

GROWTH AND MORPHOLOGY OF PHASE SEPARATING SUPERCRITICAL FLUIDS

John Hegseth
Department of Physics
University of New Orleans, New Orleans, Louisiana 70148

Daniel Beysens
Commissariat à l'Énergie Atomique
Département de Recherche Fondamentale sur la Matière Condensée
CEN-Grenoble
17, Avenue des Martyrs
38054 Grenoble Cedex 9, France

Françoise Perrot and Vadim Nikolayev
Commissariat à l'Énergie Atomique
Service de Physique de l'État Condensé
Centre d'Études de Saclay
F 91191 Gif sur Yvette Cedex, France

Yves Garrabos
Laboratoire de Chimie du Solide du Centre National de Recherches Scientifiques
CNRS-Université de Bordeaux I
351, Cours de la Libération
33405 Talence Cedex, France

SCIENCE OBJECTIVES

The scientific objective is to study the relation between the morphology and the growth kinetics of domains during phase separation. We know from previous experiments performed near the critical point of pure fluids and binary liquids that there are two simple growth laws at late times. The "fast" growth appears when the volumes of the phases are nearly equal and the droplet pattern is interconnected. In this case the size of the droplets grows linearly in time. The "slow" growth appears when the pattern of droplets embedded in the majority phase is disconnected. In this case the size of the droplets increases in proportion to time to the power $1/3$. The volume fraction of the minority phase is a good candidate to determine this change of behavior. All previous attempts to vary the volume fraction in a single experimental cell have failed because of the extreme experimental difficulties.

RELEVANCE OF THE SCIENCE AND POTENTIAL APPLICATIONS

Phase separation in liquid mixtures and pure fluids is a common process that occurs in many areas of natural science, engineering, and industry. Engineering applications are especially important in heat and mass transfer processes that occur in many industries. Phase separation is also ubiquitous in materials processing, e.g., metallic alloys, polymer alloys¹, and flat panel displays. A clearer understanding of the exact physics of phase separation is desirable for improving industrial efficiency and in developing new products. Phase

separation is also an important fundamental scientific problem in which low gravity facilities are needed to improve understanding. A particularly important feature in the phase separation process, especially in applications, is the growth and morphology of domains (e.g., liquid droplets) after the process has been started. The connection between the morphology of the domains and the growth laws is still unclear. Only a few experimental results are available where density or concentration has been systematically varied^{2,3}. In the region of the critical point, it has been found very easy to continuously vary the physical parameters that control phase separation (c.f., Figure 1). In addition, the critical slowing down of dynamics processes that occurs near the critical point enables a detailed investigation of the mechanisms involved in the separation process. Results from phase separation experiments done near the critical point can be described by scaled master curves¹ that are universal, i.e., curves that are *valid for all fluids* within two scale factors.

Binary liquids near a critical point of miscibility belong to the same universality class as pure fluids for static properties (c.f., the three dimensional Ising Model⁴). However, their dynamic behavior can be markedly different, especially in a gravitational field. This difference can be seen from the order parameter M (M is a generic variable that describes or controls a phase transition). M is the concentration difference $M = c - c_c$ for liquid mixtures where c is the concentration and c_c is the critical concentration where phase separation occurs. At c_c the osmotic compressibility diverges and the mutual diffusion coefficient goes to zero. When M is changed to induce phase separation, sedimentation usually occurs because one phase is more dense than the other. In pure fluids, M is the density difference $\rho - \rho_c$ (ρ is the density, ρ_c is the critical density). At the critical point in pure fluids the isothermal compressibility diverges and the thermal diffusivity goes to zero. Because pure fluids have a very large isothermal compressibility, they are very sensitive to the earth's gravitational field (acceleration g_0)³. Experiments are complicated by the very high compressibility of the fluid that induces density gradients even in the one-phase region. Convective flows, often turbulent, are also observed.

During phase separation, pure fluids and binary liquids are always sensitive to gravitational fields, through convection and/or sedimentation. Attempts have been made to avoid convection by preparing density-matched liquid mixtures, e.g., by adding a small amount of deuterated cyclohexane in a cyclohexane-methanol mixture⁶. These attempts show that it is impossible to avoid long-term sedimentation because density-matching can never be perfect. In a pure fluid near the critical point the thermal diffusivity becomes very small and the compressibility become very large. These two properties leads to a heat transport mechanism that becomes very fast, the so-called "piston effect." This effect allows thermalization of a fluid to be limited only by the thermal response of the thermostat⁷. Previous experiments with density-matched binary liquids and pure fluid CO_2 under reduced gravity have shown⁸ that when $M=0$ (at $M=0$ the volume fraction of the minority phase is $\phi = 1/2$ where $\phi = \text{ratio of the minority phase volume/total volume}$), an interconnected pattern of domains that coalesces continuously is formed. The characteristic wavelength L_m , at late times, grows linearly with time t . When expressed in the scaled units the corresponding wave number is $K_m^* = 2\pi\xi/L_m$ (ξ is the correlation length for fluctuations of M that, at temperature T_f , is given by $\xi = \xi_0(1 - T_f/T_c)^\nu$, where ξ_0 is the correlation length amplitude, T_c is the critical temperature, and $\nu = 0.63$ is a universal exponent). The corresponding time is $t^* = t/t_\xi$ (t_ξ is the relaxation time for fluctuations of M given by $t_\xi = 6\pi\eta\xi^3/k_B T_f$, where k_B is the Boltzmann constant and η is the shear viscosity). Using these scaled variables the results obtained in all liquid mixtures and in CO_2 during the gravity-free experiment can be placed on the same master curve⁸ strongly supporting universality.

