FLUID-PHASE TRANSITIONS IN LIGHT WATER AND HEAVY WATER

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Abstract

Phase transitions are important phenomena in water-cooled nuclear-fission reactors. In this study, liquid-vapour phase transitions and critical-point behaviour are considered. Special attention is given to the van der Waals model, asymptotic critical scaling, thermodynamic potentials and steam properties. Models and data are shown for light water and heavy water. The relevance to advanced Generation III reactors and proposed Generation IV reactors is assessed.

1. Introduction

An important study of the future of nuclear power [1] was motivated by the belief that this technology is a means of meeting future energy needs without emitting carbon dioxide and pollutants into the Earth's atmosphere. That study identified four unresolved problems that limit the prospects for nuclear power; these problems include high economic costs, and long-term management of radioactive wastes.

A useful classification of nuclear-power systems involves four generations. Early prototype reactors of the 1950s and 1960s are in Generation I. Most commercial power reactors are in Generation II. Advanced light-water reactors are in Generation III. Future reactors for the year 2030 and beyond are in Generation IV. An international program for research and development of Generation IV nuclear-power systems [2] involves six types of nuclear-fission reactors; one type is the supercritical-water-cooled reactor (SCWR) [3].

Most of the nuclear-fission reactors used currently in electrical power generation are cooled by water. This coolant can be either light water (hydrogen oxide) or heavy water (deuterium oxide). These water-cooled reactors operate with a liquid-vapour mixture flowing through fuel channels in the reactor core. The thermodynamic properties of water restrict the maximum temperature of the coolant, and the thermal-hydraulic characteristics of liquid-vapour flow restrict the maximum vapour fraction of the flow. These restrictions limit the thermal efficiency of present water-cooled power reactors. A decrease in the cost of nuclear-generated electricity, and an increase in the efficiency of nuclear-fuel utilization, would result from overcoming these restrictions.

The development of the Canada Deuterium Uranium (CANDU) reactor by Atomic Energy of Canada Limited (AECL) provides an example of the development of water-cooled power reactors. The CANDU pressurized heavy-water reactor (CANDU PHWR) has operated successfully in generating stations for about forty years. The Advanced CANDU Reactor (ACR) is being designed as a successor to the CANDU PHWR [4]. The ACR will have light-water coolant; the CANDU PHWR has heavy-water coolant. The ACR will be an advanced Generation III (Generation III+) reactor. The temperatures and pressures in Table 1 indicate that the coolant is a subcritical liquid-vapour mixture in both types of reactor.

The future development of the CANDU reactor, beyond the ACR, will involve major changes to the nuclear steam-supply system, in pursuit of greater thermal efficiency [3, 5]. An SCWR is a likely successor to the ACR. A conceptual SCWR using an indirect thermodynamic cycle is given the type SCWR 1 in Table 1. A conceptual SCWR using a direct thermodynamic cycle is given the type SCWR 2 in Table 1. The temperatures and pressures in Table 1 are for the designs CANDU-X Mark 1 (type SCWR 1) and CANDUal-X2 (type SCWR 2) [5]. The temperatures and pressures indicate that the coolant is a supercritical fluid in both types of reactor.

Table 1 Temperature and pressure of the coolant at the reactor outlet.

Type of reactor	Outlet temperature T' (°C)	T (K)	Outlet pressure p (MPa, abs)
CANDU PHWR [4]	310	583	10.0
ACR [4]	319	592	11.2
SCWR 1 [5]	430	703	25
SCWR 2 [5]	625	898	25

The future development of nuclear-power systems with water coolant will depend on new information about the thermodynamic and fluid-dynamic properties of water. A previous study [6] indicated the need for new practical methods of calculation for the critical-point neighbourhood and the supercritical thermodynamic states. The present study involves the thermodynamic properties of water, with an emphasis on phase transitions and critical phenomena.

2. Liquid-vapour phase transitions

2.1 Thermodynamic potentials and steam properties

The theory of thermodynamics can be based on a set of postulates about a thermodynamic system and its fundamental relation [7]. The present study is based on this formulation of thermodynamics.

The primary fundamental relation of a simple thermodynamic system with one chemical component is the function $S(U, V, N)$, where S is the entropy, U is the internal energy, V is the volume, and N is the number of moles of substance. The equilibrium state of a system is determined by the entropy-maximum postulate. Lower-case letters are used to denote specific (per unit mass) quantities, so $s = S / m$, $u = U / m$, $v = V / m$, and m represents the mass of a system. The quantity N / m is a constant for a given substance. The entropy function is a homogeneous first-order function of its three independent variables. Thus, the specific entropy function $s(u, v)$ is a homogeneous zero-order function of its two independent variables.

