

A New Four-Parameter Equation of State and Its Application in Predicting the Spinodal Temperature of Water

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Summary

A new four-parameter equation of state (EoS) is presented here. It has the form $p = RT/(v - b) - a/T^m v(v + c)$, which can be thought of as a modified Redlich-Kwong equation. This EoS is designed to permit a special parameter adjustment technique that leads to great accuracy in the calculation of the spinodal temperature (or limit of superheat) of a liquid. This p - v - T relationship yields a predicted spinodal temperature of 331.7°C for water at 1 atm, which is in good agreement with an extrapolation of experimental kinetic limits of superheat that falls in the range of $330 \pm 2^\circ\text{C}$. A knowledge of the spinodal temperature of water is an important dimension in the understanding of the vapor explosions (or steam explosions, in the case of water) that sometimes occur in marine volcano eruptions, nuclear-reactor accidents, and foundry molten-metal spills.

Introduction

To represent the behavior of a fluid as unusual as water over an extremely wide range of temperatures and pressures is an incredibly challenging task and requires an equation of state (EoS) of great complexity. Saul and Wagner [1] have successfully carried out this undertaking with a 58-parameter equation that accurately predicts a wide variety of thermodynamic properties of water. An EoS with several adjustable

parameters cannot hope to compete with a relationship of this complexity, but can sometimes provide useful practical results if the parameters are adjusted to carry out a specific prediction over a narrow range of temperatures and pressures. Such equations have the advantage of simplicity and can lead to results of acceptable accuracy for some practical applications. Such an equation and application are described here.

This study presents a new four-parameter EoS for characterizing liquid-and-vapor-phase behavior and the predictions of this equation for the liquid spinodal temperature or limit of superheat [2-4] for water. The parameters in the EoS are adjusted via a technique [5] that has been previously explored for a closely related, three-parameter EoS [6]. This parameter-adjustment approach guarantees that the equilibrium curve and the liquid and vapor spinodal curves not only terminate at the critical temperature and pressure, but do so with the correct tangent, or Riedel constant [4,5], at the critical point. Use of the Riedel constant in parameter adjustment yields great accuracy in the prediction of the above pressure-temperature relationships. The new EoS presented here is constructed so that it includes all of the above features and, in addition, has the correct molar volume at the critical point. This feature leads to greater accuracy in equilibrium and spinodal density-temperature relationships or coexis-

tence curves.

The spinodal temperature is the maximum temperature to which a liquid can be superheated. A liquid superheated to this temperature will undergo a vapor explosion [7], which, in the case of water, is often called a steam explosion. These physical explosions are possible in situations where water (or some other liquid) comes into contact with a hotter, immiscible second liquid. Steam explosions have occurred in marine volcano eruptions; nuclear reactor, loss-of-flow accidents; and in foundry molten-metal spills. The spinodal temperature of water is thus a key parameter in the mathematical modeling of these physical explosions. The use of this new EoS for the prediction of the spinodal temperature of water is described below.

The Equation of State

The EoS of a pure fluid is a mathematical relationship between the molar volume, v , and the temperature, T , and pressure, p . It is often expressed through the functional notation

$$[1] \quad p = f(T, v)$$

The EoS studied here is the outgrowth of past explorations of other equations with three or four parameters and employs the best features of these p - v - T relationships [4-6]. This new, four-parameter EoS is

$$[2] \quad p = RT/(v - b) - a/T^m v(v + c)$$

where R is the molar gas constant, b is a constant related to the size of the fluid molecules, and c , a and m are constants which characterize the attractive force between pairs of fluid molecules. This EoS contains some well-known, simpler equations as special cases. Eq [2] reduces to the van der Waals EoS when $m = 0$ and $c = 0$ [8] and to the Redlich-Kwong EoS when $b = c$ and $m = 1/2$ [9]. Thus, it is appropriate to refer to this new relationship as a modified Redlich-Kwong EoS. The original Redlich-Kwong EoS [9] and this new modification can be thought of as empirical refinements of the van der Waals EoS.

