Thermo Manual

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1 Introduction to Thermo

Thermo is a software that calculates an estimation of the thermodynamics quantities of a molecular system based on closed-form expressions derived from a statistical mechanics approach. This involves the calculation of energy, entropy and free energy of molecules from their molecular properties like the mass, the moments of inertia, or the vibrational frequencies.

In the next chapters, it will be described how to download and install the code and how to use it with some examples. Next, a Theory chapter aims at describing in details the underlying statistical mechanics to understand how this works and under which approximations and limits the obtained results can be interpreted (currently it is a work in progress).

1.1 License and Copyright

This code and manual has been written by Simone Conti at work a the University of Strasbourg:

1.2 Citation References

If you use the Thermo software in scientific publications, please cite[1]

> S. Conti and M. Cecchini "Predicting molecular self-assembly at surfaces: a statistical thermodynamics and modeling approach", PCCP, 2016, 18, pp. 1480-31493

2 Install instructions

The last version of the code can be downloaded from git via:

```
git clone https://github.com/SimoneCnt/thermo.git thermo
```

which will copy the latest available version inside the `thermo` directory. If you do not have git installed and - you want to install it, take a look at http://git-scm.com - you do not want to install it, you can get the code as a zip archive directly from the git project page at https://github.com/SimoneCnt/thermo

Once downloaded the installation is straighforward. The code is written in standard C and the compilation is managed by a CMake script. So to compile the code the following list of commands will easily do the work:

```
mkdir build
cd build
cmake ..
make
```

If you are missing CMake, you can get if from http://www.cmake.org.

Once the compilation finishes, you can find the `thermo` binary inside the `build` directory.

This procedure has been tested on Linux (Ubuntu) and MacOsX machines. On Ubuntu, and probably also in other Linux distributions, you can find both CMake and git on the standard packaging tools. So in Ubuntu this line should smoothly install both applications:

```
sudo apt-get install git cmake
```

No test has been performed on Windows machines.

3 Usage Examples

Here a small description on how to use the code is given. Inside the `examples` directory it is possible to find some ready to use input files for some more applications. A reference output is normally present with the `.ref` suffix.

3.1 Water

The easiest system we can take as example is water. Here a sample input script to evaluate the thermodynamic properties of an hypotetical box of 22.465 liters which contains 1 mol of gas water at 298.15 kelvin (1 atm pressure). Each water molecule will have three translational degrees of freedom, three rotational (with the associated moments of inertia), and $3N - 6 = 3$ vibrations (and associated frequencies). The simmetry number is also reported: since water symmetry pointgroup is C2v, the symmetry number is 2. The mass is also specified.

```
# Set temperature in Kelvin
T 298.15

# Set number of mols and volume (1 atm pressure)
n 1
V 22.465

# Mass in g/mol
m 18.01528

# Translational degrees of freedom
t 3

# Rotational degrees of freedom and moments of inertia in g/mol Ang^2
r 3
1.7704
```

```
0.6169
1.1535

# Symmetry number
s 2

# Number of vibrations and their frequencies in cm-1
v 3
1635.618
3849.420
3974.869
```

Save this input as e.g. `water.inp` and run it with `thermo -A water.inp` The output will print all parsed options and at the end all thermodynamic quantites, like energy, entropy, free energy, and chemical potential, are printed. For example, the evaluated translational molar entropy is evaluated to be 32.452 cal mol-1 K-1 and the zero point vibrational energy to be 13.524 kcal mol-1.

Input and reference output can be found in the `water` subdirectory.

3.2 Dimerization of Insulin

A second example in based on the reference paper by B. Tidor and M. Karplus[2], published in 1994:

> B. Tidor and M.Karplus, "The Contribution of Vibrational Entropy to Molecular Association: The Dimerization of Insulin", Journal of Molecular Biology, 238(3) 1994 pp. 405-414

In this work the effect of vibrations in the stabilization of the insulin dimer is discussed as example of how the vibrational entropy can partially counterbalance the net lost in translational and rotational degrees of freedom. Translational and rotational contribution are calculated in good agreement with the data reported in the paper, while the vibrational ones are incorrect due to the limited number of frequences reported in the main text.

The input files are inside the `insulin` subdirectory. Since we want to study the dimerization reaction, it is possible to run at the same time both the monomer and the dimer, and, thanks to the '–stechio" command line option, the differences for the dimerization reaction are automatically printed. The Thermo command line can thus be:

```
thermo -A monomer.inp -B dimer.inp --stechio 2:1 > insulin.out
```

The reference output is `insulin.out.ref`. At the moment only reactions between two species can be studied (so only `-A` and `-B` command are available).

