Free Fluid Manual

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Part I.

Introduction and usage

1. Introduction

Th FreeFluids soft has been developed along years as an aid for personal chemical engineering calculations, and is now licensed as open source according to the General Public License version 3. It is formed for five different applications. The first and basic application is a physical properties calculation module called FreeFluidsC. It uses correlations, EOS, and activity models, for the calculation of physical properties and equilibrium between phases and, as its name indicates, it has been developed in C. The second module is a GUI for the calculation module, called FreeFluidsGui, that allows to do the most normal calculations needed for pure substances and mixtures, and has been developed in C++ using QT 5.

In order to perform the calculations we will need always some data about the substances used: Tc, Pc, coefficients for correlations..., so a way of storing and retrieving this information is needed, and this is the third module: a database that has been implemented in MS Access (with a graphical interface for its consultation and update). And in SqLite without the dedicated graphical interface, although we can manipulate the database with any of the existing tools for SqLite, and FreeFluidsGui gives also some access to it.

The direct interactive use of the calculation module is interesting, but its real power is developed when we automatize the access to it from engineering packages that are normally strongly needed of physical properties calculations. This interphase is done, for Modelica, by FreeFluidsMedia, that uses external objects, created with FreeFluidsGui from the database, to keep the basic information of the substances to be used, and external functions to perform the calculations. Finally FreeFluidsModelica provides models, based on connectors, for some typical chemical engineering applications.

At the moment only FreeFluidsC and FreeFluidsGui have been published under open source license (General Public License v.3)

2. How to use FreeFluids

There are two basic ways of using FreeFluids. The first is to use the GUI for obtaining immediate access to the normal calculations. The second, for programmers, is to link against the C routines in FreeFluidsC to obtain full access to the possibilities of the software. But before it is necessary to speak about how the necessary data will be accessed.

2.1. Substances and mixtures data

For all the calculations we need data regarding the products used, for example the critical temperature and pressure, or other properties, depending on the calculation to be done. The pass of the data to the calculation functions is done in FreeFluids mainly in the form of structures. These structures are in fact containers for data of the products we are using. The used structures are defined in the file 'FF_basic.h'. We can, inside a program, to declare such structures, to fill them with data and to use them for performing calculations. Of course this is impractical, the data should be gathered once, stored, and re-used when needed, so it is necessary some form of storage of data. In some programs, like in CoolProp, this storage is done in files (one file for each substance normally). As the normal place for storing data seems a database this has been the solution used in FreeFluids. There is a database called 'Substances.mdb' with all the tables needed for data storage and a GUI to interact with them. There is also a second database called 'Substances.db3', with the same information in SqLite format, but without the interface. Although it is easy to use the same interface for it, if we register the 'Substances.db3' database in Windows as an ODBC data source, later we can link the interface with the tables of this data source.

The problem with this approach is the difficulty to connect from the program to the database for retrieving the information. In C++ it is very easy, as Qt comes already with the necessary libraries to connect with ODBC data sources in Windows or, if we have not registered the data source or we are not in windows, natively with different databases. In C this is not so easy and the adopted solution has been to use files containing the data. When you are using the GUI, as it is written in C++ with the Qt5 libraries, it retrieves the data from the database, fills the needed structures with the data, and calls the needed function, passing it the structures. Nevertheless, also in the GUI, there is one information that is retrieved always from files, it is the information related with the UNIFAC subgroups and the interaction between groups. As this information needs to be accessed directly by the C program it has been stored in files. These files must be in a subdirectory labelled 'Data' located in the same directory that the main program.

2. How to use FreeFluids

When we want to use the database information in a C program we need previously to export it as a binary file, and place this file in a subdirectory labelled 'Data', just as with UNIFAC data.

The database stores:

1. Basic data for the substances: MW, CAS number, boiling temperature, critical properties etc. All data are in SI units, with the exception of dipole moment (Debye), quadrupole moment(Debye·m), and Van der Waals area and volume (A). The data is stored in the Products table, and each product is identified by an unique Id.

