

Phase transformations in liquids and the liquid–gas transition in fluids at supercritical pressures

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Abstract. It is an experimental fact that in the neighborhood of melting curves, including those measured at above-critical pressures and temperatures, all fluids have some short- and intermediate-range order and their excitation spectra contain high-frequency transverse waves. At high pressure, both smooth and sharp first-order phase transitions involving changes in the liquid structure and properties can occur between various liquid states. However, at sufficiently high temperatures, any liquid loses its identity and turns into an unstructured dense gas in which only longitudinal waves can propagate. We discuss theoretical and experimental evidence for the existence of a boundary between a ‘solid-like’ melt and a dense gas at supercritical pressures.

Keywords: supercritical fluids, high pressures, phase transformations, dynamical crossover

Approaches treating a liquid as a dense nonideal gas have been prevalent since the early 20th century and even now, with their mathematical language updated, are to some extent the basis of the theory of liquids — and quite understandably so, because a liquid, similarly to a gas, possesses fluidity (which is the origin of the common term, ‘fluid’). A liquid, like a gas, has a zero static shear modulus (which is in fact why it flows) and shows no long-range order in its structure. In simple van der Waals type models, a liquid and a gas are described by the same equation of state, such that beyond certain pressures and temperatures they become indistinguishable.

On the other hand, it has been realized in recent decades that a liquid at a temperature close to the melting point has much more in common with a solid than with a gas. Liquids and their corresponding crystals are close in density. When cooled at a sufficient rate, a liquid continuously transforms into a glassy solid. At sufficiently high frequencies, liquids exhibit nonzero shear strength, with the result that many physical quantities such as heat capacity, thermal conductivity, and electrical conductivity vary very weakly as the crystal is melted, despite the loss of the long-range order. Of particular interest are ‘solid-state’ heat capacity values of liquids at temperatures close to the melting point; for most

polyatomic substances, the heat capacity per particle of a liquid is close to $3k_B$, where k_B is Boltzmann’s constant. Despite the absence of long-range order in the structure, many liquids have well-structured long- and intermediate-range orders.

As a consequence, a range of phenomena occur that until recently were not even suspected to be possible for liquids. In all liquids, there are intrinsic excitations of the transverse phonon type, which ensure a nonzero shear modulus at high frequencies. The heat capacity of a liquid is well described by the Debye model, originally proposed for describing the behavior of crystals. In many liquids, varying the temperature and pressure causes phase transitions (both sharp first-order and smooth) involving dramatic changes in the material structure and properties. And finally, it was recognized quite recently that in the supercritical region, liquids and gases retain their distinction and there is a corresponding dynamic crossover line between them.

Supercritical fluid is a commonly accepted term for the state of a substance at temperatures and pressures exceeding the critical values (T_{crit} , P_{crit}). In fact, this concept is of little or no constructive value, and the only thing this definition says is that no first-order phase transition (boiling) can be observed on the isobars and isotherms of the system. In reality, far from the critical point, neither the structure nor properties of the system change in any way at all at the intersection of the lines $T = T_{\text{crit}}$, and $P = P_{\text{crit}}$, and in this sense a supercritical fluid does not differ in any way from its ‘subcritical’ counterpart [1]. We note that close to the melting point, all liquids, even well above the critical temperature, retain their well-defined close-range ordered structure, which can either remain virtually unchanged (as exemplified by liquid argon [2]) or undergo a strong transformation (for example, in the case of water [3]).

The transformation of a close- and intermediate-range ordered structure under pressure can occur discontinuously as a result of a first-order phase transition. The first experimental example of a sharp transformation in a melt is the semiconductor–metal transition in liquid selenium [4]. The most spectacular example of a first-order transition in a liquid is the transformation occurring in phosphorus [5, 6] (Fig. 1). There is a range of other candidate materials exhibiting sharp transitions in liquids: nitrogen, bismuth, tellurium, sulfur, AlCl_3 , AsS , P_2O_5 , CdTe , overcooled water (hence the possible reason for the plethora of anomalies in water), overcooled liquid silicon, etc. At the same time, in most melts, pressure-induced changes in the properties and close-range ordered structure occur smoothly. Interestingly, both sharp and smooth transitions in melts can lead to a change (either increase or decrease) in viscosity by three to four (!) orders of magnitude [7]. As a result, some systems (Se,

