Development of an online application for determination of thermo-physical properties of substances

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Abstract. The article deals with development of a web application for determining thermo-physical properties of substances. A distinctive feature of the application is in using the method of forming functional dependencies in order to determine thermodynamic properties of a working medium for the regions of their liquid, steam, and gas phases that have first-order discontinuities at the inter-phase boundaries. The software package for mathematical modeling of thermodynamic processes, which includes a web application, is considered. Reference systems and computing services for performing mathematical calculations online are described. Examples of procedures used in the application to determine the properties of substances on the experimental data tables are given. The areas of using the application are identified.

1. Introduction

Mathematical modeling of thermodynamic processes takes into account many factors. For example, the process of compressing a working medium in a piston compressor in real conditions is accompanied by a whole complex of interrelated phenomena. These include: changes in volume, pressure and temperature of the working medium; change in the mass of the working medium due to leakage through the seals; changes in the composition and mass of the gaseous form during compression of wet steam; the influence of thermal effects of phase transitions; heat exchange of the working medium and structural elements.

One of the main stages in modeling of such processes is determining thermodynamic properties of gases, liquids and solutions used as working mediums, heating mediums, and refrigerants. Methods for calculating thermodynamic properties of a working medium in the process of mathematical modeling of various thermodynamic processes ultimately determine quality and reliability of the resulting solution.

Currently, various scientific and educational as well as commercial organizations have accumulated a huge amount of information on the properties of substances, which are usually presented in various reference sources: traditional paper based sources [1], electronic databases on thermo-physical properties of substances [2,3] and various automated information systems. The latter is by far the most...
attractive for a number of reasons: first, they do not need to be looked for as they are in open access via the Internet; secondly, they are usually certified; thirdly, they have an advanced search service for finding and processing necessary information about the properties of substances.

Let us consider some of these systems.

The program REFPROP [3,4], provides calculation of thermo-physical properties of technically important substances, contains a database with constants for state equations. It was developed by the National Institute of Standards and Technology (USA), which, together with studying the properties of individual substances, collects previously obtained data from around the world, processes it and creates free or commercial software products on their basis - databases with properties of substances.

Together with thermodynamic properties and their derivatives, transport properties (viscosity, thermal conductivity, as well as the dielectric constant, the highest and the lowest calorific value) are calculated.

For a number of pure products, the boundaries of the solid phase (melting and sublimation lines) are also calculated. The system also makes it possible to depict thermodynamic processes on diagrams $T, s; T, h; p, h$. This program can be directly connected to Mathcad through the DLL (Dynamic Link Library) mechanism.

The GERG2008 library [5,6] is the author’s realization of thermodynamic library based on the GERG2008 state equation proposed by doctor of engineering, professor W.Wagner and his colleagues. This equation of state provides the most accurate (at present) estimate of thermodynamic properties of natural gases and other mixtures consisting of natural gas components. It can be used to calculate the mixtures of 21 components of natural gas (12 alkanes, hydrogen, nitrogen, oxygen, carbon monoxide and dioxide, hydrogen sulfide, water, helium and argon) in a wide range of pressures (up to 70 MPa) and temperatures (from 60 to 700 K). Users of this equation and software are more than 80 leading companies and universities, as well as state research institutes in Germany, France, Norway, the United States and other countries.

Simulis Thermodynamics of the French company ProSim is a powerful modern software system for calculating thermo-physical properties and phase equilibria (TPP and PE) for a wide range of products on a modern methodical basis [7]. Simulis Thermodynamics provides the ability to calculate a large set of thermodynamic and transport properties of products by their molar or mass composition: density, compressibility factor, isobaric and isochoric heat capacity, internal energy, enthalpy, entropy, sound velocity, Joule-Thompson coefficient, dynamic and kinematic viscosity, thermal conductivity, coefficient of surface tension. At the same time, the derivative of the calculated property by pressure, temperature, or the content of one of the components can be determined simultaneously. If necessary, one can immediately perform phase equilibrium calculation, find phase compositions and determine the value of the desired property for each phase. In addition, the system allows calculating phase equilibrium of two immiscible liquids, determining composition and content of phases by temperature and pressure. The coefficients of phase equilibrium and their derivatives by pressure, temperature, or content of one of the components are also calculated.

