On the characterization of transcritical fluid states

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1. Motivation and objectives

Utilization of supercritical fluids has emerged as a key technology for energy efficiency, addressing the needs imposed by climate change: a higher operating pressure increases the combustion efficiency in gas turbines, Diesel engines, and rocket engines (Oschwald et al. 2006; Oefelein et al. 2012); CO$_2$ sequestration, i.e., deposition of supercritical CO$_2$ in subterranean reservoirs, is pursued as a way to effectively reduce the amount of atmospheric CO$_2$ (Benson & Cole 2008). Furthermore, supercritical fluids may play a fascinating role in the origin of life itself in the neighborhood of deep-sea hydrothermal vents (Martin et al. 2008).

The classical thermodynamic presentation splits the pure fluid $p$-$T$ state diagram into four quadrants (Candel et al. 2006), centered around the critical point. The state-space is thus divided into liquid, vapor, gaseous, transcritical, and supercritical states, with transitions implied at the critical pressure $p_{cr}$ and temperature $T_{cr}$. Recently, another structuring line, the Widom line as an extension to the coexistence line (Sciortino et al. 1997), has been popularized. This line divides liquid-like and gas-like supercritical states (Gorelli et al. 2006; Simeoni et al. 2010), and exhibits some properties of a phase transition (Banuti 2015). The Widom line has since been shown to differ between species as a function of the acentric factor (Banuti et al. 2016b, 2017a), and even to occur multiply in certain mixtures (Raju et al. 2017).

However, open questions remain: Specifically, it is unclear whether a physical difference between liquid, transcritical, and liquid-like states exists. Furthermore, a number of competing supercritical transition lines have been proposed (Nishikawa & Tanaka 1995; Brazhkin et al. 2012; Gorelli et al. 2006; Banuti 2015), which differ in their definitions and yield contradictory results.

The objective of this article is thus to identify the specific differences and similarities between states and transition lines using macroscopic (continuum) and microscopic (molecular) methods, with the goal of providing a unified view of the fluid state space based on physical characteristics.

2. Methods

This paper combines theoretical and numerical data, applying continuum and molecular perspectives in the study of supercritical fluid behavior. We selected argon as the reference fluid of interest: Following the extended corresponding states principle (Reid et al. 1987), the state plane topology of supercritical fluids can be assumed to be general (Banuti et al. 2017a), and thus this study can be expected to be of relevance for other, perhaps more complex, fluids. At the same time, molecular dynamics (MD) modeling influences are minimized due to the monatomic structure (Tegeler et al. 2016). The critical temperature and pressure of argon are $T_{cr} = 150.7$ K and $p_{cr} = 4.863$ MPa, respectively. In order to allow for interspecies comparison, the reduced values of temperature $T_r = T/T_{cr}$ and pressure $p_r = p/p_{cr}$ are used in the following discussion.
The macroscopic continuum behavior was analyzed using reference fluid data from the NIST database (Linstrom & Mallard 2016). The data are based on a fundamental Helmholtz equation of state developed specifically for argon by Tegeler et al. (2016). The equation is fit to experimental and numerical data from an extensive literature review. Partial derivatives were obtained from numerical differentiation of these data.

The microscopic view is obtained from MD simulations. We used the LAMMPS package (Plimpton 1995) to run a system with 25,600 Ar atoms in the canonical N-p-T (constant number of atoms N, constant pressure p, and constant temperature T) ensemble at different temperatures and pressures. The Ar force field was developed by training the van der Waals parameters in the ReaxFF reactive force field (van Duin et al. 2001) against experimental Ar dimer potential energy curves (Ogilvie & Wang 1992, 1993). To validate the developed ReaxFF force field (Raju et al. 2017), we compared the enthalpy obtained from isobaric MD-simulations with experimental enthalpy curves obtained from NIST (Linstrom & Mallard 2016). The MD simulations were performed with a time step of 0.25 fs using the Nose-Hoover thermostat with a coupling time constant of 10 fs and Nose-Hoover barostat with a coupling time constant of 100 fs to control the temperature and pressure of the system, respectively. For each simulation, the system was first energy-minimized with convergence criterion of 0.1 kcal/Å. The system was then equilibrated over 62.5 ps and the system energy and other properties were averaged for the following 62.5 ps of the production run. To quantitatively investigate the structural characteristics, we computed the radial distribution function (RDF) (Levine et al. 2011)

\[ g(r) = \lim_{dr \to 0} \frac{p(r)}{4\pi(N_{\text{pairs}}/V)r^2dr}, \]

with the distance between a pair of atoms \( r \), the average number of atom pairs \( p(r) \) at a distance between \( r \) and \( r + dr \), the total volume of the system \( V \), and the number of pairs of atoms \( N_{\text{pairs}} \). The self-diffusion coefficient was obtained from the mean-square displacement \( \Delta(t) \propto \langle [r(t) - r(0)]^2 \rangle \) through Einstein's relation (Frenkel & Smit 2001).

