

ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 2. Equations of State on Demand and Dynamic Updates over the Web

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ThermoData Engine (TDE) is the first full-scale software implementation of the dynamic data evaluation concept, as reported recently in this journal. The present paper describes two major software enhancements to TDE: (1) generation of equation of state (EOS) representations on demand and (2) establishment of a dynamically updated experimental data resource for use in the critical evaluation process. Four EOS formulations have been implemented in TDE for on-demand evaluation: the volume translated Peng–Robinson, modified Sanchez-Lacombe, PC-SAFT, and Span Wagner EOS. The equations are fully described with their general application. The class structure of the program is described with particular emphasis on special features required to implement an equation, such as an EOS, that represents multiple properties simultaneously. Full implementation of the dynamic data evaluation concept requires that evaluations be based on an up-to-date “body of knowledge” or, in the case of TDE, an up-to-date collection of experimental results. A method to provide updates through the World Wide Web is described that meets the challenges of maintenance of data integrity with full traceability. Directions for future enhancements are outlined.

1. INTRODUCTION

As discussed in the first paper of this series,¹ *NIST ThermoData Engine* (TDE)² software represents the first full-scale implementation of the dynamic data evaluation concept for thermodynamic and thermophysical properties.^{3,4} This concept requires large electronic databases capable of storing essentially all relevant experimental data known to date with detailed descriptions of metadata and uncertainties. The combination of these electronic databases with expert-system software, designed to automatically generate recommended data based on available experimental and predicted data, leads to the ability to produce critically evaluated data dynamically or ‘to order’.

Critical evaluation of thermodynamic and thermophysical property data can be performed based on one of three general methods: (1) single-property data analysis; (2) simultaneous analysis of multiple properties with enforced mutual consistency; or (3) through application of an equation-of-state (EOS).^{5,6} The first two approaches were implemented previously in TDE for dynamic data evaluation.^{1,2} Implementation of dynamically evaluated EOS representations is addressed in the present paper. At this time, all discussions are restricted to pure molecular compounds only.

Implementation of the EOS technology allows, in principle, evaluation of all thermodynamic properties of the system simultaneously. In general, an EOS establishes a relationship between the thermodynamic variables of the system, temperature T , volume V , and pressure p . For one mole of pure substance, the equation of state can generally be expressed as

$$pV = RT + f(T, p) \quad (1)$$

where R is the gas constant.

In the case of an ideal gas, where interactions between molecules are absent, the function $f(T, p)$ is equal to zero. In practice, this term is rarely negligible and has been calculated with a wide variety of numerical approximations leading to the development of hundreds of empirical EOS formulations during the last century.⁷ More precise equations of state often contain numerous parameters for characterizing $f(T, p)$. These equations can be deployed only if the compound of interest has been studied adequately to allow determination of the fitting parameters. Data of high quality and broad range are often required for a high-precision EOS. Some less precise EOS formulations containing only a few parameters can be deployed for a large variety of “data scenarios”, including compounds for which data are sparse. In either event, until now, EOS technology has been deployed in only static data evaluations.^{8,9} EOS deployment in dynamic data evaluation is particularly challenging for complex, high-precision equations, due to mathematical complexities, the sensitivity of results to data quality, the necessity to meet special validity criteria, and the need to function without human intervention. Dynamic evaluation provides new opportunities for generating EOS representations for a wide variety of chemical species. A key aspect is the establishment of criteria for deployment of a specific type of EOS based on a particular data scenario, i.e., the data quality and extent.

Full implementation of the dynamic data evaluation concept requires that evaluations be based on an up-to-date “body of knowledge”.^{3,4} To meet this requirement, a system must be established to provide regular updates of available experimental thermodynamic property data. The World Wide Web can provide a path for such updates, but important challenges include maintenance of data integrity and full traceability.

The present paper describes a software implementation¹⁰ of the dynamic data evaluation concept for both principal areas outlined above: (1) generation of EOS representations on-demand and (2) establishment of a dynamically updated experimental data resource for use in the critical evaluation process.

In order to adequately represent a range of data scenarios, four different equations of state of various complexity and precision were selected for implementation: Peng–Robinson,¹¹ PC-SAFT,¹² Sanchez-Lacombe,^{13,14} and fundamental equations based on the Helmholtz energy.^{15,16} A dynamically updated TDE-SOURCE^{1,17} data storage facility was developed, in part, using the multitier Web-Oracle dissemination system¹⁸ recently established in development of the NIST Ionic Liquids Database, ILThermo.¹⁹

2. SELECTED EQUATIONS OF STATE

Equations of state are the underlying basis for the calculation of thermodynamic properties for any fluid. Often, the properties of a pure fluid are represented by a variety of equations; for example, the vapor pressure can be represented by a Wagner type equation and the liquid density with a Tait type equation (cf. ref 20). Multiple equations may be used to span wide ranges of density, where one equation is often used for the liquid, one for the vapor, and possibly a third for supercritical conditions. The critical region may be represented by scaling law equations. The application of multiple equations often results in discontinuities at the borders between equations and inconsistencies between mathematically related properties, such as the vapor pressure and the enthalpy of vaporization.

Fundamental EOS Formulations based on the Helmholtz Energy. These shortcomings can be avoided by using a single equation of state to represent all of the thermodynamic properties for the fluid of interest. Most modern, wide-range, high-precision equations of state for pure fluid properties are fundamental equations explicit in the Helmholtz energy as a function of density and temperature. The advantage of using fundamental equations of state is that all single-phase thermodynamic properties can be calculated as derivatives of the Helmholtz energy. For example

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

where p is the pressure, ρ is the density, and a is the specific Helmholtz energy. Equations for other properties such as the speed of sound are more complex but still require only derivatives of the Helmholtz energy. The location of the saturation boundaries requires an iterative solution of the physical constraints on saturation (the so-called Maxwell criterion that pressures and Gibbs energies are equal at constant temperature during phase changes). Such computational complexities are readily justified, as the result is a fully consistent set of property values.

Equations of state explicit in the Helmholtz energy as the fundamental property with independent variables of density and temperature can be expressed as

$$a(\rho, T) = a^0(\rho, T) + a^r(\rho, T) \quad (3)$$

where $a^0(\rho, T)$ is the ideal gas contribution to the Helmholtz

energy and $a^r(\rho, T)$ is the residual Helmholtz energy, which corresponds to the influence of intermolecular forces. The Helmholtz energy of the ideal gas can be formulated in terms of the ideal gas heat capacity c_p^0 . Equations for $a^0(\rho, T)$ are developed by fitting experimental data for either heat capacities at low pressures, speeds of sound in the gas phase, or values derived from spectroscopic information and the methods of statistical mechanics.

Unlike the case of an ideal gas, the real fluid behavior is often described with empirical models that are only loosely supported by theoretical considerations. Although it is possible to extract values such as second and third virial coefficients from the fundamental equation, the terms in the equation are empirical, and any functional connection to theory is not entirely justified. The coefficients of the equation depend on the experimental data for the fitted fluid.

A common functional form for Helmholtz energy equations of state^{21,22} is

$$a^r(\delta, \tau) = \sum N_k \delta^{d_k} \tau^{t_k} + \sum N_k \delta^{d_k} \tau^{t_k} \exp(-\delta^{l_k}) \quad (4)$$

where δ is the reduced density ($\delta = \rho/\rho_c$) and τ is the inverse reduced temperature ($\tau = T_c/T$). Each summation typically contains 4–20 terms, where the index k points to each individual term. The values of d_k , t_k , and l_k are restricted so that the t_k are generally expected to be greater than zero, and d_k and l_k are integers greater than zero. Further information on equations of state and their applications to several fluids is given by Lemmon and Jacobsen²¹ and Lemmon and Span.²²

Span–Wagner EOS Formulations. The fundamental equations of state used in TDE are based on the work of Span and Wagner.¹⁶ Their work describes the development of two 12-term equations with fixed functional forms: one for nonpolar or slightly polar substances and one for polar fluids. Data sets of high quality were used to develop the functional forms and assess the quality of the resulting data representations. Although the new technical equations suffer from a slight loss in representation accuracy for some compounds with very extensive high-quality data, their shorter forms allow for computations that are as much as ten times faster, depending on the number of terms in the other equations and on the use of special constraints for fitting in the critical region.

