

CDA-EOS: Curvature–Driven Hydrogen-Bond Cooperativity in an Extension of IAPWS-95 for Liquid Water

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Abstract

We introduce the Curvature-Driven Association Equation of State (CDA-EOS) for liquid water. The model combines (i) the IAPWS-95 Helmholtz equation as a high-accuracy reference for bulk thermodynamics, (ii) a SAFT-style four-site association term representing hydrogen bonding, and (iii) thermodynamic curvature in the sense of Ruppeiner computed from the IAPWS-95 free energy as a scalar proxy for correlation strength. The curvature field $R(T, \rho)$ is mapped to a bounded network factor that modulates the effective association strength, producing a curvature-dependent association contribution added to the IAPWS reference. All thermodynamic properties follow by differentiation of a closed-form molar Helmholtz free energy $a_{\text{tot}}(T, \rho)$. Here ρ denotes molar density; IAPWS-95 is evaluated using its standard mass-density variable via $\rho_m = M_w \rho$. We present explicit expressions for the association contribution and its pressure and response-function corrections, and we discuss qualitative implications for the temperature of maximum density and heat-capacity anomalies. CDA-EOS provides a framework for connecting curvature-based correlation measures to association physics within an engineering-grade reference EOS.

1 Introduction

Liquid water exhibits a set of anomalous thermodynamic behaviours that distinguish it sharply from simple liquids. At ambient pressure there is a

temperature of maximum density (TMD) near 4°C, and on supercooling both the isothermal compressibility and the isobaric heat capacity rise steeply [5, 4]. These anomalies have often been interpreted in terms of competition between more open, tetrahedral local structures and more compact, high-density structures, and a possible liquid–liquid critical point in the deeply supercooled regime has been discussed in a wide range of simulation and theoretical studies [4, 3].

For practical thermodynamic calculations, the IAPWS-95 formulation provides a widely used reference equation of state (EOS) for ordinary water. It expresses the Helmholtz free energy in terms of reduced variables and a residual contribution $\phi^{(r)}(\tau, \delta)$ that is fitted to a large body of experimental data over broad ranges of temperature and pressure [1, 2]. From this single Helmholtz function, one can obtain pressure, entropy, internal energy, and response functions for engineering use with high accuracy. IAPWS-95, however, is essentially empirical: it does not expose explicit microscopic degrees of freedom for hydrogen bonding or local structural states.

In contrast, the Statistical Associating Fluid Theory (SAFT) and its variants treat associating fluids by decomposing the Helmholtz free energy into ideal, reference, chain, and association parts, with the association term derived from Wertheim’s theory for site–site bonding [6, 7]. For water, SAFT and PC-SAFT models often represent hydrogen bonding through multi-site association schemes and, in some cases, explicit two-state or multi-state descriptions of high-density and low-density local structures [8, 9, 11]. In these models, the association parameters are fitted to reproduce known anomalies such as the TMD and the shape of $C_p(T, p)$.

A third line of work applies thermodynamic geometry to fluid equations of state. In Ruppeiner’s formulation, one defines a Riemannian metric from second derivatives of the entropy and computes a scalar curvature R that is related to the correlation volume of the fluid [12, 14]. For several real substances, including water, $R(T, p)$ has been evaluated from experimental or reference EOS and used to identify regimes of large correlations and “solid-like” liquid states [13, 15]. In these studies, the EOS is taken as given and the curvature is used as a diagnostic; it is not typically fed back into the EOS as an active ingredient.

The central aim of this work is to connect these three strands in a minimal, explicit way. We propose the Curvature–Driven Association Equation of State (CDA-EOS) for liquid water, in which:

1. The IAPWS-95 molar Helmholtz free energy $a_{\text{IAPWS}}(T, \rho)$ is used as a fixed base EOS for water in the liquid and supercooled regions.
2. Thermodynamic curvature $R(T, \rho)$ is computed from a_{IAPWS} and mapped to a dimensionless network factor $n(T, \rho)$, which increases with correlation strength.
3. A four-site SAFT-style association term, representing hydrogen bonding, is added on top of a_{IAPWS} , with its effective association strength multiplied by a simple function of $n(T, \rho)$.

