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Preparation of the KIBILI experiment

Jean-Claude Legros^{a,*}, Vitaliy Sechenyh^a, Denis Melnikov^a, Dirk van Merode^b,
Valentina Shevtsova^a^a MRC, EP – CP165/62, ULB, av. Roosevelt, B1050, Brussels, Belgium^b Lessius University College, Campus De Nayer, Mechelen, Belgium

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ABSTRACT

An effective way to solve the issue of global warming is reduction of CO₂ emissions through its capture from stationary sources of energy production. A large amount can be stored in depleted oil and gas reservoirs being mixed with impurities and hydrocarbons in states close to the critical point. Thermodiffusion may result in accumulation of chemically active impurities near the bottom of the cap rock, thus leading to provoke leakages. The objective of the KIBILI project aims to study the kinetic of the mass transport in a binary mixture in the gas/liquid critical region. The measurements of diffusion and Soret coefficients are foreseen to be carried out in a CO₂–hydrocarbon system, which could be representative of those mixtures stored in depleted oil and gas reservoirs. The microgravity conditions provided by nano-satellites of the project QB50 would be a very nice opportunity to realize accurate measurements of these delicate phenomena.

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1. Introduction

The aim of the project KIBILI (Kinetic of thermodiffusion in Binary Liquids near the critical point) is to join the QB50 project with a double CubeSat orbiting in low Earth orbit for 90 days with a sophisticated hardware allowing studying the thermodiffusion in the region of the gas/liquid critical point under microgravity conditions.

Our project is aimed at understanding the diffusive phenomena near the critical point. The ground experiments dealing with temperature gradients in gravity field may face serious problem of accuracy due to buoyancy-induced convection. One of the ways for solving this problem is to conduct an experiment in the absence of gravity inside a nano-satellite of the QB50 project [1], with the purpose to provide incontestable benchmark results for ground experiments. Such an experiment should be carefully prepared, keeping in mind constraints related to small volume, weight, and power. This project is a close collaboration between MRC-ULB and LESSIUS. The first one is responsible for the KIBILI science experiment, while the second one is responsible for the JULES platform in a CubeSat.

A CubeSat is a miniaturized satellite (10 × 10 × 10 cm³, weighing 1 kg) which offers all the standard functions of a normal satellite: attitude determination and control, uplink and downlink telecommunications, power subsystem including a battery and body-mounted solar panels, on-board data handling and storage by a CPU, plus either a technology package or a small sensor or camera. They can even have deployable solar panels, antennas or booms. Limited orbit control using micropropulsion, S-band instead of VHF/UHF and wireless data transfer inside the CubeSat are now beginning to be used. It takes about two years to develop a CubeSat from the provision of funding until launch. The hardware composed of standard

* Corresponding author.

E-mail addresses: jcleghros@ulb.ac.be (J.-C. Legros), vsecheny@ulb.ac.be (V. Sechenyh), dirk.vanmerode@lessius.eu (D. van Merode), vshev@ulb.ac.be (V. Shevtsova).

kits is rather cheap to acquire and until now, about 50 CubeSats have been successfully launched, worldwide an estimated 100–150 CubeSats are being ready for launch in the next few years.

The project QB50 has the scientific objective to study in situ the temporal and spatial variations in the lower atmosphere (90–320 km) with a network of 50 double CubeSats, separated by a few hundred kilometers and carrying identical sensors. QB50 will also study the re-entry process by measuring a number of key parameters during re-entry and by comparing predicted and actual CubeSat trajectories and orbital lifetimes. There exists also an opportunity for scientific experiments like KIBILI to join the QB50 on the same launcher.

KIBILI experiment is aimed at the investigation of diffusion and thermodiffusion in supercritical fluid composed by CO₂ and a hydrocarbon. On the experimental side, the behavior of such fluids in the vicinity of the critical point is poorly studied. The most relevant study to a suggested work is a pioneer experiment by Rutherford and Roof [2] in 1959 at which the Soret coefficient were measured in methane/*n*-butane mixtures, using the membrane cell technique. There were a few attempts to measure this coefficient using thermogravimetric columns [3]. However, in these columns the hydrodynamics of the convective system is rather complex and involves knowledge of a variety of physical properties of the system. Furthermore, it does not allow studying the accumulations near the walls.

