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Methodology Article

Universal Gas Transitions for Pure Substances

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Abstract

Classical models of phase transitions have traditionally assumed that at the critical point of a pure substance, the temperature, pressure, and density simultaneously reach unique critical values. However, experimental findings demonstrate that along the liquid–vapor equilibrium curve, only the temperature (Tcr) attains a true critical state, while the pressure and density vary depending on experimental conditions. Furthermore, for the liquid–solid equilibrium curve at high pressures, a critical point associated with the disappearance of the metastable liquid phase has been experimentally identified, leading to the definition of a critical pressure (Pcr). To comprehensively address these phenomena, a Universal Phase Transition Equation (UPTE) is proposed, extending the classical Van der Waals framework by incorporating dynamic interaction parameters dependent on both temperature and pressure. The UPTE successfully integrates the solid, liquid, gas, and plasma phases into a unified model within the pressure–temperature (P–T) diagram. By accounting for metastability, critical phenomena, and non-equilibrium behaviors, the UPTE offers a more complete and realistic framework for describing phase transitions in pure substances.

Keywords

Phase Transitions, Critical Temperature, Critical Pressure, Metastability, Universal Phase Transition Equation, Liquid–solid Transition, Liquid–vapor Transition, Plasma Formation, Non-equilibrium Thermodynamics

1. Introduction

The classical understanding of critical phenomena in pure substances is based primarily on the assumption that temperature, pressure, and density simultaneously reach well-defined critical values at the termination of a phase transition. However, recent experimental studies have demonstrated that, at the critical point associated with the termination of the liquid ⇄ vapor phase transition, only the temperature (Tcr) attains a truly critical state, while the corresponding pressure and density vary depending on experimental conditions (Figure 1).

The point at which the liquid phase transitions into the gas phase along the liquid ⇄ vapor equilibrium curve [1] is traditionally defined as the critical point, where temperature, pressure, and density are assumed to be critical simultaneously [2]. Nevertheless, more precise investigations reveal that while the critical temperature (Tcr) is valid for both phases, the critical pressure (Pcr) exists within a pressure range ($p_1 < pcr < p_2$) in the liquid phase but does not fully characterize the gas phase behavior (Figure 1). In this context, the pressure at the critical point is determined primarily by temperature and cannot independently represent the critical state [3].

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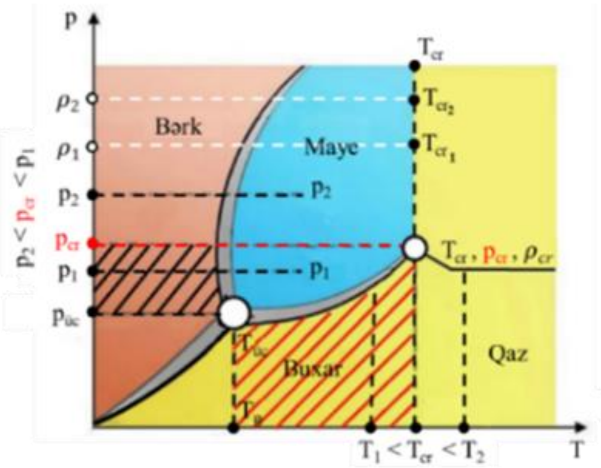

Figure 1. *Pressure–Temperature (P–T) Diagram of a Pure Substance.*

Extensive studies on the termination of the liquid phase during the liquid ⇄ vapor transition have led to a detailed generalization of this phenomenon. In contrast, the understanding of the termination point of the liquid phase under high-pressure conditions during the liquid ⇄ solid phase transition remains relatively underdeveloped. This gap is likely influenced by the experimental findings of Nobel laureate P. W. Bridgman [4] and the theoretical framework established by L. D. Landau [5], both of whom argued that no critical point exists along the solid ⇄ liquid equilibrium curve.

