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Anomalous Properties of Some Fluids − with High Relevance in Energy Engineering − in Their Pseudo-critical (Widom) Region

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Abstract
Recent results are shown about the peculiarities of the pseudo-critical region, with special emphasis on properties important for energy production and conversion. The property-map of some materials, which are relevant as model fluids or as working / cooling fluids in energy engineering (argon, methane, water and carbon dioxide) and their relative positions to various adiabats – influencing their stability through the anomalous properties – are presented. Some potential technological problems related to the existence of these anomalies are discussed.

Keywords
adiabatic processes, stability, compressibility, specific heat, speed of sound, thermal expansion

1 Introduction

The conversion of heat to a generally more "useable" form of energy, namely electricity, often requires thermodynamic cycles [1]. They are used in various thermal power plants including fossil, nuclear, solar and geothermal ones. Most of these cycles are built from a few basic processes like adiabatic expansion / compression, isobaric or isochoric heat exchange, isenthalpic expansion, etc. For example the archetype of thermodynamic cycles, the Carnot cycle consists of two isothermal and two adiabatic steps, while the Rankine cycle [2] – developed in the mid-19th century – which is applied in most commercial power plants using steam turbines, consists of two isobaric and two adiabatic steps. It is also important to mention that some of these steps are used in other applications, which are important in energy production and conversion; one could mention for example the gas liquefaction or the inverse process – liquid evaporation – connected for example with LNG (Liquefied Natural Gas) technology.

In most cases, the thermodynamic cycles are performed far from the critical point, either in much higher temperatures (gas cycles) or in lower pressures and temperatures (liquid / vapor cycles). This situation started to change only a century after the development of Rankine cycle by introducing transcritical (some part is below and some part is above the critical point) or supercritical (the full cycle is above the critical point, but not far enough to handle the fluid as almost ideal gas) cycles [3, 4].

The description of the basic steps of the cycles in single-phase regions should be simple, assuming smooth, monotonously changing properties and similar "simplicity" were assumed for the description of the processes in the supercritical region. But this assumption is not valid, at least not for the entire ($p > p_c$; $T > T_c$) region. The so-called supercritical region cannot be handled as a homogeneous region; some part can be considered as liquid-like, some as vapor-like, while there is a region which is really different from the liquid and vapor states. This is the so-called Widom region, also called pseudo-critical, pseudo-boiling or pseudo-spinodal region; the existence of this anomalous region seems to be a general phenomenon for all fluids, rather than the peculiarity of a few chosen ones [5-14].

We are going to present a systematic study of a model fluid (van der Waals argon) and several real fluids (real argon, carbon dioxide, water and methane) with regard to

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the relative positions of reversible adiabats and Widom lines (see definition later). In particular, we will show how to find favourable as well as unfavourable adiabats by a detailed thermodynamic analysis, and demonstrate how an adiabatic process might be perturbed by temperature- and pressure-noise (caused by some external source), which might destabilize the trajectory and might shift the process into another less favourable course. Potential applications to optimize thermodynamic cycles (Carnot, super- or transcritical Rankine, etc.) will be discussed.

2 The internal structure of the supercritical region

Historically, one can define supercritical states quite simply in temperature – pressure diagram as states where both properties (temperature as well as pressure) are above the corresponding critical values. The fluid phase diagram of water calculated by IAPWS reference equation of state (REoS) [15] implemented into ThermoC [16] can be seen in Fig. 1. The borders of the supercritical region according to the traditional definition are marked by grey dashed lines.

Although this is a straightforward and simple definition, it can be easily seen that it does not have real physical-chemical background. In Fig. 2, density of water at 23 MPa (slightly above the critical value, 22.06 MPa) can be seen. For better comparison, the densities of liquid water and steam in equilibrium at 12 MPa (which is a typical operating pressure for the primary circuit of a nuclear Pressurized Water Reactor) where the liquid and vapor phases are still very well distinguishable, with densities of 0.65 and 0.07 g/cm^3, respectively. The critical temperature is marked by a dashed line; for convenience, critical point data for the substances relevant to this paper are summarized in Table 1. Comparing states shown by arrows A, B and C, one can see that they are almost identical (concerning their density, as well as other properties, not shown here), but while state A is a subcritical liquid state, states B and C are supercritical fluid states. In similar way, comparing states C and E; according to the traditional classification, both of them are supercritical fluid states, yet as it can be seen concerning density (and other properties, not shown here), C is rather a liquid-like state, while E is a vapor-like one. Therefore, one might conclude that the previously homogeneous supercritical region should be divided into three sub-regions; one for liquid-like states, one for vapor-like ones and the remaining one (located between the two dotted arrows in Fig. 1) for the "real" supercritical ones with properties between liquid and vapor. As it can be seen on the density curve in Fig. 2, it is not possible to separate this mid-region sharply from the liquid- and vapor-like ones, because the transition is smooth.

One can see that in this "real" supercritical region at least regarding density, the fluid behaves as a transitional one between liquid and vapor; at lower pressure and temperature one could construct a system with the same density by

Table 1 Critical point data of the materials studied in the paper (taken from NIST WebBook [17]).