The technical equations of Span and Wagner¹⁶ were developed with keen insight into the proper behavior of an equation of state. They extrapolate properly at low temperatures (as demonstrated by the curvature of the isobaric and isochoric heat capacities, and the speed of sound) and at high temperatures (for example, along the “ideal curve” with compressibility factor $Z = 1$). In addition, the number of terms in the eqs (12 each) was kept to a minimum, which decreases the extent of correlation among terms and overfitting. Although the smaller number of terms decreases the flexibility of the equation, and thus its ability to accurately represent a fluid’s properties, its rigid shape allows greater application to substances with limited data. In this way, the fitted equation becomes a reliable tool to fill in gaps in the thermodynamic surface. These fixed functional forms are ideal for use in TDE to represent fluids that are often characterized by limited data sets; however, they are not

recommended for representation of highly polar molecules, such as acids and alcohols.

Other EOS Formulations Implemented in TDE. Three EOS formulations that are used in the engineering community are (a) the volume-translated Peng–Robinson equation¹¹ with a substance-dependent constant volume-translation term (described later), (b) the PC-SAFT equation,¹² and (c) the volume-translated (commonly referred to as the “modified”) Sanchez-Lacombe equation.^{13,14} Although none of these equations approach the precision possible with the fundamental EOS formulations described above, they do have numerous engineering applications, particularly when few or only low-quality experimental data are available. These equations are implemented in TDE, and their formulations are described in the following paragraphs.

The Volume-Translated Peng–Robinson EOS. The Peng–Robinson equation is

$$Z = V(V - b)^{-1} - \Theta V / \{ (RT)(V^2 + \delta V + \epsilon) \}^{-1} \quad (5)$$

where Z is the compressibility factor (pV/RT), p is the pressure, V is the molar volume, R is the gas constant, and T is the temperature. The quantity Θ is defined based on the following expressions

$$\Theta = a\alpha \quad (6)$$

where

$$\alpha = \{ (-0.26992\omega^2 + 1.54226\omega + 0.37464)(1 - T_r^{0.5}) + 1 \}^2 \quad (7)$$

$$a = 0.45724(RT_c)^2/p_c \quad (8)$$

and

$$T_r = T/T_c \quad (9)$$

where ω is the acentric factor, T_c is the critical temperature, and p_c is the critical pressure. Finally, the equation quantities b , δ , and ϵ are defined as follows:

$$b = 0.0778RT_c/p_c \quad (10)$$

$$\delta = 2b \quad (11)$$

$$\epsilon = -b^2 \quad (12)$$

The dimensionless residual Helmholtz energy a^r for the Peng–Robinson equation was obtained by integration

$$a^r = (A - A^0)/RT = \int (Z - 1)\rho^{-1}d\rho \quad (13)$$

where A is the Helmholtz energy for the real-fluid, A^0 is the ideal-gas Helmholtz energy at the same temperature and molar density, and ρ is the molar density.

As described later in the section *The EOS Fitting Process*, the critical temperature, critical pressure, and acentric factor are fixed through an initial critical evaluation by TDE prior to the EOS implementation. Consequently, there is only one adjustable parameter in fitting the Peng–Robinson equation, the volume-translation term v_{tr} . The initial value is calculated by the formula²³

$$v_{tr} = (RT_c/p_c)(-0.014471 + 0.067498\omega - 0.084852\omega^2 + 0.067287\omega^3 - 0.017366\omega^4) \quad (14)$$

“Volume translation”²⁴ means that the volume V , calculated with the original Peng–Robinson equation (eq 5, without volume translation) as a function of temperature and pressure in the single phase region or as a function of temperature on the vapor–liquid saturation line, is shifted by the volume-translation term

$$V_t = V - v_{tr} \quad (15)$$

where V is the volume (of eq 5) that is thermodynamically consistent with all other properties, v_{tr} is the volume-translation term, and V_t is the adjusted volume. It is important to note that V_t is not consistent with all other properties derived with the volume-translated equation. However, this adjusted volume is a better approximation to the observed volume that can be measured experimentally. As follows from this, the volume-translation term affects only single-phase and saturated liquid and gas-phase densities and, in theory, can be refined by fitting any combination of experimental values for these properties. This option as well as the particular state-variable region to fit can be selected by the user. The volume-translated Peng–Robinson equation generally provides a representation that often lies well outside the experimental uncertainty, but calculations are very fast and are widely used in industrial applications.

The Modified Sanchez-Lacombe EOS. The Sanchez-Lacombe equation is another EOS formulation that includes volume translation. Its mathematical form (without volume translation) and application was described by Koak and Heidemann.¹³ The equation is defined in terms of the compressibility factor Z as follows

$$Z = pV/(RT) \quad (16)$$

where p is expressed as

$$p = (-\delta^2\epsilon\nu/V^2) - RT[(\delta - 1)/V + \ln\{1 - \delta\nu/V\}/\nu] \quad (17)$$

with the equation parameters δ , ϵ , and ν defined as follows

$$\delta = 5.1178 + 13.5698\omega + 5.9404\omega^2 - 1.2952\omega^3 \quad (18)$$

$$\epsilon = RT_c(1 + \delta^{0.5})^2/2\delta \quad (19)$$

$$\nu = (RT_c/p_c)[\ln(\delta^{-0.5} + 1) - \{(\delta^{0.5} - 0.5)/\delta\}] \quad (20)$$

All other symbols (V , R , T , ω , T_c , and p_c) are as defined for the Peng–Robinson equation.

Volume translation for the Sanchez-Lacombe EOS was proposed by Krenz.¹⁴ The volume-translation term v_{tr} is expressed as

$$v_{tr} = (3.297\delta - 0.1092M)/1000 \quad (21)$$

where M is the molar mass in $\text{g}\cdot\text{mol}^{-1}$, and v_{tr} is in units of $\text{dm}^3\cdot\text{mol}^{-1}$.

The PC-SAFT EOS. The PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory) equation is based on intermolecular potential theory and is not a volume-translated equation. It is implemented in TDE in the formulation described by Gross and Sadowski,¹² where the primary

Table 1. General Characteristics of the EOS Formulations in the ThermoData Engine (TDE) Software

equation of state (EOS)	required properties	adjustable parameters	thermodynamic consistency	data extent for optimal representation	precision of representation
volume-translated Peng–Robinson	T_c, p_c, ω	1	no	low	low
modified Sanchez-Lacombe	T_c, p_c, ω	1	no	low	low
PC-SAFT	none	3	yes	medium	medium
Span–Wagner	T_c, ρ_c	12	yes	high	high

quantity calculated is the dimensionless residual Helmholtz energy a^r . (Gross and Sadowski later published a formulation that included an association term,²⁵ but this is not implemented in the version of TDE described here.) For the PC-SAFT equation, a^r is calculated with three adjustable parameters, m , σ , and ϵ , and two constant arrays, a and b .¹² The mathematical formulation of the PC-SAFT EOS is complex. For the purpose of completeness, the formulation is included as an Appendix to this article. Due to the complexity of the mathematics, the derivatives of the residual Helmholtz energy with respect to temperature and density that are necessary for the calculation of thermodynamic properties were derived with a symbolic mathematics package²⁶ and then translated to the C++ programming language.

The PC-SAFT EOS can describe vapor pressure and saturation density with good precision but commonly overestimates the critical temperature T_c . Experimental vapor pressures are well represented even to the experimental T_c ; however, saturation densities near T_c are often erroneous because of the overestimation of T_c .

Summary. General characteristics of the four EOS formulations presently in TDE are summarized in Table 1. As can be seen in the table, the volume-translated Peng–Robinson EOS and modified Sanchez-Lacombe EOS have the same requirements and general expectations for quality of property representation. In comparison with the Peng–Robinson EOS (with the original α function, eq 7, implemented in TDE 2.0), the modified Sanchez-Lacombe equation better describes vapor pressure but diverges from the saturation density for the liquid at high temperatures. Also, the extent of the volume-translation adjustment is greater for the modified Sanchez-Lacombe EOS than that for the volume-translated Peng–Robinson EOS. Consequently, parametrization for a restricted temperature range is suggested for a particular application for the volume-translated equations of state. While the volume-translation method works well in the variable range where the translation is made, a volume-translated EOS can give results that are worse than a simple cubic EOS under conditions away from where the translation parameters were established. Among the four equations provided, optimum equation selection is necessarily dependent on the target application and the data scenario for the target compound.