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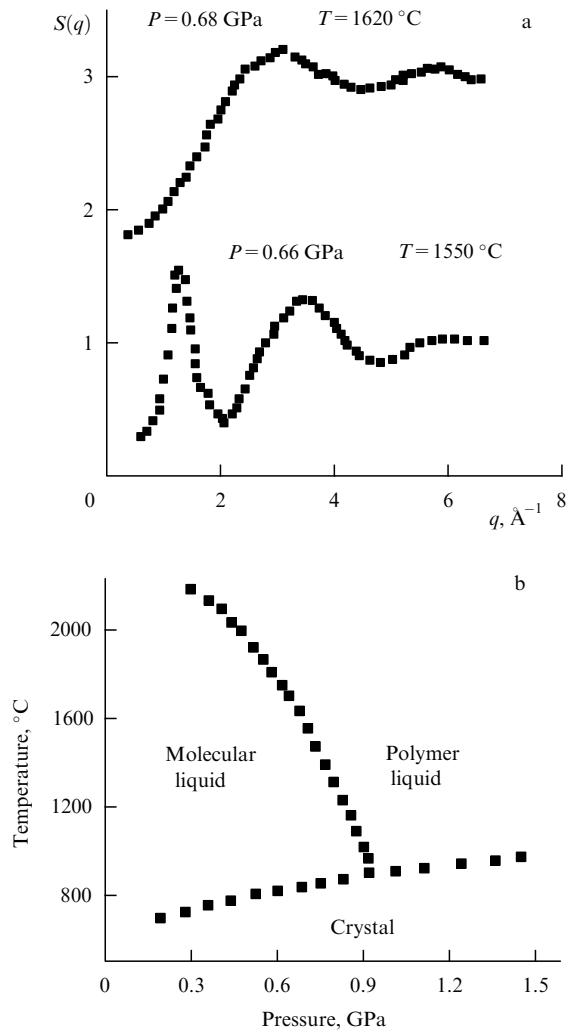


Figure 1. (a) Structure factors of two liquid phosphorus modifications [5] and (b) phosphorus phase diagram demonstrating a first-order phase transition to a liquid state.

P, B_2O_3 , $ZnCl_2$, As_2S_3 , $GeSe_2$) allow the growth of large crystals under pressure (which is difficult under normal conditions), whereas others (AsS , P_4Se_3), on the contrary, allow the easy vitrification of the melt (which is virtually impossible under normal pressure).

The high-frequency shear strength and the possibility of transverse wave propagation in viscous liquids (such as honey, glycerin, and boron oxide melt) have been known since the mid-20th century. In such liquids, shear strength can be and indeed is easily observed by ultrasound and Brillouin scattering methods at frequencies ranging from a few kHz to a few GHz [8, 9]. In the last two decades, an indirect method, the observation of positive sound dispersion, has been used to discover transverse excitations in low-viscosity liquids at terahertz frequencies (see, e.g., Ref. [10]). In these studies, inelastic X-ray scattering was also used. Quite recently, the same technique was used to directly observe transverse excitations in the melts of Ga, Sn, Fe, Cu, Zn, etc., at terahertz frequencies [11–13] (Fig. 2). Together with a certain amount of close-range order, high-frequency shear strength is conserved in melts close to the melting curve at superhigh pressures at temperatures well above the critical value [14].

Thus, all liquids have a certain amount of close- and intermediate-range order and contain high-frequency trans-