The entropy function can be inverted with respect to U, giving an internal-energy function that serves as a secondary fundamental relation. A set of tertiary fundamental relations can be obtained with Legendre transformations. The tertiary relations obtained from the internal-energy function are the thermodynamic potentials.

The specific Helmholtz potential f is obtained by the transformation

$$f = u - Ts \tag{1}$$

where T is the absolute temperature. The function $f(T, v)$ contains the complete thermodynamic information about a system. The specific enthalpy potential h is obtained by the transformation

$$h = u + pv \tag{2}$$

where p is the absolute pressure. The function $h(s, p)$ contains the complete thermodynamic information about a system. The specific Gibbs potential g is obtained by the transformation

$$g = u - Ts + pv\ . \tag{3}$$

The function $g(T, p)$ contains the complete thermodynamic information about a system.

The thermodynamic system is a sample of water in the present study. The reader may be familiar with steam tables that contain numerical information about the thermodynamic properties of water. Such tables are calculated from equations with coefficients that are determined from experimental data. These equations typically represent specific thermodynamic potentials with high accuracy and many coefficients. The International Association for the Properties of Water and Steam (IAPWS) has published such equations for ordinary (light) water [8] and heavy water [9]. These general IAPWS formulations are based on the specific Helmholtz potential. The formulation for ordinary water represents stable fluid states for temperatures from

–22°C to 1000°C (251 K to 1273 K), and for absolute pressures from 0.0002 MPa to 1000 MPa. The formulation for heavy water represents stable fluid states for temperatures from 3.80°C to 527°C (276.95 K to 800 K), and for absolute pressures from 0 MPa to 100 MPa.

The evaluation of the general function for a specific thermodynamic potential, and functions for derived properties, is complicated and slow. Steam tables are useful for hand calculation, but using interpolation algorithms with stored steam tables can require a large amount of computer memory. As an alternative to approximating the functions for thermodynamic properties with steam-table interpolation, these functions can be approximated with simpler functions [6].

2.2 The van der Waals model and phase transitions

The reader is familiar with the transition between the liquid phase of water and the vapour phase of water. This first-order phase transition is related closely to the thermodynamic stability of the system (a sample of water).

A system with one chemical component has the intensive parameters T, p and μ. The electrochemical potential μ is proportional to the specific Gibbs potential g. Thermodynamic equilibrium requires equality of the electrochemical potential of the two phases (liquid and vapour), so there is equality of the specific Gibbs potential of the two phases. This equality determines a liquid-vapour coexistence curve on a graph of p versus T. One terminus of this curve is the triple point, where the solid, liquid and vapour phases coexist. The other terminus of this curve is the critical point, where the liquid and vapour phases are indistinguishable. This curve corresponds to the "saturated" states, where the liquid and vapour phases are in equilibrium. The triple points and critical points of light water and heavy water are described in Table 2.

Table 2 Triple points and critical points of light water and heavy water [8, 9].

	Light water		Heavy water	
Property	Triple pt.	Critical pt.	Triple pt.	Critical pt.
Temperature, T' (°C)	0.01	373.946	3.80	370.697
Absolute temperature, T (K)	273.16	647.096	276.95	643.847
Absolute pressure, p (MPa)	0.0006117	22.064	0.0006601	21.671

The van der Waals model of a fluid can be derived with statistical mechanics and the mean-field approximation [10]. The van der Waals equation is

$$p = RT / (Mv - b) \; - \; a / (Mv)^2 \; . \tag{4}$$

In this equation, $R = 8.314$ J/(K·mol), M is the molar mass, and a and b are constants for the fluid. The constants a and b represent the interaction between two molecules of the fluid; the constant b is the molar volume of the molecules in the model. The constants a and b can be calculated from the critical-point values of temperature and pressure. For ordinary (light) water, $M = 18.015$ g/mol, $a = 0.5534$ Pa·(m^3/mol)^2, and $b = 0.00003048$ m^3/mol. For heavy water, $M = 20.028$ g/mol, $a = 0.5578$ Pa·(m^3/mol)^2, and $b = 0.00003088$ m^3/mol.

The function $g(T, p)$ can be determined for the van der Waals model, and this function can be used to study thermodynamic stability [7, 10]. The consideration of stability accounts for the difference in the values of a thermodynamic property (other than g) between the liquid and vapour phases, at a given temperature and pressure.

The van der Waals model provides a molecular interpretation of thermodynamic properties, but it is generally less accurate for the determination of properties of stable states than the empirical models of the IAPWS formulations and the authoritative steam tables. These formulations and tables do not represent most non-stable states, but the van der Waals model does represent those states. Some non-stable states can be observed experimentally and they may persist in the absence of external perturbations.