This yields a total molar Helmholtz free energy

$$a_{\text{tot}}(T, \rho) = a_{\text{IAPWS}}(T, \rho) + \lambda a_{\text{assoc}}(T, \rho; R), \quad (1)$$

which we refer to as the CDA-EOS. In this sense, the present work introduces a new EOS construction and theoretical framework: the association contribution is not chosen independently of the reference EOS, but is regulated by the correlation structure implied by IAPWS-95 itself.

The rest of this note sets out the explicit form of the curvature–driven association term, derives expressions for pressure and selected response functions, and discusses how the CDA-EOS could be parameterised and compared with existing two-state and SAFT-type models for water. The intention is not to provide a final, fully fitted EOS, but to define a concrete, closed-form structure that can be implemented on top of existing IAPWS codes and tested against data and simulations in follow-up work.

2 Background

2.1 IAPWS-95 Helmholtz free energy and density convention

Throughout this paper, ρ denotes the *molar density* (mol/m^3), and $a(T, \rho)$ denotes the *molar Helmholtz free energy* (J/mol). IAPWS-95 is commonly expressed using the *mass density* ρ_{mass} (kg/m^3). The two are related by

$$\rho_{\text{mass}} = M_w \rho, \quad (2)$$

where M_w is the molar mass of water.

To avoid ambiguity, we treat IAPWS-95 as providing a Helmholtz free energy in its native variable $a_{\text{IAPWS}}(T, \rho_{\text{mass}})$ and then define the molar-density form used in this paper by composition:

$$a_{\text{IAPWS}}(T, \rho) \equiv a_{\text{IAPWS}}(T, \rho_{\text{mass}}) \Big|_{\rho_{\text{mass}} = M_w \rho}. \quad (3)$$

Any derivative with respect to ρ therefore uses the chain rule, for example

$$\left(\frac{\partial a_{\text{IAPWS}}}{\partial \rho} \right)_T = M_w \left(\frac{\partial a_{\text{IAPWS}}}{\partial \rho_{\text{mass}}} \right)_T. \quad (4)$$

We use IAPWS-95 in its standard reduced variables

$$\tau = \frac{T_c}{T}, \quad \delta = \frac{\rho_{\text{mass}}}{\rho_{c,\text{mass}}} = \frac{M_w \rho}{\rho_{c,\text{mass}}}, \quad (5)$$

where T_c and $\rho_{c,\text{mass}}$ are the critical temperature and *critical mass density* used by IAPWS-95.

The IAPWS-95 formulation expresses the Helmholtz free energy as [1, 2]

$$a_{\text{IAPWS}}(T, \rho_{\text{mass}}) = RT \phi(\tau, \delta), \quad (6)$$

with

$$\phi(\tau, \delta) = \phi^{(0)}(\tau, \delta) + \phi^{(r)}(\tau, \delta). \quad (7)$$

Here ϕ is the standard IAPWS-95 dimensionless Helmholtz function, and R is the *molar* gas constant. This is equivalent to the more common mass-specific form $f = R_{\text{spec}} T \phi$ with $R_{\text{spec}} = R/M_w$ and $a = M_w f$.

Once a is known, all thermodynamic properties follow from standard relations; for example,

$$p(T, \rho) = \rho^2 \left(\frac{\partial a}{\partial \rho} \right)_T, \quad (8)$$

$$s(T, \rho) = - \left(\frac{\partial a}{\partial T} \right)_\rho, \quad (9)$$

$$u(T, \rho) = a + Ts, \quad (10)$$

where s and u are molar entropy and molar internal energy.