P. W. Bridgman, using a piston–cylinder apparatus in his pioneering high-pressure experiments, systematically investigated the volume change (ΔV) and entropy change (ΔS) associated with solid ⇄ liquid transitions in various substances, including benzene. His results suggested the absence of a classical critical point along the melting curve. The challenges inherent in such measurements stem from the minimal density difference between the solid and liquid phases under high pressure, leading to considerable experimental uncertainties—up to 30%—which complicate the accurate determination of critical parameters. Similarly, L. D. Landau's theoretical framework concluded that no critical point exists along the melting line, instead describing phase transitions primarily in terms of symmetry breaking and thermodynamic potentials [5]. However, Frenkel [6] later critiqued Landau's model, arguing that it neglects metastable and unstable states inherent to liquid ⇄ solid transformations. The determination of critical points in phase transitions began with Cagniard de la Tour's 1822 discovery in the liquid–vapor system. By heating sealed tubes containing liquids such as water, alcohol, ether, and carbon disulfide, he observed that beyond a certain temperature the liquid disappeared and became indistinguishable from its vapor phase—marking the critical point. In phase diagrams, both vaporization and solidification processes occur along the equilibrium boundaries of the liquid phase (Figure 1). By analogy with the liquid–vapor system, the critical point in the liquid–solid transition may be approached by cooling under constant pressure, leading to complete solidification. However, P. W. Bridgman did not apply this analogy in his work. To explore this possibility, our team developed a custom high-pressure experimental apparatus [7], enabling the study of discrete metastable states under elevated pressure and temperature. Using this setup, we have provided compelling evidence for the existence of a pressure-dependent critical point along the liquid ⇄ solid equilibrium curve for substances such as benzene (C_6H_6) and benzonitrile (C_7H_5N) (Figure 2). These findings challenge the traditional assumptions of classical thermodynamics and highlight the necessity of a revised, unified thermodynamic framework capable of integrating solid, liquid, gas, and plasma phases within a single, coherent model [10, 11]. Furthermore, our application of thermo-axiomatic geometry at high pressures [8, 9] has offered new perspectives on phase boundaries and metastability.

Accordingly, this study proposes the Universal Phase Transition Equation (UPTE), which extends classical models by incorporating temperature- and pressure-dependent dynamic interaction parameters, offering a comprehensive approach to the phase behaviors of pure substances across different phase boundaries.

2. Determination of the Critical Point in Liquid ⇄ Vapor and Liquid ⇄ Solid Phase Transitions

The liquid ⇄ vapor and liquid ⇄ solid equilibrium curves for a pure substance represent two-phase systems. Along the liquid ⇄ vapor equilibrium curve, the liquid evaporates into the gas phase due to temperature increase. The point at which the liquid fully transitions into gas marks the critical point. Similarly, for the liquid ⇄ solid transition, the critical point emerges from the disappearance of the metastable liquid phase under high pressures.

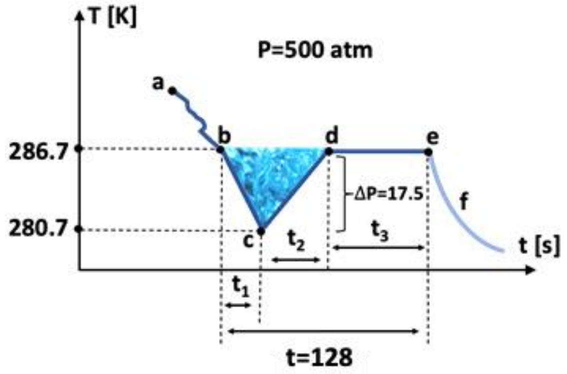

Figure 2. *Discrete Metastability of Benzene along the Liquid ⇄ Solid Equilibrium Curve at 500 atm.*

The critical pressure along the liquid⇄solid equilibrium curve indicates the point at which the metastable liquid phase suddenly disappears as Pcr = 2229.2 bar, thus defining the pressure-dependent limit of the liquid phase [12-15].

3. Linear Extrapolation of Density–pressure Isotherms and the Identification of Liquid–solid Critical Points

Isotherms showing the variation of density with pressure at different temperatures have been plotted. It has been determined that the isotherms are linear, meaning they follow an equation of the form $\rho = ap + b$, and that the extensions of the ρ-p graph intersect at the same point. A sample graph for benzene is shown in Figure 3. The position L, where the densities at different temperatures are equal, has been assumed to be the critical point (L) of the liquid-solid thermodynamic equilibrium boundary for benzene. From the graph, it can be seen that the pressure at this critical point is P = 2229.2 bar, and the density is ρL = 1200 kg/m³. The fact that this critical pressure matches the value found from the freezing thermograms confirms the validity of the extrapolation method applied. The PL and ρL values determined in the same way for other liquids are given in Table 1.

