



# Extended Phase Diagram of Supercritical Carbon Dioxide and its Applications

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## Motivations and Discoveries

- Supercritical CO<sub>2</sub> is central to power cycles, carbon capture and storage (CCS), pipeline transport, and planetary/environmental modeling.
- Near and above the critical point, CO<sub>2</sub> exhibits non-linear property variations, which can cause non-equilibrium thermodynamics, flow instabilities, and heat-transfer deterioration.
- We present a Gibbs free energy-based thermodynamic analysis that
  - Predicts the **boundaries of the anomalous region**
  - Extends Liquid-Vapor line beyond the critical point to DP
  - Finds the boundary of the Liquid/Liquid-like region
  - Discovers and characterizes the **Dwij point (DP)** beyond which **only two phases** – gas and solid, exist,
  - Creates **new Phase Diagrams** to very high pressures, temperatures
  - Identifies three supercritical pseudo phases:
    - SC Gas-like (SCGL), SC Liquid-like (SCLL), and SC Solid-like (SCSL)**

## Anomalous Region

- Gibbs free energy model:
  - Leads to  $c_p^* = \left(\frac{c_p}{T}\right)$ ,  $\beta^* = (v\beta)$ , and  $\kappa^* = (v\kappa)$  as crucial parameters to analyze fluids from their Subcritical to Supercritical States via the Anomalous Region.
- Nishikawa's condition at Critical Point,  $d^3g = 0$ :
  - Leads to two extrema (maxima and minima) of  $c_p^*$ ,  $\beta^*$ , and  $\kappa^*$
  - Only maxima reported for  $c_p$ ,  $\beta$ , and  $\kappa$
  - Loci of extrema of these parameters,  $c_p^*$ ,  $\beta^*$ , and  $\kappa^*$  form (P,T) loops.
- Three loops together form the anomalous region as shown below.
- For CO<sub>2</sub>,  $P_{max} = 24$  MPa and  $T_{max} = 419.4$  K (Point C), SC region  
 $P_{min} = 1.5$  MPa and  $T_{min} = 243.6$  K (Point A), Subcritical, Liquid-vapor