2.3 Examples of subcritical-water coolant

Thermodynamic properties in the examples are represented by symbols with subscripts: "c" for the critical point, "i" for the inlet of a reactor, "o" for the outlet of a reactor, "s" for a steam-generator outlet, and "l" for the liquid formed in a condenser. The Carnot-cycle efficiency is

$$\eta_C = 1 - T_l / T_s \tag{5}$$

and the turbine-generator efficiency is

$$\eta_T = P_e / P_{th} \tag{6}$$

where P_e is the gross electrical power output and P_{th} is the thermal power (heat-transfer rate) input. Temperature conversions in the reactor examples use $T \approx T' + 273$ K.

The Darlington Nuclear Generating Station is located near Bowmanville, Ontario, and it contains four CANDU PHWR units [4]. The heavy-water coolant ($T_c = 643.847$ K) has $p_i = 11.4$ MPa, $T_i' = 267$°C, $p_o = 10.0$ MPa, and $T_o' = 310$°C. Thus, the fluid is mainly a liquid, with $T_o = 583$ K and $T_o / T_c = 0.905$. The light-water power cycle has $T_s' = 265$°C, $T_l' \approx 30$°C, $P_{th} = 2650$ MW, and $P_e = 935$ MW, for each of the four units. Thus, $T_s = 538$ K, $T_l \approx 303$ K, $\eta_C = 43.7\%$, and $\eta_T = 35.3\%$.

The ACR-1000 is an Advanced CANDU Reactor that is being designed by AECL [4]. The light-water coolant (T_c = 647.096 K) has p_i = 12.7 MPa, T_i' =275°C, p_o = 11.2 MPa, and T_o' = 319°C. Thus, the fluid is mainly a liquid, with T_o = 592 K and T_o / T_c = 0.915. The light-water power cycle has T_s' = 275.5°C, $T_l' \approx$ 32°C, P_{th} = 3180 MW, and P_e = 1165 MW, for one unit. Thus, T_s = 548.5 K, $T_l \approx$ 305 K, η_C = 44.4%, and η_T = 36.6%.

An increase in coolant temperatures in a reactor would provide an increase in steam temperatures in the power cycle, an increase in η_C, and an increase in η_T. However, increasing coolant temperatures and pressures substantially toward the critical-point values would require a larger, higher-pressure reactor core, giving a system that would probably be worse economically than existent power systems with pressurized water reactors [11].

If a modified ACR-1000 with T_o' = 360°C is compared with a basic ACR-1000 with T_o' = 319°C, estimates of thermal conditions suggest that the modified power system has η_C equal to 1.09 times the value for the basic power system. However, the modified reactor has p_o equal to 1.67 times the value for the basic reactor. Also, the modified reactor has v_o equal to 1.27 times the value for the basic reactor, so the modified reactor may require a larger core to provide sufficient neutron moderation.

3. Critical-point behaviour

3.1 Critical phenomena and fluid properties

The phenomenon of critical opalescence was observed experimentally in the 1860s. Critical opalescence is an optical effect that results from large-scale density fluctuations in a fluid near its critical point [12]. These density fluctuations are very effective at scattering light, so a transparent fluid becomes highly reflective at temperatures and pressures near the critical-point values.

On a graph of p versus v, the isotherm with the critical temperature T_c has a point of inflection at the critical pressure p_c. This inflection is predicted by the van der Waals model, and it is indicated by experimental data. This inflection suggests that the isothermal compressibility approaches infinity near the critical point. Thus, small statistical fluctuations in pressure can produce large fluctuations in specific volume v and density ρ ($\rho = 1 / v$).

A supercritical thermodynamic state has a temperature greater than the critical temperature and a pressure greater than the critical pressure. A subcritical thermodynamic state has a temperature less than the critical temperature or a pressure less than the critical pressure; an inclusive "or" applies. The critical thermodynamic state has a temperature equal to the critical temperature and a pressure equal to the critical pressure; it is represented in thermodynamic-state space by the critical point.

Recent critical-point data for light water and heavy water are available [13]. Basic thermodynamic properties of light water and heavy water at the critical points are shown in Table 3. The coexistence curve for light water is close to the coexistence curve for heavy water, on a graph of p versus T. There are significant differences in the termini of the liquid-vapour coexistence curves, as described in Tables 2 and 3.

Table 3 Thermodynamic properties of light water and heavy water at the critical points [13].

Property	Light water (hydrogen oxide)	Heavy water (deuterium oxide)
Temperature, T' (°C)	373.946	370.697
Absolute temperature, T (K)	647.096	643.847
Absolute pressure, p (MPa)	22.064	21.671
Specific volume, v (m^3/kg)	0.003106	0.002809
Density, ρ (kg/m^3)	322	356

3.2 Asymptotic critical scaling and specific heat capacity

The foregoing theory of the first-order phase transition is not valid at, or near, a critical point. A valid theory of the second-order phase transition in a small neighbourhood of a critical point was achieved in the 1970s. The valid theory of critical phenomena incorporates a correct treatment of the correspondence between thermodynamics and statistical mechanics [7].