2. Coefficients for the correlation of physical properties. The equations used are defined in the table CorrelationEquations. The combination of equation, and input and output units, identifies completely how the correlation is used. The different combinations are defined in the table Correlations. And in the table CorrelationParam we have the value of the parameters, identifying the substance and the correlation for which these parameters apply.

3. EOS data. The different EOS used are defined in the table EOS. In the table EosParam you will find the parameters for each EOS, referencing the product and EOS for which they apply. Due to the special complexity of the parametric EOS, in this table only the number of terms of each type is indicated for these EOS, and the values for the parameters are stored in the table SWparam.

4. Substance description for different group contribution models: different flavours of UNIFAC, Bondi, Joback. The description is stored in tables that link the substance Id, the group Id and the number of occurrences of the group in the substance. The tables are named Product_Model

5. Binary interaction parameters (BIP) for EOS and activity models. The supported activity models are defined in the table ActivityModels. The BIP are stored in the tables EosInteraction and ActInteraction. There are 12 parameters for each pair, the first 6 are for the pair i,j and the last 6 for the pair j,i. So, if you need to enter the BIP for the mixture acetone-water, you use the first 6 values for the acetone-water pair, and the last 6 for the water-acetone pair. It seems too many parameters, but the number has been selected in order to give compatibility with the Aspen format. Each register in the table identifies the first and second elements of the pair, the EOS type and mixing rule (the model in case of activity) for which they apply, and the formula to use for the computation of the BIP from the parameters. The different formulas are defined in the table InteractEquations. For cubic EOS with VdW or PR mixing rules, the first 3 parameters are for the calculation of k, using the formula $k = a + b * T + \frac{c}{T}$, and the forth for the calculation of l. In this case $k_{i,j} = k_{ji}$ and $l_{i,j} = l_{ji}$. For MKP mixing rule, only the first 3 parameters are used for the calculation of k, but $k_{i,j} \neq k_{ji}$. For SAFT type EOS the first 3 parameters are used to compute the k for the ε_{ij} calculation, using also the formula: $k = a + b * T + \frac{c}{T}$. For activity models it is also necessary to take into account the units used for the energy.

The database has been filled from different sources but only a small part is delivered with the program. Nevertheless you can populate it with data from several interesting projects as: Caleb Bell's Thermo, J.J. Gomera's PychemQt, Chemsep, CoolProp, CHERIC, AIST, GESTIS, ... I have used Python scripts to automate the transfer and probably I will publicate them in the future.

2.2. The GUI

2.2.1. Download and installation

If you are using Windows the only thing you need to do is to download the repository FreeFluidsGui as a zip compressed file, decompress it in your computer and copy the folder «windowsexe» in your preferred place. If you are just going to use the program you can delete all the other folders, that are intended for compiling or modify the program. The program needs no installation and is run just double clicking on the FreeFluidsGui.exe file. If the MS Access database 'Substances.mdb' has been previously registered as an ODBC source, the program will use it. If not, it will look for a database called 'Substances.db3' in its same directory. Of course if you use a registered ODBC source you can put 'Substances.mdb' in the directory you want.

2.2.2. Single substance calculations

2.2.2.1. General and Substance EOS calc tab

You select the substance to use (from the connected database) at the combo-box located at the top of the program window. The substances are now arranged in alphabetical order, but I expect to add a CAS based alternative. When you select a substance a FF_SubstanceData structure is loaded with its basic data, and two more combo-box are loaded with the options available for this substance. You will find these combo-boxes at the top of the 'Substance EOS calc' tab. These combo-boxes allow you to select the EOS and the ideal gas heat capacity correlation to use. The selection of an EOS is mandatory. If you do not select a Cp0 correlation the energy related properties will not be computed. When you select an EOS or a correlation, its data is charged in the FF_SubstanceData structure.

The EOS implemented are: different flavours of Cubics, PCSAFT including association, polar PCSAFT using the dipole terms of Gross & Vrabeck or that of Jog & Chapman, VR SAFT with Mie potential, and high precision reference equations using the multi-parameter methodology of Schmidt &Wagner.