3. Thermodynamic states

3.1. Distinguishing state properties

Supercritical fluids have been studied for a long time. Figure 1(a) shows the projected p-T state space of a pure fluid, which is classically divided into four quadrants, centered around the critical point. Baron Cagnard de la Tour (1822) discovered that fluids no longer exhibit a liquid-vapor interface when subjected to sufficiently high pressures; instead, they transform to a uniform medium. This transformation was later explained with the existence of a critical point (CP), representing an endpoint of the vapor-pressure curve (Andrews 1869). No unified terminology of the supercritical state space is established. Fluids in quadrant I of Figure 1(a) are commonly referred to as liquids (I_L) and vapors (I_V). Higher temperatures identify gases in II, that cannot be compressed to a liquid state (Atkins & de Paula 2010). When instead the pressure is raised, the fluid state in quadrant IV has been referred to as compressed liquid (Oefelein et al. 2012), compressible liquid (Bolmatov et al. 2014), transcritical fluid (Oschwald et al. 2006; Candel et al. 2006), liquid (Younglove 1982), or a supercritical fluid (Bellan 2000). When both pressure and temperature exceed the fluid critical values, fluids are commonly considered supercritical. Banuti et al. (2016a, b, 2017b) pointed out that a supercritical fluid behaves like an ideal gas for \( T_r \gtrsim 2 \) and \( p_r \lesssim 3 \).
States can be distinguished not only quantitatively (e.g., the liquid density is higher than the gaseous density), but also by qualitative criteria: In a solid, molecules are bound in a rigid, orderly structure. Neighboring molecules can be found in a periodic pattern from other molecules and do not change their place. Movement of molecules is oscillatory (Atkins & de Paula 2010). Liquids exhibit a similar structure. Movement is still primarily oscillatory (Brazhkin et al. 2012), but molecules may switch their position (Bolmatov et al. 2013). As in solids, the molecules are densely packed and can hardly be compressed further when pressure is applied. Brazhkin et al. (2012) describe liquids as an intermediate state, sharing properties from both solids and gases. Gases exhibit no inherent structure. Movement is ballistic-collisional (Brazhkin et al. 2012; Bolmatov et al. 2015), and compressibility is comparably high. Supercritical fluids form the intermediary between liquids and gases due to the large density inhomogeneities (Nishikawa & Tanaka 1995; Tucker 1999).

3.2. Atomistic analysis

We analyzed the properties of the fluid states in Figure 1(b) with the goal of assessing whether a physical differentiation of supercritical fluids from liquids and gases can be justified. The criterion is based on interatomic interaction, where an ideal gas is considered as the limiting case of vanishing interaction. The corresponding ideal gas RDF introduced in Eq. (2.1) is then a translated Heavyside function with $g = 0$ within an atomic diameter, and $g = 1$ outside, indicative of no spatial preference of the atoms. A single peak of the RDF with $g > 1$ signifies limited interatomic interaction within a real gas, a higher number of peaks corresponds to a long- range order, characteristic of a liquid (Fisher & Widom 1969). In order to study the transition from liquid to gas for various pressures, we carried out MD-simulations of argon, scanning a temperature range in increments of 5 K at reduced pressures of $p_r = \{0.7, 1.4, 3.0, 9.4\}$. The profiles of the specific enthalpy computed from the scans are shown in the left column of Figure 2.

The results of the MD-calculations are in good agreement with NIST-data, although the transition temperatures are slightly overpredicted. The subcritical temperature scan at $p_r = 0.7$ shows the familiar phase-transition discontinuity in the enthalpy. It is replaced by a continuous, yet pronounced, crossover at a supercritical pressure of $1.4 p_{cr}$, occurring over a finite temperature interval $0.9 < T_r < 1.13$. We refer to this henceforth as the ‘transitional region’. The transition is weakly discernible at $p_r = 3$ and has completely vanished at $p_r = 9.4$. 

