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Introduction

1.1 Reactor Accident Analysis and Fuel Equation of State

For more than fifty years, uranium dioxide was world-wide used as the main fuel for two generations of nuclear power plants. Chosen first as the most convenient uranium compound for easy fabrication of sintered pellets, UO_2 displayed in the long run an excellent combination of thermophysical properties as well as an uncommon resistance to burn-up and radiation damage. Furthermore, some features of the dioxide crystallographic structure (fluorite face centred cubic), in conjunction with the electronic properties of uranium, allowing for different oxidation states, enable solid solutions, MO_2, to be formed with all existing fissile elements, in particular, with plutonium and thorium. Furthermore, mixed oxides (*MOX*) with variable oxygen stoichiometry can be obtained, so that the oxygen chemical activity may be adjusted in the fabricated fuel to avoid chemical interaction with metallic cladding. For this reason, uranium-plutonium *MOX* could be successfully adopted also for fast breeder reactors. In this application, the fuel is submitted to a severe thermal regime, with centreline pellet temperatures of up to near the melting point, and gradients of the order of 500 K/mm . Though under these conditions the fuel undergoes almost complete in-pile restructuring, the MO_2 rods still exhibit an excellent chemical and mechanical performance up to very high burn-ups. It was, indeed, in the context of the safety studies of liquid-metal cooled fast breeder reactors (*LMFBR*) that the properties of the oxide fuel were invoked to describe hypothetical core disruptive accidents where extremely high temperatures far above the melting point are reached. In fact, the worst conceivable accident sequence in a nuclear reactor can be conjectured in a *LMFBR* scenario, starting from a supercritical reactivity excursion, initiated, for example, by a loss of the liquid sodium coolant. Such an excursion entails a rapid release of energy, which - if large enough - can result in the explosive disassembly of the completely molten reactor core. Upon melting, the uranium-plutonium oxide fuel and its cladding collapse to the bottom of the core, and, should the compaction of fissile atoms lead to a supercritical configuration, even more energy will be released in the fuel. This results in even higher temperatures, and - in consequence of the inertia of the molten fuel (and core debris) which prevents instantaneous adjustment to the rapid input of energy - also in high pressures. Both act to terminate the transient - the high temperature expansion of the fuel reducing the macroscopic nuclear cross-sections (and hence the fission rate), whilst the pressure pulse ultimately results in the hydrodynamic dispersal of the fuel. This hypothetical sequence of events may occur within a very short time, and the fission energy released during the reactivity ramp - which is a measure of the gravity level of the accident - results from the competition between the lifetime of prompt and delayed neutrons, and the quasi-adiabatic rate of expansion of the core, governed, in the most conservative case, by the vapour pressure of the molten fuel.

In the context of the current *LMFBR* technology, this type of accident is highly improbable, however, the frightening scenario of an explosive core disassembly at temperatures at which also refractory materials melt and vaporise within seconds or even fraction of seconds, has produced a strong impact in the public debate on peaceful uses of nuclear energy.

At present, the objectives of the nuclear technology developments are aiming at understanding and preventing less severe reactor accidents, in which however, core melting is contemplated as well as radionuclide dispersion by fuel vaporisation. Even in this scenario, the high temperature thermodynamic properties of molten fuel represent a key issue in the evolution and consequences of the accidents. On the one side, licensing authorities are demanding trustworthy information on the physical processes taking place during these hypothetical accidents, on the other one, engineers and physicists must admit that certain predictions are to a large extent based on conjectures and estimates. Small scale simulation tests of reactor core behaviour under high and fast power excursions have been conducted worldwide, but a realistic assessment of the reactor materials properties, and in particular of fuel at temperatures far above the melting point still remains a challenge. In the last three decades, in spite of the uncertain and fluctuating context of the nuclear energy development, groups of specialists have not ceased to work on this problem, which is centred on the definition of a thermodynamic equation of state of the fuel applicable from the melting up to the critical point.

