves finding the temperature and density that make

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \left(\frac{\partial^2 p}{\partial \rho^2}\right)_T = 0$$

by 2D non-linear rootfinding. Newton steps are taken, and the analytic Jacobian is used (thanks to the ability to do derivatives with automatic differentiation). This is all handily wrapped up in the `solve_pure_critical` method which requires the user to provide guess values for temperature and density

[2]:
```
# Values taken from http://dx.doi.org/10.6028/jres.121.011
modelPR = teqp.canonical_PR([190.564], [4599200], [0.011])

# Solve for the critical point from a point close to the critical point
T0 = 192.0
# Critical compressibility factor of P-R is 0.307401308698.. (see https://doi.org/10.
↪1021/acs.iecr.1c00847)
rhoc = (4599200/(8.31446261815324*190.564))/0.3074
rho0 = rhoc*1.2345 # Perturb to make sure we are doing something in the solver
modelPR.solve_pure_critical(T0, rho0)
```

[2]:
```
(190.564, 9442.816240022832)
```

5.5.2 Mixtures

A pure fluid has a single vapor-liquid critical point, but mixtures are different:

- They may have multiple (or zero!) critical points for a given mixture composition
- The critical curves may not emanate from the pure fluid endpoints

When it comes to critical points, intuition from pure fluids is not helpful, or sometimes even counter-productive.

teqp has methods for working with the critical loci of binary mixtures (only binary mixtures, for now) and especially, methods for tracing the critical curves emanating from the pure fluid endpoints.

The tracing method in teqp is based explicitly on the isochoric thermodynamics formalism introduced by Ulrich Deiters and Sergio Quinones-Cisneros. It uses the Helmholtz energy density as the fundamental potential and all other properties are derived from it. For critical curves it is based upon the integration of sets of ordinary differential equations; the differential equations are in the form of derivatives of the molar concentrations of each component in the mixture with respect to an integration variable. The set of ODE is then integrated.

Here is an example of the construction of the critical curves emanating from the pure fluid endpoints for the mixture nitrogen + ethane.

[3]:
```
import timeit
import numpy as np
import matplotlib.pyplot as plt
import pandas
import teqp

def get_critical_curve(ipure):
    """ Return curve as pandas DataFrame """
    names = ['Nitrogen', 'Ethane']
    model = teqp.build_multifluid_model(names, teqp.get_datapath())
    T0 = model.get_Tcvec()[ipure]
    rho0 = np.array([1.0/model.get_vcvec()[ipure]]*2)
    rho0[1-ipure] = 0
    o = teqp.TCABOptions()
    o.init_dt = 1.0 # step in the arclength tracing parameter
    o.rel_err = 1e-8
    o.abs_err = 1e-5
    o.integration_order = 5
    o.calc_stability = True
    o.polish = True
    curveJSON = model.trace_critical_arclength_binary(T0, rho0, '', o)
    df = pandas.DataFrame(curveJSON)
    rhotot = df['rho0 / mol/m^3']+df['rho1 / mol/m^3']
```

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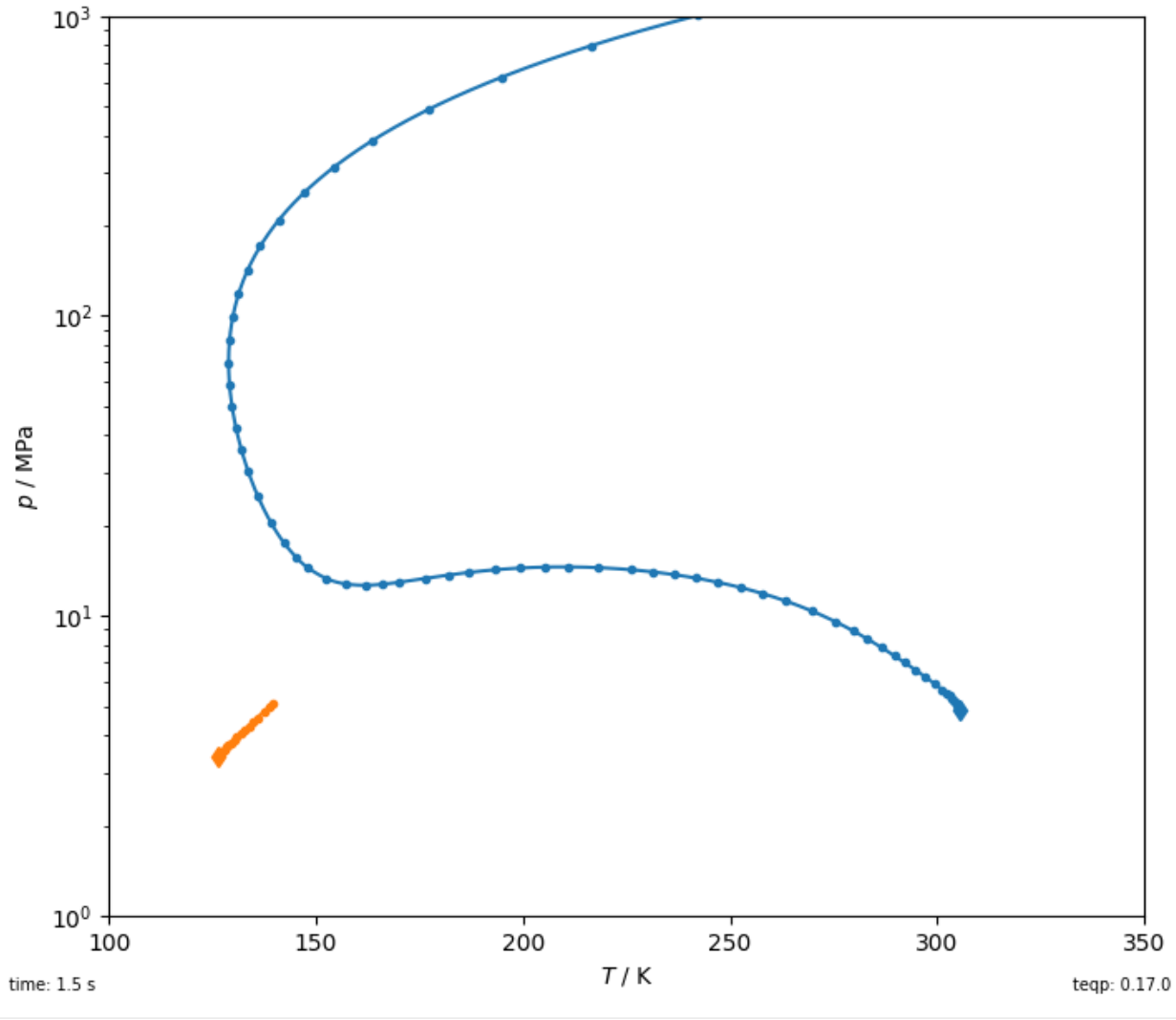
```
    df['z0 / mole frac.'] = df['rho0 / mol/m^3']/rhotot
    return df

fig, ax = plt.subplots(1,1,figsize=(7, 6))
tic = timeit.default_timer()
for ipure in [1,0]:
    df = get_critical_curve(ipure)
    first_unstable = np.argmax(~df['locally stable'])
    df = df.iloc[0:(first_unstable if first_unstable else len(df))]
    line, = plt.plot(df['T / K'], df['p / Pa']/1e6, '.')

    # And interpolate to smooth out the curve using the arclength
    # parameter (which must be monotonically increasing) as
    # the interpolation variable
    tinterp = np.linspace(df['t'].min(), df['t'].max(), 10000)
    Tinterp = scipy.interpolate.interp1d(df['t'], df['T / K'], kind='cubic')(tinterp)
    pinterp = scipy.interpolate.interp1d(df['t'], df['p / Pa'], kind='cubic')(tinterp)
    plt.plot(Tinterp, pinterp/1e6, color=line.get_color())

    plt.plot(df['T / K'].iloc[0], df['p / Pa'].iloc[0]/1e6, 'd',
        color=line.get_color())

elap = timeit.default_timer()-tic
plt.gca().set(xlabel='$T$ / K', ylabel='$p$ / MPa',
    xlim=(100, 350), ylim=(1, 1e3))
plt.yscale('log')
plt.tight_layout(pad=0.2)
plt.gcf().text(0,0,f'time: {elap:0.1f} s', ha='left', va='bottom', fontsize=7)
plt.gcf().text(1,0,f'teqp: {teqp.__version__}', ha='right', va='bottom', fontsize=7);
```