The Parameter Evaluation

Before an EoS can be applied to the task of pre-

dicting thermodynamic properties, a method of estimation for the parameters must be devised. Although there are many possible approaches to this task, the usual method is to employ the mathematical conditions obeyed by any fluid at the critical point, as well as the critical constants of the particular fluid of interest [5]. The usual statement of the critical conditions is that the critical isotherm of a fluid must pass through the critical point with a horizontal inflection point. At a horizontal inflection point on an isotherm, both the derivatives $(\partial p/\partial v)_T$ and $(\partial^2 p/\partial v^2)_T$ vanish. In functional notation this leads to the three mathematical conditions

$$[3] \quad f(T_c, v_c) = p_c$$

$$[4] \quad f_v(T_c, v_c) = 0$$

$$[5] \quad f_{2v}(T_c, v_c) = 0$$

where the v subscripts indicate partial differentiation with respect to v and p_c , T_c , and v_c are the critical pressure, temperature, and molar volume of the fluid, respectively. Eqs [3]-[5] provide only three equations for the determination of the four parameters: b , c , a , and m . Thus, a fourth mathematical condition and critical constant is necessary. The Riedel relationship [5] is employed to meet this need, which states that the tangent to the vapor pressure curve at the critical point, s_c , can also be found from the EoS by partial differentiation with respect to T , namely,

$$[6] \quad f_T(T_c, v_c) = s_c = (dp_e/dT)_c$$

where p_e is the equilibrium vapor pressure of the liquid and s_c is the Riedel constant. The four constraints, eqs [3]-[6], and the four critical constants p_c , T_c , v_c , and s_c , can thus be used to determine the four parameters: b , c , a , and m .

For a two-parameter EoS (like that of van der Waals or of Redlich and Kwong) eqs [4] and [5] and the constants T_c and p_c are usually employed for parameter estimation [5,10]. This choice guarantees that predictions of the equilibrium (or saturation) curve and the liquid and vapor spinodal curves will terminate at the critical point with the correct temperature and pressure. This new four-parameter EoS will, in addition, have the correct tangent to the equilibrium and spinodal curves at the criti-

cal point, and, furthermore, the correct molar volume. These latter features greatly increase the accuracy of equilibrium and spinodal predictions, an expectation that is borne out by the computational results ultimately obtained.

The four parameters for the EoS can be found more easily by expressing them in dimensionless or reduced form. The reduced parameters β , γ , and α are defined through the equations

$$[7] \quad \lambda = RT_c/p_c v_c = Z_c^{-1}$$

$$[8] \quad b = \beta v_c$$

$$[9] \quad c = \gamma v_c$$

$$[10] \quad a = \alpha p_c v_c^2 T_c^m$$

$$[11] \quad \sigma_c = (T_c/p_c)(dp_c/dT_c) = T_c s_c/p_c$$

where Z_c is the critical compression factor and σ_c is the reduced Riedel constant. The dimensionless unknowns β , γ , and α are the reduced values of b , c , and a , respectively, while the exponent m is already dimensionless. Application of eqs [3]-[6] to eq [2] then leads to the four constraints

$$[12] \quad \lambda/(1 - \beta) - \alpha/(1 + \gamma) = 1$$

$$[13] \quad -\lambda/(1 + \beta)^2 + \alpha[1/(1 + \gamma)^2 + 1/(1 + \gamma)] = 0$$

$$[14] \quad 2\lambda/(1 - \beta)^3 - 2\alpha[1/(1 + \gamma)^3 + 1/(1 + \gamma)^2 + 1/(1 + \gamma)] = 0$$

$$[15] \quad \lambda/(1 - \beta) + \alpha m/(1 + \gamma) = \sigma_c$$

where $\lambda = Z_c^{-1}$ and σ_c are known experimentally. These equations can be further simplified with the substitutions

$$[16] \quad \delta = 1 - \beta$$

$$[17] \quad \varepsilon = 1 + \gamma$$

$$[18] \quad \rho = \varepsilon/\delta$$

The resulting four equations in the four unknowns— δ , ε , ρ and m —can be reduced to the single, nonlinear equation in ε

$$[19] \quad \varepsilon^3 + (3 - \lambda)\varepsilon^2 + (3 - \lambda)\varepsilon + (1 - \lambda) = 0$$