One of the perspective areas for using electronic databases on thermodynamic properties of substances is mobile devices. Wide spread of mobile devices, growth of their performance, and free access to the Internet significantly expand the areas of their application and allows creating mobile applications in various areas of human activity. The choice of web technologies for creating of an application is based on the need to make it as accessible as possible on different devices (computers, tablets, smartphones) and on different operating systems. At present, there are many operating systems, both for personal computers and mobile devices and making applications for each operating system is an intensive and time consuming process. Therefore, transferring application development into the field of web technologies makes it possible to develop a cross-platform application available for various operating systems. An additional advantage of web application is the ability to quickly update, correct errors and add new features.
In this regard, the paper deals with development of a web application for calculating thermo-physical properties of substances using experimental data tables. This application is a part of the set of programs for mathematical modeling of thermodynamic processes.

2. Aim and objectives of the study

The aim of creating a web application is to improve the software complex for mathematical modeling of thermodynamic processes and its methods.

To achieve this goal, the following problems ought to be solved:
- analysis of existing methods of calculating thermodynamic properties of a working medium in modeling of thermodynamic processes;
- development of a numerical method for processing experimental dependencies on the properties of substances for existence regions of liquid, steam, and gas phases with first-type discontinuities at interphase boundaries;
- development of algorithms for solving equations of models of interrelated thermodynamic and hydrodynamic processes in real gases;
- development of software for mathematical modeling of thermodynamic problems for real gases.

3. Description of the software complex for mathematical modeling of thermodynamic processes

As a result, the following elements were developed:
- a set of programs for supporting thermodynamic processes modeling comprising the following blocks (Figure 1):
  - block of initial data origination (block 1);
  - library of experimental data processing algorithms (block 2);
  - decision block (block 3);
  - mathematical models of gas compression process in a piston compressor and changes in the state of saturated water steam when moving through a pipeline (block 4);
  - decision block (block 4), which includes the blocks for choosing the method for experimental data processing;
  - tables of experimental data (block 5);
  - storage of functional dependencies obtained during processing of experimental data tables (block 6);
  - block of online calculations (7);
  - user interface.

The block of initial data origination (block 1) is intended for processing tables of experimental data obtained from various sources. In particular, it can be data from existing databases or scanned data tables from reference books, which are placed in block 5 for storage.

The library of experimental data processing algorithms (block 2) includes approximation and interpolation methods of experimental data for two variables: linear interpolation method for areas without phase transformations, spline interpolation method for data areas with phase transitions, Akima algorithm for areas bordering with phase transition areas and the least squares method for finding coefficients of approximating polynomials for functions of one variable for constructing equations on the saturation line.

The decision block (block 3) is a computing module that performs the following main functions: selection of experimental data tables with the properties of substances and their preliminary processing; selection of an algorithm for tabular data processing; obtaining functional dependencies used in compilation of process models; testing of obtained dependencies.

The library of models (block 4) includes models of thermodynamic processes of gas compression in a piston compressor and changes in the state of saturated water steam when moving through a pipeline.
Figure 1. The block diagram of the software complex.

The block of functional dependencies (block 6) contains functional dependencies obtained by modeling various thermodynamic processes on the basis of experimental data tables processing containing the properties of substances acquired from various sources. During experimental data processing functional dependencies are formed to be used in further calculations.

In order to determine thermodynamic properties of a working medium while forming functional dependencies, we have developed a method for the regions of existence of liquid, steam and gas phases with first-type discontinuities at interphase boundaries, which includes the following steps (Figure 2):

1) Splitting tabular data by the region. Single-phase areas (liquid, gaseous) and a mixed area are distinguished. The criterion for a point belonging to a particular area is the position of the current coordinate of the point $t$ relative to the points $t_i$ and $t_{i+1}$ in which $f(t_i) - f(t_{i+1})$ is maximal over the entire range of the parameter.

