



Supercritical Fluids

Fundamentals and Applications

Edited by

Erdogan Kiran, Pablo G. Debenedetti and
Cor J. Peters

NATO Science Series

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SUPERCRITICAL FLUIDS: THEIR PROPERTIES AND APPLICATIONS

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1. Introduction

This introductory chapter is intended to acquaint the reader with the unusual properties of supercritical fluids, and with the ways these properties are exploited for a variety of applications in the chemical process industry. The presentation is closely tied to the program of this Advanced Study Institute (ASI), and points to chapters to follow in various subject areas. The behavior of thermodynamic and transport properties near a critical point is described, with water as an example. The structure of the supercritical fluid is discussed. The unusual solvent properties of supercritical fluids are explained within the framework of binary fluid phase diagrams, including a solid solute. Tunable solvent properties and environmental compatibility make supercritical fluids desirable agents in the chemical process industry. This ASI will focus on their role as extractants of food and other products, as carriers in chromatography, and as media for chemical reactions and for materials processing; moreover, virtually all aspects of polymer processing may involve the use of supercritical solvents. In this chapter, the basic knowledge and terminology required for an understanding of the chapters to follow will be introduced at an elementary level. For more advanced treatments, see [1], [2].

2. What is a Supercritical Fluid?

A one-component fluid is loosely defined to be supercritical when its temperature and pressure exceed its critical temperature and pressure, respectively, while it is not far from its critical state. In Fig. 1a, the region in pressure (P) - temperature (T) phase space is delineated where the fluid is supercritical according to the above definition, namely the right upper quadrant (cross-hatched).

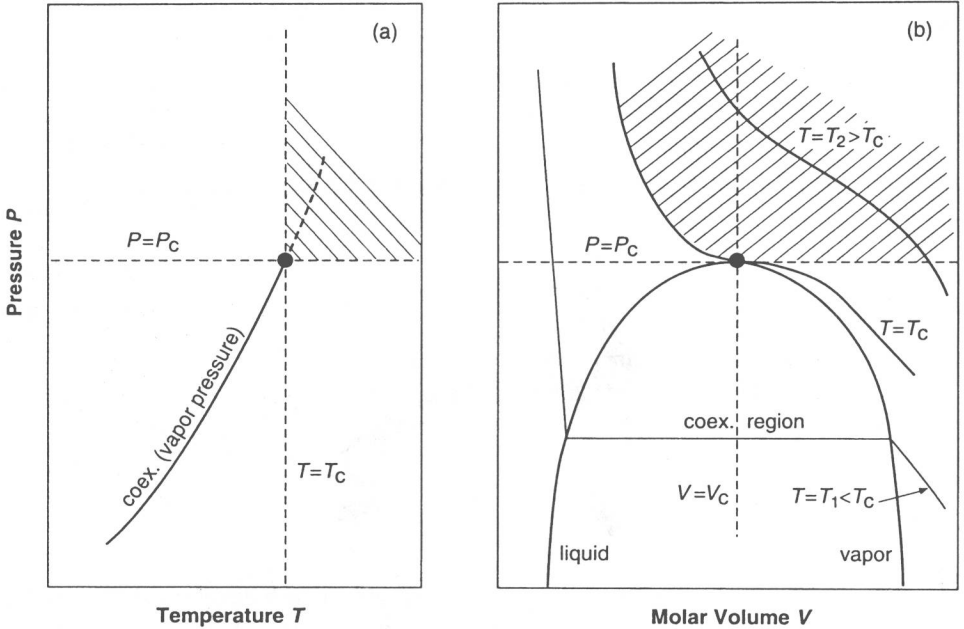


Figure 1. (a) The P - T phase diagram of a one-component fluid, with the vapor pressure curve and critical point. (b) The same diagram in P - V space with coexistence curve and several isotherms, including the critical. The cross-hatched region is considered supercritical.

