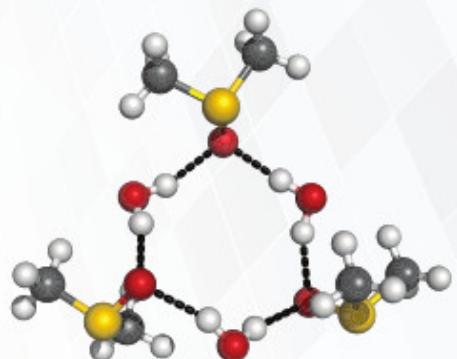
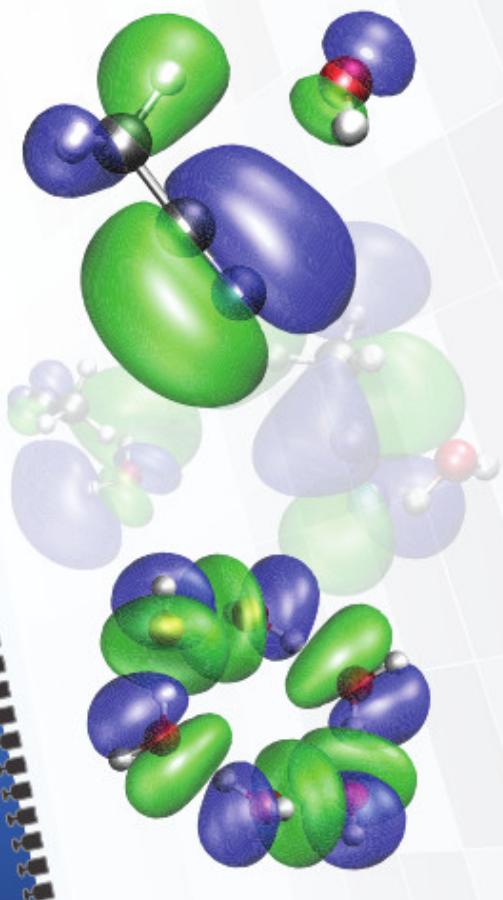


$$N_\beta = q_\beta^{\text{tot}} \left[\frac{N_1}{q_1^{\text{tot}}} \right]^{i(\beta)}$$



$$FC = SC\epsilon$$



Peacemaker Manual

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1 What is Peacemaker?

Peacemaker uses the laws of statistical thermodynamics to calculate the thermodynamic properties of pure liquids and liquid mixtures. It is based on the **Quantum Cluster Equilibrium** (QCE) method, which is the idea, that the liquid bulk system can be described as a dense distribution of statistically reoccurring molecular cluster motifs.

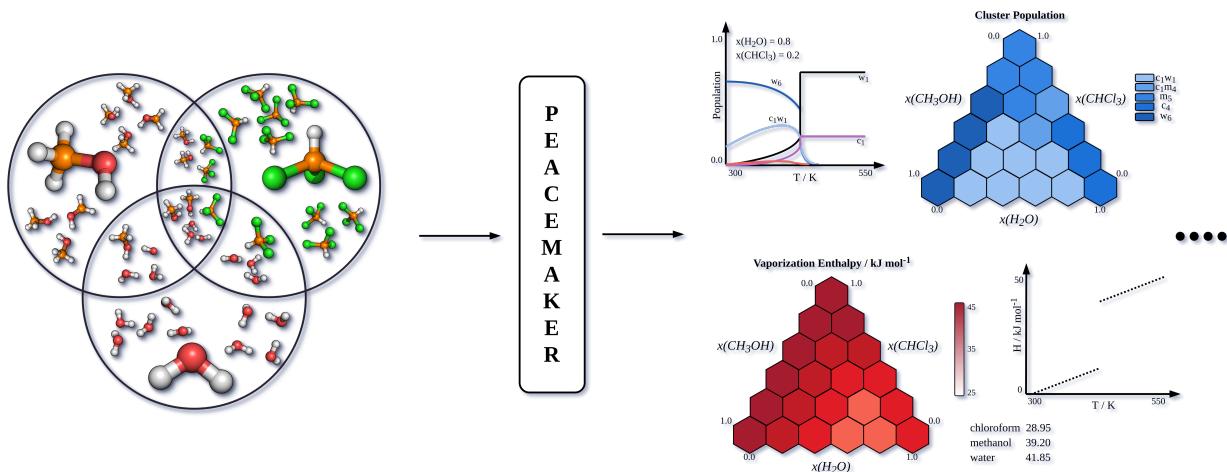
What you need to provide in order to use Peacemaker:

