Bubble streams in Titan’s seas as product of liquid $\text{N}_2$-$\text{CH}_4$-$\text{C}_2\text{H}_6$ cryogenic mixture

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Titan, Saturn’s largest moon, is the only extraterrestrial body known to support stable liquid on its surface, in the form of seas and lakes that dot the polar regions. Many indications suggest that the liquid should be composed of a mixture of $\text{N}_2$, $\text{CH}_4$ and $\text{C}_2\text{H}_6$. Recent RADAR observations of Titan’s large sea, called “Ligeia Mare”, have shown unexplained and ephemeral bright features, possibly due to rising bubbles. Here we report that our numerical model, when combined with experimental data found in the literature, shows that Ligeia Mare’s bed is a favourable place for nitrogen exsolution. This process could
produce centimeter-sized and radar-detectable bubbles.

Introduction

Titan, the main satellite of the giant planet Saturn, is the only moon in the solar system harboring a dense atmosphere. Among many unique features, this gaseous envelope, mainly composed by nitrogen and methane, is the place of a “hydrological” cycle of methane. In addition, the complex photochemistry of its atmosphere produces a wide variety of organic species with ethane being, in terms of quantity, its main product. The RAdio Detection And Ranging (RADAR) instrument, onboard the Cassini spacecraft, allowed for the discovery of dark features, partially covering Titan’s polar regions. Long suspected to be there (refs), they are interpreted as seas or lakes of liquid hydrocarbons. While their exact chemical composition is not known, the lower atmosphere contains around 5% of CH$_4$ and 95% of N$_2$ and together with C$_2$H$_6$, produced by photochemistry, these species should be the main components of Titan’s seas. Titan’s maritime environments exhibit an absence of ocean waves, but strange transient RADAR over-brightness events have been reported in two places at the surface of the northern sea, Ligeia Mare. In order to explain these episodes, the formation of gas bubbles has been proposed together with potential suspended/floatiing solids. In this work, we focus on thermodynamic instabilities that can produce a nitrogen exsolution, and consequently feed streams of bubbles, which can explain the events observed by RADAR.

Existence of Liquid-Liquid-Vapor Equilibria for hydrocarbon mixtures

The most straightforward inter-phases equilibrium, of a N$_2$-CH$_4$-C$_2$H$_6$ ternary system, is a liquid-vapor equilibrium (LVE). However, liquid-liquid-vapor equilibria (LLVE) do occur under
certain conditions in ternary and liquefied natural gas (LNG) systems, including liquid phase inversion\textsuperscript{12}. LLVE equilibria consist in the coexistence of two liquids, of different compositions, with a vapor. In the laboratory, LLVEs have been observed for systems, under cryogenic conditions, comparable to Titan’s liquid phases: nitrogen + methane + (ethane, or propane, or \textit{n}-butane)\textsuperscript{12–16}.

At the \textit{Huygens} landsite, \textit{i.e.} in Titan’s tropical regions, the temperature was 93.65 ± 0.25 K\textsuperscript{17}. Using the CIRS (The Composite Infrared Spectrometer) instrument aboard Cassini, Titan’s atmospheric temperature has been retrieved as a function of latitude, for the lowest 1 km. The average temperature of the northern polar region, during mid-northern spring, has been found around 91 K\textsuperscript{18}. However, the question of the specific temperature at the surface of Ligeia Mare remains open, since the thermal properties of the liquid could differ, compared to those of surrounding lands. Moreover, the behavior of temperature with depth is not well constrained. Most estimations rely only on numerical simulations that depend on many parameters, like the light extinction coefficient of the sea\textsuperscript{19,20}. Nevertheless, all models agree with a with a temperature cooling of a few degrees between the surface and the sea bottom\textsuperscript{20,21}. We therefore adopted a characteristic range of Ligeia Mare temperatures from 80 to 90 K.