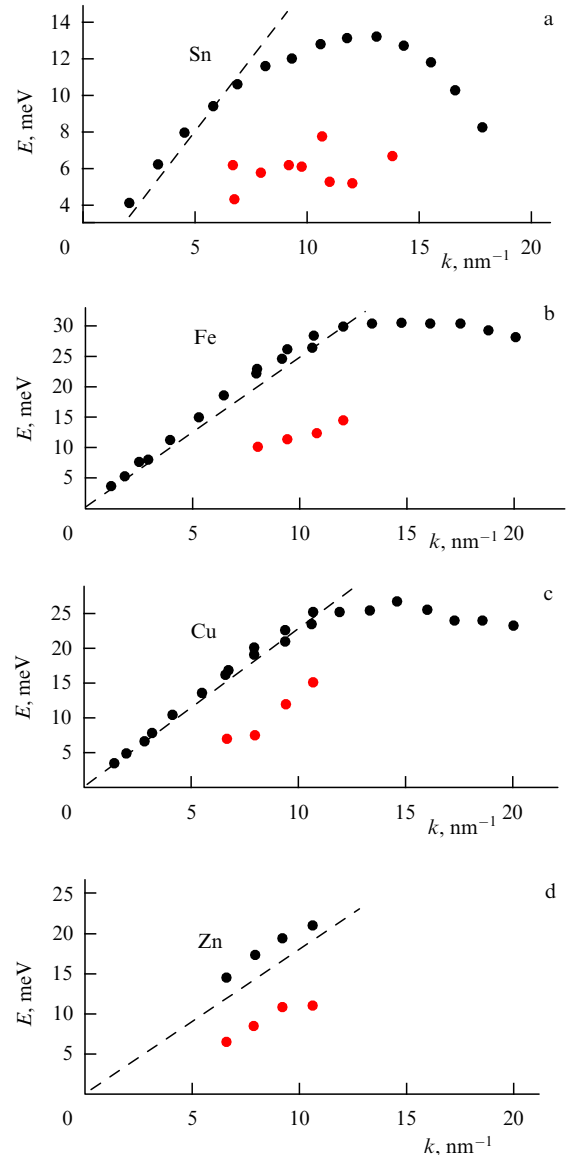


Figure 2. (Color online.) Measured dispersion curves of longitudinal and transverse excitations in liquid metals [11–13]. Upper lines indicate longitudinal branches and lower lines (red circles) indicate transverse branches. Dotted lines show tilted dispersions corresponding to long-wavelength sound velocities.

verse waves in their excitation spectra, close to the melting curve at pressures up to supercritical. Importantly, smooth or sharp transformations involving changes in structure and properties can occur between various states of liquids. At the same time, when intensely heated, all liquids should lose their individuality and make the transition to a structureless dense gas in which only longitudinal waves propagate. In recent years, experimental confirmation of this has been found for both the structure and the dynamics (see, e.g., Ref. [15]).

The question naturally arises as to the boundary between the liquid and the dense structureless gas on the phase diagram. In 2012, we proposed defining this boundary as the line where nonlocalized transverse vibrations cease to exist in the fluid [1, 16–19]. On this Frenkel line (as we called it), the motion of particles changes from a mixture of vibrations and jumps to ballistic-collisional motion, and the relaxation time of the liquid becomes comparable to the shortest period of transverse vibrations. As a result, most of the system proper-

