Research Article

Structural Transition in Supercritical Fluids

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The extension of the saturation curve $P_s(T)$ on the PT diagram in the supercritical region for a number of monocomponent supercritical fluids by peak values for different thermophysical properties, such as heat capacities C_p and C_v and compressibility has been studied. These peaks signal about some sort of fluid structural transition in the supercritical region. Different methods give similar but progressively diverging curves $P_{st}(T)$ for this transition. The zone of temperatures and pressures near these curves can be named as the zone of the fluid structural transition. The outstanding properties of supercritical fluids in this zone help to understand the physical sense of the fluid structural transition.

1. Introduction

It is well known that the saturation curve $P_s(T)$, marking the first order phase transition between liquid and gaseous phases on the PT diagram, terminates at the critical point (P_c, T_c) . The liquid and gaseous phases have quite different structures. The liquid phase is characterized by a continuous net of molecules with varying number of bonds, interrupted by pores of varying dimensions. The gas phase is characterized by vacuum filled with molecular clusters of varying dimensions and isomer configurations. This difference cannot disappear leaving no traces, when we move from one phase to another around the critical point. Some sort of structural transition takes place in the supercritical fluid.

In this paper, this transition is named as the fluid structural transition. It differs from the well-known structural transition in solids [1]. The structure in solids is the short-range structure of their elementary cells repeated in space. The short-range structure of fluids is not homogeneous in space and dynamically changes. The aim of this work is to trace the fluid structural transition $P_{st}(T)$ on the PT diagram and to understand better its nature.

This investigation tries to find answers on questions that arise frequently in courses of molecular physics and thermal physics of fluids, such as the following.

- (i) Does the remarkable saturation curve leave no traces in the supercritical region?
- (ii) What happens with fluid structure, when we come from one phase, for example, gaseous, to a quite different liquid phase moving continuously around the critical point?
- (iii) What are principal differences between the fluid structures across the saturation curve and what is the nature of structural transformation in the supercritical fluid?

The principal goal of this paper is to trace the extension, $P_{st}(T)$, of the Saturation curve to the Supercritical region by a number of ways. Another goal is to understand the mechanism of the structural transition that takes place when we cross the extension of the Saturation line in the supercritical fluid zone.

The investigation is based on experimental data accumulated in databases of thermophysical properties of fluids. The principal source of initial data: all initial data for this paper have been taken from the NIST Thermophysical Properties of Fluid Systems Database [2].

FIGURE 1: The pressure dependences of the heat capacities in CO₂ over the $T_c = 304.1282$ K. (a) $C_v(P)$ at 305 K; (b) $C_p(P)$ at 310 K (wide line); 315 K (narrow line); 320 K (dashed line).

FIGURE 2: The step-like transitions in the CO₂ fluid transition zone: (a) The Joule-Thomson coefficient (JTC) at $T = 315$ K. (b) The thermal conductivity of CO₂ at $T = 310$ K.

2. The Methods to Build the Extension of the Saturation Line

The extension line $P_{st}(T)$ can be traced as the peaks line on the PT diagram for different thermophysical properties, for example,

- (i) the heat capacity at constant pressure, C_p ,
- (ii) the heat capacity at constant volume, C_v ,
- (iii) the compressibility coefficient $K_{compr} = P/D \partial D / \partial P|_T = \partial \ln(D) / \partial \ln(P)|_T$.

It is known that at the saturation line both C_v and C_p possess δ -function peak. But over T_c , this peak degenerates to the resonance-like form. The isothermal pressure dependences of the heat capacities $C_v(P)$ or $C_p(P)$ in supercritical fluids at temperatures T over the critical temperature, T_c , clearly show resonance-like peaks that shift to higher pressures, when temperature grows; see Figure 1. The height of the peak falls and its width grows as $(T - T_c)$ grows.

The fluid transition differs from the first-order phase transition, with abrupt changes of thermophysical properties, possessing significant but not abrupt changes of thermophysical properties. In the fluid structural transition zone some thermophysical properties, like density, viscosity, thermal conductivity, or Joule-Thomson coefficient, perform the step-like transition, Figure 2. The thermal conductivity

fluid transition joins both mechanisms: the step-like from the density and the resonance-like from the heat capacity dependences on pressure; see Figure 2(b).

The used here logarithmic version of the compressibility coefficient is no dimensional that simplifies its analysis. Some other thermophysical properties, performing the step-like transition in the supercritical region, such as the Joule-Thomson coefficient, viscosity, and thermal conductivity, may be transformed to their no dimensional logarithmic derivatives by

$$K_W = \frac{P}{W} \frac{\partial W}{\partial P} \bigg|_T, \quad (1)$$

where $W(P, T)$ is the value of this thermophysical property. Their peaks give corresponding $P_{st}(T)$ curves.

It is useful to consider the potential energy to density ratio, as a measure of the molecular binding power in fluids. Potential energy U of a fluid may be given a phenomenological definition as the difference between the molar internal energy E and molar ideal gas energy E_0 at the same temperature

$$U = E - E_0. \quad (2)$$

This value takes into account both the change of microscopic potential energies of interacting particles in the fluid and the possible change of the particles' kinetic energy due to

FIGURE 3: The potential energy to density ratio in the CO₂ fluid transition zone: (a) $T = 310$ K (wide line); 350 K (narrow line); (b) $P = 80$ bar.