Table 1*. Pressure-dependent critical points of the liquid phase of benzene and some substances and density values corresponding to critical pressure.*

Matter	Chemical Name of Matter	Critical Pressure [MPa]	density at critical pressure [kg/m3]
N- Dekan	$C_{10}H_{22}$	130	839
N- Nonan	C_9H_{20}	150	820
N- Ksilen	C_8H_{10}	200	990
O -Ksilen	C_8H_{10}	205	1000
O-toloudin	C_7H_9N	150	1400
M-toloudin	C_7H_9N	140	1450
P-toloudin	C_7H_9N	200	1350
Benzonitril	C_7H_5N	270	1110
Benzen	C_6H_6	220	1200

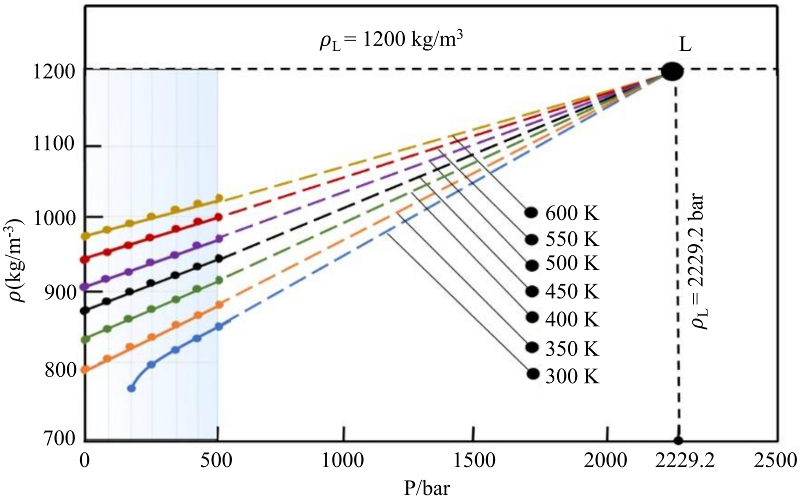

Figure 3*. The critical point of the liquid-solid thermodynamic equilibrium boundary for benzene is assumed to be where the densities at different temperatures are equal.*

4. Thermodynamic Foundations of the Universal Phase Transition Equation (UPTE)

Phase transitions in real substances, especially under extreme conditions such as high pressure and high temperature, cannot be accurately described by classical models that consider only temperature and pressure. A more comprehensive representation must also incorporate the effects of density (ρ) and the presence of metastable states, which often act as precursors or transitional configurations in the transformation between phases. Recognizing this complexity, the Universal Phase Transition Equation (UPTE) was developed to unify phase behaviors across all known states of matter—solid, liquid, gas, and plasma.

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5. The Connection Between Critical Points and the Construction of the Unified Phase Diagram

The identification of distinct critical parameters—temperature (Tcr) in liquid–gas transitions and pressure (Pcr) in liquid–solid transitions—provides the necessary framework for constructing a unified phase diagram that includes the plasma phase. By integrating these two critical constraints, a new ionization boundary can be introduced, describing the transition from high-density liquids to fully ionized plasma at elevated temperatures and pressures.

This integration leads to the development of a generalized P–T phase diagram, where all four phases—solid, liquid, gas, and plasma—are located within a continuous thermodynamic surface. The intersection and extrapolation of the Pcr and Tcr axes define the limit of the liquid phase and the onset of ionization. This unified approach underpins the Universal Phase Transition Equation (UPTE) and provides a geometric foundation for the topological connection between classical and non-classical phase transitions.

6. The Universal Phase Transition Equation

6.1. Classical Background and Limitations

The Van der Waals equation (PV=nRT) has historically modeled phase transitions but fails at high pressures and temperatures, especially regarding plasma formation and metastable states.

6.2. The Universal Phase Equation: A Unified Model

The Universal Phase Transition Equation (UPTE) reformulates the relationship between pressure, temperature, and density:

$$P\rho = \Phi(\mathrm{T}, \rho_1, \rho_2)$$

where Φ adapts based on the phase type.