2) Input of additional data specifying a phase transition region (for example, data on the properties of steam on the saturation line). Phase transition points are determined by checking the conditions: $0 < Cl - Cs$.

$$ |Cl - Cs| > 0, \text{ where } \lim_{t \to 0+} f(t) = Cl, \lim_{t \to 0} f(t) = Cs,$$

where $Cl$ and $Cs$ are heat capacity of liquid and steam, respectively.
Calculation of \( f(t) \) at the point \((i,j)\)

Selection of interpolation formula

Detection of interphase boundaries

Start

Experimental data input

Detection of interphase boundaries

\( i = x_0, x_n \)

Selection of interpolation formula

\( j = y_0, y_n \)

Calculation of \( f(t) \) at the point \((i,j)\)

Database entry

End

**Figure 2.** The block diagram of the experimental data processing algorithm.

3) Interpolation for each region. For single-phase areas interpolation is performed using bilinear or spline interpolation method. For areas adjacent to the phase transition line we use the method of inverse weighted distances for interpolation. The interpolation formula used in this method is:

\[
C_{i,j} = \sum_{k=1}^{m} \frac{C_k}{r_{ijk}^\beta} \left( \sum_{k=1}^{m} \frac{1}{r_{ijk}^\beta} \right)
\]

where \( C_{i,j} \) – interpolation value for the \((i,j)\)-th grid node; \( C_k \) – the value at the \(k\)-th point of the data table; \( r_{ijk} \) – distance between the \((i,j)\)-th node and the \(k\)-th point; \( m \) – the number of points taken into account when calculating the value in the \((i,j)\)-th node; \( \beta > 0 \) is the degree of inverse distance.

The block of online calculations (block 7). It is a web application located on the server. It has several procedures with tables of experimental data from reference materials and allows obtaining intermediate values from tables of experimental data. In order to obtain the results, it is required to select the procedure and specify pressure and temperature values.

4. Implementation of the block of online calculations (block 7)

1. When implementing this block, various existing services were considered that could be suitable, in particular:

- Mathcad Gateway developed by the PTC (Parametric Technology Corporation) [7]. This is a server that provides universal and secure access to engineering calculations online from any device. Users can access calculations through a web browser and can calculate specific problems. The server is installed in an organization and it is protected from unauthorized access.

- online service for mathematical calculations CoCalc (Collaborative Calculation in the Cloud / Co-Computing in the Cloud) [8] allows to perform various calculations, work with text, graphs and databases, create interactive applications. A programming language Python is used for calculations.
Calculations are combined with HTML, CSS, JavaScript, CoffeeScript, Go, Fortran, Julia, GAP, Axiom, Ruby, Perl, Maxima, Maple, Markdown, and Wiki. Editing is supported by multi-cursor, Vim or Sublime Text bindings can be enabled. The user can also use an Ubuntu console and access the project via SSH (Secure Shell). LaTeX documents can be created with the Python code embedded in them, which will not be displayed in the final pdf file.

Other services offering mathematical calculations online were also considered. They offer interesting solutions, but they are not suitable for different reasons, for example, Mathcad Gateway requires a license, CoCalc requires programming skills from the user.

This gave an incentive to development of a web application, which is included in the program complex for determining thermo-physical properties of substances (Figure 3).

Web application work is distributed between a client and a server; data is exchanged through the network. The client uses a browser window that displays user’s interface. Any modern browser is suitable for this application. The server stores: library of experimental data; algorithms for calculations; dynamic visualization library.

The main programming language for the application is php; for interface visualization the HTML hypertext markup language and CSS styles are used. 3D graphics visualization is done by the vis.js library written in JavaScript; it consists of several components: DataSet, Timeline, Network, Graph2d, and Graph3d. Vis.js is a browser-based dynamic rendering library. The library allows simplifying processing of large-scale dynamic data and implements data visualization. The library is freely distributed and available for download from http://visjs.org/ [9].

The application operation scheme can be described in several stages: data entry, data processing on the server, output of the obtained results. At the input stage, the user selects an experimental data table, sets the required parameters and sends a request to the server, where the corresponding calculations are made. After performing the calculations, the results are returned to the client in textual form and in the form of a 3D graph.

The application interface consists of a data entry block and a result block. The data entry block is a form that needs to be filled in by uploading a table of experimental data, and also indicating the required parameters.