2.2 SAFT association free energy (molar form)

In SAFT, the Helmholtz free energy is commonly decomposed as [6, 7]

$$a = a^{\text{id}} + a^{\text{ref}} + a^{\text{chain}} + a^{\text{assoc}}, \quad (11)$$

where a^{assoc} accounts for specific site-site association such as hydrogen bonding. For a single associating species with association sites a , the association term in molar form is

$$\frac{a^{\text{assoc}}}{RT} = \sum_a \left(\ln X_a - \frac{X_a}{2} + \frac{1}{2} \right), \quad (12)$$

where X_a is the fraction of sites of type a that are not bonded. The fractions X_a are determined by mass-action equations of the form

$$X_a = \left[1 + \rho \sum_b X_b \Delta_{ab}(T, \rho) \right]^{-1}, \quad (13)$$

where ρ is molar density (mol/m^3), and Δ_{ab} has units of (m^3/mol) so that $\rho \Delta_{ab}$ is dimensionless. A typical choice is

$$\Delta_{ab}(T) = K_{ab} \left(e^{\varepsilon_{ab}/(RT)} - 1 \right), \quad (14)$$

with parameters K_{ab} (m^3/mol) and ε_{ab} (J/mol).

For water, SAFT and PC-SAFT variants with appropriately chosen association schemes have been shown to reproduce many anomalous properties when combined with a two-state picture [8, 9, 11, 10].

2.3 Thermodynamic curvature

Thermodynamic geometry defines a Riemannian metric on the space of equilibrium states. In the entropy representation $s = s(u, v)$, where u is molar internal energy and v is molar volume, the Ruppeiner metric is [12, 14]

$$g_{ij} = -\frac{\partial^2 s}{\partial x^i \partial x^j}, \quad (15)$$

with coordinates $x^1 = u$, $x^2 = v$. From g_{ij} one computes the scalar curvature R , which has been argued to scale with a correlation volume and

to change sign across different interaction regimes [12, 13, 14]. For several simple fluids, including water, $R(T, p)$ has been evaluated along coexistence curves and inside the liquid region, revealing regimes with large negative R (strong attractive correlations) and narrow slabs of positive R interpreted as “solid-like” liquid states [13, 15].

The scalar curvature carries units of volume in the standard fluctuation interpretation. With molar variables, it is natural to treat R as having units of molar volume (m^3/mol), up to a conventional multiplicative factor that depends on the exact coordinate choice. The CDA-EOS construction uses R only through ratios (for example R_{abs}/R_0), so any fixed convention is acceptable as long as it is used consistently.

3 Curvature–Driven Association Model

We now construct a curvature–driven association contribution on top of IAPWS-95.

3.1 Base equation of state

We treat IAPWS-95 as a fixed base molar Helmholtz free energy, evaluated in its native mass-density form and then mapped into the paper’s molar-density variable via $\rho_{\text{mass}} = M_w \rho$:

$$a_{\text{IAPWS}}(T, \rho) \equiv a_{\text{IAPWS}}(T, \rho_{\text{mass}}) \Big|_{\rho_{\text{mass}}=M_w\rho} = RT \phi(\tau, \delta). \quad (16)$$

3.2 Curvature and network factor

From $a_{\text{IAPWS}}(T, \rho)$ we can obtain $u(T, \rho)$ and $s(T, \rho)$ and thus the metric g_{ij} and its scalar curvature $R(T, \rho)$. We do not reproduce those lengthy expressions here; we assume that $R(T, \rho)$ can be computed numerically for any state point using IAPWS-95 (see [13, 15] for examples based on experimental EOS). Because the CDA-EOS uses derivatives of $a_{\text{tot}}(T, \rho)$, it is helpful for the network factor to be smooth even if $R(T, \rho)$ crosses zero. We therefore define a smoothed magnitude

$$R_{\text{abs}}(T, \rho) = \sqrt{R(T, \rho)^2 + R_\epsilon^2}, \quad (17)$$

where $R_\epsilon > 0$ is a small regularisation scale. R_ϵ has the same units as R , and is chosen small enough to only matter very near $R = 0$. We define a dimensionless network factor

$$n(T, \rho) = 1 - \exp\left(-\frac{R_{\text{abs}}(T, \rho)}{R_0}\right), \quad (18)$$