And now for something a bit more interesting: ethane + alkane critical curves

[4]:
```
import timeit
import numpy as np
import matplotlib.pyplot as plt
import pandas
import teqp

def get_critical_curve(names, ipure):
    """ Return curve as pandas DataFrame """
    model = teqp.build_multifluid_model(names, teqp.get_datapath())
    T0 = model.get_Tcvec()[ipure]
    rho0 = np.array([1.0/model.get_vcvec()[ipure]]*2)
    rho0[1-ipure] = 0
    o = teqp.TCABOptions()
#     print(dir(o))
    o.init_dt = 1.0 # step in the parameter
    o.rel_err = 1e-6 # relative error on the step
    o.abs_err = 1e-6 # absolute error on the step
    o.max_dt = 100 # cap the size of the allowed step
```

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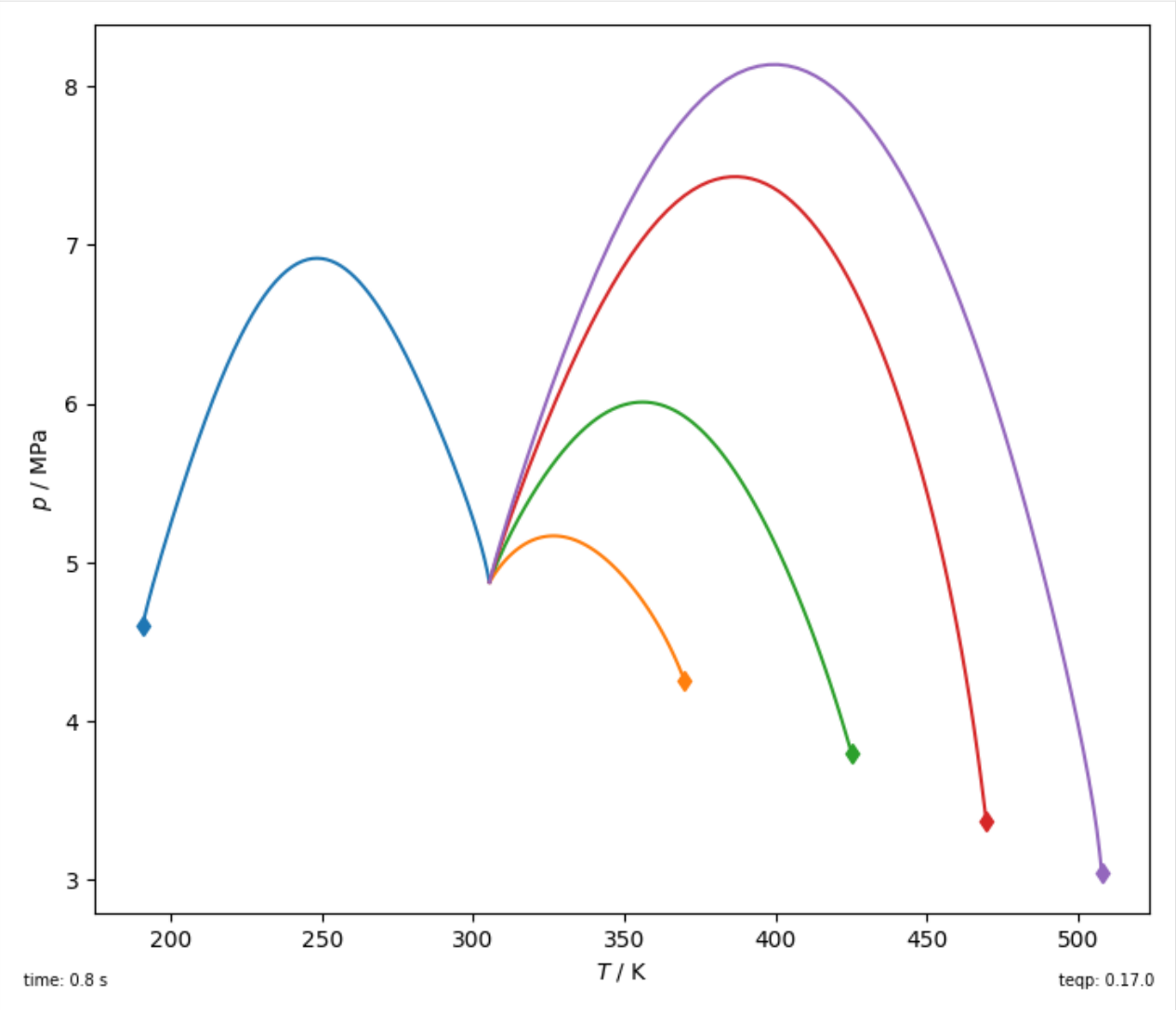
```
    o.calc_stability = True
    o.polish = True
    curveJSON = model.trace_critical_arclength_binary(T0, rho0, '', o)
    df = pandas.DataFrame(curveJSON)
    rhotot = df['rho0 / mol/m^3']+df['rho1 / mol/m^3']
    df['z0 / mole frac.'] = df['rho0 / mol/m^3']/rhotot
    return df

fig, ax = plt.subplots(1,1,figsize=(7, 6))
tic = timeit.default_timer()
name0 = 'ETHANE'
for othername in ['METHANE','PROPANE','BUTANE','PENTANE','HEXANE']:
    for ipure in [1]:
        df = get_critical_curve([name0, othername], ipure)
        line, = plt.plot(df['T / K'], df['p / Pa']/1e6, '-')
        plt.plot(df['T / K'].iloc[0], df['p / Pa'].iloc[0]/1e6, 'd',
            color=line.get_color())

elap = timeit.default_timer()-tic
plt.gca().set(xlabel='$T$ / K', ylabel='$p$ / MPa')#,xlim=(100, 350), ylim=(1, 1e3))
plt.tight_layout(pad=0.2)
plt.gcf().text(0,0,f'time: {elap:0.1f} s', ha='left', va='bottom', fontsize=7)
plt.gcf().text(1,0,f'teqp: {teqp.__version__}', ha='right', va='bottom', fontsize=7);
```