which can readily be solved numerically for

ε using Newton's Method [11]. The other unknowns can then be found from eqs [12]-[18] and are given by the expressions

$$[20] \quad \rho = (1 + \varepsilon + \varepsilon^2)/(1 + \varepsilon)$$

$$[21] \quad \delta = \varepsilon/\rho$$

$$[22] \quad \alpha = \lambda\rho - \varepsilon$$

$$[23] \quad \beta = 1 - \delta$$

$$[24] \quad \gamma = \varepsilon - 1$$

$$[25] \quad m = (\sigma_c - 1)\varepsilon/\alpha - 1$$

Once the dimensionless unknowns are found as indicated above, then b , c , and a are easily obtained from eqs [8]-[10].

The experimental critical data for water needed to perform these calculations are $T_c = 647.30$ K, $p_c = 218.3$ atm, $Z_c = 0.235$ (or $\lambda = 4.2553$), [12] and $\sigma_c = 8.28$ [4]. Application of eqs [19]-[25] then yields, for the dimensionless parameters, $\varepsilon = 2.3668$, $\rho = 2.6638$, $\delta = 0.88850$, $m = 0.92119$, $\alpha = 8.9686$, $\beta = 0.11150$, and $\gamma = 1.3668$. The remaining three parameters in eq [2] are found from eqs [8]-[10] to be $b = 0.0063755$ L mol⁻¹, $c = 0.078154$ L mol⁻¹, and $a = 2487.8$ atm K^m L² mol⁻².

The Liquid Spinodal Temperature

Once all the parameters are available for this new EoS, the liquid spinodal temperature or limit of superheat, T_s , and the corresponding spinodal molar volume, v_s , can be calculated at any pressure.

A superheated liquid is a metastable liquid that is at a temperature higher than the equilibrium temperature or boiling point, T_c . The upper limit of this superheated state is the spinodal temperature T_s . For stable liquids (where $T < T_c$) and for metastable liquids (where $T_c < T < T_s$), the liquid obeys the mechanical stability condition $(\partial p/\partial v)_T < 0$ [13]. For an unstable fluid (where $T > T_s$), $(\partial p/\partial v)_T > 0$. Thus, the boundary between the metastable and unstable states, the so-called spinodal condition, is $(\partial p/\partial v)_T = 0$ [4,6,14]. In functional notation, then, the spinodal temperature and molar volume for a particular pressure p is obtained from the solution of the two, nonlinear equations:

$$[26] \quad f(T_s, v_s) = p$$

$$[27] \quad f_v(T_s, v_s) = 0$$

For this particular EoS, then, T_s and v_s are obtained from the constraints

$$[28] \quad p = RT_s/(v_s - b) - a/T_s^m v_s (v_s + c)$$

$$[29] \quad \frac{RT_s}{(v_s - b)^2} = (a/T_s^m)[1/v_s(v_s + c)^2 + 1/v_s^2(v_s + c)]$$

Based on eqs [28] and [29] the values of T_s and v_s can be obtained by successive substitution [14,15] using the algorithm

$$[30] \quad T_{s2} = \{[a(v_{s1} - b)^2/R][1/v_{s1}(v_{s1} + c)^2 + 1/v_{s1}^2(v_{s1} + c)]\}^{1/(m+1)}$$

$$[31] \quad v_{s2} = a/T_{s2}^m(v_{s1} + c)[RT_{s2}/(v_{s1} - b) - p]$$

The initial approximations selected for starting the calculation were $T_{s1} = 0.9 T_c$ and $v_{s1} = 2b$.

The results of solving eqs [30] and [31] with the parameter values appropriate for water yield $T_s = 331.7^\circ\text{C}$ and $v_s = 0.02962 \text{ L mol}^{-1}$ at a pressure of $p = 1 \text{ atm}$.

This prediction of the spinodal temperature of water compares well with previously made extrapolations of measured kinetic limits of superheat to the thermodynamic limit of superheat or spinodal temperature [4,6] and leads to a range of values of $T_s = 330 \pm 2^\circ\text{C}$. The extrapolations were carried out for water and six other liquids [4] and are based on measurements made over a wide range of nucleation fluxes (10 to 13 orders of magnitude) and a maximum possible nucleation flux (corresponding to a maximum heating rate and a minimum volume) of about $10^{30} \text{ nuclei cm}^{-3} \text{ s}^{-1}$.