3. CRITERIA FOR EOS DEPLOYMENT

As noted, the equations of state chosen for inclusion in TDE are a very small subset of the plethora of published formulations. The selected equations were chosen, in part, to provide choices that would be serviceable for a broad variety of data scenarios ranging from extensive, high quality data, such as that available for the common hydrocarbon

gases, to effectively none, such as for new or hypothetical compounds.

There are specific sets of properties that are necessary to define each EOS. For the volume-translated Peng–Robinson and modified Sanchez-Lacombe equations, only the critical temperature T_c , critical pressure p_c , and acentric factor ω are required. Technically, no constants are needed to define a PC-SAFT equation, but in practice, application is restricted to compounds with a defined critical temperature, either experimental or predicted by TDE.

Due to the greater number of adjustable parameters, the criteria for successful deployment of the Span–Wagner EOS are more complex and are shown as a flow diagram in Figure 1. If the available data allow definition of an equation (i.e., if the critical temperature T_c and critical density ρ_c are available), a series of additional criteria is used to provide warnings to the user during the EOS fitting process. If ideal-gas heat capacities are not available, the Span–Wagner equation cannot be deployed for energy related properties. Available validated ideal-gas heat capacities²⁷ are stored in the TDE database. The ideal-gas heat capacities are necessary for EOS-based calculation of heat capacities and speeds of sound. Based on the available data, a prognosis for fitting success is made, and the user is warned in the case of a negative or doubtful prognosis (Figure 1). Warnings are provided for compounds with strong intermolecular association (e.g., water, alcohols, and acids) and compounds with normal boiling temperatures above 700 K (e.g., the branched hydrocarbon squalane with empirical formula $C_{30}H_{62}$). In our experience, properties for such compounds are not well described by the 12-parameter Span–Wagner EOS. (It is unclear whether this is due to a limitation of the EOS formulation or the quality of the available predicted and experimental property data.) The absence of experimental vapor pressures, saturated liquid densities, and saturated liquid heat capacities, also, gives a negative prognosis for fitting. In addition, the lack of single-phase liquid densities at pressures $p > 200$ kPa limit the quality of a Span–Wagner EOS representation.

4. THE EOS FITTING PROCESS

In order to define an EOS, there are specific properties (e.g., the critical temperature, acentric factor, etc., depending upon the specific EOS) that must be evaluated prior to deployment of an EOS. The first paper in this series¹ described in detail the dynamic data evaluation methods used in TDE for evaluation of such properties. Fitting an EOS within TDE involves two steps: initial evaluation to provide needed constants and parameters, followed by EOS fitting.

Interface options support the process of EOS deployment for a compound, including equation scaling, fitting, plotting,

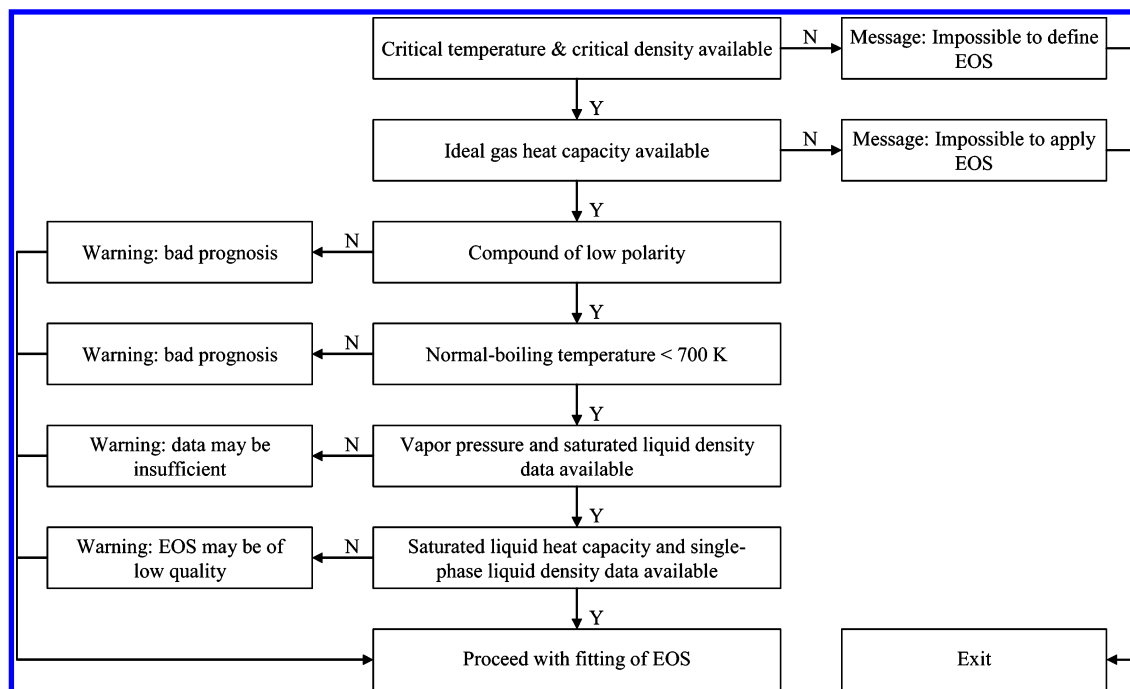


Figure 1. Algorithm for deployment criteria for the Span–Wagner equation of state.

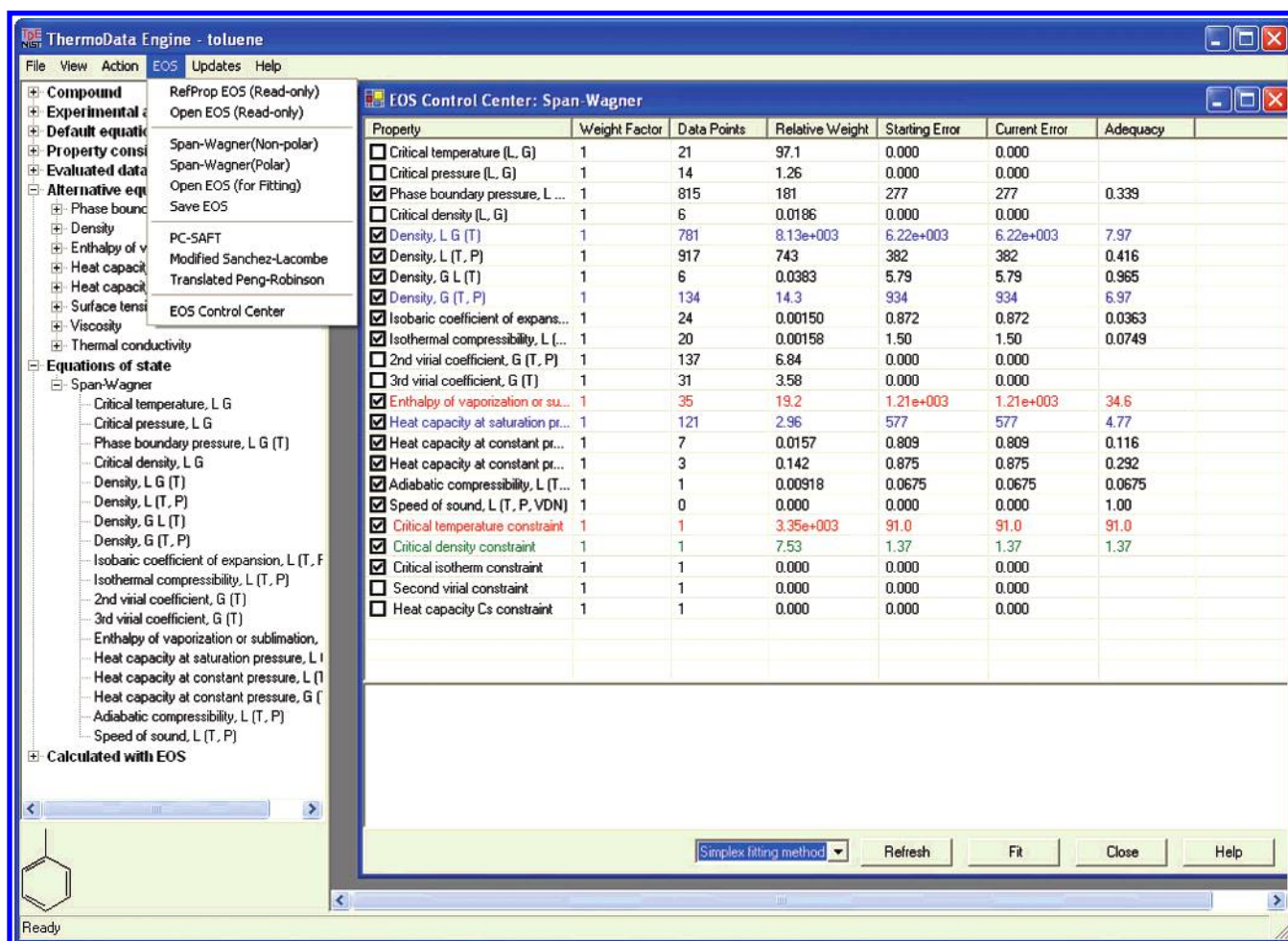


Figure 2. The EOS menu (expanded) and the EOS Control Center interface within the TDE software.