1.2 The Role of Equation of State

The pressure-volume-temperature relation is provided by the *thermal* equation of state (*EOS*), $P = P(T, V)$, in which the pressure P, temperature T, and volume, V, of the given system enter. However, like the internal energy U, the volume is not fixed by the *thermal EOS*, but requires, instead, a *caloric* equation of state, such as is afforded, for example, by the heat capacity at constant volume, $C_V(T)$. It is thus the equations of state of the fuel which provide the essential link between the nuclear aspects of a supercritical excursion and the dynamic response of the molten core; $T(U,V)$ controls the nuclear fission cross-sections *via* the Doppler coefficient, whilst $P(U,V)$ controls the time-dependence of the fuel-mass geometry *via* hydrodynamics. The reliability of reactor safety analyses is thus contingent on the accuracy to which the equations of state of the fuel are known - in particular, in the liquid-vapour coexistence region, which extends to the critical point - a most important invariant point on the phase diagram of any material.

As mentioned before, fuels of different compositions may be concerned. In particular, in fast reactors the fuel is normally a mixed oxide of uranium and plutonium. The description of the high temperature thermodynamic behaviour of *MOX* is obviously more complicated than for uranium oxide. Yet, the difference in the extrapolated thermodynamic properties of UO_2 and MO_2 at temperatures far above the melting point are very likely much smaller than the uncertainties of the current theoretical models. Therefore, the first objective should be to obtain a sufficiently accurate description of UO_2, the simplest and most known compound[1].

In the context of the above mentioned *LMFBR* reactivity excursions, any increase of hydrostatic pressure in the molten core contributes to an earlier termination of the power ramp. From this point of view, an accident occurring in a fresh core is expected to be more severe than in a core at high burn-up. As for the effect of the fuel composition, under anoxic conditions, *MOX* is slightly more volatile than uranium dioxide. Therefore, a fast reactor core composed of enriched UO_2 does probably provide the case of the highest possible energy insertion during core disruption.

Despite considerable effort over the past thirty years, the high-temperature phase diagram of the U-O system in the vicinity of stoichiometric UO_2 was still very incomplete in the middle of the 90's, due primarily to three features:

- *the very high melting temperature* ($\sim 3150\ K$), which, until the advent of rapid laser heating techniques, not only restricted the acquisition of experimental data, but also posed problems for the containment of the sample, with the attendant possibility its significant contamination,
- *the rather wide range of stoichiometries* over which urania, $UO_{2\pm x}$, can exist as a single phase system, and the related problem of controlling the stoichiometry of any *given* sample throughout the course of an experiment,
- *the non-congruency of the melting and vaporisation* of the material under conditions of thermodynamic equilibrium.

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[1] Furthermore, the fuel irradiated at high burn-ups contains significant amounts of fission products, some of which are gaseous or highly volatile. In this case, under temperature ramps above the melting point, pressures are created in addition to the equilibrium vapour pressure of the matrix. In a first approximation, the pressures of components not reacting with the matrix can be evaluated independently.

Given, however, the recent advances both in high temperature experimental technology and in the theoretical understanding of binary systems of variable composition, the possibility of further progress presented itself, involving not only further refinements, but also, more importantly, the possibility of exploring hitherto experimentally inaccessible regions of the *phase diagram.*

1.3 Equation of State for Liquid UO_2: Historical

Thirty years ago, when the first attempts were being made to construct an *EOS*, which describes in a unified and self-consistent way the thermodynamics of the coexisting liquid and vapour phases of urania, the portfolio of experimental data, which was then available to act as empirical constraints on such an *EOS*, was rather limited. In an attempt to fill this lacuna, much attention and effort was accordingly directed towards theoretical modelling in order to permit what little data there was to be extrapolated to experimentally inaccessible areas of the phase diagram - in particular, the critical region; the results obtained prior to *INTAS* 93-66 project are summarised in Table 1.1.