Titan’s ground pressure, measured \textit{in situ} by the \textit{Huygens} probe, is close to $P_0 = 1.5$ bar and should not undergo significant variations over the satellite surface\textsuperscript{17}. Since the maximum depths of Ligeia Mare have been determined to be between $\sim 100$ m and $\sim 200$ m\textsuperscript{19,22,23}, we estimated the pressure at these depths. As a first approximation, liquids can be considered as incompressible. In that frame, the pressure $P$ at a given depth $z$ within a Titan’s sea follows the law

$$P = P_0 + \bar{\rho} g_{\text{Tit}} z$$

where $\bar{\rho}$ represents the mean density of the liquid between the considered depth and the surface, $g_{\text{Tit}}$ denotes the gravity. Values for the density of liquid CH$_4$, C$_2$H$_6$ or N$_2$ can be found in the
literature\textsuperscript{24,25}, for instance under 1 bar $\rho_{\text{CH}_4} = 451.8$ kg.m\(^{-3}\), $\rho_{\text{C}_2\text{H}_6} = 651.6$ kg.m\(^{-3}\), while $\rho_{\text{N}_2} \sim 800$ kg.m\(^{-3}\). We check that these values are only weakly dependent of pressure: \textit{e.g.} at 10 bars $\rho_{\text{C}_2\text{H}_6} = 651.8$ kg.m\(^{-3}\) and $\rho_{\text{CH}_4} = 452.1$ kg.m\(^{-3}\). Using these numbers we found $P_{100} \simeq 2.1$ bar at 100 m (resp. $P_{200} = 2.7$ bar at 200 m) for pure methane layers. For layers composed exclusively of ethane the pressure at 100 m reaches $P_{100} = 2.4$ bar (resp. $P_{200} = 3.3$ bar). Due to the higher density of N\(_2\) (870 kg.m\(^{-3}\) at its triple point where $T_t = 63$ K, probably $\sim 800$ kg.m\(^{-3}\) at $\sim 90$ K), some amount of nitrogen would increase the mean density of the mixture, and then, the pressure at 100 or 200 m. If we consider the heaviest hydrocarbon under consideration, \textit{i.e.} ethane, and if we consider a nitrogen mean abundances of 40\% (in mole fraction), which represents probably a very high solubility of N\(_2\), we found $P_{100} = 2.5$ bar and $P_{200} = 3.5$ bar. In addition to these estimations, we developed a more sophisticated model based on the law of hydrostatics and the equation of state (EoS) PC-SAFT\textsuperscript{7,26}(see Methods). This way, the compressibility of the fluid was taken into account. We also investigated the influence of temperature in the range 80 – 90 K. With this model, we arrived to the same conclusion: the pressure at 100 – 200 m, should be in the range 2 – 3.5 bar.

\textbf{Stability Analysis of the Ternary System CH\(_4\)-N\(_2\)-C\(_2\)H\(_6\)}

The most relevant laboratory experiments of LLVEs have been acquired at 94.3 K under a pressure between 4.2 and 4.55 bars\textsuperscript{14}. These conditions are inconsistent with Ligeia Mare’s expected bathymetry and temperature profile. As a consequence, we investigated the stability of the N\(_2\)-CH\(_4\)-C\(_2\)H\(_6\) system at a lower pressure, and cooler temperature. To do so, we used a numerical method allowing phase stability analysis, originally introduced for the industry of gas and oil.

First, we have investigated whether the lake’s surface could be the location of phase splitting events, \textit{i.e.} the appearence of two liquids of distinct compositions, in equilibrium with the
atmosphere. For a temperature and pressure appropriate for Titan’s surface, i.e. 90 K and 1.5 bars, we found that –by varying the mole fraction of nitrogen– the binary system N\textsubscript{2}+CH\textsubscript{4} does not undergo any demixing, it remains either in vapor or in a vapor-liquid equilibrium. Same results were obtained for N\textsubscript{2}+C\textsubscript{2}H\textsubscript{6}. For the ternary mixture N\textsubscript{2}+CH\textsubscript{4}+C\textsubscript{2}H\textsubscript{6}, we have followed two distinct scenarios, in order to maximise the range of parameter space we explore: (1) we fixed the abundance in N\textsubscript{2}, of the entire system (i.e. including the vapor and the liquid(s)) and only varied the abundances of CH\textsubscript{4} from 0.05 to 0.001 (letting ethane making up the remainder) in mole fraction and (2) we fixed the overall composition of CH\textsubscript{4} and gradually changed the fraction of N\textsubscript{2} from 0.95 to 0.90. All cases resulted in an simple liquid-vapor equilibrium. The vapor, representing the Titan’s atmosphere, was always largely dominated by N\textsubscript{2}. In the light of these results, we can safely conclude that, at the expected polar ground conditions, the Titan’s seas surface is thermodynamically stable and should not split into two liquids.