Another approach to the determination of spinodal temperatures is possible through the extrapolation of p - v - T data for superheated liquid to the spinodal state. Skripov [16] has carried out such an extrapolation and obtained $T_s = 324^\circ\text{C}$, a result which is not in as close accord with the prediction obtained here of $T_s = 331.7^\circ\text{C}$. Which of these two approaches provides the more reliable experimental value of the spinodal temperature of water must await further study.

Spinodal temperatures were also calculated for the two special cases of eq [2] mentioned previously and yield values of $T_s = 273.2^\circ\text{C}$ and 306.5°C for the van der Waals and the Redlich-Kwong equations, respectively. It is thus apparent that the additional two parameters built into the modified Redlich-Kwong EoS and the particular parameter adjustment method employed for the exponent m greatly improve spinodal predictions over those of the simpler and more familiar two-parameter formulas.

Experimental determinations of the spinodal temperature of n -pentane are also available [4,6] and indicate that $T_s = 158 \pm 2^\circ\text{C}$. Based again on the appropriate critical data [4,12], the prediction of this new EoS is $T_s = 159.2^\circ\text{C}$ and $v_s = 0.1681 \text{ L mol}^{-1}$, in close agreement with experiment.

Conclusions

A modified version of the Redlich-Kwong EoS is presented. When the four parameters in the equation are evaluated from critical constant data that includes the Riedel constant, the EoS yields a spinodal temperature prediction for water, 331.7°C , that is in good accord with experiment.

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Discussion With Reviewers

Ted Lindeman¹: It is often of interest to understand in a general way what intermolecular forces and phenomena underlie the parameters of a new EoS. For the “parent” van der Waals equation, b and a clearly account for, respectively, the repulsive and attractive intermolecular forces. Does one dare to attach comparable molecular significance to your c and m results?

Jim Eberhart: This new 4-parameter EoS provides a pressure given by the difference between a repulsive term and an attractive term. Thus, the general format of this equation is, indeed, the same as that of the original van der Waals EoS. As with the van der Waals EoS, the constant b is a measure of the size of the fluid molecules and the constants a , c , and m are related to the pair-wise attraction between molecules. That said, the EoS is also empirical in nature and, thus, it does not appear possible to be more quantitative about the relationship between a , c , and m and the attraction between molecules.

From a utilitarian point of view, the parameter m was introduced into the EoS to make possible a correct value for the tangent to the vapor pressure curve at the critical point (and, thus, also a correct tangent to the spinodal curves). The parameter c was introduced to make possible a

correct value for the critical compression factor at the critical point.

Lionel Mercury²: The exact position of the spinodal temperature at 1 atm is connected to the question of the spinodal shape, especially discussed in the case of liquid water. Globally speaking, a retracing behaviour is supported by most of the empirical equations of state extrapolated inside the superheating domain (e.g., Speedy, 1982), while monotonous decreasing behaviour is predicted by molecular modelling approaches (e.g., Poole et al., 1992; Sastry et al., 1996). Which side does this new equation of state support? Do you think that the simplicity of your equation is an advantage or a disadvantage in this debate?

Eberhart: The format of this new equation of state (EoS) is similar to that of the van der Waals EoS and the Redlich-Kwong EoS in that all three of these equations are polynomials of the third degree in molar volume with the pressure given by the difference between a repulsive and an attractive term. Every EoS of this type has a liquid spinodal pressure, $p_s(l)$, that increases monotonically with temperature, T , with a slight downward concavity. Thus, $dp_s(l)/dT > 0$, while $d^2p_s(l)/dT^2 < 0$. This type of behavior is illustrated with calculated liquid spinodal curves generated previously [J.G. Eberhart and H.C. Snyders, “Application of the Mechanical Stability Condition to the Prediction of the Limit of Superheat for Normal Alkanes, Ether, and Water,” *Journal of Physical Chemistry* 77, 2730-2736 (1973)] for a variety of fluid models having the above features.