**Figure 1.** Projected $p$-$T$ state plane and supercritical states structure, with coexistence line and critical point. Subscripts L, V, LL, GL denote liquid, vapor, liquid-like, and gas-like, respectively. (a) Classical division into four quadrants with critical isotherm and isobar. (b) Four quadrants and supercritical transition line.
Figure 2. Enthalpy (left column) and visualization of the molecular structure of liquid, transitional, and vapor states (from left to right) from MD computations for argon. The temperature increases from left to right, the pressure from bottom to top. Reduced temperature for the liquid and vapor columns of the molecular structure, respectively, are $T_r = 0.5$, and $T_r = 1.56$. The transitional reduced temperatures are 0.95, 1.03, 1.16, and 1.26, from bottom to top.

Twelve representative conditions were chosen for liquid, transitional, and vapor states. The instantaneous atomic distributions in a slice through the computational domain indicate qualitatively that no appreciable difference can be seen between the low temperature states in the left column. Regardless of pressure, the molecules form a densely packed liquid. The right column depicts the vapor states at $T_r = 1.56$. At low pressures,
they exhibit a diluted gaseous character, with little interaction between the molecules. With increasing pressure, the vapor states approach liquid-like conditions. The transitional states are shown in the center column. We observe a heterogeneous molecular distribution that homogenizes as the pressure is increased.

A quantitative analysis of the molecular structure using the respective RDF, shown in Figure 3, supports this assessment. At $T_r = 0.5$, the RDF is practically indistinguishable between the four pressures and shows the characteristic multi-peak structure of a long-range ordered liquid. The transitional fluid exhibits three distinct peaks, indicating a correlated interaction across three shells surrounding an atom. We see that the peaks become more pronounced at higher pressures, signifying a higher degree of order. At $T_r = 1.56$, the fluid resembles a gas. As the compression continues, a second peak is observed at $p_r = 3$, and a third at a pressure of 9.4 $p_r$, indicative of a liquid molecular structure (Fisher & Widom 1969). The behavior of the specific enthalpy and RDF suggests that up to pressures of 3 $p_r$, the system exhibits a transitional region. At pressures greater than 3 $p_r$, the system continuously transforms from a liquid-like to a vapor-like region with no physically observable difference to distinguish these phases. This suggests that a homogeneous supercritical fluid phase extends from pressures greater than 3 $p_r$.

We can conclude that there is no physical difference between liquids and transcritical fluids. Supercritical fluids may behave like liquids or gases, depending on the exact conditions. Furthermore, we see that even gases at supercritical temperatures can be compressed to liquids.

4. Supercritical state transition lines

A number of supercritical transition lines have been proposed in the literature. The first was by Fisher & Widom (1969), showing that a transition must exist between the oscillatory decay of the pair correlation function linked to the predominantly repulsive potential in liquids, and a monotonous decay indicative of the attractive potential in gases. Fisher & Widom emphasized that this transition does not involve thermodynamic singularities and thus does not constitute a phase transition. The first experimental evidence for a supercritical transition was found by Nishikawa & Tanaka (1995), who identified a distinct maximum in the correlation length when crossing a supercritical extrapolation of the coexistence line, which they dubbed 'extension curve'. Stanley’s ‘Widom line’ (Sciortino et al. 1997) was also originally introduced as the locus of maximum correlation lengths. However, to facilitate evaluation using thermodynamic properties, it is often ap-
proximated as the locus of the thermodynamic response functions (Liu et al. 2005; Xu et al. 2005), such as isobaric specific heat capacity \(c_p\) (Xu et al. 2005; Santoro & Gorelli 2008; Ruppeiner et al. 2012; Banuti 2015); isothermal compressibility \(\kappa_T\) (Sciortino et al. 1997; Abascal & Vega 2010; Nishikawa & Tanaka 1995; Nishikawa & Morita 1997); or the thermal expansion \(\alpha_p\) (Okamoto et al. 2003). More recently, the Frenkel-line was introduced by Brazhkin et al. (2012) and extended by Bolmatov et al. (2013), dividing rigid from nonrigid liquids, corresponding to a change in molecular motion from primarily oscillatory to primarily ballistic. The crossover takes place where the fluid is no longer capable of propagating high-frequency tangential shear sound modes. It extends to arbitrarily high fluid pressures and does not constitute a phase transition (Brazhkin et al. 2012).