2. Scientific backgrounds of the KIBILI project

Thermodiffusion (or Soret effect) is a mass flux leading to the establishment of a concentration distribution in a confined fluid mixture under the action of a temperature difference. It causes mass diffusion, which aims at eliminating concentration variations. A steady state is attained when the separating effect of thermodiffusion is balanced by the remixing effect of mass diffusion. In theoretical and experimental approaches, the separation by thermodiffusion is studied in a system where two opposite walls are kept at two different constant temperatures. The separation starts as a localized increase of the concentration of one of the components near the hotter wall, while the other component accumulates near the colder wall. The steady state in a two-component fluid system with initial mass fractions C_1, C_2 corresponds to a linear distribution of concentration that can be described as:

$$\Delta C = (D_T/D)C_1C_2\Delta T = S_T C_1(1 - C_1)\Delta T$$

Here $S_T = D_T/D$ is the Soret coefficient, D_T the thermodiffusion coefficient and D the mass diffusion coefficient. The characteristic time τ for the establishment of the steady concentration distribution is generally large as it is a diffusion-controlled process: $\tau = l^2/\pi^2 D$, where l is the length that the temperature difference ΔT is acting on.

Since these transport coefficients (D, S_T) display a different behavior in a wide region around the critical point [4–6], knowledge of their critical behavior is important for technical and scientific applications in such fields as supercritical-fluid chemistry, treatment of hazardous waste, geochemistry of hydrocarbon reservoirs, etc. Far away from the critical point, these coefficients (D, S_T) are slowly varying functions of temperature and density. Very close to the critical point, the correlation length of the fluctuations diverges, leading to universal scaling laws for the critical enhancements of the transport coefficients. This asymptotic critical region is much smaller than the region where critical enhancements of transport properties are observed experimentally. The transport coefficients in this so-called crossover region cannot be described in terms of simple power laws and depend on details of the physical system under consideration.

From a detailed asymptotic analysis [5,6] around the critical point, it is expected that the mass diffusion coefficient D vanishes while the thermodiffusion coefficient D_T approaches a constant. This means that, on the one hand, the segregation of components may diverge due to thermodiffusion but, on the other hand, the steady state needs an infinite time to establish.

These theoretical findings are in line with the experimental results by Rutherford and Roof [2], who measured the Soret coefficient in methane/*n*-butane mixtures. The experimental procedure is outlined in Fig. 1. Three different temperatures were studied: $T = 46.1^\circ\text{C}$, 71.1°C , and 121.1°C . Each experiment was performed at constant temperature in gas/liquid supercritical fluid, see Fig. 1. Variation of a pressure at constant temperatures allowed observing evolution of Soret coefficients at different distances from the critical point, as shown in Fig. 2. Evidently, the Soret coefficient starts to increase rather far from the critical point, which is shown by the rhombic symbol in Fig. 1 ($T_{cr} = 115^\circ\text{C}$, $P_{cr} = 80$ bar at methane mole fraction 0.4).

Up to now, there is no other experimental data investigating such a behavior in the crossover region near critical point, where the diffusion coefficient is vanishing (or reduced dramatically). Taking into account that different theoretical approaches does not always arrive to the same conclusions, so the need for trustworthy experimental results is obvious.

3. Experiment

3.1. Choice of the fluid

The goal of the KIBILI project is to study the formation of the concentration gradient and first to quantify its behavior near the hot and cold walls and then in the whole volume, while the diffusion coefficient is becoming smaller as it approaches the critical conditions.

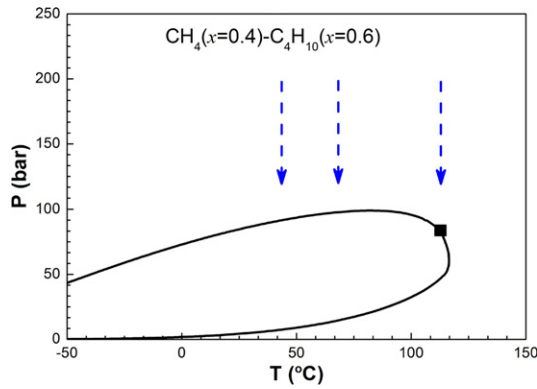


Fig. 1. Schematic phase diagram for methane/*n*-butane. Mole fraction of methane is 0.4. Symbol ■ is the critical point. Measurements were performed along the blue arrows [2].