and calculation of property values. Access is provided through the EOS menu shown expanded in Figure 2. The first two menu items allow display of a REFPROP⁹ EOS (if available) or a previously fitted Span–Wagner EOS read

from a file. (A REFPROP EOS is a reference standard EOS for a particular compound distributed with NIST Standard Reference Database 23, version 7. There are EOS representations for 48 compounds in version 7.) These are “read-only”

in the sense that properties derived with the EOS can be displayed and compared with available experimental data, but no refitting or other modifications can be made. Selection of an EOS that is not indicated as read-only initializes the EOS fitting process for the specific equation and opens the EOS Control Center screen, shown at the right in Figure 2. The menu item *Open EOS (for Fitting)* opens (from a file) a Span–Wagner type EOS as an initial condition for further fitting. When opened, the EOS is scaled with the critical temperature and critical density for the compound of interest.

Depending on the selected EOS, the TDE interface provides either basic support or full support. Basic support is provided for read-only equations and includes plotting of EOS curves against experimental data and calculation of property values. Full support further includes fitting of the EOS to experimental data, calculation of covariance and uncertainties, and saving/opening Span–Wagner EOS files. Uncertainties are not calculated for the volume-translated equations, which do not provide the precision of data representation possible with the Span–Wagner EOS.

Fitting an EOS is initiated and monitored through the EOS Control Center (Figure 2). The EOS Control Center shows all properties supported by the EOS and allows full access to the data, including editing, plotting, adjustment of statistical weights for EOS fitting, and selection of the fitting method (Simplex or Simulated Annealing). Adjustment of statistical weights is done directly on the EOS Control Center form through modification of the Weight Factor (column 2) for a particular property. Only the number of data points (column 3) is shown explicitly in the form, but complete access to the underlying numerical experimental and predicted data, including bibliographic sources, is available through interface commands similar to those described previously.¹ The Relative Weight (column 4) is a function that represents the relative importance of the property in the fitting process and is calculated as the sum of the squared property values multiplied by their statistical weights (as determined by TDE). The statistical weights are the reciprocal squares of the estimated uncertainties for the predicted and experimental property data. Any change by the user to the Weight Factor is directly reflected here. The Starting Error (column 5) is the error function for the property before fitting and is calculated as the sum of the squared deviations of the calculated values (with the EOS) from the experimental and predicted data multiplied by their statistical weights. The Current Error (column 6) is the error function for the property after the last completed fitting cycle.

The final column of the EOS Control Center (column 7; Adequacy) is a special function that indicates the accuracy of representation for each property. This quantity is regularly recalculated and displayed during the fitting process. By monitoring this quantity, the user can decide to interrupt a long calculation, if the results are adequate for a particular purpose. The adequacy function is defined as

$$A = (1/n)\sum(d_i/u_i)^2 \quad (22)$$

where n is the number of data points, d_i is the curve deviation of the i th data point, and u_i is the uncertainty associated with it. Achieving an adequacy A value near or less than 1 indicates good property representation and is the goal of the fitting process. To ease monitoring by the user, the property

rows are displayed in colors that are changed during the fit based on the value of the adequacy A . Fitting times for complex equations can be long, and the user can interrupt the fit at any time to review the results achieved.

Fitting of an EOS is complex and involves minimization of a multiproperty objective function, where the relative importance of properties is controlled by weighting factors for each property multiplied by data point weights, when calculating the objective function. Properties can also be excluded from fitting and calculation of the objective function based on information maintained within the EOS class.

In the case of the Span–Wagner EOS, fitting of the properties alone does not ensure that the resulting EOS will have a shape that is thermodynamically valid. Consequently, in addition to the fitting of properties, fitting constraints were added that contribute to the objective function as properties but represent deviations from certain conditions of validity for property representation. The five constraints used in TDE version 2.0 are listed at the bottom of the EOS Control Center property list (Figure 2); (1) critical temperature constraint, (2) critical density constraint, (3) critical isotherm constraint, (4) second virial constraint, and (5) heat capacity $C_{\text{sat,m}}(\text{liquid})$ constraint.

The critical temperature T_c and critical density ρ_c constraints are used to ensure that differences between the EOS fitting parameters (nominally T_c and ρ_c) and the T_c and ρ_c values derived in the preliminary dynamic critical evaluation are in accord with the uncertainties from the evaluation. This is analogous to the usual EOS fitting procedure in which these properties are used as fixed parameters.

The critical isotherm constraint helps to ensure that only one inflection point occurs in the curve for the critical isotherm. Figure 3 shows a valid shape for the critical isotherm of a compound with a critical density ρ_c near 300 kg·m⁻³. The final two constraints concern the shapes of the second virial coefficient B variance with temperature (Figure 4) and for the $C_{\text{sat,m}}(\text{liquid})$ variance with temperature (Figure 5). The first derivative with respect to temperature is enforced to be positive for B , and the second derivative with respect to temperature is enforced to be positive for $C_{\text{sat}}(\text{liquid})$. This latter constraint is not valid for highly associating liquids, such as alcohols or acids.

The fitting methods used in TDE, involving the combination of experimental data, predicted data, and fitting constraints, allow building Span–Wagner type equations of state even for compounds with little experimental data. Such equations had previously been impossible to derive without this comprehensive approach. As with all other properties, the user can increase or decrease the relative weights of the fitting constraints and has the option to include or exclude them from fitting. Based on the selected EOS, data availability, and the known behavior of the selected EOS, TDE preselects properties and constraints as an initial guide for the user.

Fitting Span–Wagner equations of state is a complex task and may require user intervention to achieve optimum results. User actions may include changing relative weights for properties and fitting constraints, careful reviewing of experimental and predicted data with explicit rejection of suspicious data, temporary exclusion of some properties during a preliminary fit, altering the fitting method (Simplex or Simulated annealing), and starting from a successful

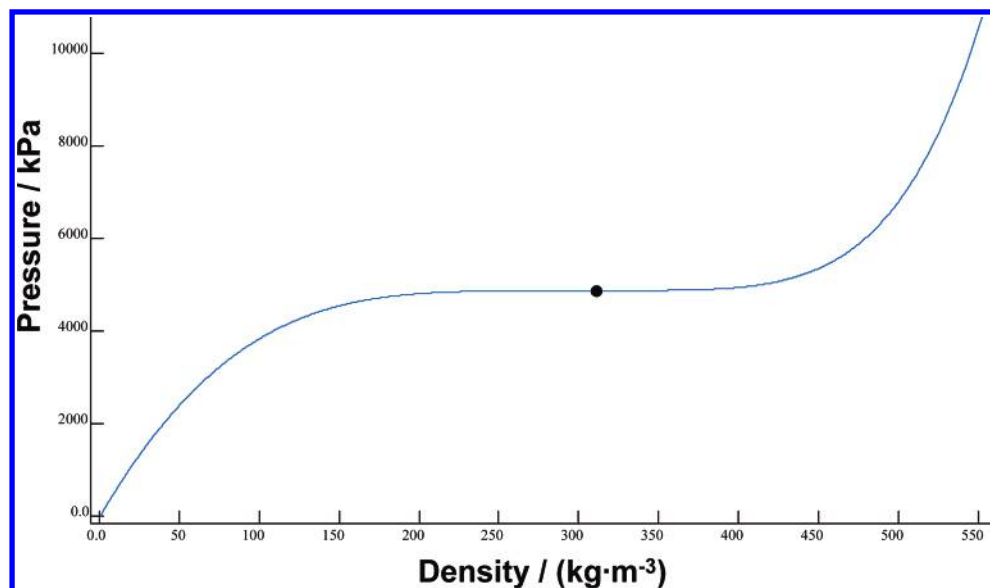


Figure 3. The line represents a valid shape for the critical isotherm showing a single inflection point at the critical density ρ_c , indicated by ●. The curve shown is for benzene.