Any EoS of this kind is only capable of predicting liquid and vapor phase properties (both stable and metastable) and can thus be used to characterize superheated or superstretched liquids (including tensile liquids) and supercooled (or supersaturated) vapors. However, these equations do not provide solid-phase behavior, and thus cannot be used to explore supercooled-liquid and superheated-solid states. Thus, this model is incapable of generating retracing behavior and has the same kind of classical liquid-vapor critical behavior as that of van der Waals’s original EoS. This means that the liquid spinodal curves generated by such an EoS should not be extended too far into the

negative pressure regime and cannot provide a minimum in the $p_s(l)$ versus T curve.

I believe it would be inappropriate to use the simple model presented here, which is not based on any explicit assumptions regarding molecular structure, to argue for either the re-tracing spinodal scenario or the metastable, low-temperature critical point scenario in water. This EoS is empirical in nature and is designed to provide a simple and reliable route to liquid spinodal predictions for any liquid, with water clearly being the fluid of greatest practical importance. Of course, there are far more complicated and accurate p - v - T relationships, such as the fifty-eight parameter EoS referred to in reference [1] of this article, that would not be subject to these limitations and would provide insight into this question.

Mercury: The spinodal curve normally is not experienced by natural fluids because the activation nucleation energy is of the same order of magnitude as the thermal fluctuations at the so-called kinetic spinodal, located at lower temperature (at constant pressure) as the spinodal one. Yet, the ability for a fluid to trespass the kinetic limit and come near the spinodal one determines the occurrence of the very explosive spinodal decomposition. What could be in your opinion the mechanism(s) or condition(s) able to provoke the spinodal decomposition in natural fluids? Especially at intermediate temperature where the gap between the two limits is large?

Eberhart: As with the previous question, I am inclined to believe that a simple EoS based on empirical ideas rather than on molecular structure assumptions cannot be used to shed light on issues such as the mechanism for spinodal decomposition (or explosive boiling) of superheated water. However, it is possible that a few general comments that would apply to any liquid would be of interest to some readers. The issue raised here centers on the difference between the thermodynamic liquid spinodal (TLS) and the kinetic liquid spinodal (KLS), which the reader can find discussed in greater detail in reference 4 of this article [J.G. Eberhart, "The Thermodynamic and the Kinetic Limit of Superheat of a Liquid," *Journal of Colloid & Interface Science* 56, 262-269 (1976)].

There are two approaches to the calculation of the liquid spinodal temperature or pressure—one is kinetic and involves the application of homogeneous nucleation theory, while the other is thermodynamic and (for a pure liquid) involves the use of the mechanical stability condition. The thermodynamic approach has the advantage of being simpler and requiring only an EoS, but has the disadvantage of providing an upper limit on the measured KLS (the TLS) rather than the KLS itself. The kinetic approach is more complicated, requires surface tension data in addition to an EoS, and yields a KLS prediction that depends on the nucleation flux, J , in the experiment. However, this approach is capable of providing good agreement with experimental KLS data rather than simply yielding an upper limit on the data. [As an example of such calculations, see J.G. Eberhart, W. Kremsner, and M. Blander, "Metastability Limits of Superheated Liquids: Bubble Nucleation Temperatures of Hydrocarbons and Their Mixtures," *Journal of Colloid & Interface Science* 50, 369-378 (1975)].

This article summarizes the most important part of reference 4, namely, that as the nucleation flux is increased to its maximum theoretical value, the KLS approach the TLS. Thus, the experimental determination of the TLS primarily used in this paper was carried out by a simple extrapolation of KLS versus J data to the thermodynamic limit. The mechanism of this vaporization is usually visualized as the fluctuation in radii of the vapor bubble nuclei as they begin the "climb" up the curve of free energy versus radius. As the temperature increases the bubble radii approach the critical radius and ultimately the liquid spontaneously decomposes into the vapor. At higher nucleation fluxes this process occurs at somewhat higher temperatures, again approaching the TLS in the limit of maximum flux. The nucleation theory approach is quasi-thermodynamic in nature and is generally independent of explicit assumptions about the molecular structure of the fluid being considered.

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