Material	T_c (K)	p_c (MPa)
argon	150.86	4.89
water	647.0	22.06
carbon dioxide	304.18	7.38
methane	190.6	4.61

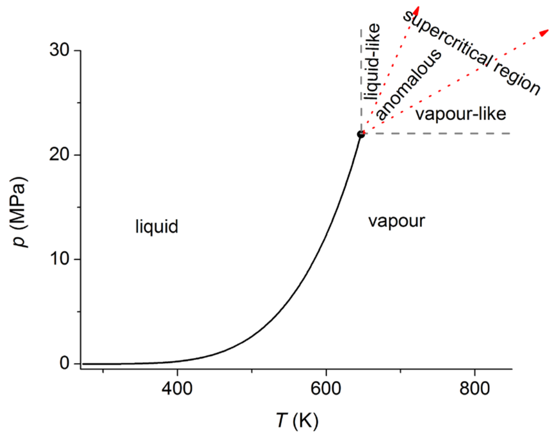

Fig. 1 Fluid phase diagram of IAPWS water [15] calculated by ThermoC [16] can be seen. The borders of the supercritical region according to the traditional definition are marked by dashed lines. Novel division of the traditional supercritical region is also shown, marking liquid-like and vapor-like supercritical parts. The borders of the anomalous Widom region are marked by dotted lines.

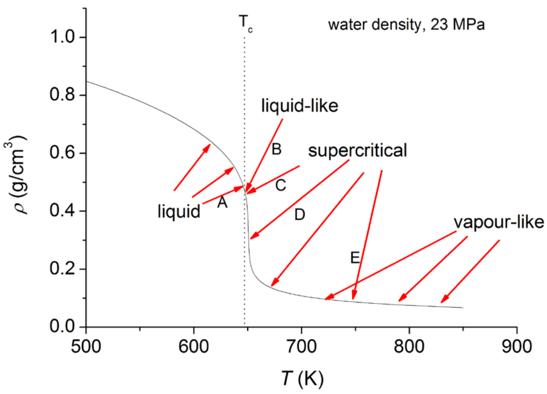

Fig. 2 Density of water at 23 MPa by IAPWS EoS [15] calculated by ThermoC [16]. Critical temperature is marked by dotted line. Various characteristics (liquid, liquid-like, supercritical and vapor-like) are marked by arrows. Further description can be found in the text.

mixing liquid with well-dispersed vapor bubbles. Therefore, supercritical state does not seem to be something very special or anomalous. Checking other properties however, one can see surprising results. In Fig. 3, isobaric molar heat capacity (c_{pm}, where m refers molar value) of water can be seen at atmospheric pressure (0.1 MPa) and at slightly supercritical pressure (23 MPa). Concerning the low-pressure case, one can see the almost constant (around 75-76 J/mol K) typical values for liquid states and the smaller, also nearly constant ones (3540 J/mol K) for vapor states; at the boiling temperature however, a jump, characteristic for first-order phase transitions appears.

The situation will be different at supercritical pressure (23 MPa). At lower temperatures, one can see a nearly constant heat capacity (between 70-80 J/mol K), typical for the pressurized liquid states followed by a part at higher temperatures, where the heat capacity starts to increase drastically (up to 90 or even to 100 J/mol K; no specific value can be established), but it is still not very far from the typical values for liquids (marked as liquid-like). The same tendency can be seen on the high temperature side; a nearly constant part with typical values for vapor states, then at lower temperatures, a part with increasing, but still vapor-like heat capacity. These results suggest that in the "real" or anomalous supercritical region, one would see heat capacity values resemble neither liquid, nor vapor values, but something in-between. Reality however is different; in that region the heat capacity reaches values unheard of even for very dense liquid states! Therefore, here the supercritical states are not simple "neither liquid, nor vapor, but something between them", rather a novel phase showing unique properties.

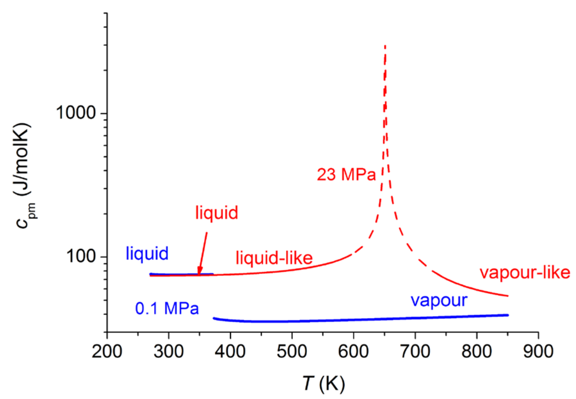

Fig. 3 Temperature dependence of the isobaric molar heat capacity of water at 0.1 MPa and 23 MPa by IAPWS EoS [15] calculated by ThermoC [16], shown in semi-logarithmic diagram. Various characteristics (liquid, liquid-like, vapor and vapor-like) are marked. Also, the anomalous heat capacity region are shown and marked by dashed line.