3.3 Free Energy Difference between Peptides and Proteins Conformers

Three examples are included to study the difference in free energy between peptides and proteins conformes:

- alanine dipeptide (`diala` directory) in its c7 equatorial (c7eq) and c7 axial (c7ax) conformations;
- beta hairpin from protein G (`bhp`) in the native beta-harpin (bhp1) and in a three-stranded beta sheet (bhp2) conformations;
- the converter of the biomolecular motor myosin VI (`conv`) in the pre-powerstroke (pps) and rigor-like (rig) conformations.

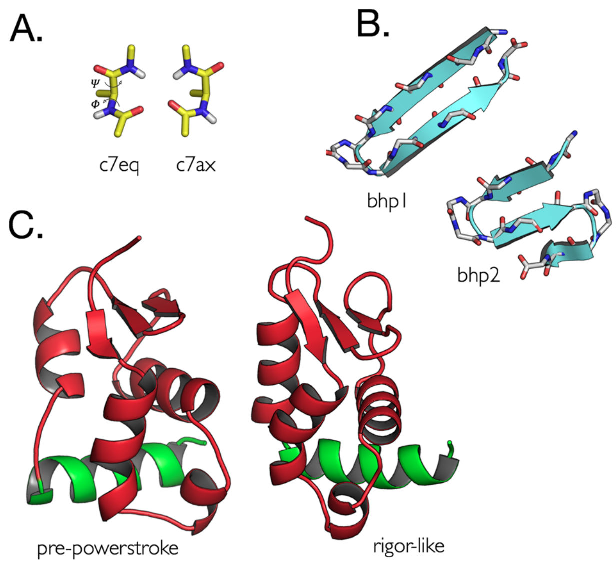

Figure 1: Representation of the three examples to study the quantum correction to the conformational free energy difference: the alanine dipeptide, the beta hairpin of protein G and the converter of myosin VI. Reproduced from ref. 3.

These examples, see Fig. 1, are taken form the work of M. Cecchini, JCTC 2015[3], where they were used to develop a quantum correction to the classical conformational free energy difference.

> M. Cecchini, "Quantum Corrections to the Free Energy Difference between Peptides and Proteins Conformers", Journal of Chemical Theory and Computation, 2015 ASAP

The quantum correction is by default calculated by Thermo; for example, for the myosin converter

```
thermo -A rig.inp -B pps.inp --stechio 1:1
```

Thermo calculates a quantum correction of 1.09 kcal mol-1, in perfect agreement with the Cecchini paper.

4 Theory

This part is still a draft. Please, see the McQuarrie "Statistical Mechanics" book[4] for more information.

4.1 Partition Function

$$Q = \frac{q^N}{N!} \tag{1}$$

$$\ln Q = N \ln q - N \ln N + N = N \ln \frac{qe}{N} \tag{2}$$

$$q = q_{tr}\, q_{rot}\, q_{vib}\, q_{elec} \tag{3}$$

Translational degrees of freedom:

$$q_{tr} = \left(\frac{2\pi m k_B T}{h^2}\right)^{t/2} V \tag{4}$$

$$\ln q_{tr} = \frac{t}{2} \ln \left(\frac{2\pi m k_B T}{h^2}\right) + \ln V \tag{5}$$

$$\frac{\partial}{\partial T} \ln q_{tr} = \frac{t}{2} \frac{1}{T} \tag{6}$$

Rotational:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2}\right)^{r/2} \left(\prod_{i=1}^{r} I_i\right)^{1/2} \tag{7}$$

$$\ln q_{rot} = \frac{1}{2} \ln \frac{\pi}{\sigma^2} + \frac{r}{2} \ln \frac{8\pi^2 k_B T}{h^2} + \frac{1}{2} \sum_{i=1}^{r} \ln I_i \tag{8}$$

$$\frac{\partial}{\partial T} \ln q_{rot} = \frac{r}{2} \frac{1}{T} \tag{9}$$

Vibrational (classical limit):

$$q_{vib,cl} = \prod_{i=1}^{f} \frac{k_B T}{h\nu_i} \tag{10}$$

$$\ln q_{vib,cl} = \sum_{i=1}^{f} \ln \frac{k_B T}{h\nu_i} \tag{11}$$

$$\frac{\partial}{\partial T} \ln q_{vib,cl} = f \frac{1}{T} \tag{12}$$

Vibrational (quantum):