5.6 Information

The algorithms are written in a very generic way; they take an instance of a thermodynamic model, and the necessary derivatives are calculated from this model with automatic differentiation (or similar). In that way, implementing a model is all that is required to enable its use in the calculation of critical curves or to trace the phase equilibria. Determining the starting values, on the other hand, may require model-specific assistance, for instance with superancillary equations.

CHAPTER

SIX

EXAMPLES

6.1 The teqp paper in I&ECR

A few minor changes have been made:

- The `get_splus` method requires the molar concentrations to be a numpy array (to avoid copies) (as of version 0.14.0
- The top-level methods `teqp.xxx` have been deprecated, and the methods attached to the instance are preferred

[1]:
```
import timeit, numpy as np
import matplotlib.pyplot as plt
plt.style.use('classic')
import teqp

def build_models():
    Tc_K, pc_Pa, acentric = 647.096, 22064000.0, 0.3442920843

    water = {
        "a0i / Pa m^6/mol^2": 0.12277 , "bi / m^3/mol": 0.000014515, "c1": 0.67359,
        "Tc / K": 647.096, "epsABi / J/mol": 16655.0, "betaABi": 0.0692, "class": "4C"
    }
    j = {"cubic": "SRK", "pures": [water], "R_gas / J/mol/K": 8.3144598}

    datapath = teqp.get_datapath()
    def get_PCSAFT():
        c = teqp.SAFTCoeffs()
        # Values from https://doi.org/10.1016/j.fluid.2017.11.015,
        # but association contribution is ignored
        c.name = 'Water'
        c.m = 2.5472
        c.sigma_Angstrom = 2.1054
        c.epsilon_over_k = 138.63
        return teqp.PCSAFTEOS(coeffs=[c])

    return [
        ('vdW', teqp.vdWEOS([Tc_K], [pc_Pa])),
        ('PR', teqp.canonical_PR([Tc_K], [pc_Pa], [acentric])),
        ('SRK', teqp.canonical_SRK([Tc_K], [pc_Pa], [acentric])),
        ('PCSAFT', get_PCSAFT()),
        ('CPA', teqp.CPAfactory(j)),
        ('IAPWS', teqp.build_multifluid_model(["Water"], datapath))
    ]
```