Readers familiar with the so-called critical anomalies (singularities) [18] might see that these peaks resemble the behavior of the same properties around the critical point; only while by approaching the critical point, heat capacities or similarly the compressibilities diverge from finite values to infinity (and comes back again to finite values on the other side of the critical point), above the critical pressure one can see only a sharp maximum. Going farther from the critical point (i.e. at higher pressures) the maxima will be less enhanced, decreasing in amplitude, while spreading into a wider temperature range and finally "disappears". This can be noticed in Fig. 4 for the isobaric heat capacity of argon modelled by and improved Wagner-Setzmann equation of state [16, 19]. Similar well-developed maximum can be seen for isobaric thermal expansion and isothermal compressibility as well. For isochoric heat capacity, one can also find a well-developed maximum (not shown here), but comparing to the other three quantities, where the values at the maximum can be one or two orders of magnitude bigger than values a few Kelvin away. For c_V, the difference is smaller than a magnitude, but still quite remarkable.

Although these Widom anomalies exist for a number of properties, we are dealing only with a few of them, which can be calculated from the equation of states, therefore for example viscosities or other properties relevant especially to flow are neglected. There are two further quantities which should be mentioned here, the speed of sound (c_s) and the isentropic compressibility (k_S). In Fig. 5, one can see these quantities for argon, calculated from

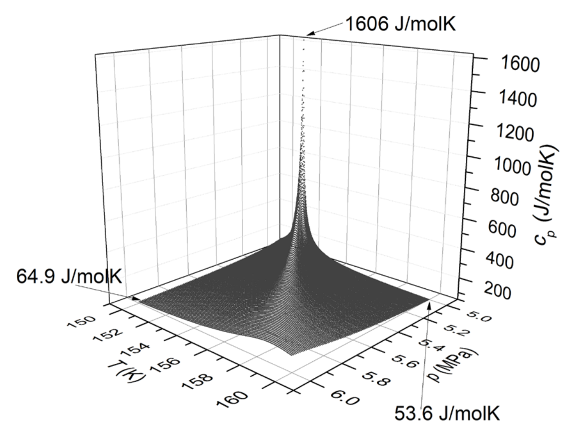

Fig. 4 Isobaric molar heat capacity of argon in the 5-6 MPa and 150-160 K pressure and temperature ranges, marking the heat capacity values at some points. Heat capacity values were calculated by Wagner-Setzmann equation of state [19] implemented into ThermoC [16]. As it can be seen, the peak is high and sharp close to the critical point and less and less significant farther from the critical region.

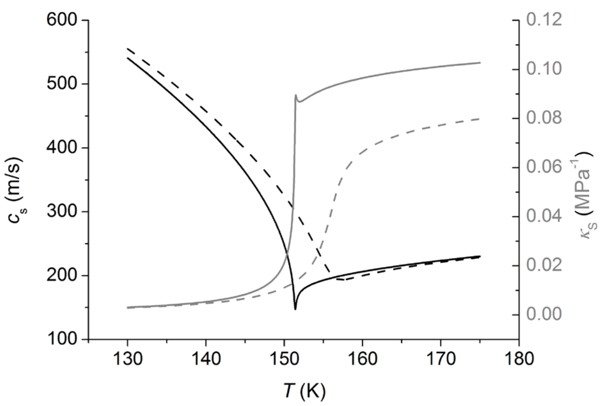

Fig. 5 Speed of sound (c_s) and isentropic compressibility (k_S) of argon, calculated from Wagner-Setzmann reference equation [19] implemented into ThermoC [16]. Solid lines: p = 5 MPa; dashed lines: p = 6 MPa.

Wagner-Setzmann reference equation. It can be seen that for the isentropic compressibility, very close to the critical pressure (p = 5 MPa, p_c = 4.89 MPa) there is a small maximum, which vanishes quite quickly by increasing the pressure leaving a sigmoidal-like change for this quantity in the anomalous region. For speed of sound, one can see a small minimum. Although the minimum is not extremely deep, it can be seen that in a given pressure, this is an absolute minimum.

The behavior of these quantities in the anomalous region is summarized in Table 2.

Concerning the anomalies itself, they can be characterized in several way including their amplitude, extent, location, etc. One of the most popular ways to characterize them is giving their "location" in temperature-pressure space. Location is given by the line connecting separately the maxima of c_p, c_V, k_T and a_p, the minima of c_s and the points of inflection of k_S and ρ, respectively. In this way, one can construct a “map”, showing the states more drastically influenced by the Widom anomalies. The map of Widom region for carbon dioxide can be seen in Fig. 6. All anomalies were determined at various constant pressures.

As it can be seen the Widom lines run very diversely. Since they do not have a sharp end, most of them are simply cut at 50 MPa or 600 K, although two of them terminate earlier, because the anomalies represented by them “disappear”, for example the maximum of c_V will be smaller than the accuracy of measured heat capacity values. In general, it can be concluded that most of the anomalies usually disappear at pressures or temperatures 2-3 times higher than the critical values [20], although this can be different for various materials [12, 13].