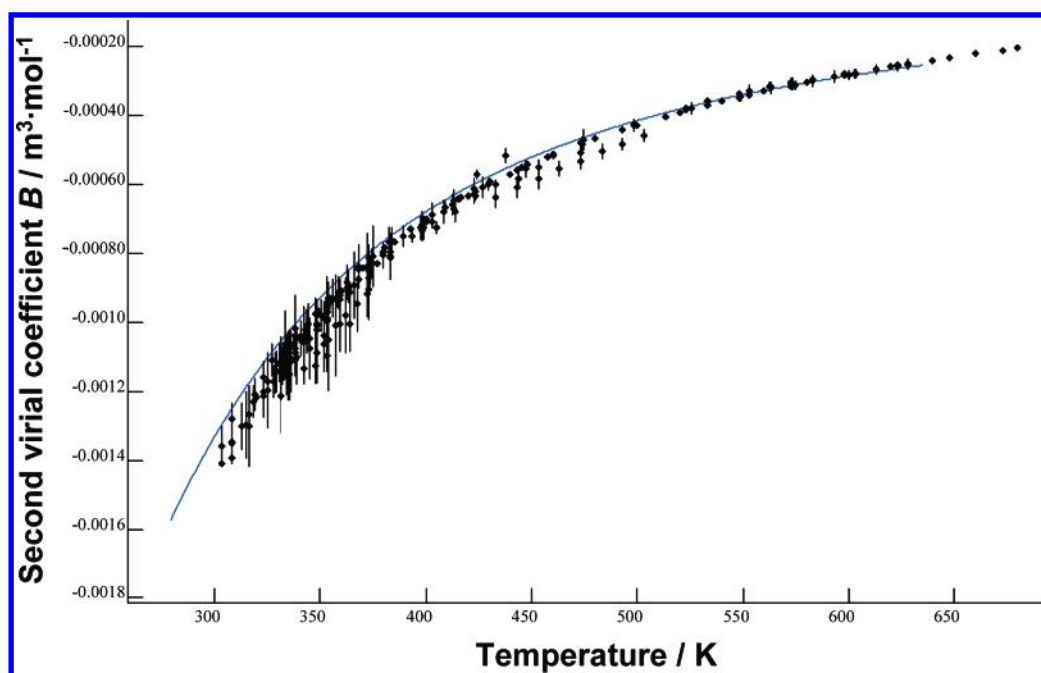


Figure 4. The curve represents a valid shape for the curve of a second virial coefficient against temperature. The data points shown are experimental values for benzene with their uncertainties.

equation (opened through the EOS menu, described earlier) for another related compound as an initial approximation. Criteria of fully successful fitting are low adequacy values (close to or less than 1) for all properties, satisfied fitting constraints (zero contributions to the objective function), valid shape of curves, and uniform scattering of experimental data along curves, as checked visually.

5. UNCERTAINTY ESTIMATES

Uncertainty estimates are based on the covariance approach. The standard uncertainty u is calculated with the equation

$$u^2 = \sum_{i=1}^n \sum_{j=1}^n C_{ij} (\partial P / \partial \phi_i) (\partial P / \partial \phi_j) \quad (23)$$

where C_{ij} is a covariance matrix element, n is the number of equation parameters, and $\partial P / \partial \phi_i$ is the derivative of property P with respect to parameter p_i . The covariance matrix is evaluated like that for any nonlinear function by assuming short-range linear dependence of the properties on the parameters.²⁸ It is the matrix reciprocal to the matrix comprised of the elements

$$M_{ij} = N^{-1} \sum_{k=1}^N w_k (\partial P / \partial \phi_i) (\partial P / \partial \phi_j) \quad (24)$$

where N is the number of data points, w_k is the statistical weight of the k th data point, and $(\partial P / \partial \phi_i)_k$ is the derivative of the property with respect to the i th parameter for the k th data point for all properties used for EOS fitting. Indices i and j vary from 1 to the number of adjustable parameters in

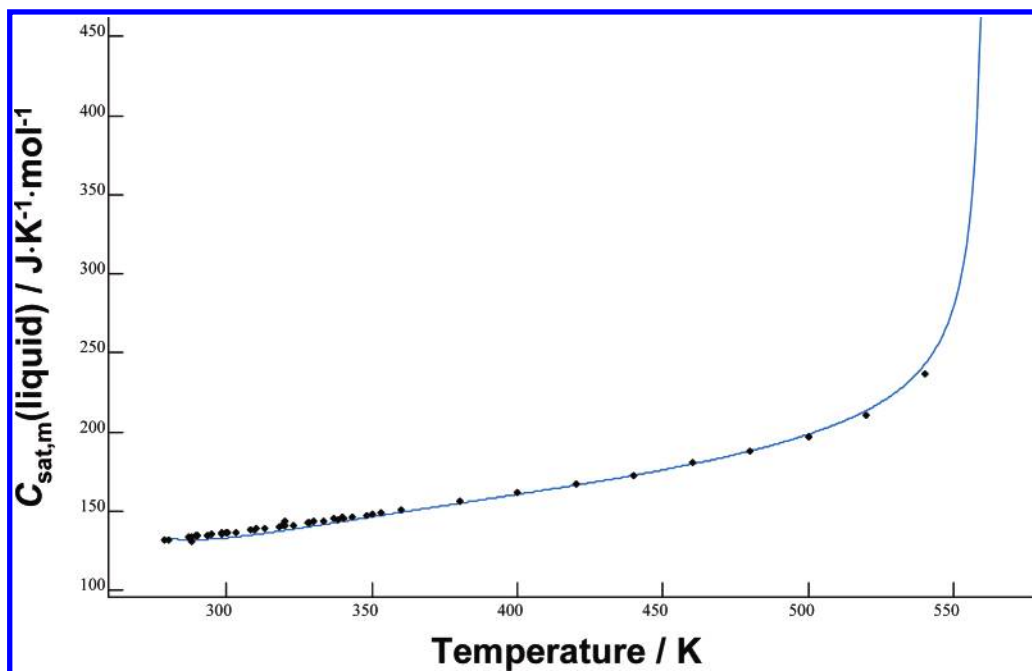


Figure 5. The curve represents a valid shape for the saturated liquid heat capacity against temperature curve. The data points shown are experimental values for benzene with their uncertainties. The sharp rise in $C_{\text{sat,m}}$ occurs as the critical temperature T_c is approached.

the EOS. As was described previously for TDE,¹ both experimental uncertainties and curve deviations are taken into account when calculating statistical weights w for the covariance matrix evaluation

$$w = 1/d^2 \quad (25)$$

where d is the greater of the experimental uncertainty or the curve deviation. Covariance determinations for equations of state are complicated by the fact that most properties are calculated with complex algorithms. Consequently, derivatives of these properties can be evaluated only numerically.