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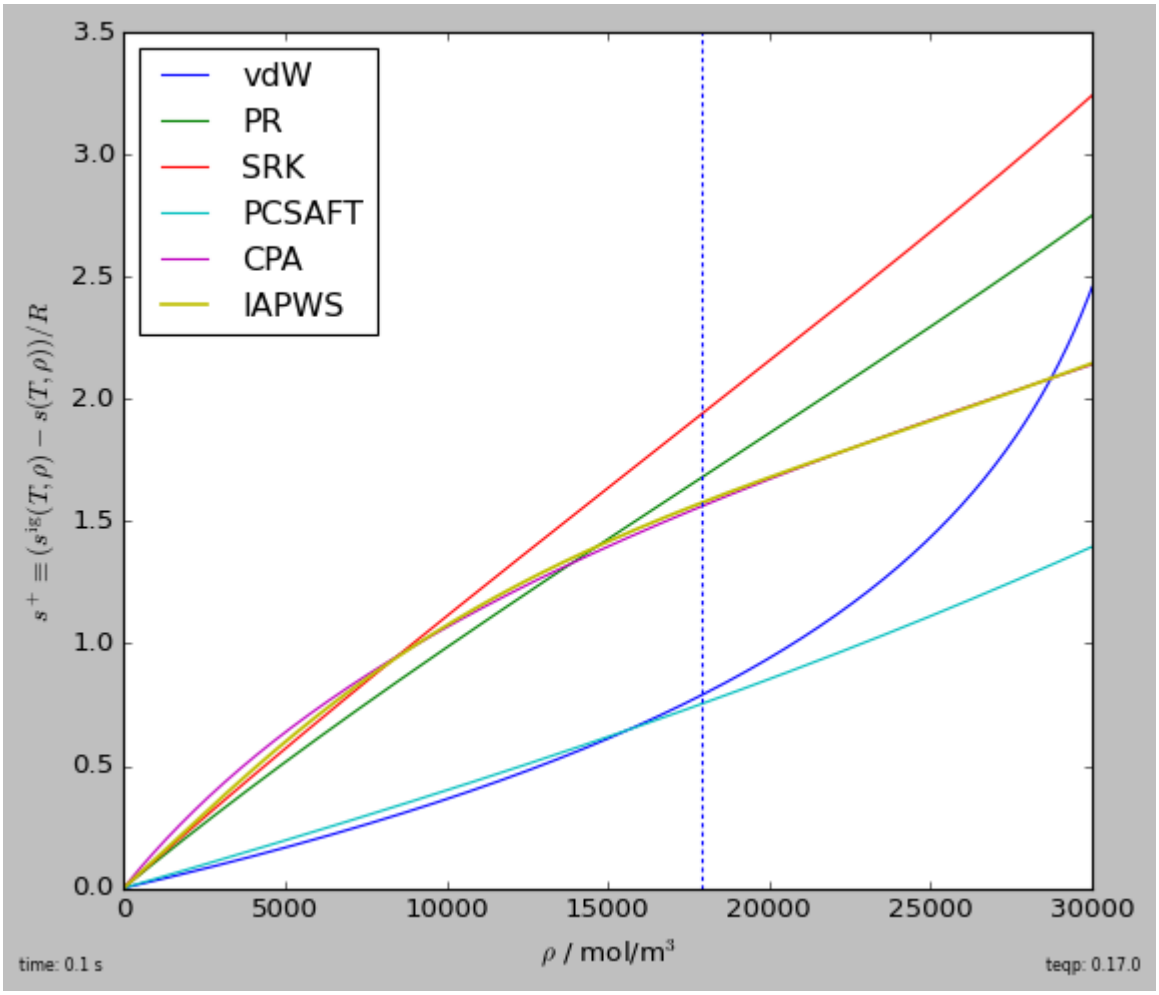
```
fig, ax = plt.subplots(1,1,figsize=(7,6))
T = 700 # K
rhovec = np.geomspace(0.1, 30e3, 10000) # mol/m^3; critical density is 17873.8... mol/
↪m^3
tic = timeit.default_timer()
for abbrv, model in build_models():
    splus = np.array([model.get_splus(T, np.array([rho])) for rho in rhovec])
    plt.plot(rhovec, splus, label=abbrv, lw = 1.5 if abbrv=='IAPWS' else 1)
elap = timeit.default_timer()-tic
plt.axvline(17873.8, dashes=[2,2])
plt.legend(loc='best')
plt.gca().set(xlabel=r'$\rho$ / mol/m$^3$', ylabel=r'$s^+\equiv (s^{\rm ig}(T,\rho)-
↪s(T,\rho))/R$')
plt.tight_layout(pad=0.2)
plt.gcf().text(0,0,f'time: {elap:0.1f} s', ha='left', va='bottom', fontsize=7)
plt.gcf().text(1,0,f'teqp: {teqp.__version__}', ha='right', va='bottom', fontsize=7)
plt.savefig('splus_water_700K.pdf')
plt.show()
```



[2]:
```
import json, timeit
import pandas, numpy as np, matplotlib.pyplot as plt
plt.style.use('classic')
```