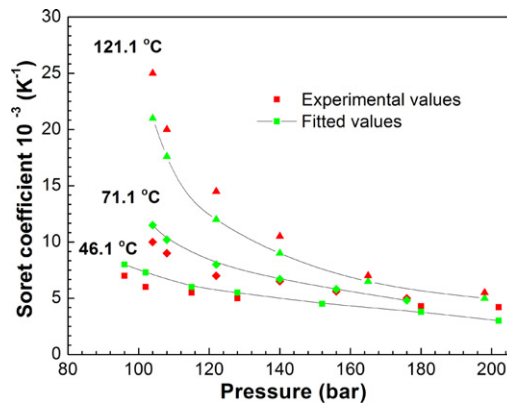


Fig. 2. Soret coefficient measurements as a function of pressure at three different temperatures for the system methane/*n*-butane; mole fraction of methane 0.4 [2].

The candidate mixture is directly relevant to the CO₂ geological storage in depleted oil reservoirs. The crude oil in a natural reservoir as well as the sequestered CO₂ is in a state close to the *critical point*. The fundamental aspects were mentioned above. The environmental aspect of fighting global warming will benefit from knowledge of the properties of geological sequestration, while this knowledge shall also be useful in oil-industry applications.

Although in the presence of the geothermal gradient (about 3 K/100 m), gravity remains the main driving force for mass transport; the thermodiffusion process is not negligible on a long-term scale. It may induce two different phenomena: first, it may concentrate components locally and so enhance various processes (chemical reactions able to modify permeability, oscillatory convective motions...); second, it may modify the migration direction of the components compared to what would have occurred without thermodiffusion. The former may result in accumulation of a layer of chemically aggressive components near the bottom of the cap rock, thus leading to increased risks in case of leakage. The latter may result in a significant error in the estimations of the gas/liquid ratio in the oil reservoir.

A strong improvement could arise from the understanding of the behavior of chemically reactive components at the limits of the system, where thermal and pressure conditions correspond to near-critical values. There is an acute lack of reliable data, particularly for mixtures near the critical point. This lack of data is mainly related to the difficulties encountered on Earth to perform accurate measurements of this property, due to buoyant convection and high compressibility of these systems [7].

It should be stressed that even if the industrial demands are related to fluids inside porous media, performing measurements in bulk fluids, as proposed in this project, is meaningful. The thermodiffusion process is, to a large extent, not affected by the presence of the porous matrix. Thus, measurements in bulk fluids will yield values that are directly usable in simulations for both porous and free media.

The mixture under high pressure to be studied in this project is a representative thermodynamic system of great interest. This mixture shall be of the type 80% CO₂ + 20% CH₄ or another light hydrocarbon, to be determined in the initial steps of the project, taking into account the thermal conditions and the power budget on board the CubeSat. The total amount of fluids would not be larger than 2 ml. Thermodynamic modeling is under development.

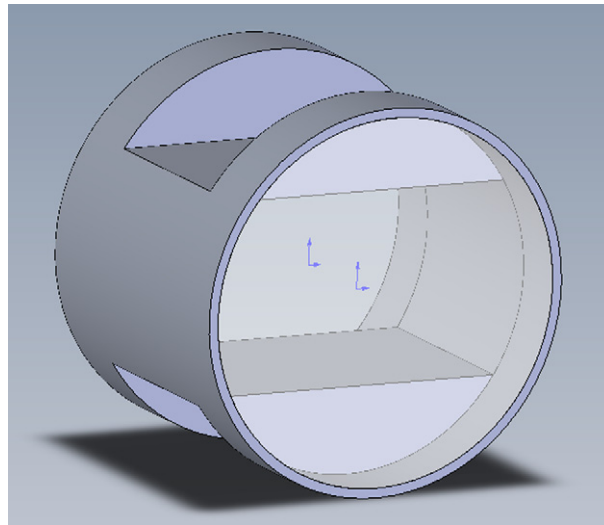


Fig. 3. Sketch of the high-pressure cell. Dark gray is corresponding to the titanium walls. The volume is closed by two sapphire windows.