where $R_0 > 0$ sets a scale at which correlations are considered strong. R_0 has the same units as R so that R_{abs}/R_0 is dimensionless. In weakly correlated regions, $R_{\text{abs}} \ll R_0$ and

$$n(T, \rho) \approx \frac{R_{\text{abs}}(T, \rho)}{R_0}, \quad (19)$$

so the boost to association strength is approximately linear in the correlation volume. Near regions of strong correlation, $R_{\text{abs}} \gg R_0$ and $n \rightarrow 1$. Because R_{abs} uses the magnitude of R , the present model deliberately ignores the sign of the curvature and treats the network factor as a proxy for correlation *strength* only. A sign-sensitive extension could be explored in later work, but is not required for the minimal curvature-feedback construction pursued here. A schematic of the overall curvature-driven association construction is shown in Fig. 1, and a qualitative example of $n(T)$ along the 1-bar isobar is shown in Fig. 2.

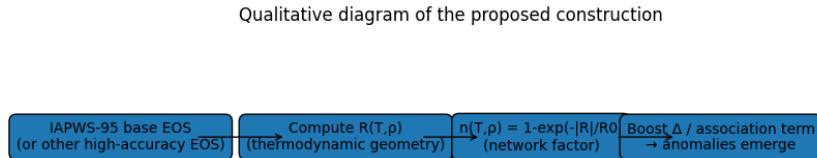


Figure 1: Schematic of the curvature-driven association construction in the proposed CDA-EOS. Thermodynamic curvature $R(T, \rho)$, computed from the IAPWS-95 base equation of state via thermodynamic geometry, is mapped to a dimensionless network factor $n(T, \rho)$ that regulates the effective hydrogen-bond strength in the added SAFT-style association term.

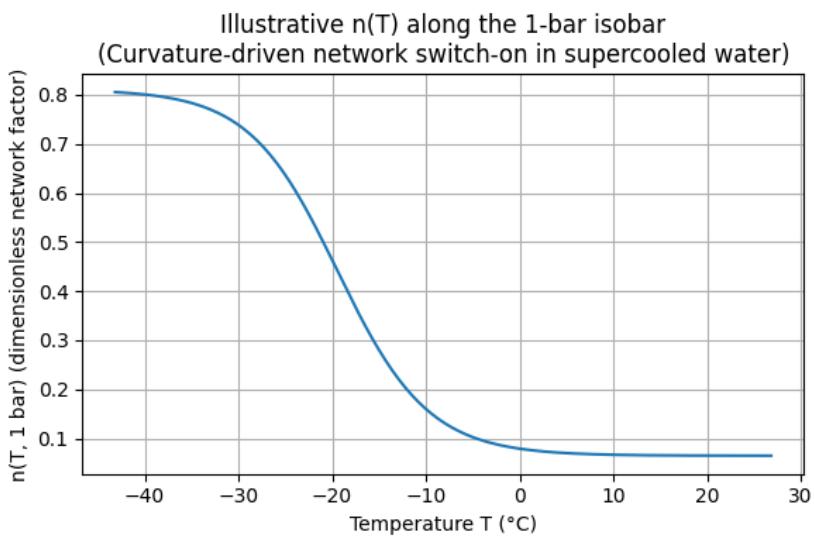


Figure 2: Qualitative behaviour of the dimensionless network factor $n(T)$ along the 1-bar isobar in the proposed CDA-EOS. The curve is constructed from a smooth model of the thermodynamic curvature $R(T)$ that reproduces the reported trend of small correlation volumes at high temperature and enhanced correlations in cold and supercooled water. The factor remains close to unity in the anomalous, strongly correlated regime and rapidly approaches zero at higher temperatures, so that hydrogen-bond cooperativity is selectively enhanced where water's thermodynamic anomalies are observed.