There are two options for uploading an experimental data table:
- first option is to choose from the list offered by the application. Sources of primary information are databases with the properties of substances [10] (existing databases, including cloud computing servers);
- second option is to upload your table from your device, the loaded table must be prepared in advance and converted into the .csv format.

The csv format is a text format intended for presentation of tabular data, each line of the file is a table row; column values separator is a comma (,) symbol. For convenience, one can use Microsoft Excel spreadsheet, enter data into a spreadsheet, and then convert it to csv format. It can be done by standard tools: one needs to go to the “File” menu, select “Save As”, “Save Document” window
opens and in the “File Type” field one should select the “CSV (comma for column separation) (*.Csv)” format.

Based on the entered data, the required parameter is calculated and a 3d graph is plotted; both are displayed in the result block.

5. Results and discussion
An example of working with experimental data tables (using the heat capacity table of water and water steam as an example) is shown in Figures 4 and 5. The experimental data table is taken from the reference book by N B Vargaftik [1].

The example illustrates the calculation of heat capacity of water at the temperature of 240° C and the pressure of 40 (bar). A 3D graph is convenient as it allows quickly changing of source data and getting the desired parameter.

The results of experimental data processing are recorded in the form of functions-procedures (in this case, a procedure called heat_capacity_water_and_steam (P,T)), and are stored in the system database for further use in modeling. Thus, in order to obtain the required parameter, it is sufficient to refer to the procedure with the current values of the parameters being changed.

Below are descriptions of some of the procedures included in the database of functional dependencies:

1) Viscosity_water_and_steam procedure is designed to determine viscosity of water and water steam. The table of experimental data from the reference book by N B Vargaftik is used as initial data source [1].

| T°C | 0   | 1   | 10  | 20  | 40  | 60  | 80  | 100 |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|     | 4.218 | 4.217 | 4.212 | 4.207 | 4.196 | 4.186 | 4.176 | 4.165 |
| 50  | 1.929 | 4.181 | 4.179 | 4.176 | 4.172 | 4.167 | 4.163 | 4.158 |
| 100 | 1.911 | 2.033 | 4.214 | 4.211 | 4.207 | 4.202 | 4.198 | 4.194 |
| 120 | 1.913 | 2.007 | 4.243 | 4.24 | 4.235 | 4.23 | 4.226 | 4.221 |
| 140 | 1.918 | 1.984 | 4.283 | 4.28 | 4.275 | 4.269 | 4.263 | 4.258 |
| 160 | 1.926 | 1.977 | 4.337 | 4.334 | 4.327 | 4.32 | 4.313 | 4.307 |
| 180 | 1.933 | 1.974 | 2.613 | 4.403 | 4.395 | 4.386 | 4.378 | 4.37 |
| 200 | 1.944 | 1.975 | 2.433 | 4.494 | 4.483 | 4.472 | 4.461 | 4.45 |
| 220 | 1.954 | 1.979 | 2.316 | 2.939 | 4.601 | 4.586 | 4.571 | 4.557 |
| 240 | 1.964 | 1.985 | 2.242 | 2.674 | 4.763 | 4.741 | 4.72 | 4.7 |
| 260 | 1.976 | 1.993 | 2.194 | 2.505 | 3.582 | 4.964 | 4.932 | 4.902 |
| 280 | 1.987 | 2.001 | 2.163 | 2.395 | 3.116 | 4.514 | 5.25 | 5.2 |
| 300 | 1.999 | 2.01 | 2.141 | 2.321 | 2.834 | 3.679 | 5.31 | 5.7 |
| 320 | 2.011 | 2.021 | 2.126 | 2.268 | 2.649 | 3.217 | 4.118 | 5.79 |
| 340 | 2.024 | 2.032 | 2.122 | 2.239 | 2.536 | 2.943 | 3.526 | 4.412 |
| 350 | 2.03 | 2.038 | 2.125 | 2.235 | 2.504 | 2.861 | 3.35 | 4.043 |

Figure 4. Table of heat capacity values of water - I and water vapor – II.