- A set of clusters, which are representative for the system you want to investigate.
- The vibrational frequencies of the clusters.
- The volumes for the monomers.
- The molar amounts of the clusters.
- The adiabatic interaction energy of the clusters in units of kJ mol^{-1} .

$$\Delta_{\text{bind}}\epsilon(t_i w_j) = \epsilon(t_i w_j) - i \cdot \epsilon(t_1) - j \cdot \epsilon(w_1)$$

What you get in return:

- The Gibbs free energy of the system in units of kJ.
- The Helmholtz free energy of the system in units of kJ.
- The internal energy of the system in units of kJ.
- The enthalpy of the system in units of kJ.
- The entropy of the system in units of JK^{-1} .
- The heat capacity at constant volume in units of JK^{-1} .
- The heat capacity at constant pressure in units of JK^{-1} .
- The volume of the system in units of dm^3 .
- The populations of each cluster.
- The concentrations of each cluster in units of mol L^{-1} .
- A set of contributions for each degree of freedom to the thermodynamic quantities.
- A set of contributions for each cluster to the thermodynamic quantities.



2 Compiling Peacemaker

Peacemaker is a modern FORTRAN code and thus requires a modern FORTRAN compiler. We recommend a recent version of gfortran which is used for active development. Before compiling Peacemaker, make sure that the following dependencies are installed:

- Meson : <https://mesonbuild.com/>
- Ninja : <https://ninja-build.org/>

To compile Peacemaker4, follow these steps:

```
$ git clone git@github.com:kirchners-manta/peacemaker4.git .
$ cd peacemaker4/pm4
$ meson setup build
$ ninja -C build
```

Optionally, you can run the tests with

```
$ ninja -C build test
$ build/test/tester
```

A run time optimized binary called peacemaker is created in the build directory. In case of errors, adjust the meson.build to your compiler. We recommend the following compiler flags or your compiler's equivalents:

```
-O3 highest optimization level that guarantees standard compliance
-fopenmp OpenMP parallelization
-flto link-time optimization
```

Note: Older versions of gfortran are subject to a bug which prevents OpenMP parallelization. If you receive the error message “Attempting to allocate already allocated variable ‘ib’ ”, compile without OpenMP support, or upgrade to a newer compiler version.

3 Running Peacemaker

Two input files are required to run Peacemaker. The first is the **QCE-input file**, which contains all necessary information about the system to be investigated as well as the parameters to be sampled. The second is the **clusterset file**, which contains the paths to the structure and the frequency files of each cluster, as well as information about the clusters, such as their composition or energy. More details on the structure of these files are given in the following sections.

Peacemaker is run by

```
$ peacemaker [QCE-input] [clusterset]
```

where [QCE-input] is the location of the QCE-input file and [clusterset] is the location of the clusterset file.

If Peacemaker was compiled with OpenMP parallelization, it can be run in parallel by

```
$ OMP_NUM_THREADS=[N] peacemaker [input] [clusterset]
```

In this case, [N] specifies the number of threads to run with.

4 Peacemaker Configuration Files

Both the input and the clusterset file are stuctured according to the **toml format**. The toml format is a simple, human-readable configuration file format. For more information visit: <https://toml.io/en/>

An example document is shown below:

```
[section1]
    keyword1 = "argument1"      # string
    keyword2 = "path/to/file"   # string
    keyword3 = true             # boolean
    ...
[section2]
    keyword1 = 1                # integer
    keyword2 = [0.0, 2.0, 201]  # array of floats
    ...
...
```

Thus there are sections, which shall be embraced in brackets, keywords, arguments, and comments. Section labels are unique. Keywords within a section are unique. Arguments are optional. **Comments** may start anywhere and are introduced by the number sign `#`. All elements are case sensitive.