Table 2 Behavior of various properties within the anomalous Widom region and its vicinity. Big, medium and small refers extrema with at least one order of magnitude bigger, a few times bigger or a few tens of percent bigger than values in the 10 K vicinity of 23 MPa for water, respectively.

Property	Behavior
mass density	sigmoidal-like with inflection
isobaric heat capacity	big maximum
isochoric heat capacity	medium maximum
isothermal compressibility	big maximum
isentropic compressibility	vanishing small maximum / sigmoidal-like with inflection
speed of sound	small minimum
isobaric thermal expansion	big maximum

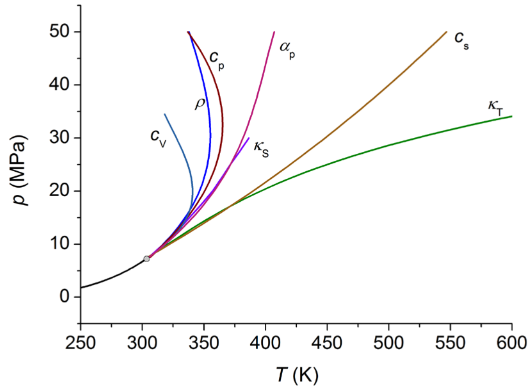

Fig. 6 Widom lines for isochoric heat capacity (c_V), density (ρ), isobaric heat capacity (cp), isobaric thermal expansion coefficient (α_p), isentropic compressibility (κ_S), speed of sound (c_s) and isothermal compressibility (κ_T) for carbon dioxide, calculated from Wagner-Span reference equation [22] implemented into ThermoC [16]. Black line represents saturation curve terminated by the critical point (small grey circle).

At this point, we are not presenting the Widom lines of other materials to avoid duplication of figures, because in the next section, the Widom lines of argon (both van der Waals argon and real one), carbon dioxide, water and methane will be shown, together with their relative position of various adiabats. Widom lines for the other materials can be seen in Fig. 9. (a)-(e). For van der Waals Argon, c_V is constant, therefore Widom anomaly does not exist for this quantity. Detailed description about the relation of Widom lines and coexistence lines of different species were given by Banuti et al. [21].

Widom lines can be fitted quite accurately with third-order polynoms. Because some of these lines turns back, therefore the fitting equations will be in $T(p)$ form, instead of $p(T)$ one. Fitting parameters can be seen in Table 3. Some of these Widom lines were already

Table 3 Cubic fits for the various Widom lines in the form of $T = A + Bp + Cp^2 + Dp^3$. Data are fitted from the critical point to the maximal (p, T) values shown on the corresponding figures.

Material	A	B	C	D	R^2
Ar (vdW)					
r	105.30 ± 0.49	11.96 ± 0.15	-0.584 ± 0.014	0.01043 ± 0.00039	0.999
c_p	108.58 ± 0.29	10.44 ± 0.09	-0.397 ± 0.008	0.00745 ± 0.00023	1
c_V	-	-	-	-	-
k_T	84.09 ± 3.86	18.22 ± 1.19	-0.242 ± 0.109	0.05359 ± 0.00306	0.999
k_S	102.63 ± 0.93	12.16 ± 0.29	-0.527 ± 0.026	0.01095 ± 0.00070	0.999
c_s	92.61 ± 0.33	13.99 ± 0.10	-0.396 ± 0.009	0.00679 ± 0.00027	1
a_p	108.11 ± 0.18	10.25 ± 0.05	-0.331 ± 0.005	0.00527 ± 0.00014	1
Ar (real)					
ρ	119.59 ± 0.93	8.10 ± 0.26	-0.374 ± 0.022	0.00627 ± 0.00058	0.999
c_p	109.72 ± 0.58	7.78 ± 0.16	-0.309 ± 0.014	0.00464 ± 0.00036	0.999
c_V	129.05 ± 6.32	2.88 ± 2.41	0.529 ± 0.293	-0.04116 ± 0.01146	0.998
k_T	116.80 ± 3.11	8.05 ± 0.87	-0.321 ± 0.074	0.01621 ± 0.00194	0.999
k_S	118.90 ± 1.51	8.02 ± 0.42	-0.352 ± 0.036	0.00794 ± 0.00094	0.999
c_s	117.28 ± 1.81	6.88 ± 0.50	-0.017 ± 0.043	-0.00141 ± 0.00113	0.999
a_p	120.84 ± 0.36	7.21 ± 0.10	-0.234 ± 0.009	0.0035 ± 0.0002	1
water					
ρ	504.28 ± 4.95	9.67 ± 0.44	-0.175 ± 0.013	0.00136 ± 0.00012	0.999
c_p	538.32 ± 0.68	6.13 ± 0.06	-0.061 ± 0.002	0.00028 ± 0.00002	1
c_V	534.42 ± 0.51	6.04 ± 0.05	-0.037 ± 0.001	-0.00024 ± 0.00001	1
k_T	584.75 ± 4.00	1.78 ± 0.36	0.058 ± 0.010	-0.00049 ± 0.00010	1
k_S	513.37 ± 24.03	9.22 ± 2.17	-0.176 ± 0.063	0.00151 ± 0.00059	0.998
c_s	572.18 ± 0.71	3.05 ± 0.06	0.022 ± 0.002	-0.00028 ± 0.00002	1
a_p	532.80 ± 2.07	6.78 ± 0.18	-0.086 ± 0.005	0.00059 ± 0.00005	1
CO_2					
ρ	260.58 ± 1.86	7.22 ± 0.28	-0.169 ± 0.012	0.00109 ± 0.00014	0.997
c_p	265.33 ± 3.30	6.18 ± 0.50	-0.097 ± 0.021	0.00004 ± 0.00025	0.993
c_V	233.18 ± 9.20	12.73 ± 2.23	-0.464 ± 0.177	0.00482 ± 0.00437	0.997
k_T	249.25 ± 3.25	8.57 ± 0.65	-0.221 ± 0.039	0.00796 ± 0.00072	0.999
k_S	259.32 ± 1.97	7.07 ± 0.40	-0.142 ± 0.024	0.00161 ± 0.00044	0.999
c_s	244.50 ± 1.23	8.37 ± 0.19	-0.062 ± 0.008	0.00031 ± 0.00009	0.999
a_p	255.70 ± 0.67	7.65 ± 0.10	-0.149 ± 0.004	0.00113 ± 0.00002	0.993
CH_4					
ρ	150.31 ± 1.17	11.33 ± 0.39	-0.608 ± 0.040	0.01243 ± 0.00132	0.999
c_p	155.34 ± 0.47	9.35 ± 0.12	-0.363 ± 0.009	0.00553 ± 0.00021	0.999
c_V	144.57 ± 1.16	13.13 ± 0.41	-0.747 ± 0.045	0.01574 ± 0.00158	0.999
k_T	98.65 ± 11.46	26.31 ± 3.15	-1.940 ± 0.264	0.06687 ± 0.00679	0.993
k_S	157.56 ± 0.69	8.20 ± 0.24	-0.237 ± 0.025	0.00315 ± 0.00087	1
c_s	147.23 ± 0.39	9.88 ± 0.10	-0.144 ± 0.007	0.00195 ± 0.00017	1
a_p	153.51 ± 0.70	9.50 ± 0.20	-0.329 ± 0.017	0.00519 ± 0.00046	1