Once you have selected the EOS and the ideal gas heat capacity correlation, you specify the pressure at which the calculation will be performed and the minimum and maximum temperatures. If you check the label 'Calc.saturation prop.', vapor pressure, saturated densities, and vaporization heat calculations will be added. When you press the button 'Calculate' you will obtain 11 calculations between the minimum and the maximum temperatures. The boiling point, at the defined pressure, is also calculated and displayed. The values of H and S displayed are always referenced to the ideal gas state at 298.15^{o}K and 101325 Pa.

In plus to the main calculation from known P and T, you can perform alternative calculations from known thermodynamic variables. On the left of the tab, you select the known variables, fill them with data and press the 'Calculate' button located at the bottom. The unknown variables will be filled.

At the left bottom of the tab you will find some check boxes and a 'Transfer' button. Checking no more than two boxes, and pressing the 'Transfer' button will copy the selected data in the columns 4 and 5 of the 'Substance Correlations/Tools' table. The finality of this will be explained in the next section.

On the top right you will find two buttons: 'Export calculations' and 'Export substance'. The first one will export the results in the table in 'csv' format, that can be imported for example by Excel for graphic representation. The second will produce the exportation of the FF_SubstanceData structure, with all the data charged, in binary format to a file. The exported file must have the '.sd' extension in order to be used later by the C program, for example in Modelica.

2.2.2.2. Substance Correlations/Tools tab

It will work with the substance selected in the upper most combo-box. There are two different functionalities: calculation and display of physical properties, for the selected substance, using the correlations stored in the database, and regression of parameters for correlations and EOS from data entered in the main table.

For the calculation and display of physical properties from the stored correlations, the use is simple: You select the correlation to use at the combo-box, the minimum and maximum temperature for the calculation, and the initial row, and number of rows to calculate. You press the 'fill table' button and you will obtain the result in SI units. The selected correlation is charged in the FF_SubstanceData structure, so when you export the substance (described in the previous tab) it will bring with it the parameters of the used correlations. The correlations that have selected (and are charged) are displayed at the top right of the tab, and you can control if they are displayed or not in the next calculation, by checking or not the check boxes.

At the bottom of the table are buttons for clear the table, exchange columns, and apply common operations to a column (normally for unit conversion)

The second functionality is the regression of parameters from data. Two type of parameters can be regressed: parameters for physical properties correlations, and parameters for EOS. Lets review the first type: You need to put the data on the main table, with the first column being always for temperature (or more generally for the independent variable). On the second column you put the data of the physical variable (dependent variable). You can fill these data manually, import from a file with ';' delimited data, of fill with a previous calculation. Once you have the data in place, tell the system from which row to which row you have filled the data, select the correlation to use for the regression and define limits and initial values for the parameters to find. This last pass is normally not necessary as the system will use normal limits, if you do not specify any. If you specify a limit for a parameter you must supply low and high limits and initial value. Once you press the 'Find corr.coef.' button the result for the best parameters will be displayed at the bottom of the tab in 30 seconds. For some calculations it is mandatory to fill previously (If it has not been filled automatically, or you want to use different values) some data, for example critical temperature and pressure for Wagner equation.

Once you have the result of the parameters you can add them to the data base. This is done at the left bottom of the tab by pressing the 'Add corr. to DB' button. Previously you must specify which correlation are you adding (not all the correlations can be added), the valid limits for the data used, and any other comment.