In P - T space, we see only two remarkable features: the vapor pressure curve, indicating the conditions under which the vapor and liquid coexist, and the critical point, at which the distinction between vapor and liquid disappears. We indicate in this figure the critical isotherm $T = T_c$ and the critical isobar $P = P_c$. If the liquid is heated at a constant pressure exceeding the critical pressure, it expands and reaches a vapor-like state without undergoing a phase transition. Andrews and Van der Waals called this phenomenon the continuity of states.

In Fig. 1b, we see the same fluid in a pressure-volume representation. The region corresponding to the supercritical states in Fig. 1a is cross-hatched in Fig. 1b. Fig. 1b looks very different from Fig. 1a. The reason is that volume, as well as density, enthalpy, energy and entropy, are very different variables compared to pressure or temperature. Pressure, temperature, and also chemical potential, called *field variables*, are equal in coexisting phases, but volume is not, nor are density, enthalpy etc., called *density variables*. So the single vapor pressure curve corresponds to a coexistence curve with two branches, one for

the vapor and another for the liquid; the branches meet in the critical point where the difference between the two phases disappears. The critical isochore, $V = V_c$, is indicated. Coexistent vapor and liquid states have the same pressure but different molar volume, so that the isothermal compressibility is infinite throughout the two-phase region. The critical point is the last point in the two-phase region, and the only point in the one-phase region, where the compressibility is infinite. All supercritical isotherms have finite slope everywhere, but the slope may be very small (the compressibility very high) in the vicinity of the critical isochore. The critical isotherm, indicated in Fig. 1b, is the first isotherm to reach zero slope, indication of infinite isothermal compressibility and incipient instability. Thermodynamics dictates that along with the isothermal compressibility K_T , the isobaric heat capacity C_P and expansion coefficient α_P become infinite at the critical point. These properties are unusually large in the supercritical regime.

In summary: a fluid is critical when the difference between coexisting liquid and vapor phases disappears. At this point the isothermal compressibility of the one-phase fluid becomes infinite. In the supercritical region, a state of liquid-like density can transform into one of vapor-like density by tuning the pressure or the temperature, without the appearance of an interface. The further from the critical point, the easier it is to gently manipulate the density by tuning pressure or temperature. In the supercritical fluid, a range of intermediate-density states can be reached which are not available at subcritical temperatures and pressures.

The critical temperature T_c and pressure P_c are characteristic points for the fluid. Table 1 lists the critical parameter values for some fluids featured at this ASI.

TABLE 1. Critical parameter values for some frequently used SCFs

Fluid	P_c/MPa	$\rho_c/\text{kg m}^{-3}$	$T_c/\text{K (ITS-90)}$	Ref.
methane	4.592	162.7	190.56	[3]
ethane	4.872	206.6	305.33	[4]
carbon dioxide	7.377	467.6	304.13	[5]
water	22.064	322	647.096	[6]

3. Properties of a Supercritical Fluid

3.1. CRITICALITY AND CRITICAL EXPONENTS

The conditions of criticality of a one-component fluid are

$$\begin{aligned}(\partial P / \partial V)_T &\equiv -(\partial^2 A / \partial V^2)_T = 0 \\ (\partial^2 P / \partial V^2)_T &\equiv -(\partial^3 A / \partial V^3)_T = 0\end{aligned}\quad (1)$$

Here A is the Helmholtz free energy and V the volume. The first condition indicates that the limit of mechanical stability is reached, the second that the Helmholtz free energy remains convex.

The criticality conditions of a mixture are different from those of a pure fluid. The fluid mixture phase-separates *at finite compressibility* because it becomes *materially* unstable: it can lower its free energy by splitting into two phases of different composition. For a binary mixture of mole fraction x , the criticality conditions, in terms of the Gibbs free energy $G(P,T)$, are

$$(\partial^2 G / \partial x^2)_{P,T} = 0; \quad (\partial^3 G / \partial x^3)_{P,T} = 0 \quad (2)$$