determined, using different temperature and pressure windows [6, 7, 10, 12-14]; the agreement between previously published results and our results are good.

When various materials are compared, one can see that the order of several Widom lines follows the same order (density, isobaric heat capacity, isobaric thermal expansion, speed of sound, isothermal compressibility, taking the temperature values at a given pressure), while two other lines (isochoric heat capacity and isentropic compressibility) move relatively freely, although they remain in the relatively low temperature region together with the lines of density, isobaric heat capacity and isobaric thermal expansion.

3 The stability of the adiabatic expansion lines in the Widom region

Thermodynamic cycles can be used to converse heat to work (and *vice versa*). These cycles usually can be divided into simple steps, like isobaric heat exchange, adiabatic compression / expansion, etc. When the process fully or partly located in the anomalous supercritical region, some of these steps might intersect one or more Widom lines.

A schematic figure of some processes used in supercritical thermodynamic cycles are introduced and can be seen in Fig. 7.

One should be aware of when we talk about isobaric, isothermal, or any other processes in a real system, external mechanical and thermal noises can kick the process out of the original path. For example by having an isothermal heat exchange (one of the basic process for the Carnot cycle and for the two-phase Rankine cycle), the noise (D*W*) through the density / volume changes (D*V*) can change the pressure, therefore the process can leave the original path and follow another, probably less good path.

The effect of DQ_p = Δ*H* and D*W* on *p* and *T* depends on the corresponding response functions, namely on the isothermal compressibility and isobaric heat capacity (Eqs. (1)-(2))

$$k_T = -\frac{1}{V}\left(\frac{dV}{dp}\right)_T \quad (1)$$

$$c_p = \left(\frac{dH}{dT}\right)_p . \quad (2)$$

Having high value for the compressibility, the same volume perturbation (D*V*) generated by external mechanical noise can make much smaller change in pressure; in similar way, systems with high heat capacities show much smaller temperature change for a given thermal perturbation than their low heat capacity counterparts. Since even adiabats (or other processes) can be approximated by isobaric / isothermal steps, therefore one might conclude, that adiabats running in high c_p – high k_T region are much stable for thermal or mechanical noises than other adiabats, running in low c_p – low k_T region. This is demonstrated in Fig. 8.