4.1. Dynamic and thermodynamic transitions

The apparent contradiction between the different definitions of the transition lines can be resolved when we realize that they can be grouped into two different physical phenomena.

On the one hand, we have a dynamic transition from liquid-like to gas-like fluid states. This transition is reflected by changes in molecular motion from primarily oscillatory to ballistic, from repulsion to attraction-dominated intermolecular interaction, from oscillatory to monotonous decay of the radial distribution function. Across this gradual transition line, dispersion and propagation of transversal sound modes vanish. This transition is distinctly not thermodynamic; it extends to arbitrarily high fluid pressures. This description fits results by Fisher & Widom (1969), Brazhkin et al. (2012), Gorelli et al. (2006), and Simeoni et al. (2010).

On the other hand, we have a thermodynamic transition reflected by maxima of the response functions, and macroscopic changes in fluid properties, such as a drop in density. The transition resembles the subcritical boiling process and occurs across a continuation of the coexistence line. The transition weakens with growing pressure. For reduced pressures exceeding three, the effect has become so weak that it is negligible. This description fits the results of Hendricks et al. (1970), Nishikawa & Tanaka (1995), Oschwald & Schik (1999), and Banuti (2015). Banuti (2015) proposed an equation that describes this supercritical line,

\[
p_r = \exp[A_s(T_r - 1)],
\]

where \(A_s = 5.280\) for argon (Banuti et al. 2017).

4.2. A closer look into the thermodynamic transition

Figure 4 compares MD transition lines for \(c_p\), \(\alpha_p\), \(\kappa_T\), and diffusivity \(D\) as extensions of the coexistence line beyond the critical point. The width of the transitional region is indicated as determined from the enthalpy (Figure 2). Figure 4 shows that the diffusion-based Frenkel line lies within the Widom lines based on different response functions. Consistent with the literature (Fomin et al. 2015; Luo et al. 2014), Figure 4 shows that the definitions based on different response functions are not equivalent; furthermore the lines diverge. There is no obvious justification to prefer one response function over any other as the ‘right’ marker of the thermodynamic crossover.

4.3. The Gibbs free enthalpy and the Widom line

The subcritical phase transition from liquid to vapor across the coexistence line is a first order phase transition. Thermodynamically, this implies a discontinuous change in the slope of the Gibbs free energy \(g = h - Ts\). At supercritical pressures, this discontinuity
has vanished. However, it is interesting to see how the Widom line definitions relate to the Gibbs energy. Using the Maxwell relations of classical thermodynamics, we obtain for the isobaric specific heat capacity

\[ c_p = \left( \frac{\partial h}{\partial T} \right)_p = -T \left( \frac{\partial^2 g}{\partial T^2} \right)_p, \tag{4.2} \]

for the isobaric thermal expansion

\[ \alpha_p = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \left( \frac{\partial^2 g}{\partial p \partial T} \right)_p, \tag{4.3} \]

and for the isothermal compressibility

\[ \kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = -\frac{1}{v} \left( \frac{\partial^2 g}{\partial p^2} \right)_T. \tag{4.4} \]

Thus, the response functions are related to second derivatives of the Gibbs energy, and hence also are closely interrelated.

The presence of the second derivatives shows that the response functions reflect the rate of change of the slope of the Gibbs energy. This suggests that while the discontinuity of \((\partial g/\partial T)_p\) at the phase transition cannot exist anymore under supercritical conditions, we may find a shadow of this transition in the form of a maximum curvature of the Gibbs energy. The curvature \(\kappa\) of a function \(y\) is \(\kappa = y''/(1 + y'^2)^{3/2}\). For the condition that \(y'' \ll y'\), this expression can be approximated as \(\kappa \approx y''\). For an isobaric heating process, \(y'\) and \(y''\) become \((\partial g/\partial T)_p\) and \((\partial^2 g/\partial T^2)_p\), respectively, with

\[ \left( \frac{\partial g}{\partial T} \right)_p = -s, \tag{4.5a} \]

\[ \left( \frac{\partial^2 g}{\partial T^2} \right)_p = - \left( \frac{\partial s}{\partial T} \right)_p = -\frac{c_p}{T}. \tag{4.5b} \]
We introduce $\kappa_g$ as the magnitude of the curvature of the Gibbs energy,

$$\kappa_g = \left| - \frac{c_p/T}{(1 + (-s)^2)^{3/2}} \right|. \quad (4.6)$$

Upon approaching the critical point on the Widom line, $c_p$ diverges and the approximation

$$\tilde{\kappa}_g = \left| - \frac{c_p}{T} \right| = \frac{c_p}{T} = -\left( \frac{\partial^2 g}{\partial T^2} \right)_p \quad (4.7)$$

is valid.