For the first 10 years, attempts toward obtaining values of the critical parameters were based on purely empirical procedures - notably the law of rectilinear diameters (*LRD*) and the principle of corresponding states (*PCS*). The values of the critical temperature, T_C, obtained by such methods are described in Table 1.2, and varied between 6400 K and 10000 K. It was eventually realised, however, that little significance could be attached to such values, since the procedures used to predict them either lacked any physical basis (as is the case with the *LRD*), or had no demonstrable validity (as is the case with the *PCS*) for non-congruently vaporising materials like urania. Accordingly, a less empirical approach based on Eyring's significant structure theory (*SST*) was initiated in 1974 (see Table 1.3), and progressively developed and refined, until by 1987 it was not only able to treat two-phase equilibria involving non-stoichiometric molten $UO_{2\pm x}$, but also incorporate the experimentally well-established [131] existence in the vapour phase - even over stoichiometric $UO_{2.00}$ - of molecular species other than UO_2(g), notably UO(g), UO_3(g) - as well as O(g), O_2(g) and U(g). For the first time, it was thus possible to consider, theoretically, the non-congruency of the vaporisation of molten urania in terms of a model which treated the liquid and vapour phases in a unified way - an attractive feature not shared by some earlier essays [37] which, through their description of the liquid and vapour phases using quite separate models, did not fully respect the coexistent equilibrium of the two phases. For the case of stoichiometric UO_2, a critical temperature around 10000 K was finally predicted [39] - a value close to that given [76] by the alternate perturbed hard sphere (*PHS*) approach, which is essentially a refinement of the classical van der Waals' treatment of two-phase equilibria. The proximity of these two values of T_C must, however, be considered fortuitous, since within the *PHS* approach the vaporisation is necessarily congruent, the

Table 1.1. Synopsis of the Main Published Works on the Equation of State of UO_2

Year	Author	Method of Evaluation	Predicted Critical Point Parameters$^{(a)}$					Input Data
			T_C	P_C	V_C	ρ_C	z_C	
1964	Meyer and Wolfe [103]	*PCS*	7300	194.0	85.5	3.01	0.27	Melting point(*MP*), density, vapour pressure
1965	Miller [104]	*LRD*	9115	124.6	170	1.59	0.27	*MP*, density, vapour pressure
1966	Menzies [102]	*PCS*	8000	200.0	90	3.16	0.27	Saturated vapour pressure(*VP*)
1966	Robbins [118]	*PCS*	5500-10000	100-280	96-120		0.2-0.4	density, heat of fusion, *VP*
1974	Booth [17]	*PCS*	6723	142.3	99	2.74	0.251	*MP*, density, *VP*, enthalpy of solid
1974	Gillan [50]	*SST*	6960	108.4		1.64	0.308	*MP*, density, *VP* of UO_2, molecular data
1974	*ibid.*	*SST*	9930	146.9		1.63	0.308	*MP*, density, different *VP* data
1976	Fischer *et al*[42]	*SST*	7560	122.6		1.66	0.316	*VP*, enthalpy of solid UO_2, molecular data (spectroscopic)
1976	Kapil [83]	*PCS*	6744	142.2		2.74	0.25	*MP*, density, linear expansion, *VP*
1977	Browning *et al*[22]	*PCS*(1)	6723	140.4	98.7		0.25	
		PCS(2)	6820	138.0	98.4		0.24	
1977	Browning *et al*[22]	*SST*(1)	7320	125.6	152		0.32	*VP*
		SST(2)	8840	142.4	158		0.31	*MP* data, liquid density, and expansion
1978	Finn *et al*[37]	*LRD*	7365	705		2.99	1.00	Liquid density, oxygen potential , liquid C_V, calculated partial pressures
			6400			3.27	0.27	

(continued)

Table 1.1. Synopsis of the Main Published Works on the Equation of State of UO_2 (end)

Year	Author	Method of Evaluation	Predicted Critical Point Parameters$^{(a)}$					Input Data
			T_C	P_C	V_C	ρ_C	z_C	
1979	Fischer [38]	*SST*	7970	$178^{(b)}$	130	2.08	$0.349^{(b)}$	O/M=1.992, solid-state defect energies, solid-state data near T_m; spectroscopic data on UO(g) and UO_2(g) molecules
		SST	7990	$182^{(b)}$	129	2.10	$0.353^{(b)}$	O/M=1.911
1982	Dharmadurai [30]	*RK-EOS*	7000	113	178	1.52	0.346	*VP* in equilibrium with UO_2(l)
1985	Mistura *et al*[105]	*PHC-EOS*	7567	141	156	1.73	0.350	*VP* and liquid molar volume at T_m
1987 (1989)	Fischer [39]	*SST*	10600	$158^{(b)}$	173	1.56	$0.310^{(b)}$	*VP* at $T = 2150\ K$ and over liquid; geometrical mean of experimental partial pressures of UO and UO_3; molecular spectroscopic data.