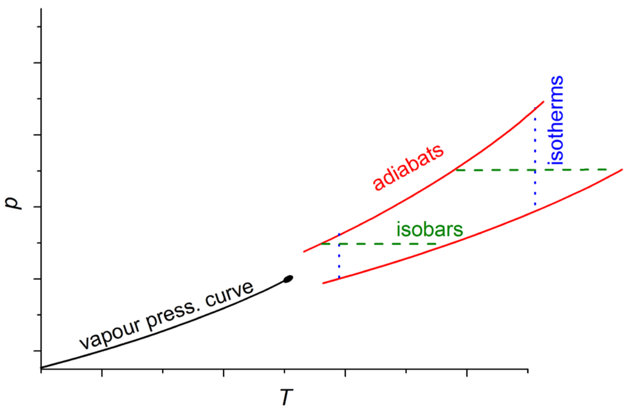

Fig. 7 Schematic diagram of various simple thermodynamic processes in the anomalous Widom region

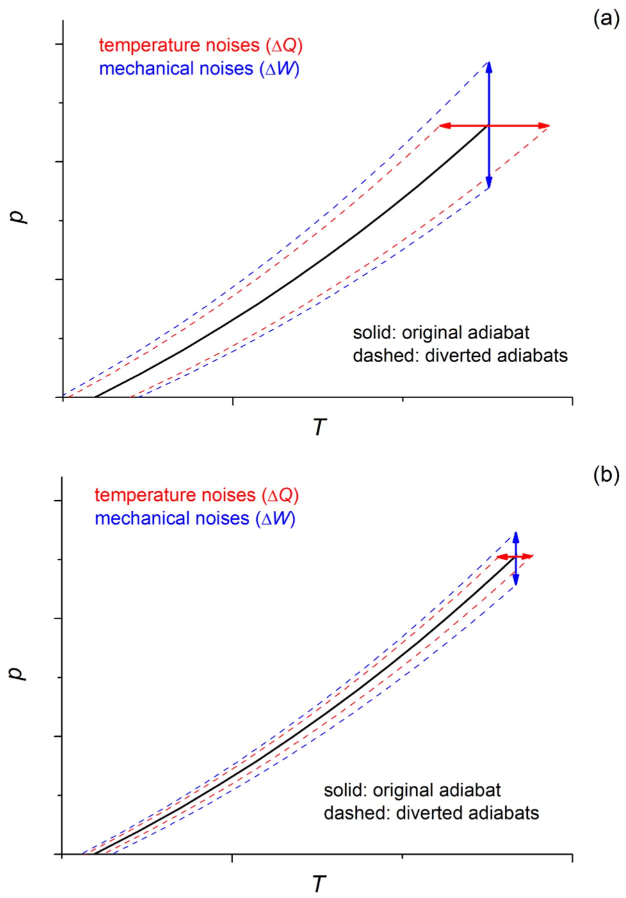

Fig. 8 Response of the systems for external thermal and mechanical noises. (a) Small heat capacity and/or isothermal compressibility make the system sensitive for noises; (b) High heat capacity and/or isothermal compressibility make the system stable against external noises.

Adiabats running in the sub- and supercritical regions are shown in Fig. 9 (a)-(e) for model argon (van der Waals argon), real argon (calculated by Wagner-Setzmann reference REoS [19]), for water (calculated with IAPWS REoS [15]), for carbon dioxide (calculated with Wagner-Span REoS [22]) and for methane (calculated with Wagner-Setzmann REoS [23]). Widom lines are drawn by various colors and also marked by their symbols. Representative adiabats – to show general *p*-*T* dependencies - are marked by grey lines, while vapor pressure curves are marked by black lines.

It can be seen that for vdW argon (Fig. 9 (a)), three Widom lines (isobaric heat capacity, isentropic compressibility and isobaric thermal expansion) run close to some adiabats from the critical point to 20 MPa, while the line for speed of sound run close to an adiabat up to 10 MPa. According to Eqs. (1)-(2), adiabats running close to or on the ridge of isobaric heat capacity maximum (represented by its Widom line) would be very resistant against external noises. Unfortunately, as it can be seen in Fig. 9 (b), for real argon, the situation is different, the Widom line of c_p deviates from the adiabats, therefore for real argon, one