Procedure reference
viscosity_water_and_steam (P,T,pn,pv,tn,tv).

Parameters description:
P – pressure (bar), pressure ranges from 1 to 800 bar;
T – temperature (°C), temperature ranges from 0 to 700 °C;

pn and pv – lower and upper limits of pressure change in the process under study, respectively;

tn and tv – limits of temperature change in the process under study.
The \( pn, pv, tn, \) and \( tv \) parameters are optional and are used to reduce the running time of the procedure.

An example of procedure reference:

\[
\text{viscosity\_water\_and\_steam}(20 \text{ bar, } 80 ^\circ \text{C}) = 3513 \text{ N}\cdot\text{s/m}^2.
\]

\[
\text{viscosity\_water\_and\_steam}(20 \text{ bar, } 230 ^\circ \text{C}) = 169 \text{ N}\cdot\text{s/m}^2.
\]

Figure 5. An example of experimental data processing with the values of heat capacity of water and water steam.

2) Thermal\_conductivity\_water\_and\_steam procedure is designed to determine thermal conductivity \( \lambda \cdot 10^3 \text{ W/(m·°C)} \) of water and water steam:

Procedure description:
The thermal\_conductivity\_water\_and\_steam procedure is intended for determining thermal conductivity of water and water steam.

Procedure reference:
thermal\_conductivity\_water\_and\_steam (P,T,pn,pv,tn,tv)

Parameters description:
\( P \) – pressure (bar), pressure ranges from 1 to 500 bar;
\( T \) – temperature (°C), temperature ranges from 0 to 700 °C;

Parameters values: \( pn, pv, tn \) and \( tv \) are identical to the preceding procedures.

An example of procedure reference:

\[
\text{thermal\_conductivity\_water\_and\_steam (20 \text{ bar, } 50 ^\circ \text{C}) = 645 \cdot 10^3 \text{ N}\cdot\text{s/m}^2.}
\]

\[
\text{thermal\_conductivity\_water\_and\_steam (20 \text{ bar, } 240 ^\circ \text{C}) = 169 \cdot 10^3 \text{ N}\cdot\text{s/m}^2.}
\]

3) Pressure\_saturation\_line procedure is designed to determine pressure \( P \) (bar) on the saturation line:

Procedure description:
The procedure pressure\_saturation\_line is intended for determining pressure on the saturation line depending on the temperature.

Procedure reference:
pressure\_saturation\_line (T,tn,tn)

Parameters description:
$P$ – pressure (bar);
$T$ – temperature (°C), temperature ranges from 0 to 373.9 °C;
$tn$ and $tv$ – limits of temperature change in the process under study.
The $tn$ and $tv$ parameters are optional and are used to reduce the running time of the procedure.
An example of procedure reference:
pressure_saturation_line (100 °C) = 1.014·10⁵ (bar).

4) Temperature_saturation_line procedure is designed to determine temperature $T$ (°C) on the saturation line:
Procedure description:
The temperature_saturation_line procedure is reverse to the previous one and is intended for
determining the temperature on the saturation line depending on the pressure.
Procedure reference
temperature_saturation_line (P,pn,pv)
Parameters description:
$P$ – pressure (bar), pressure ranges from $1\cdot10^3$ to $2.206\cdot10^7$ bar;
$T$ – temperature (°C);
$tn$ and $tv$ – limits of temperature change in the process under study.
The $tn$ and $tv$ parameters are optional and are used to reduce the running time of the procedure.
An example of procedure reference:
temperature_saturation_line (1·10⁵ bar) = 99.61 (°C).
Application of the developed complex of programs allows increasing the speed of obtaining results
of experimental data tables processing on thermo-physical properties of substances and is convenient
in operation as it allows getting the results of calculations in a remote mode.

6. Conclusion
The mobile application can be useful to students in the learning process and to engineers working in
relevant areas for rapid determination of thermodynamic parameters of substances.
Also, being a part of a software complex for modeling thermodynamic processes, a web application
can be used both for modeling of processes which uses gases and liquids, and for solving applied
problems associated with design of chemical and oil refining industries [11-14].
The application is located at http://vitahost.tambov.ru/dtpm/

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