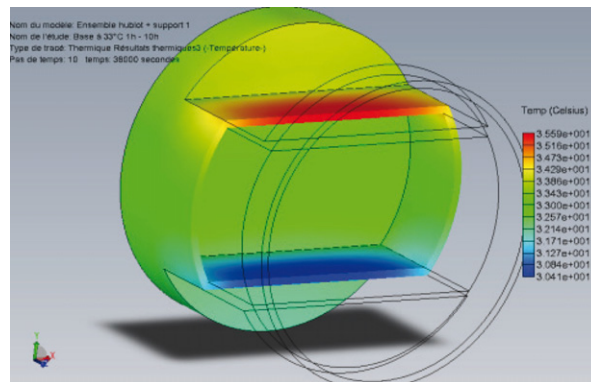


Fig. 4. The results of preliminary thermal analysis with sapphire windows with imposed temperature gradient 6 °C.

3.2. Diffusion cell

For the proposed project, experimental cells have to be designed for high pressures, and must be compatible with the interferometric analysis method (expected conditions: $T = 10^\circ\text{C}$ and $P = 80$ bar). The design should foresee that similar cells will be used in laboratory and in microgravity conditions. This needs dedicated high-pressure equipment and experienced operators. Presently, the authors are cooperating with a company that is able to produce a perfectly leak-proof cell without any sealing system. Integration of the cell will be done by welding to avoid any risk of leakage during the storage period. The preliminary design includes two circular optical windows welded on the body of the cell (see Fig. 3). The windows are made of sapphire and the body is made of titanium. For reliability reasons, any connection between the inside and the outside of the cell has to be prevented (no valve).

The results of a preliminary feasibility study of the thermal design are shown in Fig. 4. The temperature distribution is imposed by heating one of the flat wall of the cell (the red upper horizontal one in Fig. 4) and cooling down the opposite one (by Peltier cells TBC). The distance between hot and cold walls is 10 mm. The temperature profile is rather rapidly established, especially in comparison with the characteristic time for the concentration distribution, which is controlled by diffusion and thus is very slow. This is even more real as we approach the critical region.

The working principle of the experimental cell is outlined in Fig. 5. To keep test fluid under high pressure during the experiment, the cell is connected to a bellows with flexible membrane, which is filled with nitrogen on the Earth at the required pressure.

3.3. Optical design

Two opposite walls are maintained at different temperatures and, correspondingly, at different distances from the critical point. The kinetic of the establishment of the concentration gradients near these two walls are expected to be different.

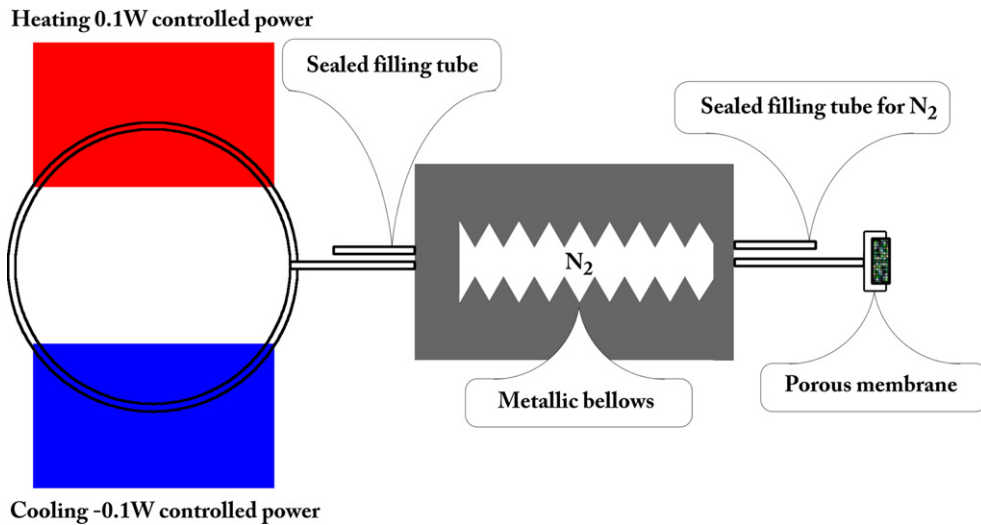


Fig. 5. A sketch of one of the options of the experimental cell with variable pressure. Nitrogen is used to pressurize the cell. For interpretation of colors, see the online version of this article.