If you want to use QCE-input and clusterset files from previous versions of Peacemaker, they need to be converted to the toml format. Two tools are provided to do this:

- `tools/convert2toml/QCEinput2toml.py`
- `tools/convert2toml/clusterset2toml.py` .

They can be run by typing the following commands in a terminal:

```
$ python3 QCEinput2toml.py [QCE-input] [QCE-input-toml]
$ python3 clusterset2toml.py [clusterset] [clusterset-toml] .
```

5 The Peacemaker QCE-Input File

All sections and their associated keywords are explained in the following.

[system]

`components = N`

The number of components in the system. $N = 1$ for a pure system, $N = 2$ for a binary mixture, $N = 3$ for a ternary mixture, etc. Note that although it is possible to run a pure system as binary system, where the amount of one of the species is set to zero, we strongly encourage you to run such calculations as a pure system. Results will be the same in either case, but slow convergence may arise for some temperatures if the amount of monomers of one component is sufficiently small. Optional. Default: 1

[qce]

`amf = A`

`amf = [A, B, N]`

The mean field parameter a_{mf} in units of $\text{J m}^3 \text{mol}^{-2}$. Can be specified either as a single value A, or as a range A, B, N, where A is the start, B the end, and N the number of data points (including both boundaries). Optional. Default: 0.0

`bxv = A`

`bxv = [A, B, N]`

The exclusion volume scaling parameter b_{xv} . Can be specified either as a single value A, or as a range A, B, N, where A is the start, B the end, and N the number of data points (including both boundaries). Optional. Default: 1.0

`amf_temp = A`

`amf_temp = [A, B, N]`

The linear temperature dependence parameter $a_{mf,temp}$ of the mean field. The specification is similar to the one for a_{mf} . This is an experimental feature and should only be used with care. Optional. Default: 0.0

`bxv_temp = A`

`bxv_temp = [A, B, N]`

The linear temperature dependence parameter $b_{xv,temp}$ of the exclusion volume. The specification is similar to the one for b_{xv} . This is an experimental feature and should only be used with care. Optional. Default: 0.0

`grid_iterations = A`

The number of iterations for the parameter sampling if a sampling grid is specified. With each iteration, the grid center is moved to the best parameter pair and the grid size is decreased with a factor of 0.2. Optional. Default: 1

```

rotor_cutoff = A
    The cutoff frequency in cm-1 at which the RRHO-correction for low frequencies
    will be used. To limit their influence on the entropy, vibrational modes with a
    frequency below A will be treated as hindered rotations, employing a switching
    function to smooth the transition between harmonic oscillator and rigid rotator. If
    set to 0, no correction will be applied. Optional. Default: 0
optimizer = ["amf", "bxv", "amf_temp", "bxv_temp"]
    Enables the Nelder–Mead algorithm for parameter optimization. The parameters
    to be optimized can be given as a list of strings in an arbitrary order. By default,
    no optimization is performed.
max_deviation = A
    The maximum relative deviation of the Gibbs energy. Used to check convergence
    of the QCE iteration. A QCE cycle has converged, if

$$\left| \frac{G(\text{current step}) - G(\text{last step})}{G(\text{last step})} \right| < A.$$

    Optional. Default: 1.0e-9
volume_damping_factor = A
    The volume damping factor used to damp the initial volume guess if one of the
    polynomials did not converge. Shall be between 0 and 1. Damping is performed
    by  $\gamma_V = 1 \pm A$ , depending on the mode of the temperature loop. Optional. De-
    fault: 0.01
qce_iterations = N
    The maximum number of iterations in a QCE cycle. Optional. Default: 100
newton_iterations = N
    The maximum number of iterations in a Newton–Raphson cycle. Optional. De-
    fault: 500