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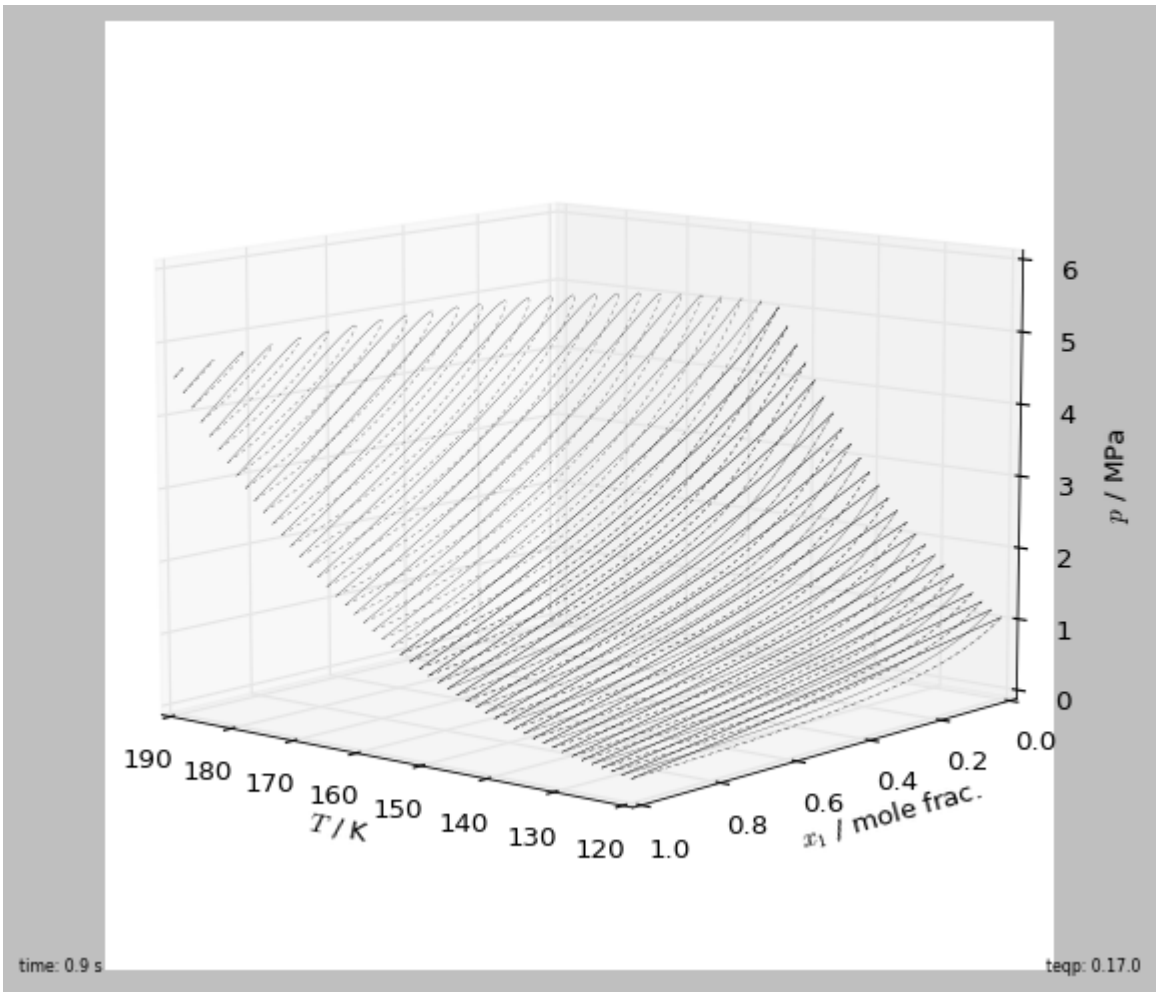
```
import teqp

Tc_K = [190.564, 154.581]
pc_Pa = [4599200, 5042800]
acentric = [0.011, 0.022]
model = teqp.canonical_PR(Tc_K, pc_Pa, acentric)
fig, ax = plt.subplots(1,1,figsize=(7, 6), subplot_kw=dict(projection='3d'))
tic = timeit.default_timer()
for ifluid in [0,1]:
    model0 = teqp.canonical_PR([Tc_K[ifluid]], [pc_Pa[ifluid]], [acentric[ifluid]])
    for T in np.linspace(190, 120, 50):
        if T > Tc_K[ifluid]: continue
        [rhoL, rhoV] = model0.superanc_rhoLV(T)
        rhovecL = np.array([0.0, 0.0]); rhovecL[ifluid] = rhoL
        rhovecV = np.array([0.0, 0.0]); rhovecV[ifluid] = rhoV
        opt = teqp.TVLEOptions(); opt.calc_criticality = True
        df = pandas.DataFrame(model.trace_VLE_isotherm_binary(T, rhovecL, rhovecV,␣
↪opt))
        df['too_critical'] = df.apply(
            lambda row: (abs(row['crit. conditions L'][0]) < 5e-8), axis=1)
        first_too_critical = np.argmax(df['too_critical'])
        df = df.iloc[0:(first_too_critical if first_too_critical else len(df))]
        line, = ax.plot(xs=df['T / K'], ys=df['xL_0 / mole frac.'], zs=df['pL / Pa']/
↪1e6,
            lw=0.2, color='k')
        ax.plot(xs=df['T / K'], ys=df['xV_0 / mole frac.'], zs=df['pL / Pa']/1e6,
            dashes=[2,2], color=line.get_color(), lw=0.2)
elap = timeit.default_timer()-tic
ax.view_init(elev=10., azim=130)
ax.set(xlabel='$T$ / K', ylabel='$x_1$ / mole frac.', zlabel='$p$ / MPa')
fig.text(0,0,f'time: {elap:0.1f} s', ha='left', va='bottom', fontsize=7)
fig.text(1,0,f'teqp: {teqp.__version__}', ha='right', va='bottom', fontsize=7)
plt.tight_layout(pad=0.2)
plt.savefig('PR_VLE_trace.pdf')
plt.show()
```



[3]:
```
import timeit
import numpy as np
import matplotlib.pyplot as plt
plt.style.use('classic')
import pandas
import teqp

def get_critical_curve(ipure):
    """ Return curve as pandas DataFrame """
    names = ['Nitrogen', 'Ethane']
    model = teqp.build_multifluid_model(names, teqp.get_datapath())
    T0 = model.get_Tcvec()[ipure]
    rho0 = np.array([1.0/model.get_vcvec()[ipure]]*2)
    rho0[1-ipure] = 0
    o = teqp.TCABOptions()
    o.init_dt = 1.0 # step in the parameter
    o.rel_err = 1e-8
    o.abs_err = 1e-5
    o.integration_order = 5
    o.calc_stability = True
    o.polish = True
    curveJSON = model.trace_critical_arclength_binary(T0, rho0, '', o)
```