3.3 Curvature-dependent association strength

We model water as a SAFT-like associating fluid with $m = 4$ identical sites (two donors and two acceptors) and a single effective association parameter. The bare association strength (without curvature) is taken as

$$\Delta_0(T) = K_0(e^{\varepsilon/(RT)} - 1), \quad (20)$$

where K_0 is a bonding volume (m^3/mol) and $\varepsilon > 0$ is a bonding energy (J/mol). Here K_0 should be read as an effective parameter that can absorb simple reference-structure prefactors (for example a contact g_{ref}) when one wants to compare against standard SAFT conventions. The curvature-dependent association strength is

$$\Delta(T, \rho) = \Delta_0(T) [\alpha + (1 - \alpha) n(T, \rho)], \quad (21)$$

where $\alpha \in (0, 1)$ sets a baseline level of association even in weakly correlated states. When $n \rightarrow 0$, $\Delta \rightarrow \alpha \Delta_0$; when $n \rightarrow 1$, $\Delta \rightarrow \Delta_0$. For a single site type with multiplicity m , the mass-action equation reduces to

$$X = \left[1 + \rho m X \Delta(T, \rho) \right]^{-1}, \quad (22)$$

where $X(T, \rho)$ is the fraction of unbonded sites. This yields a quadratic equation

$$(\rho m \Delta) X^2 + X - 1 = 0, \quad (23)$$

with physically relevant solution

$$X(T, \rho) = \frac{-1 + \sqrt{1 + 4 \rho m \Delta(T, \rho)}}{2 \rho m \Delta(T, \rho)}. \quad (24)$$

The bonded fraction per site is $B(T, \rho) = 1 - X(T, \rho)$.

3.4 Association free energy and total Helmholtz energy

The association contribution in molar form is

$$\frac{a_{\text{assoc}}(T, \rho)}{RT} = m \left(\ln X(T, \rho) - \frac{X(T, \rho)}{2} + \frac{1}{2} \right). \quad (25)$$

We propose the total molar Helmholtz free energy

$$a_{\text{tot}}(T, \rho) = a_{\text{IAPWS}}(T, \rho) + \lambda a_{\text{assoc}}(T, \rho), \quad (26)$$

with λ a dimensionless prefactor intended to reduce double counting of association physics already encoded empirically in the IAPWS residual term. In the simplest implementation one can set $\lambda = 1$ and treat the association term as a structured correction, then adjust $(K_0, \varepsilon, \alpha, R_0, R_\epsilon, \lambda)$ so that macroscopic properties remain consistent with data.

4 Derived Thermodynamic Properties

4.1 Pressure

The pressure is

$$p(T, \rho) = \rho^2 \left(\frac{\partial a_{\text{tot}}}{\partial \rho} \right)_T = p_{\text{IAPWS}}(T, \rho) + p_{\text{assoc}}(T, \rho), \quad (27)$$

with

$$p_{\text{IAPWS}}(T, \rho) = \rho^2 \left(\frac{\partial a_{\text{IAPWS}}}{\partial \rho} \right)_T, \quad (28)$$

and

$$p_{\text{assoc}}(T, \rho) = \lambda \rho^2 \left(\frac{\partial a_{\text{assoc}}}{\partial \rho} \right)_T. \quad (29)$$

Using the explicit form of a_{assoc} ,

$$\frac{\partial a_{\text{assoc}}}{\partial \rho} = RT m \left(\frac{1}{X} - \frac{1}{2} \right) \left(\frac{\partial X}{\partial \rho} \right)_T, \quad (30)$$

so that

$$p_{\text{assoc}}(T, \rho) = \lambda RT m \rho^2 \left(\frac{1}{X} - \frac{1}{2} \right) \left(\frac{\partial X}{\partial \rho} \right)_T. \quad (31)$$

It can be useful to express $(\partial X / \partial \rho)_T$ in terms of the auxiliary variable

$$A(T, \rho) \equiv \rho m \Delta(T, \rho), \quad (32)$$

so that

$$X(A) = \frac{-1 + \sqrt{1 + 4A}}{2A}. \quad (33)$$

Then

$$\left(\frac{\partial X}{\partial \rho} \right)_T = \frac{dX}{dA} \left(\frac{\partial A}{\partial \rho} \right)_T, \quad (34)$$

with

$$\frac{dX}{dA} = \frac{1}{A\sqrt{1+4A}} - \frac{\sqrt{1+4A}-1}{2A^2}, \quad (35)$$

and

$$\left(\frac{\partial A}{\partial \rho} \right)_T = m \Delta(T, \rho) + \rho m \left(\frac{\partial \Delta}{\partial \rho} \right)_T. \quad (36)$$