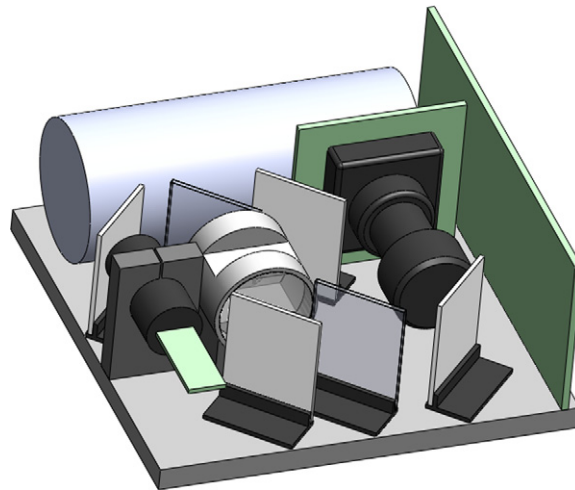


Fig. 6. Sketch of a possible arrangement of the experimental setup in 1/3 CubeSat unit.

This would be observed for the first time, and would yield important information on this physical phenomenon. A Mach Zehnder interferometer will be used to analyze the evolution of the concentration gradient after a temperature gradient is established through the cell. This type of optical scheme has been successfully used in different microgravity experiments [8–11].

The changes of temperature and concentration will be monitored via the variation of the refractive index. An important part of the project is to build the pool of data for refractive index changes near the critical point. Such data is not fully available in the literature. A dedicated refractometer is under development in collaboration with Université de Pau et des pays de l'Adour, France (Dr. H. Bataller). After performing laboratory tests, the fine-tuning of the experimental technique will be carried out on an engineering model.

Fig. 6 shows a sketch of a possible arrangement of the diffusion cell, a Mach Zehnder interferometer with the laser light source and a camera on a support plate of $90 \times 90 \text{ mm}^2$. In the middle of the plate, from the left to the right: a laser diode and its driver, a high-pressure cell, and a camera. The large cylinder in the back is the pressure compensation volume with the bellow inside. The height of the experiment volume is not larger than 35 mm but it has still to be optimized. The camera will be also miniaturized. The optical system will be built without mirrors using instead compact prisms with integrated semi-transparent face and wedges. The optical digital interferograms will be the only data downloaded during the experiment.

Table 1
The physical properties of an arbitrary model liquid [13].

Viscosity [m ² /s]	ν	3.40×10^{-6}
Thermal diffusivity [m ² /s]	a	8.50×10^{-8}
Diffusion coefficient [m ² /s]	D	1.62×10^{-10}
Density [kg/m ³]	ρ	981.6
Soret coefficient [1/°C]	S_T	5.88×10^{-3}
Thermal expansion [1/°C]	β_T	3.10×10^{-4}
Solutal expansion	β_C	0.1386
Concentration	C_0	0.5