Next, we searched for LLVE for conditions relevant to environments below the sea surface (pressure up to \( \sim 3.5 \) bars and temperature possibly down to \( \sim 80 - 85 \) K). Our results are summarized in Fig. 1. For all three considered temperatures, we found LLVE. In all cases, these three-phases equilibria consist in two liquids in coexistence with a vapor phase composed almost exclusively of nitrogen (empty squares in Fig. 1). The existence of this almost pure nitrogen vapor requires the exsolution of some amount of N\textsubscript{2} contained in the liquid before the occurrence of the LLVE. One liquid is a nitrogen-rich phase (filled squares in Fig. 1); the other is enriched in ethane (empty circles in Fig. 1). We have also evaluated the densities of the phases involved in our study. A set of values, corresponding to a specific LLVE, is presented in the insert included in Fig. 1. The higher density of the nitrogen-rich liquid is a trend confirmed for all the LLVEs we found. Low temperature and high pressure both favor the occurrence of a phase splitting that results in a LLVE. At \( T = 90 \) K, the temperature at the surface of the
sea or slightly below, a LLVE appears at a pressure as low as \( \sim 2.7 \) bars. These conditions allow the occurrences of LLVEs at depths between 130 – 170 m, compatible with Ligeia Mare’s bathymetry. Clearly, the lower temperature, due –for instance– to infrared absorption in layers near the surface, would favor phase splitting at much shallower depths in the range 20–30 m (see Fig. 1 panels a and b). The temperature strongly influences the depth required to obtain a pressure high enough to reach conditions for an exsolution.

**Implication for Titan**

A sea with a homogeneous composition that matches the one required for the occurrence of a LLVE, at some depth, is an improbable scenario. In addition, such a case would imply a nitrogen degassing through the whole extent of the system. Instead, we propose a scenario where the sea is vertically stratified with ethane enriched bottom layers and methane-rich upper layers, the latter containing more dissolved nitrogen. This is supported by the higher density of ethane-rich mixtures and the larger solubility of nitrogen in methane than in ethane\(^7\). In addition, surface layers are in contact with the nitrogen rich atmosphere, situation that favors the dissolution of \( \text{N}_2 \). In addition, given Ligeia Mare’s surface area of several thousand square kilometers, local episodes of evaporation and precipitation of methane can lead to a horizontal gradient of compound abundances\(^{20}\). 3D modeling of ocean circulation with a modified version of the Bergen Ocean Model suggests the existence of maritime streams produced by tides, wind or generated by solar heating\(^{20, 27}\). We propose that the vertical sea circulation feeds locally the lowest sea layers with methane and nitrogen enriched liquid. Depending on how exactly the composition has been altered at the surface (by local rain, evaporation or \( \text{N}_2 \) dissolution), the downward flow can meet the deep ethane-rich layers, this fulfilling the composition, pressure and temperature required for the occurrence of a LLVE. Our thermodynamically modeling informs us only about
which equilibria are possible under given conditions, but is unable to predict either the involved amounts of matter, or the kinetics of the described process. Nevertheless, in our scenario, circumstances favorable to LLVE, are ephemeral: composition of liquid sinking from the surface has a composition varying with time, first due to weather over the sea, and second due to mixing during downward flow. Once the phase splitting begins, at a specific reached depth, the droplets of the denser liquid (nitrogen-rich) tend to sink while the lighter ones (ethane-rich) rise toward the surface. Of course, this phases separation process tends to stop naturally the formation of a LLVE, by the exhaustion of one or several required constituents. Both kind of mentioned droplets should redissolve into the ambient liquid during their descent or ascent, because the pressure and temperature move away from those required for a LLVE. It is worth noting that buoyancy-driven bubbles of almost pure nitrogen rapidly rise through the upper N$_2$-rich layers to the surface, and for this reason probably do not redissolve into surrounding liquid. This scenario matches the Ligeia Mare observations of RADAR over-brightness events. It is also striking that the locations of the Transient Feature Ligeia 1 (TFL1) and TFL2