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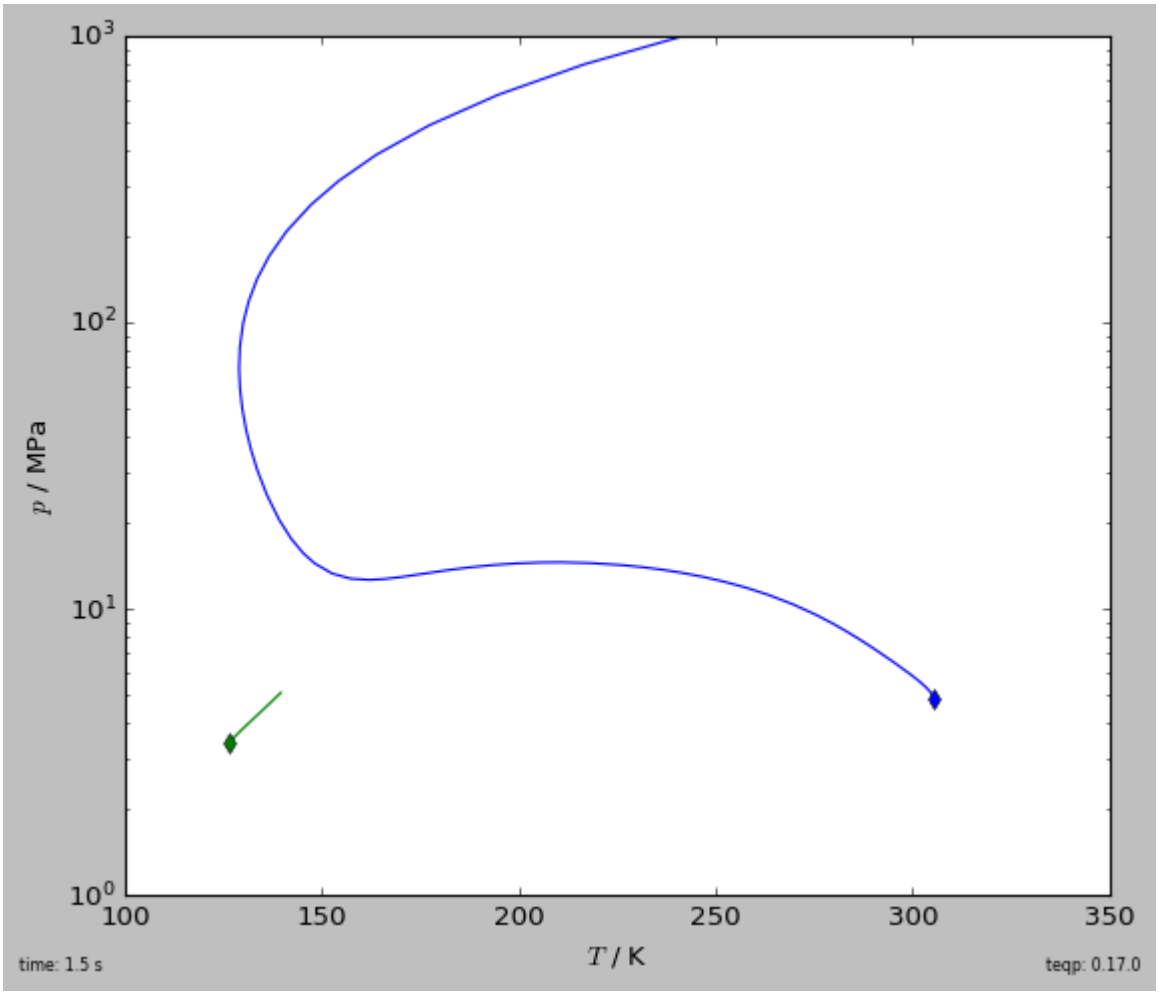
```
    df = pandas.DataFrame(curveJSON)
    rhotot = df['rho0 / mol/m^3']+df['rho1 / mol/m^3']
    df['z0 / mole frac.'] = df['rho0 / mol/m^3']/rhotot
    return df

if __name__ == '__main__':
    fig, ax = plt.subplots(1,1,figsize=(7, 6))
    tic = timeit.default_timer()
    for ipure in [1,0]:
        df = get_critical_curve(ipure)
        first_unstable = np.argmax(~df['locally stable'])
        df = df.iloc[0:(first_unstable if first_unstable else len(df))]
        line, = plt.plot(df['T / K'], df['p / Pa']/1e6, '-')
        plt.plot(df['T / K'].iloc[0], df['p / Pa'].iloc[0]/1e6, 'd',
            color=line.get_color())

    elap = timeit.default_timer()-tic
    plt.gca().set(xlabel='$T$ / K', ylabel='$p$ / MPa',
        xlim=(100, 350), ylim=(1, 1e3))
    plt.yscale('log')
    plt.tight_layout(pad=0.2)
    plt.gcf().text(0,0,f'time: {elap:0.1f} s', ha='left', va='bottom', fontsize=7)
    plt.gcf().text(1,0,f'teqp: {teqp.__version__}', ha='right', va='bottom',␣
↪fontsize=7)
    plt.savefig('N2_ethane_critical.pdf')
    plt.show()
```


10^3
10^2
10^1
10^0
p / MPa
100
150
200
250
300
350
T / K
time: 1.5 s
teqp: 0.17.0

CHAPTER

SEVEN

TEQP

7.1 teqp package

7.1.1 Submodules

7.1.2 teqp.teqp module

TEQP: Templated Equation of State Package

class teqp.teqp.**AbstractModel**

Bases: pybind11_object

build_Psi_Hessian_autodiff(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, n]]

build_Psir_Hessian_autodiff(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, n]]

build_Psir_gradient_autodiff(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

build_d2PsirdTdrhoi_autodiff(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

dpsatdT_pure(*self:* teqp.teqp.AbstractModel, *T: float*, *rhoL: float*, *rhoV: float*) → float

eigen_problem(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*, *alignment_v0: numpy.ndarray[numpy.float64[m, 1]] | None = None*) → teqp::EigenData

extrapolate_from_critical(*self:* teqp.teqp.AbstractModel, *Tc: float*, *rhoc: float*, *T: float*) → numpy.ndarray[numpy.float64[2, 1]]

find_VLLE_T_binary(*self:* teqp.teqp.AbstractModel, *traces: List[json]*, *options:* teqp.teqp.VLLEFinderOptions *| None = None*) → List[json]

find_VLLE_p_binary(*self:* teqp.teqp.AbstractModel, *traces: List[json]*, *options:* teqp.teqp.VLLEFinderOptions *| None = None*) → List[json]

get_Ar00 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar00n (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_Ar01 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar01n (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_Ar02 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar02n (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_Ar03 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar03n (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_Ar04 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar04n (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_Ar05n (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_Ar06n (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_Ar10 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar11 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar12 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar13 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar14 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar20 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar21 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar22 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar23 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Ar24 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Arxy (*self:* teqp.teqp.AbstractModel, *NT: int*, *ND: int*, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_B12vir (*self:* teqp.teqp.AbstractModel, *T: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_B2vir (*self:* teqp.teqp.AbstractModel, *T: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_Bnvir (*self:* teqp.teqp.AbstractModel, *Nderiv: int*, *T: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → Dict[int, float]

get_R (*self:* teqp.teqp.AbstractModel, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_chempotVLE_autodiff (*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_criticality_conditions (*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[2, 1]]

get_dchempotdT_autodiff (*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_deriv_mat2 (*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[3, 3]]

get_dmBnvirdTm (*self:* teqp.teqp.AbstractModel, *Nderiv: int*, *NTderiv: int*, *T: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_dp_dT_crit (*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_dpsat_dTsat_isopleth (*self:* teqp.teqp.AbstractModel, *T: float*, *rhovecL: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecV: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_drhovec_dT_crit (*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_drhovecdT_psat (*self:* teqp.teqp.AbstractModel, *T: float*, *rhovecL: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecV: numpy.ndarray[numpy.float64[m, 1]]*) → Tuple[numpy.ndarray[numpy.float64[m, 1]], numpy.ndarray[numpy.float64[m, 1]]]