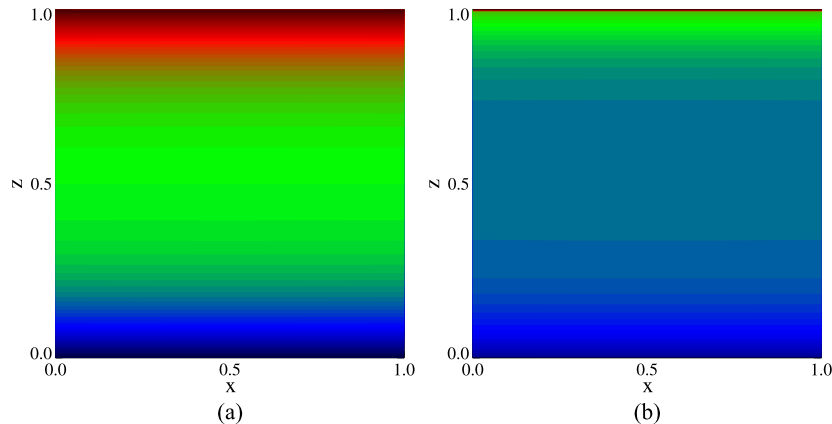


Fig. 7. The concentration field as a result of Soret separation at $t = 60$ min, $\Delta T = 3$ K, $\varepsilon(T \text{ mean}) = 0.0063$. (a) normal liquid, $\alpha = 0$; (b) near-critical liquid, $\alpha = 2/3$.

3.4. Experimental procedure

Presently, we intend to use the mixture 80% CO₂ + 20% CH₄, and it has to be confirmed by numerical modeling and preliminary ground experiments. For this fluid the experimental conditions frame will be between 10 and 15 °C for the mean temperature and between 85 and 100 bars for the pressure. To optimize the energy budget, these temperatures and pressures (and consequently the mixture composition) have to be confirmed by modeling the thermal performance of the system. The present preliminary design of the cell guarantees utilization (with the right margin) up to 100 °C and 200 bars. The experimental conditions have to be in the monophasic domain of compressible liquid region ($T < T_{\text{crit}}$ and $p > p_{\text{crit}}$).

There exist two main options for the experimental procedure:

- (1) to keep the mean the temperature constant, e.g., at 16 °C, and diminish pressure by accurately control leakage;
- (2) to keep the pressure constant, e.g., at 85 bars, and modify stepwise the mean temperature.

4. Numerical simulation

The goal of computer simulations is to visualize the expected dissymmetry of the concentration field, as the distances from the critical point are different for the cold and the hot wall of the experiment cell. In these route-finder simulations, the fluid is assumed to be non-compressible. The governing Navier–Stokes, heat and mass transfer equations are similar to that used in [12], as well as the notations. The numerical code, used in [13], was slightly modified by removing gravity and introducing temperature-dependent diffusion:

$$D = D_0 \varepsilon^\alpha, \quad \varepsilon = T/T^{\text{crit}} - 1$$

Here D_0 is the mass diffusion coefficients far from critical point and ε the distance from critical point. The physical parameters of the model liquid used in this simulation are given in Table 1.

The calculations were conducted assuming the critical temperature of the fluid is $T_{\text{crit}} = 28$ °C and walls are kept at temperatures $T_{\text{cold}} = 24.0$ °C, $T_{\text{hot}} = 27.6$ °C. It corresponds to $\Delta T = 3$ °C and the hot wall is ten times closer to the critical point than the cold one; $\varepsilon = 0.0013$ and 0.013 , respectively. The results of computer simulations are presented in Fig. 7 as concentration fields of the initially homogeneous fluid 60 min after imposing the temperature gradient. The Soret separation progressively develops, although the system is still far from its steady state.

Fig. 7(a) shows the concentration field of the normal liquid when its diffusion coefficient is constant in the critical region, $D = D_0$, $\alpha = 0$. Fig. 7(b) corresponds to the case with a diffusion coefficient slowing down with a power law $\alpha = 2/3$, i.e. $D = D_0 \varepsilon^{2/3}$. In the case of normal liquid, the similar concentration fronts develop near the hot and cold walls and propagate

toward each other (Fig. 7(a)). In the case of near-critical fluid, the concentration fronts are not symmetric near the hot and cold walls. The concentration gradient is much stronger near the hot wall, but its extension towards the cell center is undersized in comparison with that one near the cold wall.

5. Conclusions

Multidisciplinary project KIBILI (Kinetic of thermodiffusion in Binary Liquids near the critical point) is aimed at performing microgravity experiments in a double CubeSat to study and understand the diffusive phenomena near critical point. We have presented the scientific scope of the project, the preliminary design of the experiment, and have highlighted the points on which attention should be focused. The results obtained during the preparation phase are very encouraging.

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