FIGURE 4: Resonance-like peaks for logarithmic derivatives of different thermophysical properties by logarithm of pressure in water at 647, 650, 655, 660, and 670 K: (a) The logarithmic derivative of density; (b) The logarithmic derivative of the potential energy to density ratio.

the density change. This definition reminds us of the well-known situation with the stretched piece of rubber potential energy that is composed mainly from microscopic changes in kinetic energies of the polymer chains at stretching.

The potential energy to density ratio is very informative, Figure 3. In a gaseous phase at small densities its absolute value is equal to the product of the dimer equilibrium constant [3, 4] by the effective pair bond energy. With growth of density in the gas-like structure, the molecular binding power falls due to competition of particles in the particle's attraction volume. In the liquid-like structure, this constant becomes less temperature- and density-dependent, because all places in the particle's attraction volume are equally shared by neighboring particles.

Figure 4 shows how the marking transition peak shifts towards higher pressures when the temperature grows. The resonance-like logarithmic derivatives of density and potential energy-to-density ratio for supercritical water at temperatures 647, 650, 655, 660, and 670 K clearly show their peaks shift towards higher pressures for higher temperatures.

The plurality of lines $P_{sc}(T)$, built by different methods, marks the fluid structural transition zone that widens when temperature grows over the T_c ; see Figure 5(a). And there are two ways of coming from the gaseous phase to the liquid phase: directly crossing the saturation curve and crossing

the fluid structural transition zone while moving around the critical point; see Figure 5(b).

So, different methods result in slightly differing curves forming together the zone of temperatures and pressures in the supercritical region that is remarkable due to its outstanding properties. This zone is interesting both for scientific research of phase equilibrium and for practical needs, as the zone of large and quick changes of thermophysical properties. This zone is characterized by large heterogeneity of density. In this aspect, the zone of the fluid structural transition inherits the properties of the near critical region [5, 6].

3. The Fluid Structural Transition

The Figure 6 shows that at the density lower than the critical point density, the supercritical fluid consists of different size clusters interacting with each other as the real gas particles, but at the density higher than the critical point density, the structure is quite opposite: the molecules are joined in a continuous net with pores and zones with smaller number of bonds.

So, there are two structures in the supercritical fluid, differing in topology. The gas-like structure has a continuous vacuum medium filled with clusters of different dimensions and with a variety of types of the intermolecular

FIGURE 5: Extension of the Saturation curve in the H_2O Supercritical region: (a) by different methods—narrow line: by peaks of the C_p ; dashed line—by peaks of the compressibility coefficient; wide line—Saturation curve. (b) two ways of coming from the gas phase to the liquid phase—wide red line—the Saturation curve; wide blue line—the extension of the Saturation curve in the Supercritical zone; wide green lines—the nominal boundaries of the Supercritical zone; thin red line—the path crossing the Saturation curve; thin green line—the path crossing the extension zone.

FIGURE 6: Gas-like (left) and liquid-like (right) structures in the supercritical zone.

bonding. Some large clusters contain pores or small density islands. The liquid-like structure has a continuous condensed medium filled with different size pores and with small density islands. Some of pores may be filled with gas. These topological features change when pressure crosses the $P_{st}(T)$ line. But this change is not quite definite. For one property, the change occurs when the clusters' maximal size reaches one value, and for others, this value may be other. Therefore, the fluid structural transition may be considered as a soft transition.

The Term Soft Transition: means that there are significant but not abrupt changes of thermophysical properties. The term soft structural transition means that far from this zone, there are two different phases with different structures and in the vicinity of this zone exist, from one side, the gas-like structure, from the other side, the liquid-like structure. Investigation of the transition's properties shows that across the $P_{st}(T)$ curve, there is a rather quick transition from a rarely and randomly packed structure to a densely packed and more ordered structure.

The boundary between these structures on the PT diagram is rather conditional: it depends on the experimental method of the boundary determination. When pressure

grows to the fluid structural transition value $P_{st}(T)$, the number of large clusters quickly grows, and they start merging giving rise to continuous liquid medium. But this medium is not totally continuous: it contains multiple pores and small density islands. Therefore, the merging of clusters in the continuous medium does not lead to abrupt changes in the thermophysical properties of the fluid. The changes are large but smooth, and that permits to name this type of structural transition as the soft transition.

This transition reminds us of the plasma formation from a neutral gas. The boundary between plasma and neutral gas is quite conditional: it depends on the percentage of ionized atoms considered as the criterion of the plasma formation.

Soft transition is also present in the glass formation from a melt that is a no equilibrium transition. But the soft structural transition in the supercritical region is quite equilibrium and cannot be equivalent to the glass-liquid transformation.

The fluid structural transition is not really the phase transition, because both phases coexist in the fluid in forms of clusters and pores. Therefore, the previous author's definition of this transition as the soft phase transition [7] should be changed on the fluid structural transition.

4. Conclusions

- (i) The zone of the fluid structural transition is very attractive for scientific research of the gas to liquid transformation due to the rather smooth, controllable, and wide-range change of quantities.
- (ii) Quick change of thermophysical properties of supercritical fluids in the zone of the fluid structural transition makes this zone very attractive for technological applications. The zone of the fluid structural transition may be very important for technological processes design as the zone of optimal mixture of gaseous and liquid properties of the fluid and the zone of large but regulated changes of the fluid's properties.
- (iii) Educational Perspectives: The idea of the soft transition is very educative. It joins together the idea of continuous gas to liquid conversion and the idea of essential transformation of their structures at this transition.

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