get_drhovecdp_Tsat (*self:* teqp.teqp.AbstractModel, *T: float*, *rhovecL: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecV: numpy.ndarray[numpy.float64[m, 1]]*) → Tuple[numpy.ndarray[numpy.float64[m, 1]], numpy.ndarray[numpy.float64[m, 1]]]

get_fugacity_coefficients(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_minimum_eigenvalue_Psi_Hessian(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_neff(*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *molefrac: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_partial_molar_volumes(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → numpy.ndarray[numpy.float64[m, 1]]

get_pr(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → float

get_pure_critical_conditions_Jacobian(*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *alternative_pure_index: int | None = None*, *alternative_length: int | None = None*) → Tuple[numpy.ndarray[numpy.float64[m, 1]], numpy.ndarray[numpy.float64[m, n]]]

get_splus(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovec: numpy.ndarray[numpy.float64[m, 1]]*) → float

mix_VLE_Tp(*self:* teqp.teqp.AbstractModel, *T: float*, *p_given: float*, *rhovecL0: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecV0: numpy.ndarray[numpy.float64[m, 1]]*, *options:* teqp.teqp.MixVLETpFlags | *None = None*) → *teqp.teqp.MixVLEReturn*

mix_VLE_Tx(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovecL0: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecV0: numpy.ndarray[numpy.float64[m, 1]]*, *xspec: numpy.ndarray[numpy.float64[m, 1]]*, *atol: float*, *reltol: float*, *axtol: float*, *relxtol: float*, *maxiter: int*) → Tuple[*teqp.teqp.VLE_return_code*, numpy.ndarray[numpy.float64[m, 1]], numpy.ndarray[numpy.float64[m, 1]]]

mix_VLLE_T(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovecVinit: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecL1init: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecL2init: numpy.ndarray[numpy.float64[m, 1]]*, *atol: float*, *reltol: float*, *axtol: float*, *relxtol: float*, *maxiter: int*) → Tuple[teqp::VLLE::VLLE_return_code, numpy.ndarray[numpy.float64[m, 1]], numpy.ndarray[numpy.float64[m, 1]], numpy.ndarray[numpy.float64[m, 1]]]

mixture_VLE_px(*self:* teqp.teqp.AbstractModel, *p_spec: float*, *xmolar_spec: numpy.ndarray[numpy.float64[m, 1]]*, *T0: float*, *rhovecL0: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecV0: numpy.ndarray[numpy.float64[m, 1]]*, *options:* teqp.teqp.MixVLEpxFlags | *None = None*) → Tuple[*teqp.teqp.VLE_return_code*, float, numpy.ndarray[numpy.float64[m, 1]], numpy.ndarray[numpy.float64[m, 1]]]

pure_VLE_T(*self:* teqp.teqp.AbstractModel, *T: float*, *rhoL: float*, *rhoV: float*, *max_iter: int*) → numpy.ndarray[numpy.float64[2, 1]]

solve_pure_critical(*self:* teqp.teqp.AbstractModel, *T: float*, *rho: float*, *flags: json | None = None*) → Tuple[float, float]

trace_VLE_isobar_binary(*self:* teqp.teqp.AbstractModel, *p: float*, *T0: float*, *rhovecL0: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecV0: numpy.ndarray[numpy.float64[m, 1]]*, *options:* teqp.teqp.PVLEOptions | *None = None*) → json

trace_VLE_isotherm_binary(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovecL0: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecV0: numpy.ndarray[numpy.float64[m, 1]]*, *options:* teqp.teqp.TVLEOptions | *None* = *None*) → json

trace_VLLE_binary(*self:* teqp.teqp.AbstractModel, *T: float*, *rhovecV: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecL1: numpy.ndarray[numpy.float64[m, 1]]*, *rhovecL2: numpy.ndarray[numpy.float64[m, 1]]*, *options:* teqp.teqp.VLLETracerOptions | *None* = *None*) → json

trace_critical_arclength_binary(*self:* teqp.teqp.AbstractModel, *T0: float*, *rhovec0: numpy.ndarray[numpy.float64[m, 1]]*, *path: str* | *None* = *None*, *options:* teqp.teqp.TCABOptions | *None* = *None*) → json

class teqp.teqp.**IterationMatrices**

Bases: pybind11_object

property J

property v

property vars

class teqp.teqp.**MixVLEReturn**

Bases: pybind11_object

property T

property initial_r

property message

property num_fev

property num_iter

property r

property return_code

property rhovecL

property rhovecV

property success

class teqp.teqp.**MixVLETpFlags**

Bases: pybind11_object

property atol

property axtol

property maxiter

property reltol

property relxtol

class teqp.teqp.**MixVLEpxFlags**

Bases: pybind11_object

property atol

property axtol

property maxiter

property reltol

property relxtol

class teqp.teqp.**MultiFluidVLEAncillaries**

Bases: pybind11_object

property pL

property pV

property rhoL

property rhoV

class teqp.teqp.**NRIterator**

Bases: pybind11_object

get_T(*self:* teqp.teqp.NRIterator) → float

get_molefrac(*self:* teqp.teqp.NRIterator) → numpy.ndarray[numpy.float64[m, 1]]

get_rho(*self:* teqp.teqp.NRIterator) → float

get_vals(*self:* teqp.teqp.NRIterator) → numpy.ndarray[numpy.float64[m, 1]]

get_vars(*self:* teqp.teqp.NRIterator) → List[str]

take_step(*self:* teqp.teqp.NRIterator) → numpy.ndarray[numpy.float64[m, 1]]