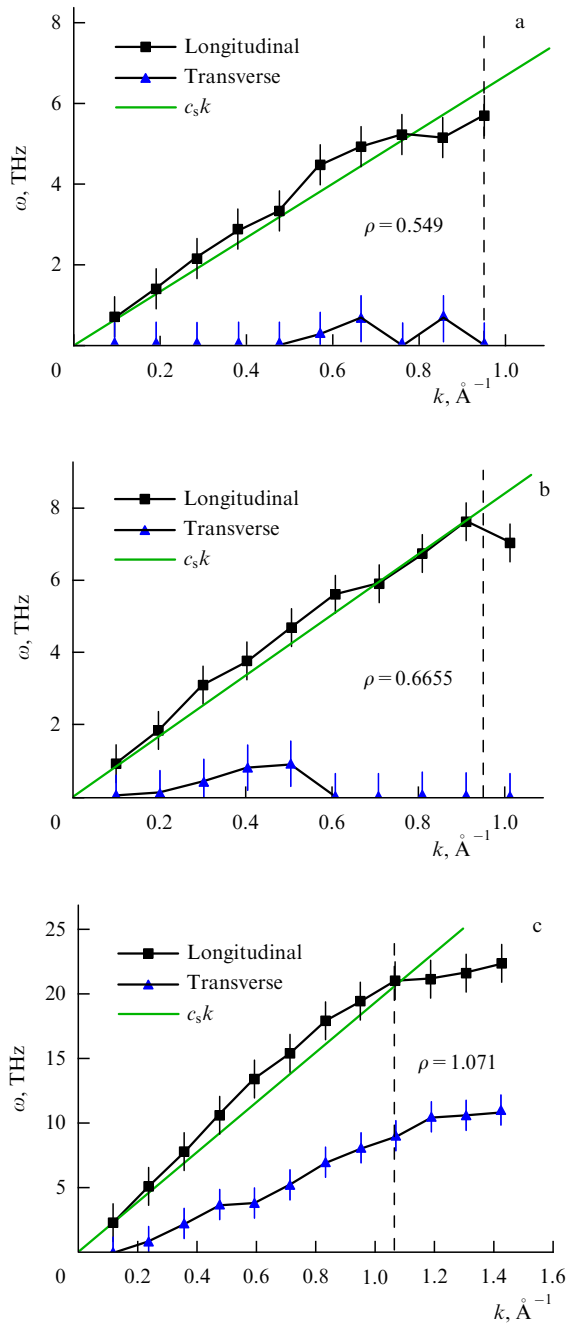


Figure 3. Dispersion curves for longitudinal and transverse excitations in argon fluid simulated by molecular dynamics [28]. Data are presented for three density values in reduced units (density of 1 for argon corresponds to 1.71 g cm^{-3}).

ties (viscosity, diffusion coefficient, thermal conductivity, speed of sound, structural characteristics, etc.) show a crossover behavior. The fact that all transverse modes disappear from the excitation spectrum has the consequence that the heat capacity per particle becomes $2k_B$ ($3/2k_B$ and $1/2k_B$ from the respective kinetic and potential energies). This dynamic boundary between the liquid and the gas exists for an arbitrarily high pressure (until quantum effects become significant).

The fact that increasingly higher-frequency modes leave the excitation spectrum of the fluid allows successfully using a simplified Debye model with a quadratic density of states to properly account for the change in the heat capacity from

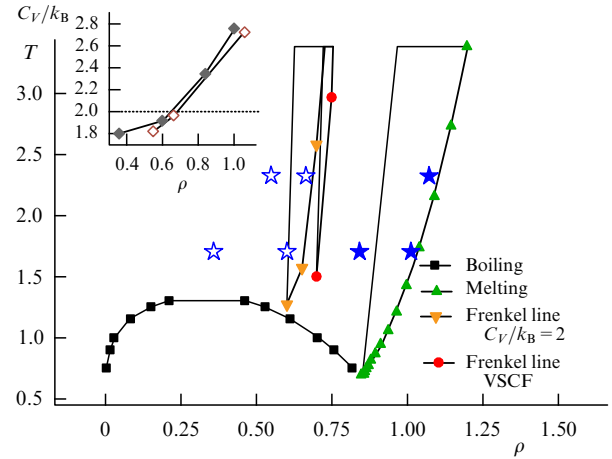


Figure 4. Density-temperature phase diagram of argon (in reduced units for both axes). Shown are Frenkel lines calculated from two criteria: $C_V = 2k_B$ and the disappearance of velocity autocorrelation function oscillations [16–20]. Unfilled and filled stars indicate those phase diagram points for which transverse excitations are respectively present or absent in the spectrum [28] (see Fig. 3). The insets show the behavior of the isochoric heat capacity on isotherms.

$3k_B$ to $2k_B$ on the Frenkel line with increasing temperature or decreasing pressure for several dozen model and real liquids [20, 21]. The further decrease in the heat capacity per particle to the gas value $1.5k_B$ occurs due to increasingly higher-frequency modes disappearing from the spectrum, because the longitudinal wavelength (in fact, the density modulation) cannot be less than the mean free path between particle collisions [20, 21].

Interestingly, a convenient criterion for the Frenkel line in molecular dynamics calculations is the disappearance of oscillations of the velocity autocorrelation function (VACF) in the course of time [18]. Physically, such oscillations are present because, on average, more than half of the particles change the sign of the projection of their acceleration, and a considerable part of them (15–20%) changes the sign of their velocity projection (which exactly corresponds to the vibrational–hopping regime of their motion).

Over the last four years, our group has used a range of criteria in computer simulations to determine the Frenkel line location both for a large number of model systems [16–19, 22, 23] and for real fluids (water, carbon dioxide, methane, iron, etc.) [24–27]. It turns out that all criteria yield nearly the same positions for the corresponding lines. Furthermore, our recent computer simulations have shown that transverse excitations indeed exist in fluids below the Frenkel line and are absent above it [28] (Figs 3 and 4). The Frenkel line has a shape similar to the melting line, with temperatures on the former greater by a factor of 2–4 than the corresponding melting points at the same pressure.