```

[reference]

This section is optional. It enables comparison to experimental reference data. It is disabled by default. Further details on parameter sampling are given in section 8.

```

density = [A, B]
density = [A, B, C]
    Reference density B in units of g cm-3 at reference temperature A in K and an
    optional error weight C. Optional.
isobar_file = "P"
isobar_weight = A
    Path to an isobar file P and an optional error weight A. Isobar files contain two
    columns representing the temperature in K and volume in L. Optional.
phase_transition = A

```

```
phase_transition = [A, B]
```

Reference temperature of phase transition A in units of K and an optional error weight B. Optional.

[output]

This section is optional. It enables output control. It is disabled by default.

```
contributions
```

```
helmholtz_contributions = true/false
```

```
internal_contributions = true/false
```

```
entropy_contributions = true/false
```

```
cv_contributions = true/false
```

Enables the output of contributions of each degree of freedom to the thermodynamic functions. If no arguments are given, contribution output is enabled for all possible thermodynamic quantities. If arguments are specified, contribution output is only enabled for the selected thermodynamic quantities. Optional.

```
progress_bar = true/false
```

Enables or disables the progress bar. Optional. Default: enabled.

Example QCE-Inputs

In the following, you find three examples of input files, for different purposes.

Single Point Calculation

The input file shown below will run a QCE "single point" calculation for a one-component system using the cluster set specified in the command line and explained in section 6. Default options are used in most cases.

```
[qce]
    amf = 0.1 # J*m^3/mol^2
    bxv = 1.3

[ensemble]
    temperature = [200.0, 400.0, 201] # K
    pressure = 1.01325 # bar
    monomer_amounts = 1.0 # mol
```

Parameter sampling

This input will perform an a_{mf} , b_{xv} parameter sampling for a pure substance. Reference data are provided by an isobar file. Further details on parameter sampling are explained in section 8.

```
[system]
    components = 1

[qce]
    amf = [0.0, 0.5, 101] # J*m^3/mol^2
    bxv = [1.0, 2.0, 101]

[ensemble]
    temperature = [200.0, 400.0, 201] # K
    pressure = 1.01325 # bar
    monomer_amounts = 1.0 # mol

[reference]
    isobar = "isobar.dat"
```

Parameter optimization

The following input will perform an a_{mf} , b_{xv} parameter optimization for a ternary mixture, following a rough sampling on a small grid. Reference data are provided by a density at 298.15 K and a temperature of phase transition.

```
[system]
    components 3
[qce]
    amf = [0.0, 2.0, 11] # J*m^3/mol^2
    bxv = [0.5, 1.5, 11]
    grid_iterations = 2
    optimizer = ["amf", "bxv"]

[ensemble]
    temperature = [273.15, 400.15, 128] # K
    pressure = 1.01325 # bar
    monomer_amounts = [0.6, 0.1, 0.3] # mol
[reference]
    density = [298.15, 0.9248] # K; g/cm^3
    phase_transition = 332.61 # K
```

6 The Peacemaker Clusterset File

6.1 Structure

Clusterset files are structured like input files. A section provides all necessary information about a cluster. The section label is used as cluster label. Cluster data may be acquired with the help of the tools provided with this distribution of Peacemaker. See the tools/README file for further information.

`monomer`

Sets the current cluster as monomer. Optional, but must be present once for each component.

`composition N M`

Composition of the cluster in number of monomers. One number for each component.

`sigma N`

The rotational symmetry number of the cluster.

`coordinates P`

Path to a coordinate file in the xyz format. Units are Å.

`frequencies P`

Path to a frequency file. It contains the number of frequencies in line 1, followed by a comment line, followed by one frequency per line. Units are cm⁻¹.

`energy A`

The adiabatic interaction energy of the cluster in units of kJ mol⁻¹ (negative energies represent stable clusters).

`volume A`

The volume of the cluster in units of Å³. Must be specified for monomers, only.

`frequency_scale A`

A frequency scaling factor. Optional.