Notes:

[a] $T_C\ in\ K$, $P_C\ in\ MPa$, V_C in $10^{-6}\ m^3 kg^{-1}$, ρ_C in $10^3 kg\ m^{-3}$, $z_C = P_C V_C / MRT_C$, $M = 0.27 kg\ mol^{-1}$

[b] only contributions from U-bearing species are included.

PCS = Principle of Corresponding States; *LRD* = Law of Rectilinear Diameters; *SST* = Significant Structure Theory; *RK-EOS* = Redlich-Kwong Equation of State; *PHC-EOS* = Perturbed Hard Core Equation of State.

Only the 1987 work of Fischer includes UO(g), UO_2(g) and UO_3(g) molecules - UO_3(g) having been *omitted* from his 1979 work. Apart from the 1974 and 1976 *SST* contributions (which treated UO_2(g) as a bent molecule), all other *SST*-based calculations have assumed a *linear* UO_2(g) molecule; all *SST* attempts (*except* 1974) have included electronic contributions in the UO_2(g) partition function.

only molecular species admitted being UO_2, in either phase; furthermore, the degree to which it can be considered realistic to treat a system such as molten UO_2 - which in its solid state is appreciably ionic - as composed of neutral molecules of UO_2 might seem slight, especially in view of the appreciable ionic conductivity exhibited by other binary molten systems having the same solid-state fluorite structure [29]. However, there exists an equivalence theorem, based on the works of Stillinger [128] and Reiss [117] which asserts that the thermodynamic properties of a binary molten salt are actually the same as those of a hypothetical non-electrolytic liquid (of the same overall density and temperature) composed of electrically neutral, identical 'molecules' of size equal to the distance of closest approach of a charged cation and an anion in the real (binary) liquid; these hypothetical molecules are considered to interact non-Coulombically by a short-range potential, identical to that to which the cations and anions in the actual liquid are subject. The asserted dependence of thermodynamic properties only on the sum of the cation and anion radii (rather than on their individual diameters) represents a *PCS* [117] - but one more subtle than that already referred to and criticised. The importance of this equivalence is, of course, that it reconciles a finite electrical conductivity (which molten UO_2 most probably has) with a description of the liquid in terms of seemingly neutral molecules. The much better overall agreement with available thermodynamic data which is obtained [76] by assuming such hypothetical spherical molecules, rather the linear form which real UO_2 molecules actually have [105], strongly suggests that the hypothetical, non-electrolytic model might form the basis of a novel approach to the *EOS* appropriate to the liquid-vapour coexistence region of the phase diagram of uranium dioxide.

The desirability of such an approach which is rooted more strongly in the liquid than is the *SST*, for example (in which the liquid is described in terms of the partition functions of the solid and gaseous phases), is indicated by certain fundamental difficulties which continued to plague even the most refined version [39] of the *SST* approach - notwithstanding heroic attempts at a realistic description of the multi-species vapour phase over a non-stoichiometric UO_2 – notably:

- certain pathologies exhibited by the derived *EOS* with respect to the composition of the vapour phase, particularly in the vicinity of the critical point where, over $UO_{2.00}^{(liq)}$, the predicted value of $(O/U)^{(vap)} \neq 2$,
- the fact that the very concept of a critical point - in the sense that it is used in the case of a mono-atomic substance - is actually ill-defined in the case of a binary system with variable stoichiometry, where the only well-defined extrema of such a system are the so-called *cricondentherm* and *cricondenbar* [151].

The former defines the highest temperature attainable on the saturation curve for which $\partial T/\partial P = 0$, whilst the latter defines the highest pressure attainable on the boiling curve for which $\partial P/\partial T = 0$; beyond these extrema, where the phenomena of retrograde condensation and vaporisation occur, lies the critical point, the precise location of which is defined by the intersection of this $P-T$ section of the phase diagram with the $T-x$ section (x =O/U-2), at the point where $T(x)$ is maximum. These boiling and saturation curves define the extent of the two-phase region, and are the $P-T$ equivalent of the more familiar (liquid-vapour) two-phase region usually depicted in the $T-x$ plane.