Equations of state such as the Span–Wagner EOS are multiparameter equations (12 parameters in TDE but as high as 56 parameters for water²⁹), and the usual covariance approach for them is often inadequate, resulting in unrealistic uncertainties that are too large in regions sparsely populated with data and too small in regions of high data density. This problem has been mentioned previously by Whiting et al.³⁰ An iterative refinement procedure was developed for such multiparameter equations in order to overcome this shortcoming for uncertainty calculations. After evaluation of the covariance matrix, uncertainties are calculated for all data points used in the fit. An “inadequacy” function f is evaluated for the covariance by summation over all property data points

$$f = N^{-1} \sum |\ln(u_i/d_i)| \quad (26)$$

where N is the number of data points, u is the calculated uncertainty, d is defined above, and the summation is over all data points from $i = 1$ to N . If the inadequacy exceeds a certain value (1/8 in TDE) and the maximum number of allowed iterations (8 in TDE) is not exceeded, the statistical weights w used for the covariance calculation are adjusted with the relation

$$w_{\text{new}} = w_{\text{old}}(u/d) \quad (27)$$

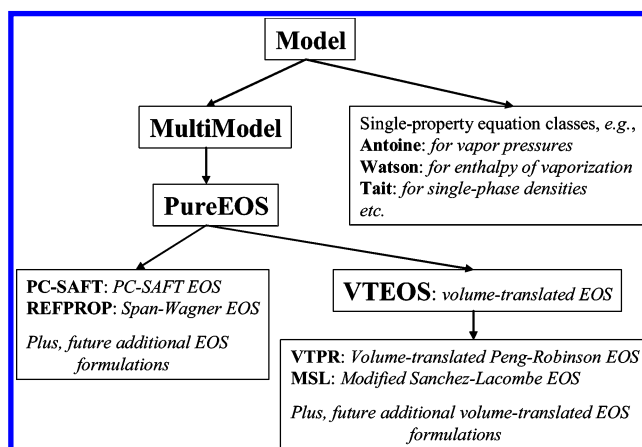


Figure 6. Hierarchy of classes (shown in boldface type) used for implementation of equations of state as property representations in TDE. The text is provided to elucidate the abbreviations used as class names.

and the covariance evaluation is repeated. The value 1/8 for the inadequacy function was determined empirically.

6. SOFTWARE ARCHITECTURE

The software architecture for TDE was described in the first paper of this series.¹ In this section, specific additions to accommodate EOS support are described, including specific C++ classes.

The hierarchy of classes supporting equations of state (Figure 6) consists of the Model, MultiModel, PureEOS, and VTEOS classes. These define common features (data and methods) of the following objects: equation fitting for a single property (Model), equation fitting for representation of multiple properties based on a single equation (MultiModel), fitting an EOS for a pure compound (PureEOS), and fitting a volume-translated EOS for a pure compound (VTEOS).

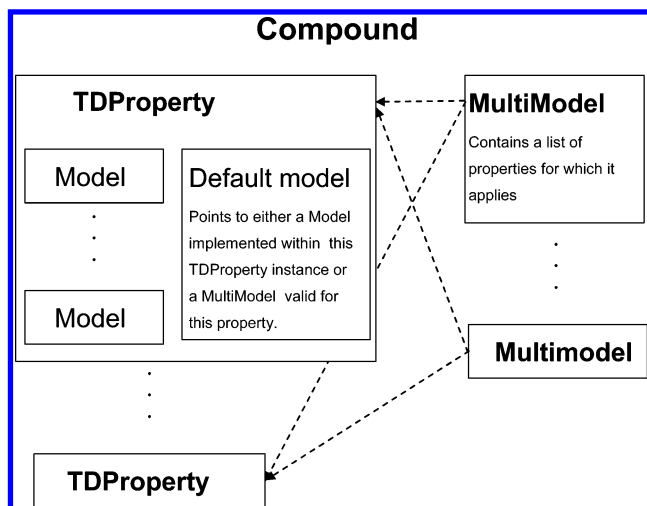


Figure 7. Structure of the Compound class in TDE.

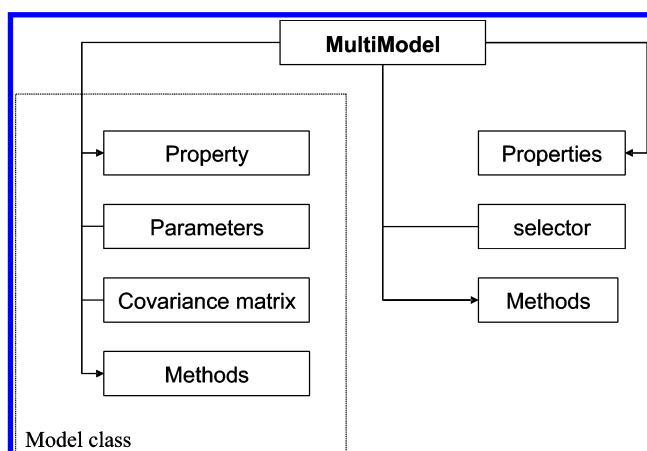


Figure 8. Structure of the MultiModel class in TDE.

The Model class stores equation parameters and provides methods for calculation of a single property together with its derivatives with respect to state variables and parameters. This class also provides methods for single property fitting and other actions. The structure of the Compound class (without the MultiModel class) was described previously in the first paper of this series,¹ and its enhanced structure (with EOS support) is shown in Figure 7. The Compound class generally contains multiple TDProperty and MultiModel classes. Each TDProperty instance may use as a default Model either an internally implemented Model that is specific to that TDProperty or a MultiModel (such as an EOS) that represents multiple properties, as indicated by the dashed lines connecting various MultiModel and TDProperty classes in Figure 7. Because they are valid for multiple properties, MultiModels are implemented at the Compound level.

The structure of the MultiModel class is shown in Figure 8. The “selector” in the MultiModel class is used to specify a property for which the Model applies. The selector can be set or passed dynamically as part of a property calculation request. The MultiModel class includes methods for equation fitting, rejection of data that are of poor quality or erroneous, and covariance calculation.

While fitting and covariance calculation methods in MultiModel differ from those of Model only because of the multiple properties involved, data rejection is a very different task and requires a special solution. In order to reject bad

data across multiple properties, it is necessary to compare curve deviations for different properties. For that purpose a covariance-based rejection method was developed. The covariance-based uncertainty is calculated for each data point, and then relative curve deviations are calculated as ratios of curve deviations to EOS uncertainties. The relative deviations can then be directly compared for different properties. The relative deviations also account for data density and local data quality because regions of state variables poorly populated with data are associated with higher uncertainties for calculated values.

The PureEOS class provides a property-specification function (a method for setting the “selector” of the MultiModel class) based on the properties, phases, and state variables involved and a function for calculation of all supported properties based on the excess Helmholtz energy and its derivatives for the EOS instance. Properties are calculated as functions of temperature and density based on published thermodynamic relationships.¹⁶ Special functions calculate (a) density as a function of temperature and pressure, (b) the saturated pressures and densities as functions of temperature, and (c) the coordinates of the critical point, i.e., where saturated liquid and gas densities converge. Instances of PureEOS provide functions for calculation of the excess Helmholtz energy based on a specific equation of state. Ideal-gas heat capacities as functions of temperature are needed by each EOS, and these are provided in TDE through an auxiliary equation.

As shown in the class hierarchy (Figure 6), PC-SAFT and REFPROP classes are directly derived from the PureEOS class. The PC-SAFT class implements all functions necessary for calculation of α' and its derivatives for a PC-SAFT EOS. The REFPROP class uses the REFPROP (NIST SRD 23)⁹ dynamic link library as the source of read-only EOS parameters for compounds included in that database. The REFPROP dynamic link library is also used as the engine for performing property calculations with Span–Wagner type equations of state.¹⁶

The VTEOS class applies the volume-translation term for the calculation of single-phase and saturated densities of the liquid and gas, as described above, after an EOS-based calculation for these properties. The volume-translated Peng–Robinson (VTPR) and modified Sanchez-Lacombe (MSL) classes are derived from the VTEOS class (Figure 6).

7. DYNAMIC UPDATES OVER THE WEB

An essential aspect of dynamic data evaluation is access by the user to a near comprehensive collection of experimental data, including the most recent data from the literature. As previously described,¹ experimental data used by TDE (version 1.0) were extracted from the NIST/TRC SOURCE¹⁷ system and distributed as a local database (TDE SOURCE) with the program. NIST/TRC SOURCE is maintained at NIST and is continuously populated with new experimental data (using Guided Data Capture GDC software³¹ developed at NIST). In order to more closely adhere to the requirements for dynamic data evaluation, TDE (version 2.0) includes a mechanism for dynamically updating the local TDE SOURCE based on additions and changes to NIST/TRC SOURCE through a central server.