For the EOS parameter regression, there are two possible situations: you are regressing for a cubic EOS, using the critical values displayed at the top of the tab. In this case the regression take into account only vapor pressure data, located at the second column of the table. This is the case for almost all cubic EOS variations, except for 'PR 78 fit Tc,Pc,w' and for 'PR fit b,a,w and Tc'. In this two cases density data (kg/m3) located on the second column is also used. For SAFT type EOS you must fill vapor pressure and density data, but the format is more flexible than for cubic EOS. As not necessarily you will have, at a defined temperature, data for both vapor pressure and density, you can enter rows with only vapor pressure or only density data. For the rows with density data it is mandatory to specify the pressure at which the data is obtained, if it is at saturation pressure you enter this pressure on the second column. If the pressure doesn't correspond to a saturation pressure, you enter this pressure on the forth column. Always in Pascal. Before to proceed with the calculation you indicate the range of rows to use, the maximum time to use in the optimization in minutes (if you left to 0 it will take 30 seconds), and the number of dipoles in the molecule (only if you are using a polar SAFT equation).

In order to speed up calculations, when density data is used, a screening system is used for the possible solutions. You specify the maximum error acceptable for the critical point (Zc) and for the the liquid density. All solutions over these limits will be automatically rejected. If you are regressing data far from the critical point you can go up with the Zc filter (20% error could be OK), but if you are regressing data close to the critical point is better to maintain it lower (7-8% could be OK). The obtained parameters and the errors are displayed at the bottom of the tab.

As with the correlations you can add the result of the optimization to the database. In this case you do not need to specify the type of EOS (it is taken automatically from the regression), but you can add limits and comments.

After the regression of an EOS the parameters are automatically charged to the FF_SubstanceData structure and you can return to the 'Substance Eos calc.' tab and perform the calculations with the parameters found. And transfer later the result of the calculations to the 'Substance Correlations/Tools' tab to compare with the regressed data.

2.2.3. Mixture calculations

2.2.3.1. Mixture Calc. tab

You define the mixture to use, and the conditions, in this tab, and you obtain the results in the 'Mixture Results' tab.

You need to begin by selecting the substances that will form part of the mixture. This is done by selecting them in the upper combo-box and by pressing the button 'Add subs.' The substance will be added to the table on the upper left. If you are going to do a calculation that need a fixed composition, you need enter the quantities in mass or moles and when pressing the 'Calc. fractions' button they will be passed to molar and mass fractions. If you are going to calculate the full envelope it is not necessary to enter these quantities.

Once specified the composition, it is necessary to establish the thermodynamic model to use. This is done by selecting options from the different combo-boxes. First it is necessary to choose the model for the liquid phase. At the combo-box 'Liquid phase model' you must choose between Activity or Fugacity(EOS). Next you must choose the EOS for the gas phase (also for the liquid if you have chosen Fugacity). Once you have selected

the EOS you must select the exact EOS you are going to use for each substance. And depending on the properties you want to calculate you must choose also the Cp0 correlation to use.

Once established the models for the gas and liquid phases, it is still necessary do some selections. Once of them is the selection of the mixing rule to use. If you have selected Activity as the liquid model, you must select 'VdW with out int.param.' if you selected cubic EOS for the gas phase, or nothing if you selected a SAFT EOS for the gas phase. Otherwise you select the mixing rule that will be used both for the liquid and gas phase.

If you selected Activity for the liquid phase, or you selected a cubic EOS with a gE mixing rule, you must select now the exact activity model to use (UNIQUAC, UNIFAC ....). Otherwise this step is not necessary. If Activity has been selected for the liquid phase, you must also choose if the reference fugacity will be the vapor pressure of the pure substances, or its fugacities at the same conditions.

Finally, if necessary, you must define the binary interaction parameters. By default they are initialized to 0 and are not necessary for UNIFAC activity models. If you are using an activity model not based on UNIFAC the interaction parameters will be used for this model, otherwise they will be used for the selected EOS. The system of entering the parameters (if needed) is the following: You touch on the left table 'Pair substances selection' the position of the pair to specify. If there are values in the database for this pair you will be able to open the combo-box 'Binary interaction parameter selection'. You select the option you want and the values will be charged on the table ready for use. Otherwise you can enter the values manually for the selected pair.

When you finish all the selections you press the 'Create system' button and the system will be ready for performing calculations. After creating the system you can still change the quantities in the composition and the thermodynamic variables at which the calculations are done. But if you need to change the substances used or the thermodynamic models you will need to press again the 'Create system' button