Critical exponents indicate how fluid properties behave near a critical point. They are defined by Sengers and Anisimov, these proceedings. By inspecting Fig. 1b, one would guess that the simplest forms the special curves could take would be a parabola for the density or volume difference along the coexistence curve, and a cubic for the pressure along the critical isotherm as function of volume or density:

$$\begin{aligned}\rho_{liq} - \rho_{vap} &\propto |T - T_c|^\beta; \beta = 1/2 \\ P - P_c &\propto |\rho - \rho_c|^\delta; \delta = 3\end{aligned}\quad (3)$$

Van der Waals and Van Laar derived these exponent values in the 1890s for the Van der Waals equation; all cubic equations and most other equations of state used by engineers have these same critical exponents. Surprisingly, this is *not* the behavior of real fluids. Although real fluids all have the same critical exponents, these differ from those of Eq. (3). The experimental coexistence curve is flatter than a parabola, with a critical exponent $\beta = 0.325$, and the critical isotherm is much flatter than a cubic, with a critical exponent $\delta = 4.8$. Because engineering equations of state do not have the correct shape near a critical point, high accuracy cannot be expected at supercritical conditions. See Sengers and Anisimov, these proceedings, for correct alternatives.

3.2. PROPERTIES INTERMEDIATE BETWEEN THOSE OF VAPOR AND LIQUID

Since the supercritical fluid can assume densities intermediate between those of vapor and liquid, it makes sense to assume that its properties are also intermediate. This is true for many properties mentioned in this section, but not for all, see Section 3.3. We have chosen water as the example, because its thermodynamic and transport properties are very well known, and are available via user-friendly software [7].

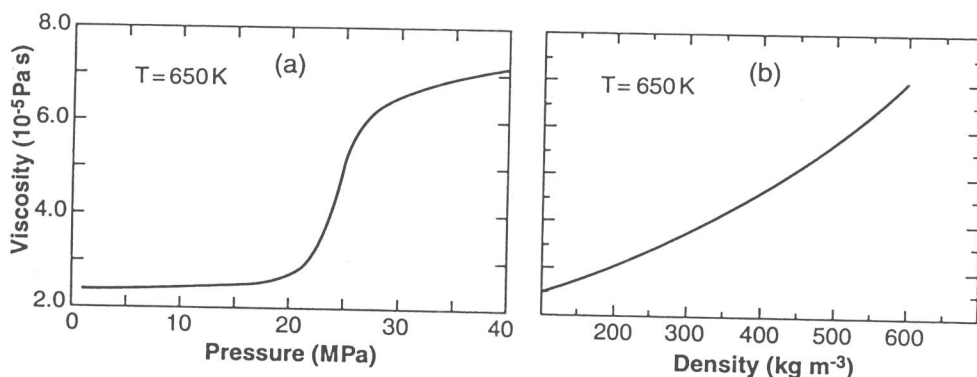


Figure 2. (a) The viscosity η of water on a supercritical isotherm as a function of pressure shows a sharp increase in the range of high compressibility. (b) On the same isotherm, the viscosity increases smoothly as a function of density.

In Fig. 2a, we show the viscosity of water along an isotherm 3 K above T_c as a function of pressure. Notice how abruptly the viscosity ascends from vapor-like to liquid-like values. In Fig. 2b, however, the viscosity is shown as a function of density along the same isotherm. Now the behavior is very simple and regular (the very weak critical divergence of the viscosity is not visible on this scale). The difference between Figs. 2a and 2b is due to the diverging compressibility. As the critical isochore is crossed, all simple functions of the density will show a sharp change when plotted against pressure: a trivial consequence of the large compressibility. When spectacular critical effects are reported in the literature, it is important to check against which variable the effect is plotted. Process engineers are better off avoiding this region of very large compressibility, because they can pressure-tune their process much better in regions where properties depend less steeply on pressure.

The viscosity of the supercritical fluid is far less than that of the liquid solvent, which is a great advantage in supercritical processing.

Many properties will behave smoothly with density. Examples are the coefficient of self-diffusion, the enthalpy, entropy, and dielectric constant. The latter three properties do have a subtle critical anomaly: a weak divergence of their first temperature derivative.