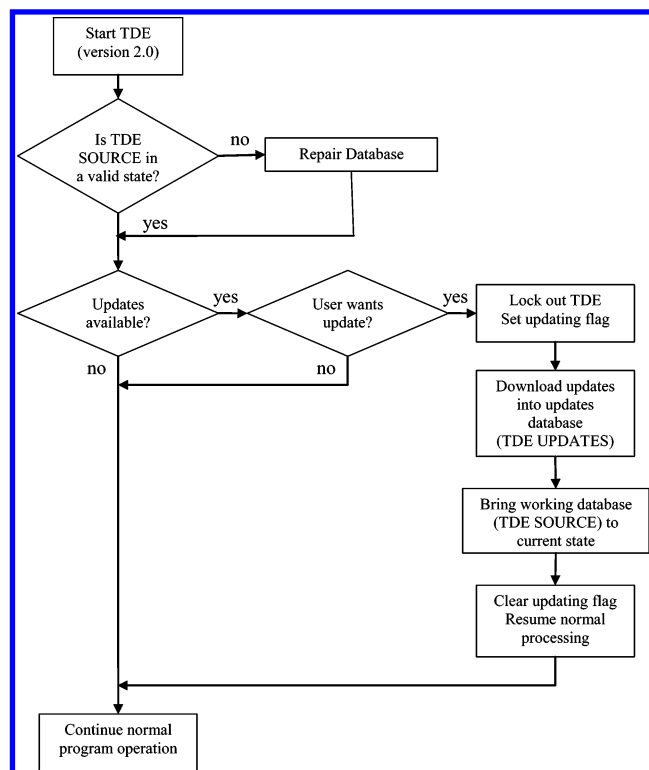


Figure 9. Flow chart for dynamic updating of the TDE SOURCE database from the Web through the local TDE UPDATES database.

Multiple technical approaches were considered for this update procedure, and a key decision was to provide periodic (quarterly) database updates rather than allowing continuous access to NIST/TRC SOURCE. This reduces the variety of possible TDE SOURCE data conditions to a small number of well defined states associated with particular dates and allows for unequivocal evaluation traceability, a key requirement for many engineering applications. A second decision was to maintain a local database of differences (TDE UPDATES) that allows each instance of TDE to set or restore the working database (TDE SOURCE) to any of the allowed discrete states rather than maintaining traceability information for every individual data point.

The process by which TDE checks for updates and maintains current TDE SOURCE information is shown as a flow chart in Figure 9. When started, TDE launches a background process that checks for the availability of a new update. If available, TDE prompts the user to download and install the update.

Once the user initiates the update process, the current update file is downloaded and merged with the local updates database (TDE UPDATES). TDE SOURCE is then set to the most recent valid state or version. Each update contains both records to be removed and records to add. When the TDE SOURCE state is changed (i.e., when the user selects an alternative TDE SOURCE version through a *Set database version* command in the Updates menu of the main toolbar), the change occurs in a stepwise fashion to neighboring states until the target state is reached, thus allowing any historical state of the database to be reproduced. The database version is stored along with evaluation results as an output of TDE, allowing for complete reproducibility and traceability for any evaluation. Setting the TDE SOURCE database to a given

version and doing an evaluation with a given version of TDE will always give the same results.

A special variable is set when the TDE SOURCE version change procedure is started and cleared when finished. This allows database integrity to be maintained and avoids the problem of TDE evaluations based on an indefinite database state. One example of an occurrence that would cause the TDE SOURCE state to be indefinite is an unexpected shutdown of the user's computer system during download of updates. When TDE is launched, the TDE SOURCE integrity (or "validity") is checked, and any database repairs are performed before any other functions are activated, as shown in the first step of the flow chart (Figure 9). Furthermore, when doing any state-change or repair operation, TDE does not allow the user to exit from the program.

Details of Implementation. The list of valid TDE SOURCE states is maintained as an index file in a coded list on the central server at NIST. The index also contains link information to the encrypted update files on the server. Each update file contains all the information necessary for transition from the preceding TDE SOURCE state to a new state. This information consists of a complete list of records to delete and new records to add. For instance, if a record has been changed since the preceding version, two records appear in the update file: a record to delete and a record to add.

To produce the difference information for updating TDE SOURCE to the current state of NIST/TRC SOURCE, software was developed that does two series of comparisons and saves two kinds of records: records present in TDE SOURCE but absent in NIST/TRC SOURCE and records present in NIST/TRC SOURCE but absent in TDE SOURCE. The first group is the set of records to delete, and the second group is the set of records to add.

8. COMPARISONS WITH PROPERTY-BY-PROPERTY AND LITERATURE EOS EVALUATIONS

As described in the first paper of this series, version 1.0 of TDE used separate equations for each evaluated property, with specific thermodynamic relationships between properties subsequently applied as constraints. As described here, version 2.0 includes this capability but further provides for deployment of equations of state that are inherently thermodynamically consistent (excluding volume-translated equations). In version 1.0, gas-phase densities were represented with the virial equation truncated at the third virial coefficient. Deployment of EOS technology in TDE version 2.0 marks a major extension into the supercritical region for property evaluations.

Span–Wagner EOS representations made with TDE for compounds included in the REFPROP database⁹ are nearly indistinguishable from those published in REFPROP. This is due, in part, to the use in TDE of the REFPROP parameters as starting conditions. Some unexpected results are displayed in Figure 10, which shows deviation plots for vapor pressures of cyclohexane derived with an EOS formulated by Span and Wagner^{16b} (upper figure) and by TDE (lower figure). In the initial EOS fits published with the equation development, Span and Wagner noted some apparent inconsistencies in the available experimental data and recommended additional measurements to resolve the discrepancies. For this com-

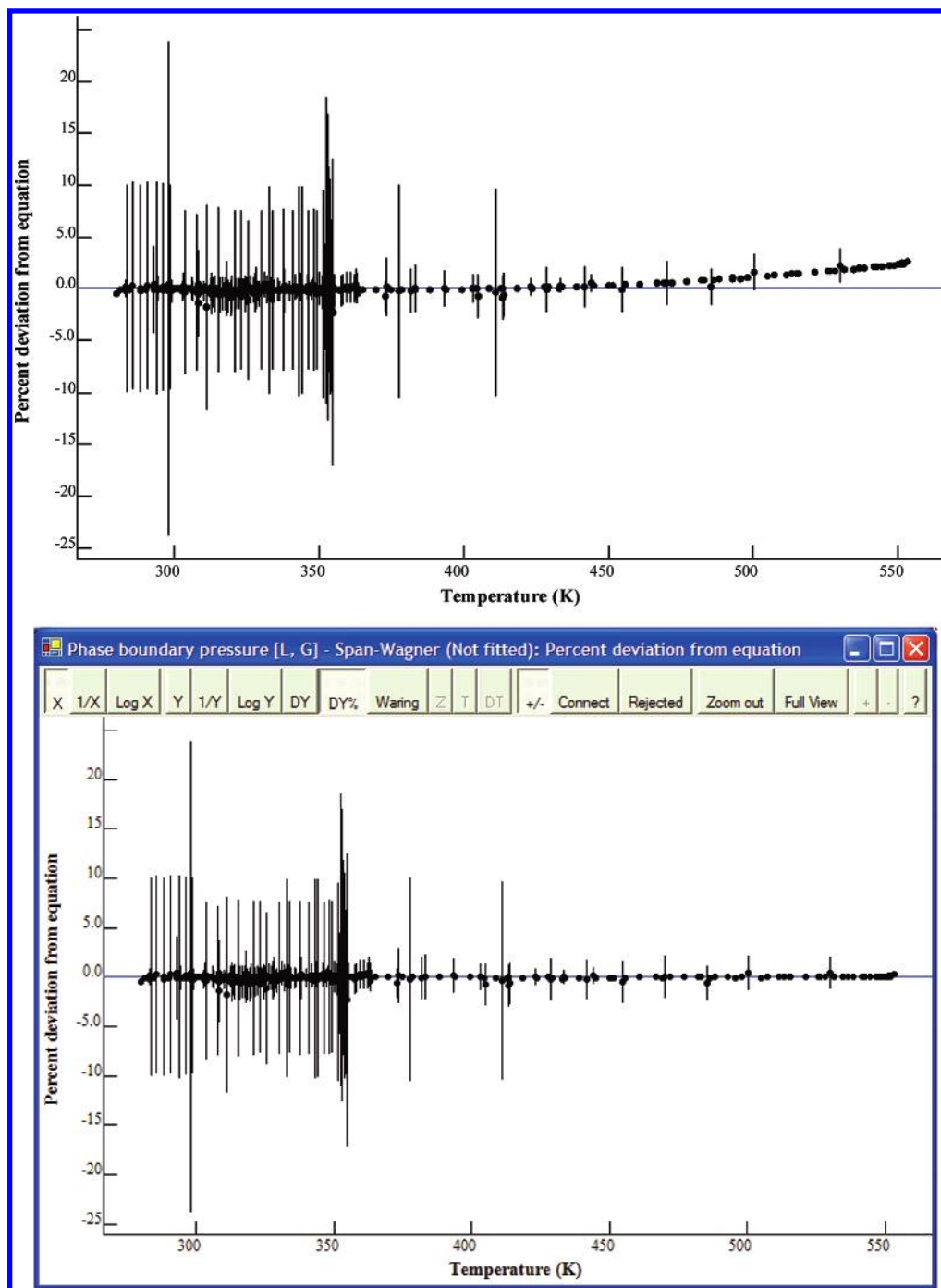


Figure 10. Deviation plots for experimental vapor pressures of cyclohexane relative to an EOS reported in the literature^{16b} (upper figure) and evaluated with TDE (lower figure).