In connection with experiments to determine the vapour pressures as functions of temperature, it is clearly essential to establish which curve corresponds to the prevailing experimental conditions. Evidently, experiments based on the classical boiling point method [16] (where a specimen, heated in a quasi-stationary way on a relatively slow timescale, evaporates against an external inert gas whose pressure can be varied) refer to the boiling curve (which separates stoichiometric liquid from a hyperstoichiometric vapour phase), whilst the conditions obtained on the saturation curve (which separates a stoichiometric vapour from a liquid phase whose surface is hypostoichiometric) are identical to those of the so-called forced-congruently vaporising mode (*FCM*), which is realised in experiments utilising very rapid laser heating (on a sub-millisecond time scale), the sample here being allowed to evaporate freely into vacuum [108]. Under these conditions, an initially stoichiometric sample is virtually instantaneously vaporised with preservation of its bulk stoichiometry, whilst the surface itself is rendered hypostoichiometric - the rate of evaporation being much greater than the rate at which oxygen can be replenished from the bulk by diffusion [20].

The T-dependence of the heat capacity, $C_P(T)$, of molten UO_2 predicted by the *SST* does not even qualitatively conform to the experimental $C_P(T)$ data which extends up to 8000 K, subsequently obtained at *ITU* [119]. This extensive set of $C_P(T)$ data, which was published in 1993, constitutes not only a most valuable contribution to the caloric *EOS* of UO_2, but also acts a powerful constraint on any acceptable thermal *EOS*, to which the *SST*-based *EOS*, for example, apparently does not conform.

The development of *EOS* for UO_2, presented in this monograph progressed through several stages. A relatively simple *EOS* based on a pure ionic model was first devised. Background, method of calibration and resulting expressions of the thermodynamic quantities are presented in Chapter 3, following a general discussion of the available models and approaches presented in Chapter 2. The pure ionic model had obviously a restricted success, since it is unable to treat the non-congruent evaporation of uranium dioxide. It also fails, at higher temperatures, to reach the vicinity of the vapour-liquid critical point. However, the experience gained on this way was important in developing an improved *EOS* model, with a first attempt to define simple physical atomic interactions having meaningful parameters expressed in terms of known ionic radii. To resolve further problems encountered in applying this *physical* model more sophisticated *chemical* models of fluid UO_2 have been invoked. The general conditions of the vapour-liquid phase equilibrium and their implementation within this more complicated context are discussed in Chapter 4. Given the problems associated with pure ionic and *SST*-based approaches, in particular in the liquid-vapour coexistence region, and the absence of any obvious way of resolving them, it was decided to base the theoretical efforts on a model which essentially generalises the single substance, neutral molecule approach already mentioned (and validated by the Stillinger-Reiss theorem), by including:

- molecular species other than just UO_2 - notably, UO and UO_3 in reactive equilibrium with UO_2,
- their associated singly charged ions (UO^+, $UO_2^\pm$, UO_3^-),
- electrons and other elemental species (U, O, O_2), together with their associated monovalent ions (U^+, O^-, O_2^-), and
- possible neutral dimers, such as U_2O_n with n = 2, 3, 4, 5.

It should be pointed out that a description of the liquid state in terms of such units is not necessarily inconsistent with the conventional *ionic* description of the bonding in the solid - if for no other reason than the stability of the O^{2-} ion is contingent on the Madelung lattice potential. Between these species the following interactions are admitted:

- short-range repulsion calculated in the *hard-spheres mixture* approximation, neglecting any difference between the radii of a given species and its associated ion,
- short-range attractions, calculated in the van der Waals' approximation, neglecting any difference between neutral and charged species, and assuming an equal attraction between all U-bearing species, and a much weaker, but still equal attraction between all combinations of O and O_2, and between either O or O_2 and any U-bearing molecule, and
- the Coulomb interaction between charged species, calculated within a variant of the modified Debye-Hückel approximation.

This further step in the development of the *EOS* was much more cumbersome but the context of the starting assumptions proved to be well grounded on principles of evidence and much more successful than those adopted in the past (Chapter 5). The results presented demonstrate the ability of a *chemical* model to reproduce the oxygen potential as a function of temperature as well as the most specific features of non-congruent evaporation of UO_2. At the same time, however, essential drawbacks were found; in particular the van der Waals - like model was still unable to reproduce the experimental temperature dependence of the heat capacity.