In Fig. 3a we plot the dielectric constant of water along the 25 MPa isobar as a function of temperature. It drops from a value of 80 near the freezing point to about 20 near 600 K. In the supercritical range, however, the dielectric constant undergoes another steep drop as the critical isochore is crossed. The critical-point value of the dielectric constant is about 4, and on the 25 MPa isobar it falls below 2 beyond 700 K.

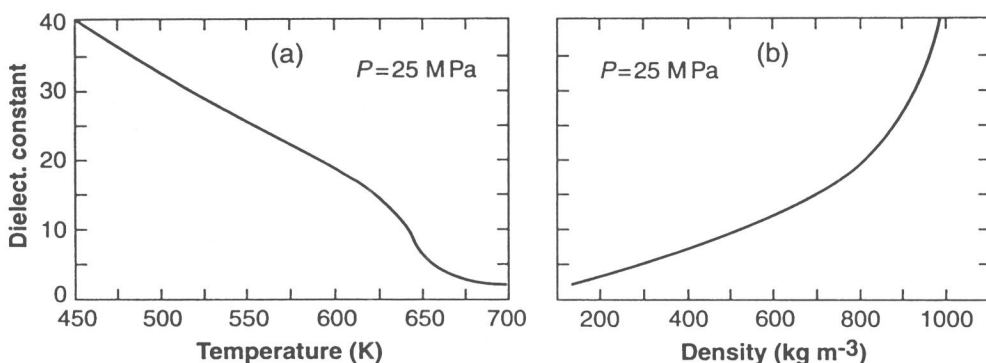


Figure 3. The dielectric constant of water along the 25 MPa isobar (a) as a function of temperature, where there is a steep drop just above the water critical temperature; (b) as a function of density, where the decrease is gradual.

In those conditions, water is a low-dielectric fluid, a poor solvent for electrolytes and a good solvent for organics. In Fig. 3b, the dielectric constant is plotted versus density along the same 25 MPa isobar. The steep drop seen near the critical point in the temperature dependence in Fig. 3a, which is due to the diverging expansion coefficient, is replaced by a smooth and gradual decrease in the density representation in Fig. 3b.

In conclusion: the properties of supercritical fluids are simplest to understand and describe as a function of the density. Unfortunately, engineers prefer measuring and controlling pressure over density. If they need the density, they may derive it from an equation of state. Engineering equations of state, however, are usually optimized for describing vapor pressures and distribution coefficients of fluid mixtures, see Sandler, [8]. Their capability of describing density is limited, and their analytic behavior at the critical point is incorrect. Inadequate knowledge of the density is a weak spot in many of the experiments performed in supercritical solvents.

3.3. PROPERTIES NOT INTERMEDIATE BETWEEN THOSE OF VAPOR AND LIQUID

It is obvious that properties such as isothermal compressibility, isobaric expansion coefficient and heat capacity, which display an extremum near the critical density, cannot be intermediate between those of vapor and liquid. As an example, we show in Figs. 4a and 4b the isobaric heat capacity of supercritical water along an isobar. The sharp spike in Fig. 4a, with temperature as the abscissa, is the equivalent of the broad maximum in Fig. 4b, with density as abscissa.