In a small neighbourhood of a critical point, interactions among parts of a system at many scales of length are equally important. Thus, a fluid exhibits both small-scale and large-scale fluctuations in density near its critical point. The long-range correlated behaviour near a critical point can be represented mathematically by asymptotic expressions for thermodynamic properties that follow from a “scaling hypothesis”.

Experimental data for specific heat capacity at constant volume, c_v, versus temperature, have strongly non-linear behaviour for temperatures within ±5 K of the critical temperature, for both light water and heavy water. An equation that incorporates the asymptotic behaviour from the valid theory of critical phenomena, predicts these data correctly. The specific heat capacity at constant volume approaches infinity near the critical point [13]. A constant-volume system exhibits a capacity to receive a large amount of heat as its temperature is increased near its critical point.

The IAPWS formulations for light water [8] and heavy water [9] represent thermodynamic properties well for both subcritical states and supercritical states, except for thermodynamic states in a small neighbourhood of a critical point. The formulation for light water exhibits unphysical behaviour in a region with temperatures from $T_c - 0.020$ K to $T_c + 5$ K, and with densities from $0.995\rho_c$ to $1.005\rho_c$. (The quantity ρ_c is the critical density.) The formulation for heavy water is not recommended in a region with temperatures from $T_c - 10$ K to $T_c + 10$ K, and with densities from $0.7\rho_c$ to $1.3\rho_c$.

Some of the thermodynamic properties, such as s and u, are finite at a critical point.

Furthermore, thermodynamic properties can have very large values at non-critical points in thermodynamic-state space. An example of this type of phenomenon occurs with the specific heat capacity at constant pressure, c_p, of light water. At a given pressure greater than the critical pressure, a graph of c_p versus T has a sharp peak at a pseudocritical temperature T_{pc} greater than the critical temperature [14]. A case of this example occurs at $p = 24.5$ MPa: $T_{pc} \approx 658$ K and $c_p \approx 87$ kJ/(kg·K). In comparison, the critical point occurs at $p = 22.064$ MPa and $T_c = 647.096$ K. A constant-pressure system exhibits a capacity to receive a large amount of heat as its temperature is increased near its pseudocritical point.

3.3 An example of supercritical-water coolant

Thermodynamic properties in this example have the same symbols and subscripts as in the previous reactor examples. The efficiencies are calculated from equations (5) and (6).

The CANDU-X Mark 1 is a conceptual design for an SCWR [5]. The light-water coolant ($T_c = 647.096$ K and $p_c = 22.064$ MPa) has $p_i = 25$ MPa, $T_i' = 380$°C, $p_o \approx 25$ MPa, and $T_o' = 430$°C. Thus, $T_i = 653$ K, $T_i / T_c = 1.009$, $T_o = 703$ K, and $T_o / T_c = 1.086$, so the coolant is a supercritical fluid. The light-water power cycle has $T_s' = 400$°C, $T_l' \approx 30$°C, $P_{th} = 2280$ MW, and $P_e = 910$ MW, for one unit. Thus, $T_s = 673$ K, $T_l \approx 303$ K, $\eta_C = 55.0\%$, and $\eta_T = 39.9\%$.

The inlet temperature and the outlet temperature were chosen so that the pseudocritical temperature of approximately 385°C (658 K) at the pressure of 25 MPa is attained in each of the fuel channels in the reactor. This temperature range provides a large heat transfer from the fuel to the coolant. This heat transfer and the large η_T are important advantages of the design.

4. Conclusion

The reader has experienced a brief tour of the transitions among the fluid phases of light water and heavy water, and the application to water-cooled nuclear-fission reactors. Liquid-vapour phase transitions can be explained by a model of short-range interaction among molecules and a consideration of thermodynamic stability. Critical-point behaviour can be explained by long-range correlated effects. Thermodynamic properties are known well for subcritical states and supercritical states, except in a small neighbourhood of a critical point. Advanced Generation III reactors will not operate near the critical points of their coolants during normal operation. Generation IV reactors with supercritical-water coolant would operate near the critical points of their coolants during transient processes that would likely occur during normal operation.

The present study indicates the need for more information about thermodynamic properties in the critical-point neighbourhoods of light water and heavy water. This study provides a useful thermodynamic framework for a nuclear-reactor analyst in studies involving water as a coolant.

A nuclear-reactor designer is advised to avoid normal operation with coolant temperatures within 10°C (10 K) of the critical temperature of water coolant. This advice is based on the strongly non-linear behaviour of some thermodynamic properties near a critical point, and the inaccuracy of empirical models of thermodynamic properties near a critical point. A designer should consider high-temperature coolant because of the potential improvement in thermal efficiency.

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