`anharmonicity A`

The anharmonicity constant. Optional.

6.2 Example

```

[Cluster 1]

monomer
composition 1
sigma 2
coordinates /home/user/clusters/cluster1.xyz
frequencies /home/user/clusters/cluster1.flist
energy 0.0
volume 60.0
frequency_scale 0.97

[Cluster 2]

composition 3
sigma 3
coordinates /home/user/clusters/cluster2.xyz
frequencies /home/user/clusters/cluster2.flist
energy -20.0
frequency_scale 0.97

...

```

7 Peacemaker Output Files

Peacemaker writes results for the best a_{mf} , b_{xv} parameter pair if it could be determined or for the first a_{mf} , b_{xv} pair otherwise. In the following, the output files shall be briefly described. All output files contain the temperature in K in column 1.

`volume.dat`

Contains the volume and related quantities: volume V in dm^3 , exclusion volume V_{excl} in dm^3 , volumetric expansion coefficient α in K^{-1} , status code for debugging purposes.

`thermo0.dat`

Contains thermodynamic quantities that do not depend on any derivative: Helmholtz free energy A in kJ, Gibbs free energy G in kJ.

`thermo1.dat`

Contains thermodynamic quantities that depend on first derivatives: internal energy U in kJ, enthalpy H in kJ, entropy S in J/K.

`thermo2.dat`

Contains thermodynamic quantities that depend on second derivatives: heat capacity at constant volume c_V in J/K, heat capacity at constant pressure c_P in J/K.

xxx_contrib.dat

Contains contributions of each degree of freedom to the quantity denoted by xxx. Possible quantities are: Helmholtz free energy, internal energy, entropy, heat capacity at constant volume.

xxx_clusters.dat

Contains the contributions of each cluster to the quantity denoted by xxx divided by its absolute population (meaning these are cluster specific quantities). Possible quantities are: the partition function and its derivatives, the indistinguishability contribution, Helmholtz free energy, internal energy, Gibbs energy, enthalpy entropy, heat capacity at constant volume and pressure.

populations.dat

Contains populations of each cluster in the order they were specified in the clusterset. Populations are monomer normalized. For example, in a binary system:

$$N'_\varphi = \frac{(i_\varphi + j_\varphi) N_\varphi}{N_{1,\text{tot}} + N_{2,\text{tot}}}. \quad (1)$$

Generally, in a multi-component system:

$$N'_\varphi = \sum_c \frac{i_c \cdot N_\varphi}{N_{c,\text{tot}}}. \quad (2)$$

concentrations.dat

Contains concentrations in mol/l of each cluster in the order they were specified in the clusterset. Concentrations are not monomer normalized.

8 Parameter Sampling

Peacemaker performs a_{mf} , b_{xv} parameter sampling on a grid, which can be specified in the [qcel] section of the input file. For each pair, the quality of the resulting isobar is compared to certain experimental quantities. The following options are available for this purpose: single density, isobar, temperature of phase transition. The isobar quality is computed according to the following equation.

$$\text{error} = w_{\text{density}} \left(\frac{\rho - \rho^{\text{exp}}}{\rho^{\text{exp}}} \right)^2 + w_{\text{isobar}} \frac{1}{N} \sum_{i=1}^N \left(\frac{V_i - V_i^{\text{exp}}}{V_i^{\text{exp}}} \right)^2 + w_{\text{phase transition}} \left(\frac{T_{\text{pt}} - T_{\text{pt}}^{\text{exp}}}{T_{\text{pt}}^{\text{exp}}} \right)^2$$

Any combination of the experimental data above can be chosen. The relative importance of each quantity can be specified by the weight w .

Isobars are specified by an isobar file. This file shall contain two columns of numbers: temperatures in K in column one and volumes in dm³ in column two. All temperatures

must be within the temperature range specified in the [qce] section. There are no requirements on the order of the temperatures. Temperatures may be included multiple times to put special weight on them. If a reference temperature is not equal to the temperature specified by the temperature range in the [qce] section, linear interpolation between the two closest temperatures is performed.