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Supercritical Casimir effect in carbon dioxide

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ABSTRACT

We present the first measurement of surface forces across supercritical carbon dioxide. An important finding is that long-range attractive surface forces are detected not just near the critical point, but along the supercritical extension of the coexistence line, which is commonly discussed as the supercritical ridge.

Using a precisely adjustable model slit pore, our experiment can measure the change of thermodynamic potential together with changes in refractive index (mass density) in the confined CO_2. The model slit pore is realized between two atomically smooth mica surfaces in a specially designed high-pressure surface forces apparatus. Our data suggest that thermal fluctuations of higher density are selectively depleted, which results in observation of a time- and space-averaged density reduction in the confined film. Direct observation of this confinement effect has consequences for theoretical understanding as well as technological applications of CO_2 in porous materials.

In the presence of small amounts of an acrylate solute (polyethyleneglycol-dimethacrylate), we found that multiple stable menisci of solute can be created between the surfaces and stretched out several micrometers. These liquid-liquid bridges are observed as an apparent birefringence effect. We demonstrate the critical character of the phenomena and discuss our findings in terms of a (super)critical Casimir effect.

1. Introduction

Supercritical CO_2 is an interesting solvent because it is non-flammable, chemically inert and non-toxic. It exhibits liquid-like density, gas-like diffusivity and its surface tension is very small. Supercritical CO_2 has great technological potential and is already found in a range of applications such as environmentally friendly solvent [1,2], in polymer syntheses [3], in materials processing [4,5], for extractions [6], tissue engineering [7], microelectronic processing. Some fundamental questions about supercritical carbon dioxide have already been raised and some answered [8,9]. This includes the microscopic and mesoscopic structure, which is believed to be responsible for much of its remarkable properties [8]. Often, supercritical CO_2 is used in confined geometries [10,11]; for example, inside porous materials. For a better fundamental understanding of confinement effects elaborate experiments are necessary. The here presented direct measurement of surface force across confined supercritical CO_2 is such an experimental approach. It has however not been previously possible due to the many technical difficulties.

At the critical point (p_c, T_c) the energetic distinction between liquid and gas disappears in the framework of thermodynamics. Density fluctuations at all length scales arise since the isothermal compressibility diverges. It was established that the compressibility has a local maximum along the supercritical extension of the coexistence line, clearly in absence of a first order phase transition [12]. The thermo-dynamical significance of the supercritical ridge is thus arguable. For example, Herbert Callen wrote in his text book on thermodynamics, that the extension of the coexistence curve into the supercritical state is "non-physical" [13].

There is yet increasing experimental evidence that the supercritical ridge demarcates a region with peculiar properties that attract attention from views of theory and application alike. This ridge collocates with a steep density gradient $d\rho/dp$ in the density–pressure phase diagram. Density fluctuations, as a consequence, seem to be enhanced along the ridge as suggested by small angle X-ray scattering (SAXS) or small angle neutron scattering (SANS) experiments [14,15]. The correlation length increases toward the critical point while it has a local maximum along the supercritical ridge [16].

Under confinement, the phase diagram may shift due to the amplified effect of interface energetics [11]. Besides this effect of interfacial energy, the confining walls also impose geometrical boundary conditions that are known to modify the fluctuation mode spectrum. The associated change of free energy depends on surface separation and can be macroscopically measured as a surface force.

For the historically original case of quantum vacuum fluctuations, which exhibit a modified mode spectrum between

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Table 1
The key specifications of the new pressurized eSFA.

	Range	Precision	Stability
Pressure, p	0.02 to 170 bar	0.007 bar	0.002 bar/h
Temperature, T	−20 to 60 °C	0.008 °C	0.002 °C/h
Surface separation, D	0 to 14 µm	0.03 nm	0.6 nm/h

conducting walls, this energetic effect was predicted by Casimir [17]. Later Fisher and de Gennes pointed out the universality of this energtic effect and extended it to fluctuating critical fluids; resulting in the so-called *critical* Casimir force [18]. The existence and bivalence (attractive or repulsive) of the *critical* Casimir force was experimentally verified in binary fluid (water/lutidine) using a colloidal probe [19]. The water–lutidine binary fluid has indeed served as a key model system for most of the fundamental and experimental work done in this field.

Supercritical CO_2 is a remarkable solvent. Motivated by technological applications, the solubility of various solutes in bulk supercritical CO_2 was investigated since the pioneering gas chromatography work in 1962 [20]. The solubility in supercritical CO_2 is often higher than expected from simple thermodynamic predictions; an effect explained at the microscopic level by special effects like local clustering [8,21,22].