pound, the TDE algorithm provided a successful representation of the experimental vapor pressures, while maintaining a high-quality fit for densities and heat capacities.

As a further test of the capabilities of TDE, Span–Wagner EOS representations for benzene were generated with two very different data scenarios: (1) with saturation line (vapor pressure and density) data, plus single phase densities, and (2) with saturation line data only. The results showed that in the region more than 10 K removed from T_c the single-phase densities calculated with the Span–Wagner EOS generated by TDE on the basis of the saturation line data only were within 4% of the experimental single-phase data for benzene. Though outside the experimental uncertainties,

such a result is excellent, considering the limited data set used.

9. DYNAMICALLY LINKED LIBRARY (DLL) VERSION OF TDE

A DLL implementation of TDE 2.0 has been developed to provide convenient mechanisms for implementation of the TDE technology into chemical engineering software applications. This version supports all aspects of property-by-property data evaluation for processing of one chemical compound at a time. All supported alternative equations for a given property are available through the DLL, and the results are returned in ThermoML⁶ format.

Table 2. Equation Parameters for the PC-SAFT Equation of State Required for Full Specification of the EOS Formulation^a

<i>i</i>	<i>a</i> ₀	<i>a</i> ₁	<i>a</i> ₂	<i>b</i> ₀	<i>b</i> ₁	<i>b</i> ₂
0	0.910563145	-0.308401692	-0.090614835	0.724094694	-0.575549808	0.097688312
1	0.636128145	0.186053116	0.452784281	2.238279186	0.699509552	-0.255757498
2	2.686134789	-2.503004726	0.596270073	-4.002584948	3.892567339	-9.155856153
3	-26.54736249	21.41979363	-1.724182913	-21.00357681	-17.21547165	20.64207597
4	97.75920878	-65.25588533	-4.130211253	26.85564136	192.6722645	-38.80443005
5	-159.5915409	83.31868048	13.77663187	206.5513384	-161.8264616	93.62677408
6	91.29777408	-33.74692293	-8.672847037	-355.6023561	-165.2076935	-29.66690559

^a The parameters are used in eqs A14 and A15.

10. CONCLUSIONS AND FUTURE DEVELOPMENT

(1) The expansion of the software implementation of the dynamic data evaluation concept within the NIST ThermoData Engine described in the present paper provides unique opportunities for generation of equations of state on-demand based on specific data scenarios. This is a new principal capability that enables critically evaluated thermodynamic property data to be used in a broad range of engineering applications and over an extensive temperature-pressure-density variable space.

(2) A new Web-based technology that provides updates for the TDE-SOURCE data storage facility used in conjunction with the critical data evaluation within the NIST ThermoData Engine makes the overall process fully dynamic.

(3) The algorithms and software tools developed for generation of the equations of state on-demand and Web-based technology for TDE-SOURCE dynamic updates complete the implementation of the dynamic data evaluation concept for pure chemical species.

(4) A DLL version of TDE makes it convenient to incorporate the TDE technology into chemical engineering software applications.

Further development will include expansion of TDE to more complex systems, such as binary mixtures and incorporation of predictive methods beyond group contribution and corresponding states techniques. Additional EOS formulations will be added to TDE based on user demand.

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APPENDIX: MATHEMATICAL FORMULATION OF THE PC-SAFT EQUATION OF STATE IN TDE

The PC-SAFT EOS is implemented in the formulation described by Gross and Sadowski,¹² where the primary quantity calculated is the dimensionless residual Helmholtz energy a^r . The quantity a^r is calculated as follows, with m , σ , and ϵ as equation parameters and a and b as arrays of constants. Aside from the molar density ρ and temperature T , all other quantities are intermediate to simplify writing of the equation. Generally, symbols used are those of Gross and Sadowski.¹² The dimensionless residual Helmholtz energy a^r is

$$a^r = (A - A^0)/(R \cdot T) \quad (\text{A1})$$

where A is the Helmholtz energy for the real-fluid, A^0 is the ideal-gas Helmholtz energy at the same temperature and molar density, and ρ is the molar density. This quantity is expressed as the sum

$$a^r = a^h + a^d \quad (\text{A2})$$

The quantity a^h is defined by the following expressions

$$a^h = m \cdot a^\phi - \{(m - 1) \cdot \ln(g)\} \quad (\text{A3})$$

where

$$a^\phi = [3\xi(1)\xi(2)/\{1 - \xi(3)\} + \xi(2)^3/(\xi(3)\{1 - \xi(3)\}^2) + \{\xi(2)^3/\xi(3)^2 - \xi(0)\}\ln\{1 - \xi(3)\}]/\xi(0) \quad (\text{A4})$$

$$g = 1/\{1 - \xi(3)\} + 3 \cdot \delta \cdot \xi(2)/[2 \cdot \{1 - \xi(3)\}^2] + \delta^2 \cdot \xi(2)^2/[2 \cdot \{1 - \xi(3)\}^3] \quad (\text{A5})$$

$$\xi(n) = (\pi/6)\rho m \delta^n \quad (\text{A6})$$

$$\delta = \sigma(1 - 0.12e^{-3\epsilon/T}) \quad (\text{A7})$$

The quantity a^d is defined by the following expressions

$$a^d = -\pi\rho(2I_1e_1 + mC_1I_2e_2) \quad (\text{A8})$$

where

$$I_1 = \sum_{i=0}^6 a_i v^i \quad (a \text{ and } v \text{ are defined below}) \quad (\text{A9})$$

$$e_1 = m^2\epsilon/T\sigma^3 \quad (\text{A10})$$

$$C_1 = 1/[1 + m(8\nu - 2\nu^2)/(1 - \nu)^4 + (1 - m)(20\nu - 27\nu^2 + 12\nu^3 - 2\nu^4)/\{(1 - \nu)(2 - \nu)^2\}] \quad (\text{A11})$$

$$I_2 = \sum_{i=0}^6 b_i \nu^i \quad (b \text{ and } \nu \text{ are defined below}) \quad (\text{A12})$$

$$e_2 = m^2(\epsilon/T)^2 \sigma^3 \quad (\text{A13})$$

The parameters a , b , and ν in eqs A8 and A11 are defined here with the coefficients $a_x(i)$ and $b_x(i)$ ($i = 0-6$) given in Table 2.

$$a_i = a_0(i) + \{(m - 1)/m\}a_1(i) + \{(m - 1)/m\}\{(m - 2)/m\}a_2(i) \quad (\text{A14})$$

$$b_i = b_0(i) + \{(m - 1)/m\}b_1(i) + \{(m - 1)/m\}\{(m - 2)/m\}b_2(i) \quad (\text{A15})$$

$$\nu = \xi(3) \quad (\text{A16})$$

Initial approximations for the three adjustable parameters m , σ , and ϵ are based on the critical temperature T_c and the molar mass M expressed in K and $\text{g}\cdot\text{mol}^{-1}$, respectively

$$m = 0.833 + 0.0000333MT_c \quad (\text{A17})$$

$$\sigma = 3.8 \quad (\text{A18})$$

$$\epsilon = 66.7 + 0.333T_c \quad (\text{A19})$$

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