Figure 5 compares Widom lines based on the maxima of $\kappa_g$, $c_p/T$ and $c_p$ with Eq. (4.1). We see that the transition temperature does not rise monotonously with pressure, but curves back to lower temperatures at sufficiently high pressures. Up to $p_r \approx 1.5$ the lines coincide. At higher pressures, first $\kappa_g$, then $c_p/T$ deviate from the $c_p$-curve, both have an end-point at supercritical conditions.

While the discontinuity in $(\partial g/\partial T)_p$ across the coexistence line vanishes at the critical point, its influence is projected into the supercritical state space as the locus of points at which the curvature of $g$ exhibits an extremum. We see that the supercritical projection of the coexistence discontinuity $\kappa_g$ coincides with the maxima of $c_p$ for $p_r < 2$.

### 4.4. An upper limit of the Widom line

Understanding the Widom line as the supercritical projection of the coexistence discontinuity suggests that this effect will weaken with growing distance from the critical point as the subcritical discontinuity smooths out.

Figure 6(a) uses NIST (Linstrom & Mallard 2016) data to show how the heat capacity peak widens, flattens, and moves to higher temperatures as pressures reach $p_r = 3$. At $p_r = 6$, Figure 6(b) shows that the excess heat capacity of the peak has become so thinly spread out that a distinct crossover temperature is no longer discernible. As shown in Figure 5, the peaks move to lower temperature beyond $p_r = 6$, before vanishing altogether at $p_r = 10$.

Figure 5 shows that the loci of maxima deviate from Eq. (4.1) when they start to curve back. For $\kappa_g$, $c_p/T$, and $c_p$, this occurs at reduced pressures of 2, 3, and 4, respectively. A look at the behavior of $\kappa_g$ and $c_p$ at the corresponding pressures provides insight into the
Figure 6. Specific isobaric heat capacity for sub- and supercritical pressures. (a) Low pressures. (b) High pressures. The peaks widen, flatten, and move to higher temperatures as the pressure is increased for \( p_r \leq 6 \). At \( p_r = 8 \), a maximum is hardly discernible and has moved to lower temperatures; at \( p_r = 10 \) the peak has vanished altogether. Note the different temperature scale at higher pressures. Data are from the NIST database (Linstrom & Mallard 2016).

Figure 7. Comparison of response functions and Gibbs curvature at two pressures. Graphs are normalized to the respective peak values. (a) \( p_r = 1.2 \). (b) \( p_r = 2.0 \). Data are calculated from the NIST database (Linstrom & Mallard 2016).

relevance of this deviation. Figure 7 compares \( \kappa_g, \frac{c_p}{T}, \alpha_p, \) and \( \kappa_T \) around the transition temperature at two pressures. Close to the critical point at \( p_r = 1.2 \), Figure 7(a) shows that their respective values at the peak by far exceeds the liquid-like and gas-like values towards lower and higher temperatures. The transition region is narrow and the peaks occur at roughly the same temperature, consistent with the validity of Eq. (4.7). The character of the curves changes when the pressure increases to \( 2p_r \) (see Figure 7(b)). The differences between peaks and tails are reduced significantly, and the differences in the temperature of the respective peaks are more pronounced and move to higher temperatures in all cases. Thus, Figure 7(b) shows that the peak of \( \kappa_g \) at \( p_r = 2 \) has almost vanished. Similarly, Figure 6 illustrates how the \( c_p \) peak has flattened and widened at reduced pressures exceeding 3. We can conclude that the Widom lines diverge when the respective peak has weakened to the point of losing its physical significance. Similarly, the peak in the thermodynamic Gibbs curvature \( \kappa_g \), Figure 5, vanishes at approximately \( 2.6 \ p_{cr} \).