$$q_{vib,qm} = \prod_{i=1}^{f} \frac{\exp \frac{h\nu}{2k_BT}}{1 - \exp \frac{h\nu}{k_BT}} = \prod_{i=1}^{f} \left[2 \sinh \left(\frac{h\nu}{2k_BT} \right) \right]^{-1} \tag{13}$$

$$\ln q_{vib,qm} = -\sum_{i=1}^{f} \ln \left[2 \sinh \left(\frac{h\nu}{2k_BT} \right) \right] \tag{14}$$

$$\frac{\partial}{\partial T} \ln q_{vib,qm} = \frac{1}{T} \sum_{i=1}^{f} \frac{\frac{h\nu}{2k_BT}}{\tanh \left(\frac{h\nu}{2k_BT} \right)} \tag{15}$$

Electronic:

$$q_{elec} = \exp \left(-\frac{E_m}{k_BT} \right) \tag{16}$$

$$\ln q_{elec} = -\frac{E_m}{k_BT} \tag{17}$$

$$\frac{\partial}{\partial T} \ln q_{elec} = \frac{E_m}{k_BT} \frac{1}{T} \tag{18}$$

4.2 Helmholtz Free energy

$$F = U - TS \tag{19}$$

$$F = -k_BT \ln Q = -Nk_BT \ln \frac{qe}{N} \tag{20}$$

$$= -Nk_BT \ln \frac{q_{tr}e}{N} - Nk_BT \ln q_{rot} - Nk_BT \ln q_{vib} - Nk_BT \ln q_{elec} \tag{21}$$

$$= F_{tr} + F_{rot} + F_{vib} + F_{elec} \tag{22}$$

$$F_{tr} = -Nk_BT \ln \frac{q_{tr}e}{N} = -Nk_BT \ln \left[\left(\frac{2\pi m k_BT}{h^2} \right)^{t/2} \frac{Ve}{N} \right] \tag{23}$$

$$= -Nk_BT \left(\frac{t}{2} \ln \frac{2\pi m k_BT}{h^2} + 1 - \ln \frac{N}{V} \right) \tag{24}$$

$$F_{rot} = -Nk_BT \ln q_{rot} = -Nk_BT \left[\frac{1}{2} \ln \frac{\pi}{\sigma^2} + \frac{r}{2} \ln \frac{8\pi^2 k_BT}{h^2} + \frac{1}{2} \sum_{i=1}^{r} \ln I_i \right] \tag{25}$$

$$F_{vib,cl} = -Nk_BT \ln q_{vib,cl} = -Nk_BT \sum_{i=1}^{f} \ln \frac{k_BT}{h\nu_i} \tag{26}$$

$$F_{vib,qm} = -Nk_BT \ln q_{vib,qm} = Nk_BT \sum_{i=1}^{f} \ln \left[2 \sinh \left(\frac{h\nu}{2k_BT} \right) \right] \tag{27}$$

$$F_{elec} = -Nk_BT \ln q_{elec} = NE_m \tag{28}$$

4.3 Molar Helmholtz free energy

$$\mu = F_m = \frac{\partial F}{\partial N} \tag{29}$$

$$= \frac{\partial F_{tr}}{\partial N} + \frac{\partial F_{rot}}{\partial N} + \frac{\partial F_{vib}}{\partial N} + \frac{\partial F_{elec}}{\partial N} \tag{30}$$

$$= \mu_{tr} + \mu_{rot} + \mu_{vib} + \mu_{elec} \tag{31}$$

$$\mu_{tr} = \frac{\partial F_{tr}}{\partial N} = -k_BT \frac{t}{2} \ln \frac{2\pi m k_BT}{h^2} + k_BT \ln \frac{N}{V} = \frac{F_{tr}}{N} + k_BT \tag{32}$$

$$\mu_{rot} = \frac{\partial F_{rot}}{\partial N} = -k_BT \left[\frac{1}{2} \ln \frac{\pi}{\sigma^2} + \frac{r}{2} \ln \frac{8\pi^2 k_BT}{h^2} + \frac{1}{2} \sum_{i=1}^{r} \ln I_i \right] = \frac{F_{rot}}{N} \tag{33}$$

$$\mu_{vib,cl} = \frac{\partial F_{vib,cl}}{\partial N} = -k_BT \sum_{i=1}^{f} \ln \frac{k_BT}{h\nu_i} = \frac{F_{vib,cl}}{N} \tag{34}$$

$$\mu_{vib,qm} = \frac{\partial F_{vib,qm}}{\partial N} = k_BT \sum_{i=1}^{f} \ln \left[2 \sinh \left(\frac{h\nu}{2k_BT} \right) \right] = \frac{F_{vib,qm}}{N} \tag{35}$$

$$\mu_{elec} = \frac{\partial F_{elec}}{\partial N} = E_m = \frac{F_{elec}}{N} \tag{36}$$