Over the last two years, the first experimental evidence for the existence of Frenkel lines in neon and methane fluids has been obtained by our group in collaboration with colleagues from the USA and Great Britain. For the methane fluid, X-ray diffraction studies have been conducted using a synchrotron source at room temperature in the pressure range 0.5–35.0 kbar. Structural characteristics (the height and position of the structure factor peaks, the coordination number, etc.) were found to exhibit a quite sharp crossover between 6 kbar and 7 kbar. Molecular dynamics calculations confirm that the Frenkel line at a given temperature intersects

the room temperature isotherm at 6.5 kbar. Experiments on the methane fluid also revealed two structural crossovers, at 1.5 kbar for room temperature and at 2.5 kbar for 500 K, in agreement with the predicted values. Also, Raman measurements in the methane fluid at the same pressures reveal a sharp crossover in the pressure dependence of the vibron frequency.

We also note that methane, like water and carbon dioxide, finds extensive application in supercritical technologies, which use fluids at supercritical pressures to ensure a high speed of chemical reactions or increase the solubility rate of various substances due to the high diffusion coefficient in supercritical fluids; this property coexists with their fairly high density.

Supercritical technologies are currently used at pressures not exceeding 1 kbar. We also note that along the Frenkel line, the density and diffusion coefficient of the fluid increase with pressure (the former considerably so), the viscosity is close to its minimum value at a given pressure, and no wetting problem exists. It can be hypothesized that many technological characteristics of supercritical fluids, such as the solving capability and chemical reaction rates, also have maximum values in the vicinity of a given ‘dynamical’ line, strongly suggesting the use of supercritical technologies in the yet unexplored range of supercritical pressures from a few thousand to a few tens of thousand atmospheres (1–30 kbar) [25, 29].

A point to note is that under extreme parameters, the technological characteristics of supercritical fluids can also be uniquely high. For example, it is known that at pressures of 20–40 kbar and a temperature of 1000 °C, water fluid dissolves silver, stainless steel, and diamond (the former two rapidly, the last at an appreciable rate). Superhigh pressure clearly allows the use of nonconventional ‘cryogenic’ fluids. Thus, for methane and nitrogen fluids, the Frenkel line lies in the room temperature region at the respective pressures of 1.5 and 2.0 kbar. We note that for these parameter values, the density of these fluids is almost 2.5 times larger than their critical point density and that their viscosity is sufficiently low.

Hence, low-cost methane and nitrogen can be used in many supercritical technologies at relatively mild parameters: room temperature and pressures of 1.5–3 kbar. It is also likely that the technological characteristics of fluid CO₂ can be considerably improved at supercritical pressures. The Frenkel line for CO₂ corresponds to a pressure of 3.5 kbar at temperatures of 300–400 °C and to pressures of 9–10 kbar at 800–1000 °C. How large the solving and extracting capabilities of carbon dioxide are under these parameters is still not known.

In conclusion, we recall L D Landau’s famous debate speech after a talk by Ya I Frenkel at a session of the USSR Academy of Sciences in 1937. Landau advocated the then most common view that “gas and liquid are rather vague concepts with no distinct boundary between them.” Still, he concluded his speech by admitting that a liquid can have some amount of definitive order (weak anisotropy). However, he noted, “at high temperatures a completely isotropic modification should exist,” thereby suggesting the existence of a temperature at which “the liquid discontinuously becomes weakly anisotropic—which is not observed.” That is, Landau actually admitted the existence of the Frenkel line as a structural crossover, but noted that no one had yet observed it. The dynamic crossover could not be discussed at

the time: it was only 50–60 years later that short-wavelength transverse excitations were discovered experimentally in liquids.

It can be concluded that the distinction between liquid and gas exists for any external parameters and is of a more fundamental nature than has been believed. Furthermore, the analysis of various states of matter from the standpoint of the dynamics of its component particles allows understanding how the problem of the theoretical description of liquids originated. Solids and gases are, in a certain sense, ‘pure’ aggregate states. In solids (crystals and glasses), the motion of particles is purely vibrational; in gases, it is purely ballistic-collisional. From a physics standpoint, this is because the kinetic energy of the particles in solids is much less than their potential interaction energy and hence much less than the barrier energy between various potential minima, whereas just the opposite occurs in a gas. When viewed from this perspective, a liquid is not a ‘pure’ state of matter but rather a ‘mixed’ aggregate state—a transitional state from solids to gases. In any liquid, both types of particle motion—vibrational and ballistic—are present, whose relative content varies smoothly with varying external parameters. In a certain sense, it is for this reason that the microscopic dynamics of a liquid state defy explanation.

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