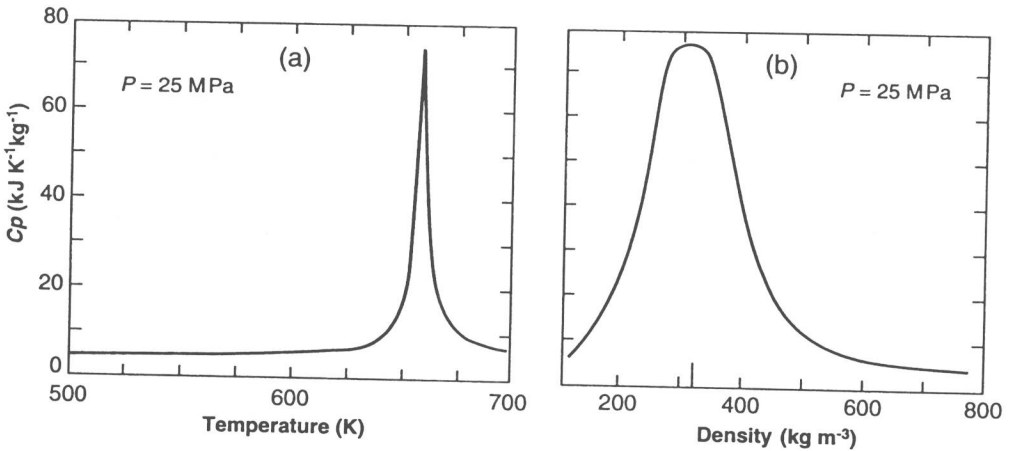


Figure 4. The isobaric heat capacity of water on a supercritical isobar (a) as function of temperature; (b) as function of density.

The diverging expansion coefficient is the reason that a small change in temperature, a field variable, causes a huge density change. Even for properties that reach very large values, the behavior is easier to understand and characterize as a function of a density, rather than a field variable.

The thermal conductivity Λ of pure fluids diverges at the critical point about half as strongly as the isobaric heat capacity (Figs. 5a and 5b), and therefore the thermal diffusivity, $\Lambda/\rho C_p$, goes to zero.

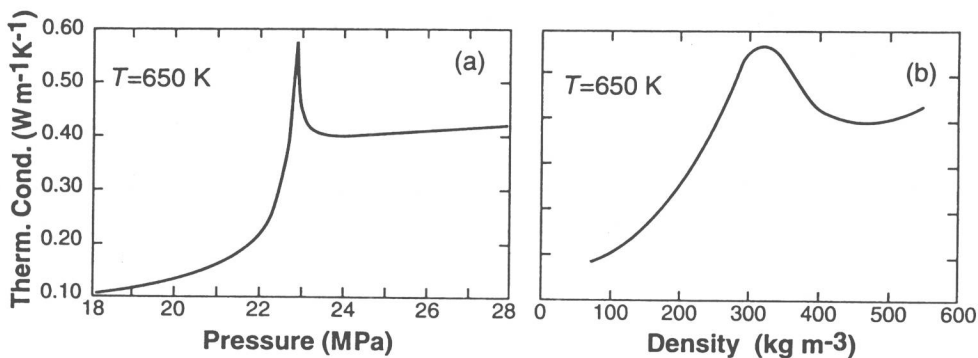


Figure 5. The thermal conductivity of water along supercritical isotherms. (a) plotted versus pressure (b) plotted versus density.

The coefficient of self-diffusion does not appear to have an anomaly near the critical point. For the engineer, however, the mutual diffusion coefficient is the more important property. The binary diffusion coefficient approaches zero at the mixture critical point ("critical slowing-down"). In dilute mixtures, however, the decrease of the binary diffusion coefficient is not seen until the critical line is approached very closely. For many practical purposes, such as supercritical extraction and chromatography, the mixture is dilute, and it can be assumed that the coefficient of binary diffusion is intermediate between that in the vapor and that in the liquid. Since the diffusion coefficient decreases roughly inversely proportional to the density, diffusion in supercritical solvents is much more rapid than in liquid solvents, thus increasing the speed of diffusion-controlled chemical processes.

3.4. STRUCTURE OF SUPERCRITICAL FLUIDS

3.4.1. The correlation function

The number density around any given molecule in a fluid is not constant, but fluctuates in time and varies with the distance from the molecule. The average, static structure of a fluid is known from X-ray and neutron scattering experiments (see Cummings, this ASI) and theoretically from integral-equation methods and from computer simulation (see Cummings, Tucker, this ASI). The structure is described by means of the correlation function $H(r)$. For spherical molecules, $\Delta H(r)$ measures the excess or deficit of the local density compared to the average density, as a function of the distance r from the center of a chosen molecule. The correlation function thus represents the average correlation in density between two points at distance r in the fluid. In a binary fluid mixture, three different correlation functions

can be defined, for two kinds of like pairs and for the unlike pair [1], [2].