4.4 Internal energy

$$U = k_BT^2 \frac{\partial}{\partial T} \ln Q = Nk_BT^2 \frac{\partial}{\partial T} \ln q \tag{37}$$

$$= Nk_BT^2 \frac{\partial}{\partial T} \ln q_{tr} + Nk_BT^2 \frac{\partial}{\partial T} \ln q_{rot} + Nk_BT^2 \frac{\partial}{\partial T} \ln q_{vib} + Nk_BT^2 \frac{\partial}{\partial T} \ln q_{elec} \tag{38}$$

$$= U_{tr} + U_{rot} + U_{vib} + U_{elec} \tag{39}$$

$$U_{tr} = Nk_BT^2 \frac{\partial}{\partial T} \ln q_{tr} = Nk_BT \frac{t}{2} \tag{40}$$

$$U_{rot} = Nk_BT^2 \frac{\partial}{\partial T} \ln q_{rot} = Nk_BT \frac{r}{2} \tag{41}$$

$$U_{vib,cl} = Nk_BT^2 \frac{\partial}{\partial T} \ln q_{vib,cl} = Nk_BTf \tag{42}$$

$$U_{vib,qm} = Nk_BT^2 \frac{\partial}{\partial T} \ln q_{vib,qm} = Nk_BT \sum_{i=1}^{f} \frac{\frac{h\nu}{2k_BT}}{\tanh\left(\frac{h\nu}{2k_BT}\right)} \tag{43}$$

$$U_{elec} = Nk_BT^2 \frac{\partial}{\partial T} \ln q_{elec} = NE_m \tag{44}$$

4.5 Molar internal energy

$$U_m = \frac{\partial U}{\partial N} = \frac{\partial U_{tr}}{\partial N} + \frac{\partial U_{rot}}{\partial N} + \frac{\partial U_{vib}}{\partial N} + \frac{\partial U_{elec}}{\partial N} = U_{m,tr} + U_{m,rot} + U_{m,vib} + U_{m,elec} \tag{45}$$

$$U_{m,tr} = \frac{\partial U_{tr}}{\partial N} = k_BT \frac{t}{2} = \frac{U_{tr}}{N} \tag{46}$$

$$U_{m,rot} = \frac{\partial U_{rot}}{\partial N} = k_BT \frac{r}{2} = \frac{U_{rot}}{N} \tag{47}$$

$$U_{m,vib,cl} = \frac{\partial U_{vib,cl}}{\partial N} = k_BTf = \frac{U_{vib,cl}}{N} \tag{48}$$

$$U_{m,vib,qm} = \frac{\partial U_{vib,qm}}{\partial N} = k_BT \sum_{i=1}^{f} \frac{\frac{h\nu}{2k_BT}}{\tanh\left(\frac{h\nu}{2k_BT}\right)} = \frac{U_{vib,qm}}{N} \tag{49}$$

$$U_{m,elec} = \frac{\partial U_{elec}}{\partial N} = E_m = \frac{U_{elec}}{N} \tag{50}$$

4.6 Entropy

$$S = \frac{\partial}{\partial T}\left(k_B T \ln Q\right) = k_B \ln Q + k_B T \frac{\partial}{\partial T} \ln Q = N k_B \ln \frac{qe}{N} + N k_B T \frac{\partial}{\partial T} \ln q \tag{51}$$

$$= \left(N k_B \ln \frac{q_{tr} e}{N} + N k_B T \frac{\partial}{\partial T} \ln q_{tr}\right) + \left(N k_B \ln q_{rot} + N k_B T \frac{\partial}{\partial T} \ln q_{rot}\right) + \left(N k_B \ln q_{vib} + N k_B T \frac{\partial}{\partial T} \ln q_{vib}\right) + \left(N k_B \ln q_{elec} + N k_B T \frac{\partial}{\partial T} \ln q_{elec}\right) \tag{52}$$