\[ \text{d}_{\text{breakup}} \sim 8 \sqrt{\frac{\gamma}{g_{\text{Tit}} \Delta \rho}} \]

where \( \gamma \) is the surface tension of the liquid, \( g_{\text{Tit}} \) stands for the Titan’s surface gravity and \( \Delta \rho = \rho_{\text{liq}} - \rho_{\text{gas}} \) with \( \rho_{\text{liq}} \) and \( \rho_{\text{gas}} \), respectively, the density of the surrounding liquid and the gas held by the bubbles\textsuperscript{28}. Using surface tensions from the Dortmund Data Bank (http://www.ddbst.com), and for a mixture of CH$_4$, C$_2$H$_6$ and N$_2$ (0.4:0.4:0.2), composition that could be typical of the upper layers of liquid, at 90 K \( \gamma_{\text{mix}} \sim 2 \times 10^{-2} \) N m$^{-1}$; \( \Delta \rho \) is estimated at a few bars for the
same mixture thanks to PC-SAFT. This yields a $d_{\text{breakup}} \sim 4.6$ cm, approximately twice the RADAR wavelength (2.2 cm). It should be noted that a composition based only on CH$_4$ and N$_2$ with a ratio 1 : 1, which is probably an extreme situation, leads also to a $d_{\text{breakup}}$ of a few centimeters. Such large bubbles can magnify the Cassini RADAR backscattering, allowing easy detection, similarly to what is suspected for pebbles in dry river beds on Titan$^{29}$ or evaporites$^{30}$. In comparison, predicted sea current speeds, of a few cm s$^{-1}$, can lift only sediment particles well below 1 cm in size$^{20}$, and, then cannot be detectable with the Cassini RADAR.

At its specific site of occurrence, the LLVE demixing should perturb the local circulation of fluids. Indeed, the densest liquid sinks below the lightest while vapor rises to the surfaces. This phase separation tends also to stop the process, since it changes locally the composition. Unfortunately, our approach can not provide the amount of matter involved in the different phases. No quantification can be then proposed concerning the influence on circulation and the magnitude of degassing. Of course, we have focused on Ligeia because “Magic Islands” (i.e. nicknames for TFL1 and TFL2) were observed at this sea. But, our argumentation can be applied to other mare like Kraken and Punga. However, the existence of depths between 100 and 200 m is a crucial point. We can reasonably think that such depths exist under the surface of Kraken, but in the case of Punga it is much more questionable as the bathymetry is not yet available and as Punga could be substantially less deep than Ligeia and Kraken, as it is suggested by its smaller size. Since, nitrogen exsolution in the deepest parts of Titan’s seas can represent a potential hazard for an in situ exploration$^{31,32}$, future laboratory experiments, specifically designed to study these ternary equilibria, would be extremely useful. As a priority, the existence of LLVEs, found in past experiments has to be confirmed by modern measurements$^{33,34}$. These investigations could then be easily extended to the pressures of a few bars higher than the Titan’s surface one, and to temperature down to a few degrees below $\sim 90$ K. This way, our numerical stability analysis
could be reinforced. Concerning the seas circulation, 3D models including a full treatment of the chemical composition, with the possibility of LLVEs, would be welcome. But, since data used as inputs of such models, and in the first place the sea beds topography, are still poorly known, the last word will come from a Titan’s submarine exploration.
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**Author contributions**

D. Cordier wrote the paper and performed PC-SAFT computations, F. García-Sánchez and D. N. Justo-García made the stability analysis of the N$_2$-CH$_4$-C$_2$H$_6$ mixtures, G. Liger-Belair provides expertise concerning the physics of bubbles and effervescence.