The correlation function equals -1 as long as r is smaller than the diameter of the hard core, or if it is well within the Lennard-Jones diameter σ . It falls off to 0 for large r . Fig. 6a shows the behavior of the correlation function in supercritical Lennard-Jonesium, at $T^* = kT/\varepsilon = 2$, about 30% above the critical point; ε is the Lennard-Jones well-depth and k Boltzmann's constant. It was calculated by De Boer in 1949, and is reported in [9].

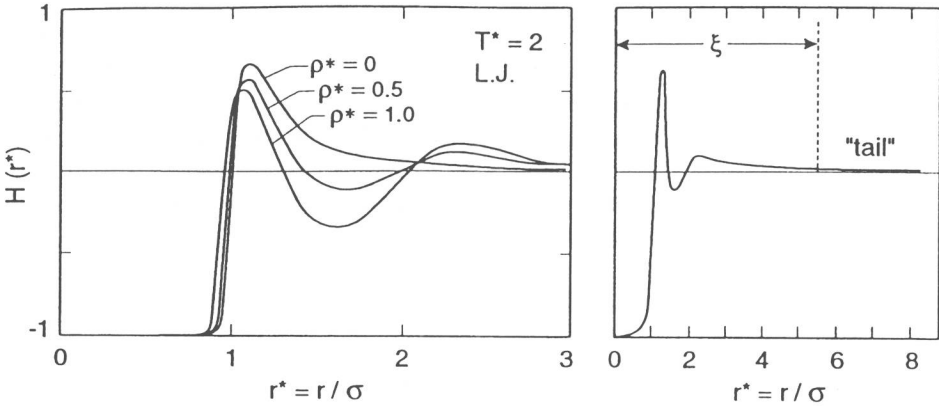


Figure 6. (a) About 30% above the critical temperature, the correlation function of 1-component Lennard-Jonesium [9], at a low density $\rho^* = 0$: one nearest- neighbor peak; at a density about 30% higher than critical $\rho^* = 0.5$: a second maximum; and at a density near close-packing $\rho^* = 1$: pronounced oscillations. (b) schematically, in a fluid near the critical point. (Reprinted from [2] Fig. 3, copyright 1994, with kind permission from Kluwer Academic Publishers)

In the vapor phase, $\rho^* = 0$ in Fig. 6a, with $\rho^* = \rho N \sigma^3$, N Avogadro's number, and ρ the molar density, molecular attraction induces an increase in local density near a chosen molecule.

In the dense liquid, $\rho^* = 1$ in Fig. 6a, several shells of molecules pack around a central molecule, leading to oscillations in $H(r)$ before it decay to 0. What happens near the critical point is described in the next section.

3.4.2. Critical fluctuations

A very striking effect is critical opalescence: a near-critical fluid looks like a dense fog. This effect implies that there must be fluctuations in the refractive index and therefore in the density over ranges comparable to the wavelength of light, hundreds of times the molecular size. The correlation function thus assumes a long tail, decaying very slowly to the average of zero, see Fig. 6b. In fact, the integral of the correlation function diverges, because it is proportional to the isothermal compressibility according to the exact relation

$$RT\rho K_T = 1 + \int_0^{\infty} H(r) 4\pi r^2 dr \quad (4)$$

with R the gas constant and ρ the molar density. It is said that the correlation function becomes *long-ranged* at the critical point. The range over which the tail extends is called the *correlation length*. The closer to the critical point, the longer the correlation length. The critical fluctuations are a consequence of the diverging compressibility, and thus a direct signature of criticality.

In Table 2, typical values of the correlation length, and of the ratio of the compressibility to that of an ideal gas at the same density, are shown for carbon dioxide and water. Parameters and asymptotic power laws are those from Ref. [10]. The correlation length is to be compared with a molecular dimension, ξ_0 , which is 0.15 nm for carbon dioxide, and 0.13 nm for water, of the order of the average molecular radius. The second and third columns show how large the ratio ξ/ξ_0 becomes in fluids and the Ising model as the critical point is approached. In two dimensions, fluctuations are even more pronounced.