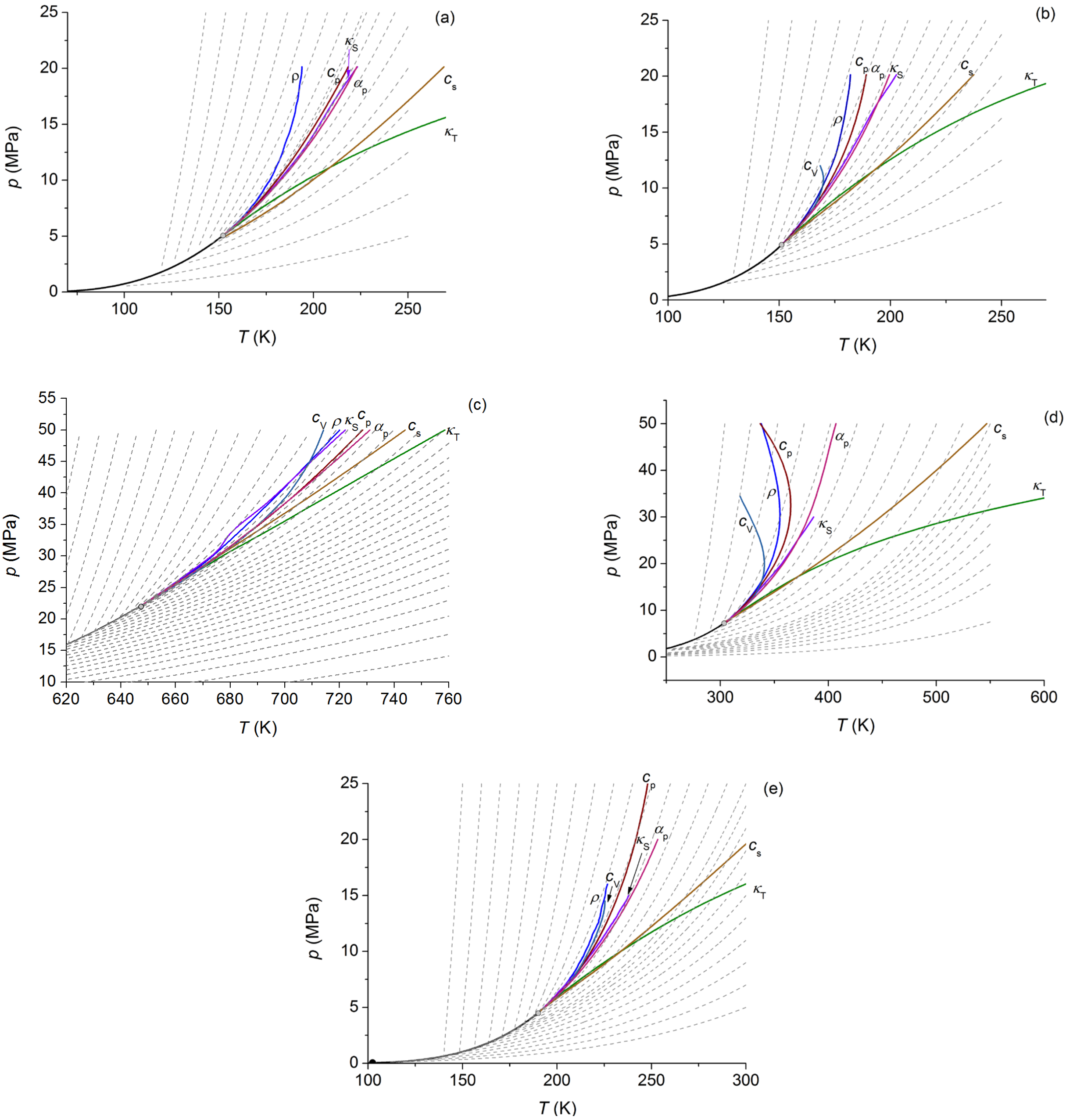

Fig. 9 Position of adiabatic expansion lines and various Widom lines for a model fluid (van der Waals Argon) (a) and for real ones; argon (b), water (c); carbon dioxide (d) and methane (e).

cannot find adiabatic expansion / compression lines with extremely high stability against external thermal noises. The only Widom line which still has "adiabat-philic" behavior is the line of isobaric thermal expansion.

Concerning water, "adiabat-philic" Widom lines (lines running close to or together with an adiabatic line) do not exist, not even in this relatively low (p_c to 2.5*p_c) pressure range. At lower pressure, isochoric heat capacity and density line run quite close to adiabats. In general, for this working fluid, one cannot find very stable adiabats, except close to the critical point. This might have some practical importance, because recent nuclear power plant designs using supercritical water as moderator and working fluids [24] goes up only to 25 MPa, where one can still find adiabats running in the favorable region.

For carbon dioxide, the situation is similar to the water; general adiabat-philic Widom line does not exist, although at pressures closer to p_c, the Widom lines of density and isobaric heat capacity run together with some adiabats.

Finally, for methane, the situation is more or less the same; at lower pressure the Widom lines of density and isochoric heat capacity run along with adiabats, while in the total range, the Widom line of isobaric heat capacity runs almost parallel to the neighboring adiabats. One of the most important quantity in this case is the speed of sound (having special importance in the re-fueling process of CNG-driven cars [14]), but its Widom line does not run together with the adiabats.

Concerning the Widom line of isentropic compressibility of water, a small hump can be seen at low pressures; it is probably caused by the existence of the small maximum for this quantity mentioned above- existing only at pressures very close to the critical point.

4 The importance of various materials in energy production and transformation

In this section, we would like to give some explanations for the choice of materials of this study. The choice for van der Waals argon is simple; this is the simplest model fluid and it is frequently used for qualitative demonstrations. The use of real argon has two reasons. First, it is good to demonstrate the difference between an ideal model (vdW Ar) and a more realistic one (real Ar). The second reason is – although it might be strange to read – that argon is a potential working fluid for power stations, although not on the Earth, but on asteroids or outer planets [25]. The choice of water does not need too much explanations; well over 90 % of all high-capacity fossil or nuclear power plants use Rankine cycle with water to turn heat into work. Carbon dioxide can be used as supercritical working fluid for the utilization of low-temperature heat sources, like geothermal, solar and other sources.