$$= S_{tr} + S_{rot} + S_{vib} + S_{elec} \tag{53}$$

$$S_{tr} = N k_B \ln \frac{q_{tr} e}{N} + N k_B T \frac{\partial}{\partial T} \ln q_{tr} = N k_B \left(\frac{t}{2} \ln \frac{2\pi m k_B T}{h^2} + \frac{t+2}{2} - \ln \frac{N}{V}\right) \tag{54}$$

$$S_{rot} = N k_B \ln q_{rot} + N k_B T \frac{\partial}{\partial T} \ln q_{rot} = N k_B \left(\frac{1}{2} \ln \frac{\pi}{\sigma^2} + \frac{r}{2} \ln \frac{8\pi^2 k_B T}{h^2} + \frac{1}{2} \sum_{i=1}^{r} \ln I_i + \frac{r}{2}\right) \tag{55}$$

$$S_{vib,cl} = N k_B \ln q_{vib,cl} + N k_B T \frac{\partial}{\partial T} \ln q_{vib,cl} = N k_B \left(f + \sum_{i=1}^{f} \ln \frac{k_B T}{h\nu_i}\right) \tag{56}$$

$$S_{vib,qm} = N k_B \ln q_{vib,qm} + N k_B T \frac{\partial}{\partial T} \ln q_{vib,qm} = N k_B \sum_{i=1}^{f} \left[\frac{\frac{h\nu}{2k_B T}}{\tanh \frac{h\nu}{2k_B T}} - \ln\left(2 \sinh \frac{h\nu}{2k_B T}\right)\right] \tag{57}$$

$$S_{elec} = N k_B \ln q_{elec} + N k_B T \frac{\partial}{\partial T} \ln q_{elec} = 0 \tag{58}$$

4.7 Molar Entropy

$$S_m = \frac{\partial S}{\partial N} = \frac{\partial S_{tr}}{\partial N} + \frac{\partial S_{rot}}{\partial N} + \frac{\partial S_{vib}}{\partial N} + \frac{\partial S_{elec}}{\partial N} = S_{m,tr} + S_{m,rot} + S_{m,vib} + S_{m,elec} \tag{59}$$

$$S_{m,tr} = \frac{\partial S_{tr}}{\partial N} = k_B \left(\frac{t}{2} \ln \frac{2\pi m k_B T}{h^2} + \frac{t}{2} - \ln \frac{N}{V}\right) = \frac{S_{tr}}{N} - k_B \tag{60}$$

$$S_{m,rot} = \frac{\partial S_{rot}}{\partial N} = k_B \left(\frac{1}{2} \ln \frac{\pi}{\sigma^2} + \frac{r}{2} \ln \frac{8\pi^2 k_B T}{h^2} + \frac{1}{2} \sum_{i=1}^{r} \ln I_i + \frac{r}{2}\right) = \frac{S_{rot}}{N} \tag{61}$$

$$S_{m,vib,cl} = \frac{\partial S_{vib,cl}}{\partial N} = k_B \left(f + \sum_{i=1}^{f} \ln \frac{k_B T}{h\nu_i} \right) = \frac{S_{vib,cl}}{N} \tag{62}$$

$$S_{m,vib,qm} = \frac{\partial S_{vib,qm}}{\partial N} = k_B \sum_{i=1}^{f} \left[\frac{\frac{h\nu}{2k_B T}}{\tanh \frac{h\nu}{2k_B T}} - \ln \left(2 \sinh \frac{h\nu}{2k_B T} \right) \right] = \frac{S_{vib,qm}}{N} \tag{63}$$

$$S_{m,elec} = \frac{\partial S_{elec}}{\partial N} = 0 \tag{64}$$

References

(1) Conti, S.; Cecchini, M. Predicting Molececular Self-Assembly at Surfaces: A Statistical Thermodynamics and Modeling Approach. *Physical Chemistry Chemical Physics* **2016**, *18*, 1480–31493.

(2) Tidor, B.; Karplus, M. The Contribution of Vibrational Entropy to Molecular Association: The Dimerization of Insulin. *Journal of molecular biology* **1994**, *238* (3), 405–414.

(3) Cecchini, M. Quantum Corrections to the Free Energy Difference Between Peptides and Proteins Conformers. *Journal of Chemical Theory and Computation* **2015**, *11* (9), 4011–4022.

(4) McQuarrie, D. A. *Statistical Mechanics*; University Science Books, 2000.