The second term contains the curvature feedback:

$$\left(\frac{\partial \Delta}{\partial \rho} \right)_T = \Delta_0(T) (1 - \alpha) \left(\frac{\partial n}{\partial \rho} \right)_T, \quad (37)$$

and, from the smooth definition of n ,

$$\left(\frac{\partial n}{\partial \rho} \right)_T = \exp\left(-\frac{R_{\text{abs}}}{R_0}\right) \frac{1}{R_0} \left(\frac{\partial R_{\text{abs}}}{\partial \rho} \right)_T, \quad (38)$$

where

$$\left(\frac{\partial R_{\text{abs}}}{\partial \rho} \right)_T = \frac{R}{\sqrt{R^2 + R_\epsilon^2}} \left(\frac{\partial R}{\partial \rho} \right)_T. \quad (39)$$

In practice, $R(T, \rho)$ and its derivatives can be computed numerically from an IAPWS-95 implementation over a local stencil in (T, ρ) , or by automatic differentiation if an AD-compatible implementation is available.

4.2 Isobaric expansion and the TMD line

At fixed pressure p^* , the density is implicitly defined by $p(T, \rho) = p^*$. Differentiating with respect to T gives

$$\left(\frac{\partial p}{\partial T} \right)_\rho + \left(\frac{\partial p}{\partial \rho} \right)_T \left(\frac{\partial \rho}{\partial T} \right)_p = 0, \quad (40)$$

so that

$$\left(\frac{\partial \rho}{\partial T} \right)_p = -\frac{(\partial p / \partial T)_\rho}{(\partial p / \partial \rho)_T}. \quad (41)$$

The isobaric expansion coefficient is

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p = \frac{1}{\rho} \frac{(\partial p / \partial T)_\rho}{(\partial p / \partial \rho)_T}. \quad (42)$$

A density maximum along a given isobar occurs where $\alpha_p = 0$, that is,

$$\left(\frac{\partial p}{\partial T} \right)_\rho = 0, \quad (43)$$

assuming mechanical stability $(\partial p / \partial \rho)_T > 0$. In the present model,

$$\left(\frac{\partial p}{\partial T} \right)_\rho = \left(\frac{\partial p_{\text{IAPWS}}}{\partial T} \right)_\rho + \left(\frac{\partial p_{\text{assoc}}}{\partial T} \right)_\rho. \quad (44)$$

The first term reproduces the TMD behaviour of the base IAPWS-95 formulation. The association term adds a correction. From

$$p_{\text{assoc}}(T, \rho) = \lambda R T m \rho^2 \left(\frac{1}{X} - \frac{1}{2} \right) \left(\frac{\partial X}{\partial \rho} \right)_T, \quad (45)$$

we obtain

$$\left(\frac{\partial p_{\text{assoc}}}{\partial T} \right)_\rho = \lambda R m \rho^2 \left[\left(\frac{1}{X} - \frac{1}{2} \right) \left(\frac{\partial X}{\partial \rho} \right)_T + T \left(\frac{\partial}{\partial T} \left\{ \left(\frac{1}{X} - \frac{1}{2} \right) \left(\frac{\partial X}{\partial \rho} \right)_T \right\} \right)_\rho \right]. \quad (46)$$

Since $X(T, \rho)$ depends on T through the Boltzmann factor $\exp(\varepsilon/RT)$ and through the curvature-driven factor $n(T, \rho)$, this term can become negative in regions where the network factor grows rapidly with decreasing temperature. This provides a mechanism for shifting the TMD line and modifying its shape relative to the base IAPWS prediction.