To overcome this difficulty a modification based on the thermodynamic perturbation theory (*TPT*) was developed. The final version of the *EOS* described in Chapter 6 is a generalisation of the approach first proposed by Barker and Henderson [10] for a Lennard-Jones fluid. This generalisation was also implemented in two stages. In the first one, the simple version of *TPT* (actually the model of a Lennard-Jones fluid) was utilised, in the second stage a more sophisticated version was constructed by taking into account the non-central character of the interactions of complex molecules in a dense fluid.

The calibration of this model and validation of its predictions with experimental data are presented in Chapter 7. Calibration of the model was performed by using as input selected thermodynamic quantities. Different choices were, obviously, possible (recommended values of pertinent thermophysical properties of urania are presented in Appendix A.1), but only few quantities, with the respective experimental uncertainties, were providing sufficiently strong constraints for unambiguous calibration. The optimal input was found to be: *i*) the density of molten UO_2, *ii*) the partial pressure of $UO_2(g)$ at the melting point, and *iii*) the value of $(O/U)^{(vap)}$ at $T = 3400\ K$.

Furthermore, elaboration of reactive equilibria considered in the model, requires a specific database containing the thermodynamic functions of the relevant gaseous species, together with the ionisation energies and electron affinities of certain atoms and molecules. These data are presented in Appendix A.2.

Calibration is implemented by treating molecular radii and van der Waals' interaction constants as *free* parameters, whose fitted values must be ultimately in reasonable agreement with measured molecular quantities. Accordingly, a detailed, independent assessment of these molecular parameters is presented in Appendix A.3.

To test the predicative accuracy of the model, experimental data on thermophysical quantities related to the *EOS* are required at temperatures well above the melting temperature. The $C_P(T)$ data (constituting the caloric *EOS*) obtained in *ITU* are extremely valuable in this respect. The situation with the thermal *EOS* is, however, less satisfactory, despite the extensive experimental attempts over the past 20 years to acquire reliable $P_S(T)$ data up to the highest possible temperatures. These temperatures vary from experiment to experiment. Those attained by using laser pulse heating - probably the most reliable technique – are based on the classical boiling point method [16]. Yet, the boiling temperature of UO_2 is relatively low ($\sim 5000\ K$), and well below the estimated critical temperature (of which there is no indication in the new $C_P(T)$ data of molten UO_2 which extends up to $8000\ K$). Pressure measurements at higher temperatures were attained either in-pile [21] with low measurement accuracy[2], or from very fast laser heating (microsecond pulses). These latter are unfortunately plagued with contributions to the total vapour pressure from ions thermo-ionically emitted from the heated surface, an artefact that establishes the intrinsic application limit of this technique. Additionally, in all these experiments vaporisation was produced in the *FCM*, where the vapour pressure is significantly lower than under thermodynamic equilib-

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[2] In-pile vaporisation experiments are to date more informative than they were prior to the acquisition of $C_P(T)$ data of molten UO_2 [119]. In fact, in these experiments only the deposited energy, H, and the generated total pressure, P, could be measured, but not the sample temperature. A conversion of $P(H)$ into $P(T)$ was therefore necessary. This conversion, which was initially performed through a complex numerical procedure, can now be obtained with much greater accuracy.

Table 1.2. Inter-comparison of Purely Empirical Theoretical Approaches for Estimating the Critical Parameters of Urania

	Law of Rectilinear Diameters (*LRD*)	**Principle of Corresponding States (*PCS*)**
Range of T_c	$6400 - 9115\ K$	$5000 - 10000\ K$
Basic Principles	$1/2(\rho^{(liq)} + \rho^{(vap)}) = a - bT$	Universal relationship in *reduced* variables
Predicted Properties	Critical point data	Critical point data, *EOS*, (transport properties)
Calculation Procedure	Intersection of $\rho^{(liq)}$ and $\rho^{(vap)}$ curves	Application of universal functions in their reduced state within the *same* class of materials
Input Data	Liquid expansion data, vapour pressure data, and density at melting	*T, P, ΔH...,* mainly near melting
Validity of Results	Dependent on the range of extrapolation of the input data, and gives only a first estimate of the range of the critical parameters	Dependent on the availability of data of *similar* substances; gives a first approach to *EOS*
Advantages	Easy to apply	Simple empirical relationship. Can be deduced from statistical mechanics under certain restrictive conditions.
Problems	Availability of input data close enough to T_c. *No theoretical basis*	Availability of data on similar substances; this is *particularly* so with UO_2!