We conclude that there is strong evidence for an upper limit to the thermodynamic
Widom line. There is no precise limiting pressure, but instead we observe a universal weakening in the thermodynamic character of the crossover. Steep property gradients and response function extrema present at near-critical pressures have weakened to the point of being negligible at \( p_r \approx 3 \), and vanish for \( p_r > 10 \), consistent with the changing character of the transitions found for \( p_r = 3.0 \) and 9.4 in Figure 2.

The respective peaks of the response functions are not isolated local events. Instead, they represent different stages of the same thermodynamic transition spanning a finite, broadening transitional region. Thus, each maximum of a response function marks a certain point during the same thermodynamic transition. We found that the \( c_p \)-based Widom line is strongly related to the curvature of the Gibbs energy, which projects the influence of the phase transition into the supercritical domain. A spreading of the transitional region then naturally causes the different loci to diverge, without stripping them of physical meaning.

4.5. A revised state diagram

We have shown that the projected \( p_r-T_r \) structure of the fluid state space is only insufficiently characterized by the states illustrated in Figure 1(b). Instead, we have presented evidence for the state regime structure depicted in Figure 8. No difference could be found between a liquid at subcritical and a compressed liquid at supercritical pressure. We further showed that a supercritical fluid may behave like a gas at sufficiently high temperatures. In Figure 8, we use the term ‘vapor’ to denote a real gas with significant intermolecular interaction, and ‘ideal gas’ to denote a gas with negligible intermolecular interaction. Only for very low pressures (\( p < 0.1 p_{cr} \)) do we find a transition from a liquid to an ideal gas across the coexistence line; for higher subcritical pressures, the liquid transitions to a real-gas vapor state instead. For \( p_{cr} < p < 3 p_{cr} \), the thermodynamic crossover occurs through a transitional domain, surrounding the heat capacity based Widom line. This process is spread over a finite temperature interval characterized by strong changes in fluid properties. When heated to \( T > 2 T_{cr} \), this supercritical fluid behaves like an ideal gas. At pressures exceeding \( 3 p_{cr} \), the phase change-like character vanishes and is replaced by an almost linear change in enthalpy with temperature. At pressures exceeding \( 10 p_{cr} \), the heat capacity peak has vanished altogether. While the thermodynamic transition ceases to play a role at \( p > 3 p_{cr} \), a structural transition across the Frenkel line may exist in the fluid for arbitrary pressures.
5. Conclusions

This paper discusses fluid states by studying similarities and differences between liquids, gases, and supercritical fluids, and the transitions between them.

There is no such thing as a homogeneous supercritical state; instead, the state space is more complex than previously anticipated. We identified four different supercritical fluid states: classical liquids, a non-rigid liquid unable to sustain transversal sound propagation, a vapor gas with significant intermolecular interaction, and an ideal gas with no intermolecular interaction.

By emphasizing the differentiation into the thermodynamic Widom line and the dynamic Frenkel line, we are able to categorize the different lines that are currently discussed in the literature. The Widom line is the supercritical extension to the coexistence line, associated with a thermodynamic crossover from the classical rigid liquid to the vapor state. Beyond \( p > 3p_{cr} \), the transition loses its thermodynamic character but retains the dynamic transition, corresponding to the Frenkel line. The Frenkel line extends to arbitrarily high fluid pressures, and marks the transition from liquids to non-rigid liquids which no longer exhibit a liquid-like dispersion behavior. Pseudoboiling is no longer relevant at these pressures.

We introduce the supercritical maximum curvature of the Gibbs energy \( \kappa_g \) as a thermodynamically meaningful interpretation for this transition, showing that the discontinuous character of the coexistence line is projected into the supercritical state space. This projection coincides with the \( c_p \)-based Widom line. The influence weakens with growing distance to the critical point and vanishes at \( 2.5 < p < 3 \). The response functions \( c_p \), \( \kappa_T \), and \( \alpha_p \) can be expressed in terms of the second derivatives of the Gibbs free energy. Correspondingly, all functions exhibit maxima in the vicinity of the transition. For temperatures lower than \( 3p_{cr} \), peaks of \( c_p \) are a valid and simple approximation for extrema of \( \kappa_g \).

Due to the continuous nature of the supercritical liquid-to-vapor crossover, the respective loci of maxima cannot be regarded as isolated events, but should instead be understood as different stages within the same transition. We demonstrate that the transition region has a finite width and widens towards higher pressures, encompassing the transition lines based on other definitions. The widening leads to a divergence of the different lines without stripping them of physical meaning.

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