4.3 Heat-capacity anomaly

The isobaric heat capacity is

$$C_p = \left(\frac{\partial h}{\partial T} \right)_p, \quad (47)$$

where the molar enthalpy is

$$h = a_{\text{tot}} + T s + \frac{p}{\rho}. \quad (48)$$

The entropy contribution from association is

$$s_{\text{assoc}} = - \left(\frac{\partial a_{\text{assoc}}}{\partial T} \right)_{\rho}, \quad (49)$$

and $h_{\text{assoc}} = a_{\text{assoc}} + Ts_{\text{assoc}}$. Taking the derivative at constant pressure,

$$\Delta C_{p,\text{assoc}} = \left(\frac{\partial h_{\text{assoc}}}{\partial T} \right)_p, \quad (50)$$

gives an association contribution to C_p dominated by first and second derivatives of $X(T, \rho)$ with respect to T . Because $X(T, \rho)$ is sensitive to both the bonding energy and the curvature-driven factor $n(T, \rho)$, the model naturally produces a broad peak in C_p in regions where $R(T, \rho)$ varies strongly with temperature, consistent with the observed enhancement of C_p on supercooling [5, 4]. A detailed quantitative evaluation requires numerical differentiation using a concrete implementation of IAPWS-95 and a chosen parameter set $(K_0, \varepsilon, \alpha, R_0, R_\epsilon, \lambda)$; this lies outside the scope of this conceptual note.

5 Relation to Existing Water Models

Two-state and multi-state models of water have a long history, beginning with early qualitative proposals of coexisting open and collapsed local structures and extending to modern parametric models for supercooled water [4, 5]. Recent work has embedded a two-state description directly into PC-SAFT, deriving a framework (PC-SAFT-TS and PC-SAFT-TS-CAF) that reproduces the characteristic extrema of water by treating high-density and low-density water as interconverting species with fitted cross-association parameters [8, 9]. At the same time, thermodynamic curvature has been used as a diagnostic tool for fluids and for water in particular, revealing regions where the correlation length becomes large and where liquid states show solid-like character [13, 15]. These studies have largely taken an existing EOS (often IAPWS-95 or related formulations) as given and evaluated $R(T, p)$ without feeding it back into the EOS. The present proposal differs in two ways:

1. It treats IAPWS-95 (or an IAPWS-consistent extension into the supercooled region [4, 17]) as the fixed macroscopic base EOS and uses thermodynamic geometry of that EOS to define a network factor $n(T, \rho)$ through the curvature $R(T, \rho)$.

- It couples this network factor into a SAFT-style association term, so that the strength of hydrogen bonding is controlled by a measure of correlation implied by the base EOS, rather than by an independent phenomenological two-state function.

In this sense the model provides a bridge between empirical high-accuracy EOS, association theory, and thermodynamic geometry. It does not attempt to replace IAPWS-95, but to augment it with an explicit network term whose intensity is tied to R .

6 Outlook

The present work is a framework rather than a completed parametrised EOS. Several steps are needed to turn it into a practical model:

- Implement IAPWS-95 (and its supercooled extension) numerically and compute $R(T, \rho)$ over the region of interest, following methods similar to Refs. [13, 15].
- Choose initial guesses for $(K_0, \varepsilon, \alpha, R_0, R_\epsilon, \lambda)$ based on typical hydrogen-bond energies and known densities, then adjust them to preserve agreement with IAPWS-95 within uncertainties for $p(T, \rho)$ while modifying the predicted TMD and C_p behaviour in a controlled way.
- Compare the resulting TMD line, C_p ridge, and compressibility anomalies with those from existing two-state PC-SAFT-type models [8, 9, 11] and with experimental data in the supercooled region [4, 5].

If successful, this curvature-driven association EOS would offer a way to embed network physics into an established engineering EOS, with all thermodynamic properties still derived from a single Helmholtz free-energy function.