Table 1.3. Inter-comparison of Less Empirical Theoretical Approaches for Estimating the Critical Parameters of Urania

	Significant Structure Theory (*SST*)	**Perturbed Hard Spheres (*PHS*)**
Range of T_c	$6960 - 10000\ K$	$7000 - 9934\ K$
Basic Principles	Liquid partition function taken as a geometrical average of solid and gas partition functions	Perturbation theory expansion about the hard sphere potential
Predicted Properties	Critical point data, *EOS*, transport properties	Critical point data, *EOS* and certain transport properties
Calculation Procedure	Construction of the partition functions. Double tangent technique to determine phase equilibrium and pressure	Calculation of free energy from first few terms of a pertinent series. Calculation of thermodynamic quantities
Input Data	Melting temperature, volume expansion upon melting, vapour pressure data, heat of fusion	Pair potential for pure substances and interaction for mixtures. Boiling point, thermal expansion coefficient
Validity of Results	Dependent on input data and validity of model, especially for ionic systems.	Depends on how close the real potential is approached. Additive assumption of pair potential
Problems	Limited validity of the model	Accuracy of the pair potential and hard sphere correlation function
Advantages	Analytic form of free energy based on a liquid model, involving reasonable amounts of computing time	Based on same physical principles as van der Waals theory. Exact treatment of hard core. Treats attractive part and soft core of potential

rium (characterised by non-congruent vaporisation). This difficulty identifies an additional key role for the thermal *EOS*, namely that of permitting conversion from *FCM* vapour pressure values to those corresponding to *global* equilibrium. Without the possibility of such a conversion, information yielded by laboratory experiments employing rapid, laser-induced evaporation into vacuum would be irrelevant for predicting real reactor conditions arising from reactivity excursions.

1.4 Summary of the New Equation of State Features

In the following Chapters, the construction of the equation of state is described step by step, by following a line of though, which started from a simple scenario, and gradually encompassed new aspects or details to attain an adequately comprehensive model.

The final model is based on the thermodynamic perturbation theory (*TPT*) modified in order to account for the specific properties of UO_2. It describes, in a unified formalism, a multi-component mixture of chemically reactive, strongly interacting molecules and atoms, both neutral and charged. The description of dense liquid UO_2 is based on the demonstrated formal correspondence of the partition function of ionic liquids to that of liquids consisting of virtual molecular clusters (Stillinger-Reiss [128, 117] theorem). In such a model, detailed information is needed to describe the contributions of the internal degrees of freedom of complex (bounded) particles, *e.g.*, energies of ionisation and dissociation, excitation energy levels, *etc.*. On the other hand, however, the offered advantage is that the renormalized effective interaction of free (unbounded) particles is relatively weak, and, furthermore, arbitrary stages of ionisation and different structures of the particles can be composed in the frame of a unified calculation procedure. In principle, once a proper definition of the effective interaction of free particles is achieved, and the bound states are properly restricted, the model can continuously describe the wide variety of states ranging from the presumably highly ionised liquid at very high temperatures, to the *cold* vapour represented by a neutral molecular mixture. Along with free UO_2, a number of 'clusters', like U_2O_4, U_2O_2, U_2O_3, U_2O_5, *etc.* , as well as free atoms and molecules of uranium and oxygen (U, U_2, O, O_2), and ions (UO_2^+, UO^+, U^+, UO_3^-, UO_2^-, O^-) are included in the picture as distinct species with own partition functions, repulsion parameters (intrinsic volumes) and short-range attraction. This model can be considered as sufficiently realistic for dense vapours as well as dense, expanded liquids in the high-temperature region of phase coexistence. The liquid phase is essentially described as a set of conventionally distinguishable clusters (mainly with one uranium in the centre surrounded by several oxygen atoms), which are allowed to freely exchange oxygen and/or electrons. The general conditions for the free-energy minimum correspond to a system of equations for the chemical potentials, or may alternatively be expressed in the form of mass action law. Once explicit expressions for the free energy are known, this minimisation becomes a mere numerical problem. The equilibrium composition is evaluated, and, consequently, all thermodynamic functions can be deduced from the *thermal* and *caloric* equations of state, which are self-consistently defined as first derivatives of the free energy. It is worth remarking that, in spite of the additional, implicit dependence of the free energy on temperature and density (through the variable equilibrium composition) its first full derivatives, *e.g.*, pressure, entropy and chemical potentials, are equal to the corresponding partial derivatives of the free energy for fixed composition, at the free energy minimum. However, wherever the second derivatives are concerned, (*e.g.*, for the calculation of heat capacity, compressibility, *etc.*), this additional dependence of the free energy must be taken into account *explicitly.* Therefore, these quantities must be calculated via a direct numerical differentiation. The method applied to obtain the results reported here, was developed by V.K. Gryaznov and is described in Ref. [58].