When the volume fraction is very small ($\phi < 0.03$), and the gravity effects are negligible, the droplets do not coalesce. In this region they grow slowly by a diffusion mechanism. Experiments⁹ show that the initial growth follows a power law in time with exponent $1/2$ or $1/3$, depending on the initial supersaturation. Experiments also show that the late stages of growth are always characterized by a $1/3$ power law exponent ("slow" growth) as described by Lifshitz and Slyosov¹⁰. Off-critical systems at a large volume fraction have been studied in a liquid mixture by Wong and Knobler². For $\phi > 0.10$ a "slow" growth characterized by a $1/3$ growth law exponent is reported at early times and a faster growth at late times. The growth exponent varies from $1/3$ to 1 as a function of ϕ ("fast" growth).

If densities of liquid mixture components are close together, gravity effects are expected to be weak in

phase separation experiments. Density matching in a binary fluid mixture has been used in recent work³. In this experiment the temperature quenches were done in the presence of a controlled concentration gradient. This made it possible, in a single experiment, to determine both the coexistence curve and the boundary between the "fast" growth zone and the "slow" growth zone. Due to intrinsic experimental difficulties, however, the errors of the experimental results were large and difficult to estimate. The experiment was also performed using a gradient whose influence is also difficult to estimate. Based on these results it was only possible to state that the threshold between "fast" and "slow" growth has a value of ϕ that is between 0.3 and 0.4.

RESEARCH APPROACH

In order for this experiment to succeed it is necessary to perform very shallow quenches in a pure fluid very slightly off-critical and in a microgravity environment. Although in principle density-matched liquid mixtures on earth or under microgravity could be used for this experiment, they suffer from extremely slow evolution for such shallow quenches. This is not so with pure fluids whose viscosity is nearly 30 times smaller than liquid mixtures. In addition, a precise determination of the concentration of density-matched liquid mixtures is extremely difficult. This is not so with pure fluids whose volume fraction dependence can be accurately determined on earth (temperature variation of the meniscus height). In this experiment we will use two or more off-critical samples ($(\rho - \rho_c)/\rho_c$ less than 1%) of SF_6 to determine the critical threshold of the volume fraction where morphology and growth change. This will be done during a flight experiment using the ESA's Critical Point Facility (CPF).

A typical phase separation experiment consists of quenching a sample from an initial state (density ρ_0 , initial temperature T_i) where it is homogeneous to another state (ρ_b, T_f). In this later state the homogeneous fluid is not stable and the process of phase separation starts. The main part of this experiment consists of a systematic variation of the quench depth, $\delta T = T_{cx} - T_f$, where T_{cx} is the liquid-gas phase transition temperature as shown in Figure 1. The starting point (ρ_0, T_i) of each quench will be the same. To know the quench depth accurately, it is necessary to first determine T_{cx} with a precision of better than 50 μK . After each quench, the system has to be heated 1K above T_{cx} to be homogenized again. The equilibrium volume fraction ϕ of the minority phase is a key parameter for this experiment. ϕ is controlled by controlling the quench depth, δT . This is possible because of the relation $\phi = 1/2 \{1 - (1 + \delta T/\Delta T)^{-\beta}\}$ where $\beta = 0.325$ is a universal exponent and $\Delta T = T_c - T_{cx}$ is calculated from the coexistence curve expression $\rho - \rho_c = \pm B(-T/T_c)^\beta$ where B is a system dependent⁴ constant.

The phase separation experiments require a very precise temperature control (temperature stability better than 50 μK per hour) with negligible temperature gradients in the cell. Temperature quenches of step size 0.1 mK will be typical with an overshoot of less than 10% of the quench depth. This experiment will also require direct real time visualization of the sample with ground-based control. These are needed for the determination of the transition temperature and for adjusting the experimental protocol.

The experiment will also require the following optical diagnostics:

- small angle light scattering for determining the coexistence point temperature, T_{cx} , and the early stages of phase separation
- direct observation of the cell for the determination of T_{cx} , the study of the pattern morphology, and for the determination of the growth laws
- interferometry for estimating the temperature gradient in the cell unit.