The last material is methane; unlike the other three real substances, it is not an existing or potential working fluid. The reason why it is included in this study because it has an increasing importance in energy engineering, namely in CNG (Compressed Natural Gas) technology, where the gas is basically pure, pressurized supercritical methane stored quite above the temperatures relevant to Widom anomalies. In addition, upon expansion (for example while filling it to the vehicles), temperature can be low enough to reach some of the Widom anomalies [14], for example speed of sound minimum might interfere with the speed of filling the fuel into the vehicle, giving an upper speed limit for re-fuelling; reaching speed of sound would damage the fuelling station as well as the vehicle. Therefore, the study of these systems is also important.

5 Further problems related to the Widom anomalies

To find the best – or at least optimal – adiabats, isobars isochores, etc. in the range where due to the Widom anomalies, material properties can go from liquid-like to vapor-like or to some super-compressible gas-like is not an easy task. But this is not the only problem caused by the unusual characteristics.

Let's assume a compressor or pump or any other equipment with rotating or sliding parts, the simplest one would be to imagine a pump, where a piston moves up and down in a cylinder. In Fig. 10, two situations can be seen. First, the pump is compressing hot carbon dioxide (400 K) from 5 MPa to 10 MPa; in this temperature, the compressibility

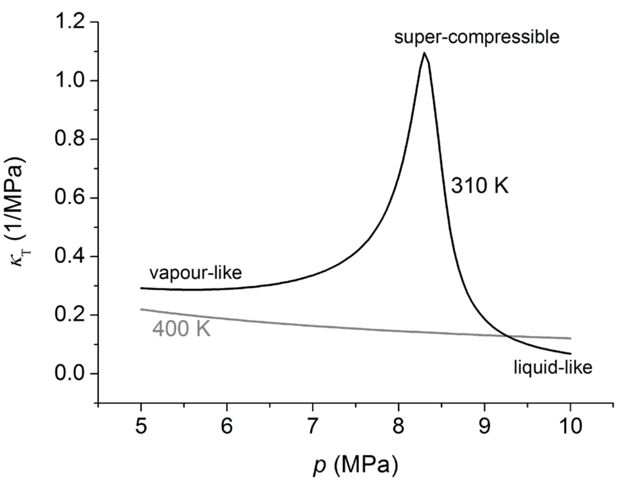

Fig. 10 The vapor-like, liquid-like and super-compressible regions for carbon dioxide.

changes slowly and smoothly and only in a small extent (grey line). It is also true for other quantities, for example density. Therefore, the resistance of the gas changes also slowly and smoothly. Second, pumping the same material in lower temperature (310 K), the piston can start its movement in a vapor-like material, finish it in a liquid-like one and – which is even worse – has to cross the region, where the material will be super-compressible (black line). This temperature-pressure range is dangerous, the piston might slide by the sudden decrease of gas resistance and it can damage the whole equipment.

Obviously, similar problems can also happen to other moving (for example rotating, vibrating or sliding) parts during operation.

One should not forget that due to the different location of the different Widom lines, one can find states, where the material has vapor-like density, liquid like compressibility, and anomalous (neither liquid nor vapor) isobaric thermal expansion coefficient; should we transfer this fluid with a pump used for liquids or with a compressor used for gases? Facing these problems, it can be easily realized that to handle supercritical phases, one might need new physics, new chemistry and even new instrumentation.

6 Summary

The supercritical region when defined as all states, where $T > T_c$ and $p > p_c$ is not a homogeneous region. Close to the low-temperature border of this region, supercritical states show rather liquid-like properties, while states close to the low-pressure border are very much vapor-like. Between this liquid- and vapor-like regions, a wedge-shaped region can be seen, where the liquid-like fluid turns to vapor – like and vice versa upon the proper change of pressure and temperature. Crossing this region, some of the properties (for example density) change smoothly from liquid-like to vapor-like, suggesting that this is a "neither liquid – nor vapor, but something between them" region, which might be handled in some sense as a mixture (i.e. one can obtain densities seen in this region by mixing normal liquid and vapor into a well-dispersed, two-phase mixture). However, the change of other properties shows entirely different characteristics; for example upon crossing this region, one can start from a state with liquid-like isobaric compressibility, reach a vapor-like value on the other side, but within the region, states with enormously high compressibility values can be seen; these are neither liquid-like, nor vapor-like materials; according to these anomalies, they might be considered as a new phase. This anomalous region is called Widom region. In this paper, the Widom regions of model and real argon as well as real water, carbon dioxide and methane have been mapped by marking the extrema or inflections of the anomalously changing properties.

Some of these properties have influence on the stability of various processes against external noises. Therefore, relative position of the mapped Widom lines and the adiabatic expansion-compression lines have been shown for the material mentioned above. For some materials, concerning regions with pressure slightly above critical pressure, one can find adiabats moving close to the Widom line of isobaric heat capacity, representing the ridge formed by the c_p-maxima. These adiabats might be more stable against internal heat-noises than other, therefore they might have special importance in thermodynamic cycles used for heat-to-work conversion.

Other problems also have been discussed briefly such as pumping or transporting fluids while they are in this anomalous region.

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