**Additional information**

Supplementary information is available for this paper.

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**Competing interests**

The authors declare no competing financial interests.
Fig. 1. The behavior of a ternary mixture N₂-CH₄-C₂H₆ at three temperature values relevant for Titan’s sea subsurface environment: (a) \( T = 80 \) K, (b) \( T = 85 \) K and (c) \( T = 90 \) K. Each set of circles, filled squares and empty squares represents a LL VE for a given pressure. While the LL VE shown at \( T = 80 \) K is an example that illustrates the influence of temperature, panels (b) and (c) provide estimations of the lowest pressures at which LL VE occur at \( T = 85 \) K and \( T = 90 \) K, respectively \( \sim 1.7 \) bar and \( \sim 2.7 \) bar. A grey-shaded panel provides composition and densities of fluids involved in the LL VE corresponding to \( T = 85 \) K and \( P = 1.8 \) bar (see panel b).
Methods

In order to evaluate the pressure at the bottom of Titan’s seas we used the well known equation

$$\frac{\partial P}{\partial z} = -\rho g_{\text{Tit}}$$

(3)

where $z$ is the depth, $\rho$ the density and $g_{\text{Tit}}$ the satellite ground gravity. The density depends on the pressure $P$, the temperature $T$ and the mole fractions of the considered species $\text{N}_2$, $\text{CH}_4$ and $\text{C}_2\text{H}_6$. The PC-SAFT equation of state (EoS)\textsuperscript{26}, widely employed in the chemical engineering community, was used to determine the density $\rho$. In the PC-SAFT EoS, the molecules are conceived to be chains composed of spherical segments, in which the pair potential for the segment of a chain is given by a modified square-well potential\textsuperscript{35}. Non-associating molecules are characterized by three pure-component parameters: the temperature independent segment diameter $\sigma$, the length of the potential $\epsilon/k_B$, and the number of segments per chain $m$. The PC-SAFT EoS, expressed in terms of the Helmholtz energy for a multicomponent mixture of non-associating chains, consists of a hard-chain reference contribution and a perturbation contribution to account for the attractive interactions. The three pure-component parameters of nitrogen, methane and ethane for the PC-SAFT EoS were taken from the literature\textsuperscript{26}. For mixtures, the PC-SAFT EoS uses classical van der Waals one-fluid mixing rules for the perturbation terms. In these mixing rules, the parameters for a pair of unlike segments are obtained through conventional Lorentz-Betherlot combining rules, where one binary interaction parameter $k_{ij}$ is introduced to correct the segment-segment interactions of unlike chains. The binary interaction parameters used in all the phase equilibrium calculations for the PC-SAFT EoS are: 0.0307 for $\text{N}_2$$-\text{CH}_4$, 0.0458 for $\text{CH}_4$$-\text{C}_2\text{H}_6$, and $-0.0058$ for $\text{CH}_4$$-\text{C}_2\text{H}_6$, and they were also taken from the literature\textsuperscript{36,37}.

Concerning the stability analysis, the employed technique relies on the above mentioned PC-SAFT EoS, and uses an efficient computational procedure for solving the isothermal multiphase
problem. Initially, the system is assumed to be monophasic. A stability test allows checking whether the system is stable or not. If stability is reached, the procedure is stopped. In the contrary case, it provides an estimation of the composition of an additional phase to take into account for the equilibrium calculation. The number of phases is then increased by one, and equilibrium is reached by minimizing the Gibbs energy. The procedure is continued until a stable solution is found\textsuperscript{12}. This approach has been validated by comparison with many laboratory measurements involving ternary mixtures. For instance, a very good agreement is found with mixtures of liquid methane, nitrogen and \textit{n}-pentane, or \textit{n}-hexane or \textit{n}-heptane at various temperatures\textsuperscript{38}. In addition, in the specific context of this work, we have paid great attention to the reproduction of laboratory data, for the system \textit{N}_2-\textit{CH}_4-\textit{C}_2\textit{H}_6 at 94.3 K under \textasciitilde 4 bars, reported in Ref.\textsuperscript{14}.

**Data availability.** The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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