A Numerical evaluation of curvature and derivatives

This paper treats $R(T, \rho)$ as an input computed from the IAPWS-95 Helmholtz function. The algebra in the main text assumes that $R(T, \rho)$ and at least its first derivatives with respect to (T, ρ) can be obtained in a numerically

stable way. Because R involves second derivatives (and nonlinear combinations of them), numerical noise can easily dominate unless the evaluation is smoothed. A practical route that stays close to the CDA-EOS needs is:

A.1 State grid and stable base derivatives

Work in (T, ρ) with ρ molar density and $\rho_{\text{mass}} = M_w \rho$. At each state, compute the base IAPWS quantities from $a_{\text{IAPWS}}(T, \rho)$:

$$p, \quad s = - \left(\frac{\partial a}{\partial T} \right)_\rho, \quad u = a + Ts, \quad v = \frac{1}{\rho}. \quad (51)$$

Also compute base response functions that you can sanity-check:

$$\left(\frac{\partial p}{\partial \rho} \right)_T > 0, \quad \kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T > 0, \quad C_p > 0. \quad (52)$$

These checks catch step-size problems early.

A.2 Finite differences for R and its derivatives

Use a local symmetric stencil around (T, ρ) :

$$T_\pm = T \pm \Delta T, \quad \rho_\pm = \rho \pm \Delta \rho, \quad (53)$$

with relative step sizes chosen small but not tiny:

$$\Delta T = \eta_T T, \quad \Delta \rho = \eta_\rho \rho, \quad (54)$$

where typical starting values are $\eta_T, \eta_\rho \sim 10^{-3}$ to 10^{-4} . In strongly varying supercooled regions you may need to increase steps to suppress noise. Compute R at the central state and neighbors using one consistent procedure. Then compute first derivatives with central differences:

$$\left(\frac{\partial R}{\partial T} \right)_\rho \approx \frac{R(T_+, \rho) - R(T_-, \rho)}{2\Delta T}, \quad (55)$$

$$\left(\frac{\partial R}{\partial \rho} \right)_T \approx \frac{R(T, \rho_+) - R(T, \rho_-)}{2\Delta \rho}. \quad (56)$$

If the derivative flips wildly when you change (η_T, η_ρ) by a factor of 2, the calculation is not stable yet and needs smoothing.

A.3 Local smoothing of R

A simple way to smooth while keeping locality is to fit a low-order polynomial surface to R values on a small (T, ρ) patch, then differentiate the polynomial. For example, fit on a 3×3 or 5×5 patch:

$$R(T, \rho) \approx \sum_{i=0}^2 \sum_{j=0}^2 c_{ij}(T - T_0)^i(\rho - \rho_0)^j, \quad (57)$$

solve for c_{ij} by least squares, then take analytic derivatives of the fit. This tends to reduce stencil noise without washing out real structure.

A.4 Regularised magnitude used in the CDA-EOS

Once R is stable, use the regularised magnitude already defined in the main text:

$$R_{\text{abs}} = \sqrt{R^2 + R_\epsilon^2}, \quad \left(\frac{\partial R_{\text{abs}}}{\partial \rho} \right)_T = \frac{R}{\sqrt{R^2 + R_\epsilon^2}} \left(\frac{\partial R}{\partial \rho} \right)_T. \quad (58)$$

This avoids singular behaviour of $n(T, \rho)$ derivatives at $R = 0$.

A.5 What the CDA-EOS actually needs

For the pressure correction p_{assoc} in Section 5.1, the curvature enters through

$$\left(\frac{\partial \Delta}{\partial \rho} \right)_T \propto \left(\frac{\partial n}{\partial \rho} \right)_T \propto \left(\frac{\partial R_{\text{abs}}}{\partial \rho} \right)_T. \quad (59)$$

So the minimum viable curvature pipeline for implementation is:

$$R(T, \rho), \quad \left(\frac{\partial R}{\partial \rho} \right)_T, \quad (60)$$

computed stably enough that the resulting $p_{\text{assoc}}(T, \rho)$ is smooth.

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formulations and organise the derivations, and xAI Grok models were used interactively to refine questions and highlight connections to existing literature. All scientific choices, interpretations, and possible errors remain the sole responsibility of the author.

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