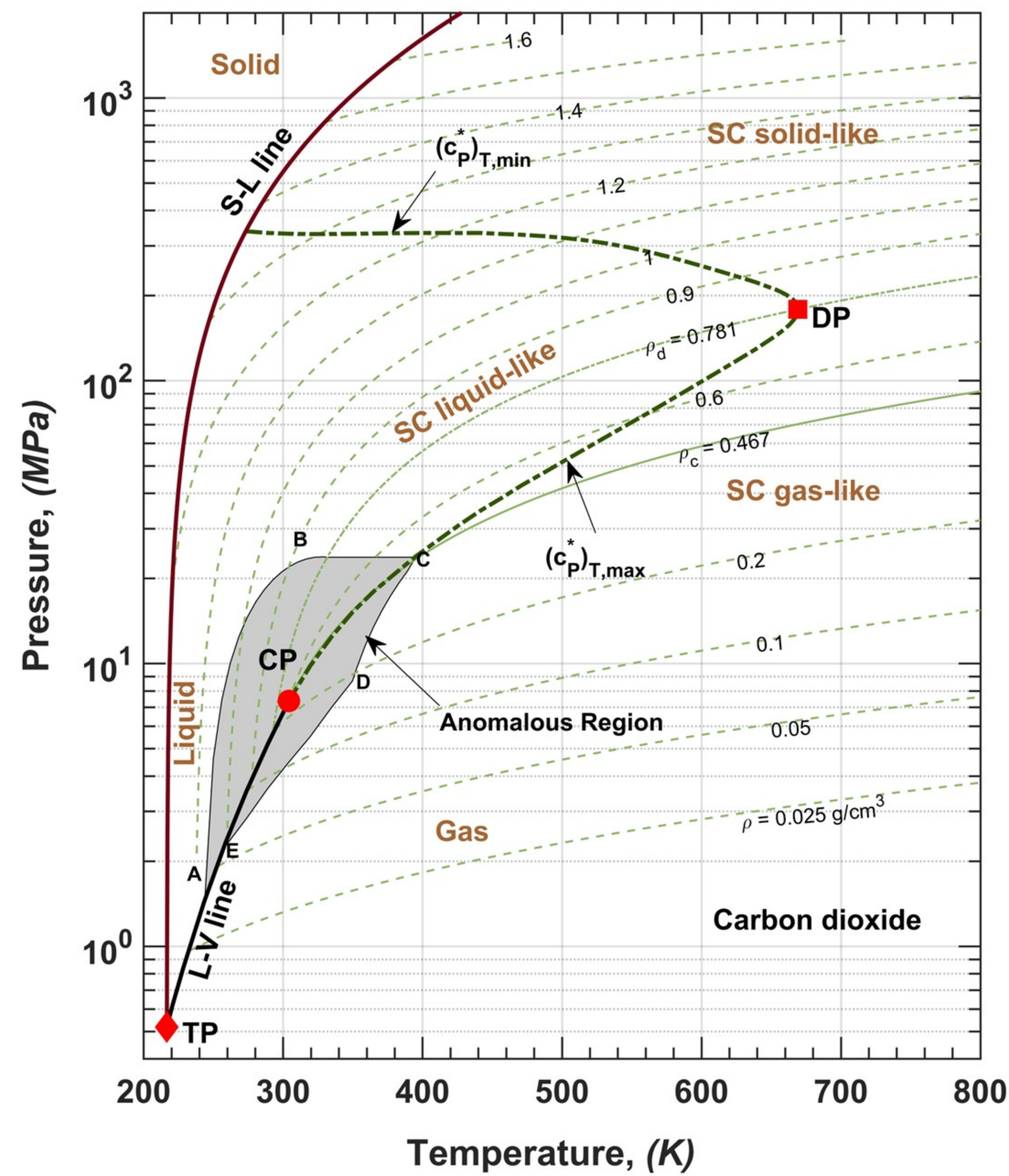


Figure 2: New Phase Diagram of CO<sub>2</sub> with the Anomalous Region

## Discovery of Liquid/ SC Liquid-like Boundary, SC Solid-Like State and Dwij Point

- Maxima and minima of  $(c_p^*)_P$  or  $\left(\frac{\partial v}{\partial T}\right)_P$  forms the fourth loop.
- Lower branch, maxima of  $\left(\frac{\partial v}{\partial T}\right)_P$  represents the natural extension of the liquid vapor line, distinguishing the boundary between SC liquid-like and SC gas-like state.
- Upper branch, minima of  $\left(\frac{\partial v}{\partial T}\right)_P$  establish the boundary between SC liquid-like and SC solid-like state.
- Dwij point (DP,  $P_d = 178.8$  MPa,  $T_d = 669$  K) marks a thermodynamic turning point:
  - Beyond DP only gas and solid states exist (connected via SCGL and SCSL), analogous to the solid-vapor regime below the triple point.
- The solid-like state is between solid-liquid (S-L) and liquid/SCLL line.
  - Density, heat capacity, viscosity, and thermal conductivity become weak functions of temperature.
- Together with the solid-liquid (S-L) and liquid-vapor (L-V) line, maxima of  $(c_p^*)_P$  forms the closed boundary of liquid/ SC liquid-like state.
- The Frenkel line intersects the Dwij point, suggests DP is the end of thermodynamically dominant transitions, while FL marks the onset of dynamics-dominated transitions.

## Applications

### sCO<sub>2</sub> Brayton Cycles

- As turbine inlet temperature, pressure increases, cycle efficiency increases.
- With the new diagram more efficient cycle can be designed where:
  - Compressor operates near, but typically inside the anomalous region.
  - Expansion occurs mainly in the SC gas-like region (smoother property).