Specific cases:

Gas:

$$P = \frac{RT}{\rho}$$

Liquid/Solid:

$$P = \frac{RT}{\rho}$$

Two-phase coexistence:

$$P = \frac{KT(\rho_1 - \rho_2)}{\rho_1 \rho_2 \rho_3}$$

For plasma formation:

$$\mu_{plasma}(T, P) = \frac{1}{1 + e^{-b(T - T_{ion})}}$$

6.3. Graphical Representation

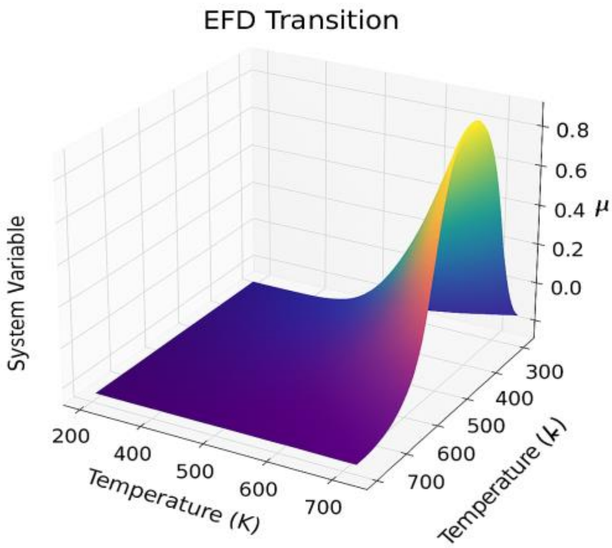

Figure 4. Schematic Representation of the Universal Phase Transition Surface integrating Solid–Liquid–Gas–Plasma Phases.

7. Scientific and Practical Significance

The Universal Phase Transition Equation (UPTE) introduces a comprehensive and unified approach to understanding phase behavior across all states of pure matter, including solid, liquid, gas, and plasma. This model addresses long-standing limitations in classical thermodynamic theories, particularly those arising from the rigid assumptions of van der Waals-like equations and the exclusion of metastable and non-equilibrium phenomena.

One of the major scientific contributions of the UPTE is its ability to reconcile classical transitions (such as boiling and melting) with complex behaviors like discrete metastability and pressure-induced phase transformation. By incorporating temperature- and pressure-dependent interaction parameters, the model accommodates the emergence and termination of critical states along both the liquid–vapor and liquid–solid boundaries.

Additionally, the inclusion of plasma as a distinct and continuous extension of high-temperature behavior in matter enhances the practical scope of the model. This has significant implications for fields such as plasma physics and astrophysics, where understanding ionization thresholds, shock waves, and supercritical conditions is essential. The UPTE also holds relevance in high-pressure material synthesis, combustion processes, energy systems, and planetary science.

In experimental settings, the model provides predictive insight into the boundaries of metastability, facilitating the design of high-precision measurements and new materials under extreme conditions. By presenting a geometrically integrated, mathematically robust, and physically accurate framework, the UPTE serves as a powerful tool for scientists and engineers working at the frontiers of thermodynamic research.

8. Conclusion

In conclusion, the Universal Phase Transition Equation (UPTE) represents a transformative framework that redefines our understanding of phase transitions in pure substances. Unlike traditional models that treat phase boundaries as abrupt and static lines, the UPTE introduces a dynamic continuum where transitions evolve through temperature, pressure, and density-driven mechanisms, often governed by metastability and non-equilibrium effects.

By integrating critical temperature (Tcr) and critical pressure (Pcr) into a single coherent formulation, the UPTE bridges the gap between classical equilibrium thermodynamics and real-world high-pressure behaviors. This model not only captures the known transitions between solid, liquid, and gas phases but also seamlessly incorporates plasma as a high-energy extension of the phase diagram.

The experimental validation of the pressure-dependent critical point in liquid–solid transitions, supported by discrete metastability and thermo-axiomatic geometry, strengthens the model’s applicability across diverse materials. The UPTE opens avenues for future research, especially in the integration of fuzzy logic, quantum mechanics, and computational thermodynamics, further enriching its theoretical and practical value.

Ultimately, the UPTE contributes to a new paradigm in phase transition science, where continuous, nonlinear, and coupled phenomena are not only acknowledged but systematically modeled within a unified and expandable thermodynamic structure.

Abbreviations

UPTE	Universal Phase Transition Equation

Conflicts of Interest

The authors declare no conflicts of interest.

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