The results of the final calculations of thermodynamic properties are discussed in detail in Chapter 7 and presented in an extended set of tables in Appendix A.

1.5 General Notations

List of Symbols

A	–	Electronic affinity	$J,\ eV$
a	–	van der Waals attraction parameter	$J\ m^3\ kmol^{-1}$
C_V	–	Isochoric heat capacity	$J\ kmol^{-1}K^{-1},\ J\ kg^{-1}K^{-1}$
C_P	–	Isobaric heat capacity	$J\ kmol^{-1}K^{-1}$
D_i	–	Dissociation energy if i-th species	$J\ kmol^{-1}$
d	–	Effective particle diameter	$m, \text{Å} \equiv 10^{-10}m$
U	–	Internal energy	$J\ kmol^{-1},\ J\ kg^{-1}$
F	–	Helmholtz free energy	$J\ kmol^{-1}$
G	–	Gibbs free energy	$J\ kmol^{-1},\ J\ kg^{-1}$
H	–	Enthalpy	$J\ kmol^{-1},\ J\ kg^{-1}$
I	–	Ionisation potential	$J,\ eV$
k	–	Boltzmann constant	$1.38\ 10^{-23} J\ K^{-1}$
L	–	Latent heat of vaporisation	$J\ kmol^{-1},\ J\ kg^{-1}$
m_i	–	Mass of i-th species	$kg\ kmol^{-1}$
N_i	–	Number of i-th species	$kmol$
N	–	Total number of particles	$N = \sum_i N_i,\ kmol$
n	–	Number density	$n = N/\mathcal{V}$
n_i	–	Number density of i-th species	$n_i = N_i/\mathcal{V}$
N_a	–	Avogadro number	$6.023\ 10^{26}\ kmol^{-1}$
P	–	Pressure	$Pa,\ bar \equiv 10^5 Pa$
R	–	Ideal-gas constant	$8.314\ J\ kmol^{-1}K^{-1}$
r_D	–	Debye radius	$m, \text{Å} \equiv 10^{-10}m$
S	–	Entropy	$J\ kmol^{-1}K^{-1},\ J\ kg^{-1}K^{-1}$
T	–	Temperature	K
$\mathcal{V}$	–	Volume	m^3
V	–	Molar volume	$V = \mathcal{V}/N,\ m^3\ kmol^{-1}$
V_s	–	Speed of sound	$m\ s^{-1}$
x	–	Non-stoichiometry parameter	$x = \mathrm{O/U} - 2$
x_i	–	Mole fraction of i-th species	$x_i = N_i/N$
z	–	Compressibility factor	$z = PV/RT$
Z_i	–	Charge of i-th species, in units of $\lvert e \rvert$	$\lvert e \rvert = 1.602\ 10^{-19} C$
α_T	–	Isobaric volume expansion	K^{-1}
β	–	Inverse temperature ($\beta = 1/kT$)	J^{-1}
$\beta_T(\beta_S)$		Isothermal (adiabatic) compressibility	Pa^{-1}, bar^{-1}
$\varGamma_D$	–	Coulomb non-ideality parameter	$\varGamma_D = d/r_D$
ε, σ	–	Parameters of the Lennard-Jones potential	J,Å
η	–	Packing fraction	$\eta = {}^1\!/_6 \pi n d^3$
μ_i	–	Chemical potential of $i-$th species	$J\ kmol^{-1}$
ρ	–	Density	$\rho = \sum_i m_i n_i, kg\ m^{-3}$
$\varPhi(r)$	–	Interaction potential	J