### Ocean and Geological CO<sub>2</sub> Sequestration

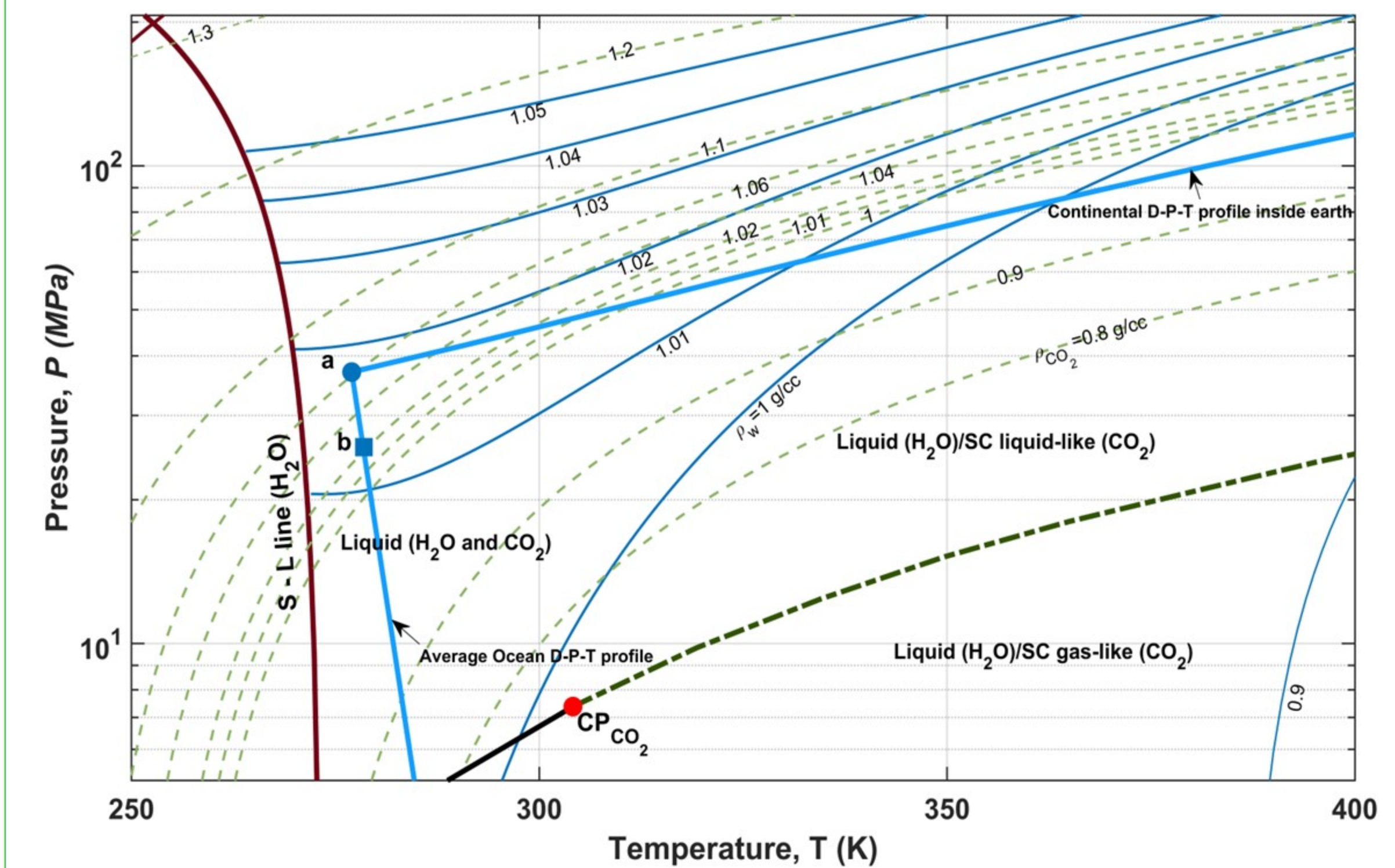


Figure 3: Combined density contours of CO<sub>2</sub> (dashed green line) and H<sub>2</sub>O (solid light-blue line). The thick blue line up to "a" presents the depth-pressure-temperature (D-P-T) profile of ocean at an average depth ("b" at 2700 m and "a" at 3700 m); further extension of this line represents the continental D-P-T

### Ocean Sequestration

- Current estimates are to store CO<sub>2</sub> below 500 m depth, whereas at the **✗** depth of 500–2700 m, CO<sub>2</sub> density is lower than that of water, CO<sub>2</sub> can rise to the surface.
  - Stable storage requires depths, where CO<sub>2</sub> is significantly denser than seawater  $\geq 3000$  m ( $P \geq 30$  MPa), point "a" (Fig. 3, where  $\rho_{CO_2} = 1.06 \frac{g}{cc} > \rho_w = 1.018 \frac{g}{cc}$ ; CO<sub>2</sub> will sink and pool at the seafloor.

### Geological Storage

- At greater depths (~8.6 km in Fig. 2), CO<sub>2</sub> may transition into SC solid-like state, promising enhanced long-term stability in "deep reservoirs."

### Long-Distance CO<sub>2</sub> Pipelines

- Using the new phase diagram, pipeline routes and pressure profiles can be better designed to avoid the anomalous region along the entire length (like proposed "ultra-long SNG transport" by Prasad et al., 2023).