TABLE 2. Values of the compressibility and the correlations length at the critical density at various distances from T_c

Ising and fluids			CO ₂			water		
$\frac{T-T_c}{T_c}$	ξ/ξ_0	ξ/ξ_0	$T-T_c$	$K_T/K_{T,id}$	ξ	$T-T_c$	$K_T/K_{T,id}$	ξ
	2D	3D	(K)		(nm)	(K)		(nm)
10^{-3}	1000	78	0.3	989	11.6	0.65	1394	10.1
10^{-2}	100	18	3.0	57	2.7	6.5	80	2.3
10^{-1}	10	4.3	30	3.3	0.63	65	4.6	0.56

The $1/r^6$ attractive potential decreases by 98% if the distance increases from 1 to 2 molecular diameters, that is, from 2 to 4 times ξ_0 . Near the critical point, the correlation length far exceeds the range of the molecular forces. This dominance of the fluctuations over the particular molecular interactions is the reason for critical-point universality.

At a temperature 10% above the critical point in three dimensions, the compressibility is still higher than that of a perfect gas at the same density, but the correlation length is only about four times the molecular radius and thus barely exceeds the range of molecular interaction. At this or at larger distances from the critical point, a clean division between long-range and short-range effects (if such a division exists) can thus no longer be made.

A fluid mixture near a critical point is opalescent just like the one-component fluid. All its correlation functions develop long tails. At a given distance from the critical point,

however, there is only one correlation length, so all correlation functions decay in the same way. See [1], [2], and Sengers and Anisimov, these proceedings.

3.4.3. Average short-range environment

Since the critical temperature of fluids is of the order of ε/k , the attractive energy is significant enough to cause a first peak in the correlation function even at low densities. The height of the first peak is largest *below* the critical density. If we speak about *local* environment, we refer to this first peak, which extends roughly from 1 to 1.5 diameters, Fig. 6a.

A solute may have considerably higher critical temperature and a much deeper potential well. Thus a solute molecule may attract solvent molecules more strongly than the latter attract each other. Therefore the solvent-solute and the solute-solute first peaks around a solute molecule may be quite pronounced, indicating considerable enhancement of the local solvent (and solute) density around a solute molecule. Again, this effect appears to be largest below the critical density.

Contrary to the tail of the correlation function, which is directly connected with the strong divergence of the compressibility, the first peak of the correlation function, as pointed out by Stell and Høye [11], bears a subtle relation to the internal energy. The latter property behaves smoothly at the critical point, but its first temperature derivative, the heat capacity C_V , has a weak divergence.

Tucker (these proceedings, and [13]) reasons that in addition to the local density enhancement due to the direct intermolecular interaction, an additional enhancement must be due to the critical-fluctuation induced long-range inhomogeneity of the fluid.

In a supercritical fluid, the departures of local density and composition from the bulk average, present over a large range away from the solvent's critical point, have an important effect on supercritical solubility. Mean-field (Van der Waals-like) equations of state ignore this effect, with serious consequences for their accuracy.

The environment of a solute molecule or reactant is probed by spectroscopic studies of light emitted or absorbed by the solute or by reacting species (See Johnston, these proceedings). Much experimental evidence has been published of local density enhancement around such solutes or species.

3.4.4. The instantaneous environment

The first peak of the correlation function represents a statistical *average* of the distribution of neighbors around a chosen molecule. The *instantaneous* short-range environment (that seen in a snapshot) of a solute molecule in a supercritical fluid may be an important factor in solvent-influenced chemical reactions. At the present time, the principal source of information on the instantaneous structure is computer simulation. One such simulation was done by Mountain in 3-dimensional supercritical water, about 10% above the critical temperature [12]. Snapshots of the fluid for densities from well above to well below the