take_steps(*self:* teqp.teqp.NRIterator, *arg0: int*) → None

class teqp.teqp.**PVLEOptions**

Bases: pybind11_object

property abs_err

property calc_criticality

property init_c

property init_dt

property integration_order

property max_dt

property max_steps

property polish

property rel_err

property terminate_unstable

class teqp.teqp.**SAFTCoeffs**

Bases: pybind11_object

property BibTeXKey

property Qstar2

property epsilon_over_k

property m

property mustar2

property nQ

property name

property nmu

property sigma_Angstrom

class teqp.teqp.**TCABOptions**

Bases: pybind11_object

property T_tol

property abs_err

property calc_stability

property init_c

property init_dt

property integration_order

property max_dt

property max_step_count

property polish

property polish_exception_on_fail

property polish_reltol_T

property polish_reltol_rho

property pure_endpoint_polish

property rel_err

property skip_dircheck_count

property small_T_count

property stability_rel_drho

property verbosity

class teqp.teqp.**TVLEOptions**

Bases: pybind11_object

property abs_err

property calc_criticality

property crit_termination

property init_c

property init_dt

property integration_order

property max_dt

property max_steps

property p_termination

property polish

property rel_err

property terminate_unstable

class teqp.teqp.**VLEAncillary**

Bases: pybind11_object

property T_r

property Tmax

property Tmin

class teqp.teqp.**VLE_return_code**

Bases: pybind11_object

Members:

unset

xtol_satisfied

functol_satisfied

maxiter_met

maxfev_met

notfinite_step

functol_satisfied = <VLE_return_code.functol_satisfied: 2>

maxfev_met = <VLE_return_code.maxfev_met: 3>

maxiter_met = <VLE_return_code.maxiter_met: 4>

property name

notfinite_step = <VLE_return_code.notfinite_step: 5>

unset = <VLE_return_code.unset: 0>

property value

xtol_satisfied = <VLE_return_code.xtol_satisfied: 1>

class teqp.teqp.**VLLEFinderOptions**

Bases: pybind11_object

property max_steps

property rho_trivial_threshold

class teqp.teqp.**VLLETracerOptions**

Bases: pybind11_object

property T_limit

property abs_err

property init_dT

property max_dT

property max_polish_steps

property max_step_count

property polish

property rel_err

property terminate_composition

property terminate_composition_tol

property verbosity

teqp.teqp.**attach_model_specific_methods**(*arg0: object*) → None

teqp.teqp.**build_alias_map**(*root: str*) → Dict[str, str]

teqp.teqp.**collect_component_json**(*identifiers: List[str]*, *root: str*) → List[json]

teqp.teqp.**convert_CoolProp_idealgas**(*arg0: str*, *arg1: int*) → json

teqp.teqp.**get_BIPdep**(*BIPcollection: json*, *identifiers: List[str]*, *flags: json = None*) → Tuple[json, bool]

teqp.teqp.**get_departure_json**(*name: str*, *root: str*) → json

7.1.3 Module contents

teqp.**AmmoniaWaterTillnerRoth**()

teqp.**CPAfactory**(*spec*)

teqp.**IdealHelmholtz**(*model*)

teqp.**PCSAFTEOS**(*coeffs*, *kmat=None*)

teqp.**build_LJ126_TholJPCRD2016**()

teqp.**build_Psi_Hessian_autodiff**(*model*, **args*, ***kwargs*)

teqp.**build_Psir_Hessian_autodiff**(*model*, **args*, ***kwargs*)

teqp.**build_Psir_gradient_autodiff**(*model*, **args*, ***kwargs*)

teqp.**build_d2PsirdTdrhoi_autodiff**(*model*, **args*, ***kwargs*)

teqp.**build_multifluid_model**(*components*, *coolprop_root*, *BIPcollectionpath=''*, *flags={}*, *departurepath=''*)

teqp.**build_multifluid_mutant**(**args*, ***kwargs*)

teqp.**canonical_PR**(*Tc_K*, *pc_Pa*, *acentric*, *kmat=None*)

teqp.**canonical_SRK**(*Tc_K*, *pc_Pa*, *acentric*, *kmat=None*)

teqp.**deprecated_caller**(*model*, **args*, ***kwargs*)

teqp.**eigen_problem**(*model*, **args*, ***kwargs*)

teqp.**extrapolate_from_critical**(*model*, **args*, ***kwargs*)

teqp.**find_VLLE_T_binary**(*model*, **args*, ***kwargs*)

teqp.**get_B2virget_B12vir**(*model*, **args*, ***kwargs*)

teqp.**get_chempotVLE_autodiff**(*model*, **args*, ***kwargs*)

teqp.**get_criticality_conditions**(*model*, **args*, ***kwargs*)

teqp.**get_datapath**()

Get the absolute path to the folder containing the root of multi-fluid data

teqp.**get_dchempotdT_autodiff**(*model*, **args*, ***kwargs*)

teqp.**get_dpsat_dTsat_isopleth**(*model*, **args*, ***kwargs*)

teqp.**get_drhovec_dT_crit**(*model*, **args*, ***kwargs*)

teqp.**get_drhovecdT_psat**(*model*, **args*, ***kwargs*)

teqp.**get_drhovecdp_Tsat**(*model*, **args*, ***kwargs*)

teqp.**get_fugacity_coefficients**(*model*, **args*, ***kwargs*)

teqp.**get_minimum_eigenvalue_Psi_Hessian**(*model*, **args*, ***kwargs*)

teqp.**get_partial_molar_volumes**(*model*, **args*, ***kwargs*)

teqp.**get_pr**(*model*, **args*, ***kwargs*)

teqp.**get_pure_critical_conditions_Jacobian**(*model*, **args*, ***kwargs*)

teqp.**get_splus**(*model*, **args*, ***kwargs*)

teqp.**make_model**(**args*, ***kwargs*)

This function is in two parts; first the make_model function (renamed to _make_model in the Python interface) is used to make the model and then the model-specific methods are attached to the instance

teqp.**make_vdW1**(*a*, *b*)

teqp.**mix_VLE_Tx**(*model*, **args*, ***kwargs*)

teqp.**mix_VLLE_T**(*model*, **args*, ***kwargs*)

teqp.**mixture_VLE_px**(*model*, **args*, ***kwargs*)

teqp.**pure_VLE_T**(*model*, **args*, ***kwargs*)

teqp.**solve_pure_critical**(*model*, **args*, ***kwargs*)

teqp.**tolist**(*a*)

teqp.**trace_VLE_isobar_binary**(*model*, **args*, ***kwargs*)

teqp.**trace_VLE_isotherm_binary**(*model*, **args*, ***kwargs*)

teqp.**trace_critical_arclength_binary**(*model*, **args*, ***kwargs*)

teqp.**vdWEOS**(*Tc_K*, *pc_Pa*)

teqp.**vdWEOS1**(**args*)

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