In the here used surface forces apparatus technique [23], two mica surfaces confine a very thin fluid film and the change of thermodynamic potential with adjustable film thickness can be studied via the sensitive measurement of the surface interaction force. The surface separation, D, can thereby be precisely controlled and monitored with sub-Å resolution. From a fundamental physical point of view, a continuous transition from bulk to quasi 2D-fluid films can be realized with this instrument, while film thickness, refractive index (i.e. film density) and surface force (i.e. thermodynamic potential) are measured simultaneously and in absolute terms.

2. Materials and methods

2.1. Measuring surface forces

The here used extended surface forces apparatus (eSFA) was previously described in detail [24]. In summary, the apparatus consists of a miniature force measurement device embracing two cylindrically shaped glass substrates, which hold and shape the two model mica surfaces as illustrated in Fig. 1(a). The upper glass substrate is connected to a permanent magnet and together they are attached to a compliant spring, k = 1750 ± 70 N/m. The spring deflection is used as a measure for the surface force. The mica surfaces are asymmetrically back-silvered (25 nm Ag lower surface and 160 nm Ag upper surface) and thus constitute a reflective optical resonator for the white-light interferometric distance measurement as seen in Fig. 2(a). The miniature eSFA can be slid into a tight autoclave, which is closed with a flange providing an optical window. A low-resistivity copper coil generates the magnetic field required to deflect the one magnetic surface and therefore control the surface separation, D (i.e. slit dimension) at sub-nanometer precision. A pressurization vessel serves at preconditioning the clean carbon dioxide to the desired pressure, p and temperature, T. Temperature control is realized using Peltier heat exchangers [25]. Some key specifications of the eSFA are summarized in Table 1. We had to slightly modify the system from the one described in [24]. Namely, all EPDM o-rings that were in contact with CO_2 were replaced by Viton o-rings, and, the titanium autoclave connectors – formerly sealed with Loctite 577 – were weld-sealed.

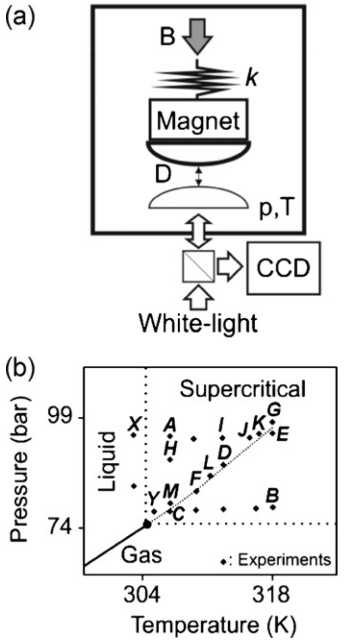

Fig. 1. (a) Schematic setup of the surface forces apparatus [24] as used in this work. One of two curved mica surfaces is attached to a permanent magnet for controlled deflection in an external magnetic field, B. Knowledge of the spring constant, k, is necessary for the surface force measurement. The separation between the surfaces, D, is measured at sub-Angstrom resolution using white light interferometry. (b) The PT-phase diagram of CO_2 with a selection of loci visited in this work designated by letters ***A*** through ***M*** and ***X***, ***Y***.

In this work, we have visited a total of 25 different loci in the bulk phase diagram of CO_2. Although we consider the full data set, only a selection of particular loci shall be designated with a letter for convenience as listed in Table 2 below:

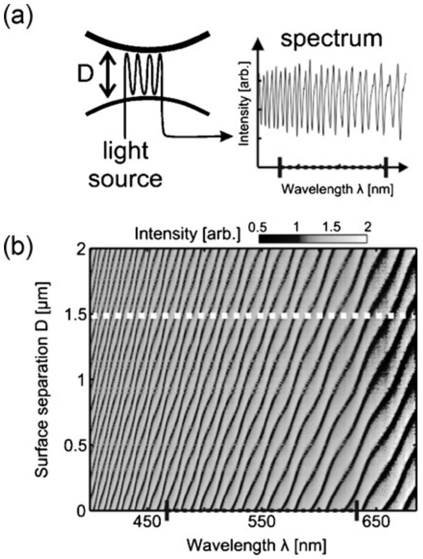

Fig. 2. (a) White-light interferes destructively in a Fabry-Pérot resonator and generates a spectrum as depicted to the top right. The surface separation D as well as the index of refraction can be determined using the exact position of the extinctions within a defined wave-length window (black dotted line). (b) Interference plot in the liquid state (p = 81 bar, T = 303.2 K). The two mica surfaces are approached toward each other in 1 nm steps. Each spectrum is recorded between 2 and 0 µm. The black lines in the (D, λ)-plane represent the destructive interference pattern, which is obtained from the interfere metric measurement. The spectrum shown in (a) corresponds to the horizontal line in the (D, λ)-plane at D = 1.5 µm (white dotted line in (b)).