## Key Conclusions

- A comprehensive extended phase diagram provides critical insights that can significantly advance both scientific understanding and technological development.
- The absence of a complete phase diagram might have led to limitations in thermodynamic analysis and even potential misinterpretations of SC fluid behavior.

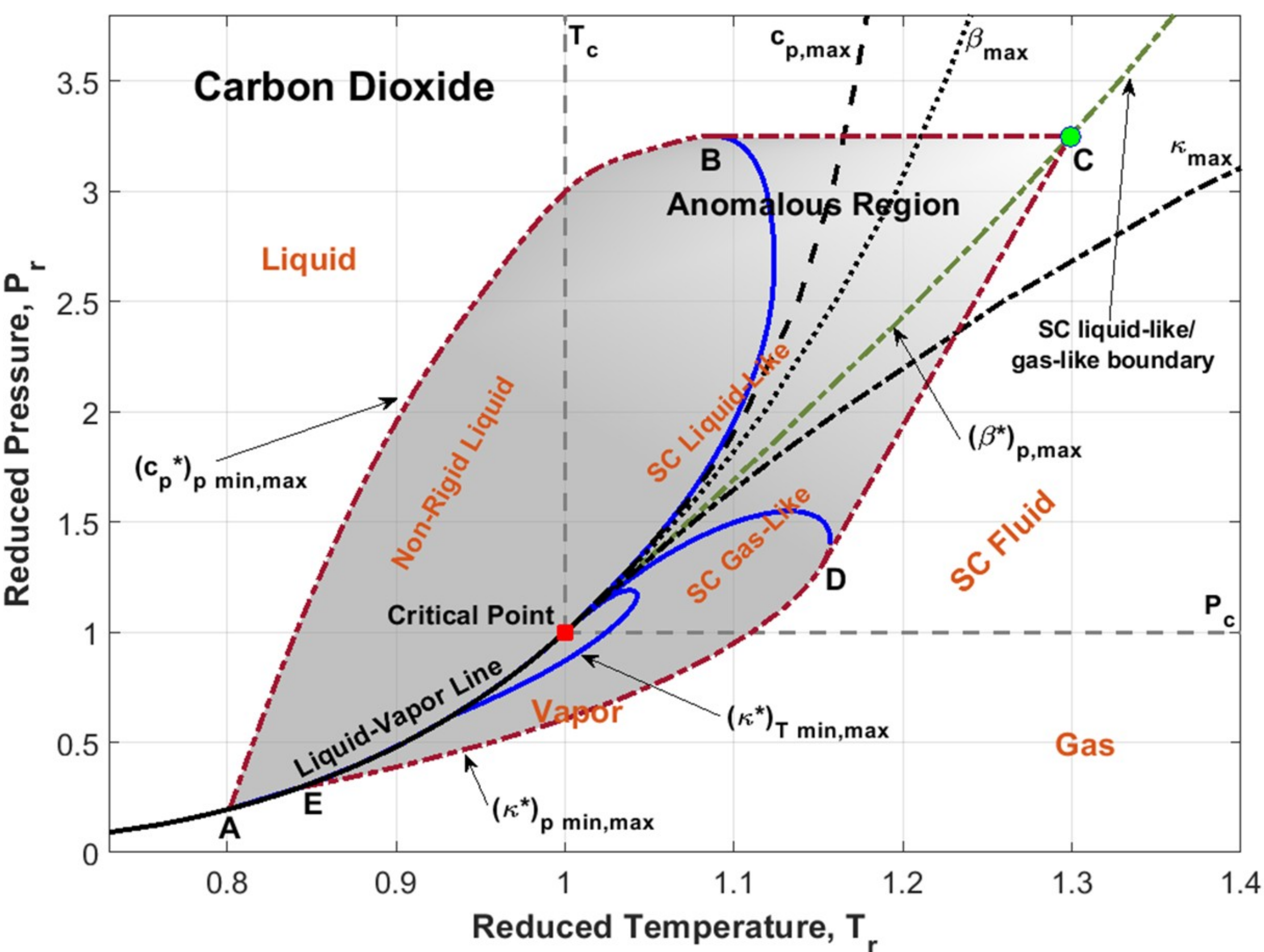


Figure 1: Anomalous region, ABCDEA for CO<sub>2</sub>; anomalies are maximal at the critical point; they vanish outside ABCDEA