SCIENCE RESULTS

Although this project has just begun, there are previous results from other experiments that are relevant. In the IML1 mission using the CPF a sample of density matched binary fluid and a sample of pure fluid were flown. The density matched binary fluid was an off-critical sample of methanol and partially deuterated

cyclohexane at concentration $c \approx c_c - 0.01$. The pure fluid was an off-critical sample of sulfur hexafluoride at $(\rho - \rho_c)/\rho_c = 0.036$. In these experiments the samples were subjected to various quench depths. All the data obtained in liquid mixtures and in pure SF_6 during the gravity-free experiments, when expressed in the scaled units $K_m^* = 2\pi\xi/L_m$ and $t^* = t/t_\xi$ fit remarkably well to the same master curve ($K_m^* \approx 1t^{*1/3}$) giving clear evidence for the universality of phase separation in fluids and liquid mixtures¹¹. Moreover, the crossover between slow and fast growth at $\phi=0.1$ reported by Wong and Knobler could not be observed when gravity effects were suppressed. It is likely that this discrepancy can be attributed to gravity effects that are difficult to see directly.

We have found that density-matched liquid mixtures could not be used on earth to study the crossover in morphology. This is because the range of interest is 0.01 in concentration around c_c . The determination of such a small concentration difference is extremely difficult to achieve. It is also necessary to perform shallow quenches to produce small volume fractions. These experimental conditions lead to very slow evolution. Typically, in partially deuterated cyclohexane-methanol at $c-c_c=0.005$, for a quench depth of 100 μK , the time to obtain droplets of $\approx 30 \mu\text{m}$ is of order 3 hours. This time is much too long in comparison to the stability of the experiment conditions that can be obtained.

To avoid these difficulties an experiment with an off-critical fluid (SF_6) was carried out in the IML2 mission. The density difference $(\rho - \rho_c)$ was measured on earth by studying the temperature dependence of the meniscus between the liquid and gas phases. This precise method gave $(\rho - \rho_c)/\rho_c = 0.0050$. Under microgravity, a determination of the transition temperature T_{cx} with a precision of 50 μK was first done. Fast growth, with interconnected patterns, occurred for quench depths of 300 μK and 1000 μK . This contrasts with the slow growth observed for quench depths of 50 μK and 100 μK . This shows that the volume fraction (related to quench depth as shown above) is the correct parameter for studying the connection between morphology and growth. The presence of a density gradient in the cell, however, (related to the very large compressibility of the fluid near its critical point) complicated the interpretation of the data. This was especially true for estimating the crossover volume fraction. To avoid density gradients during the determination of T_{cx} , it is necessary to use considerable time during the approach. These experiments were hampered by the short time allowed. The T_{cx} determination can only be done on earth to within a few mK because of the gravity-induced gradients present (the fluid is compressed under its own weight).

Another attempt to suppress gravity effects has been considered by Tanaka¹² who studied phase separation with oligomer mixtures between closely spaced plates. During the late stages of growth, when the sizes of the domains were of the order of the thickness of the liquid mixture layer, he also observed two different kinetics of growth. However, in this case the phase separation is controlled by the wetting phenomena from the plates and cannot reveal many interesting bulk effects.

Although the experimental results are few, phase separation has been the object of great theoretical interest over the last several decades. The work by Siggia¹³ has initiated many attempts to explain the two growth laws by considering hydrodynamic arguments. Recently, several groups¹⁴⁻¹⁸ have done large scale direct numerical simulations by using different approaches to solve coupled equations involving diffusion and hydrodynamics. Some of these simulations have recovered a t^1 growth law^{14,15}. Others were unable to reach the late stages of separation but did calculate the transient values of the growth exponent (between 1/3 and 1). In spite of these efforts, the physical mechanism for the linear growth has not been clarified. To our knowledge, the simulations have never shown the two asymptotic growth laws: the exponents are either larger than 1/3 when accounting for hydrodynamics or 1/3 for pure diffusion. Thus the simulations still do not explain the transition from one regime to the other. Recently, a new theoretical approach has been suggested by some of us that explains the existence of the two different regimes and their relation to the pattern morphology. One purpose of the present project is to check the predictions of this model.

RESEARCH PLANS

From two space shuttle missions in the ESA's Critical Point Facility several important results have already

been obtained. In the IML1 experiment the universality of phase separation in fluids and liquid mixtures has been shown. The IML2 experiment yielded preliminary results in a 0.5% off-critical sulfur hexafluoride cell where a transition between disconnected-slow growth and the interconnected fast growth was observed. This has been obtained in a single cell, showing that the volume fraction is a crucial parameter. Nevertheless, the presence of a density gradient in the cell, related to the very large compressibility of the fluid near its critical point, complicated the interpretation of the data and prevented any precise determination of the volume fraction threshold, estimated to be within 30-40%.

To understand why morphology and growth undergo such a dramatic change at this "critical" value of the volume fraction, it is necessary to reproduce and refine the experiments. Systematic variations of the temperature quench depths must be made and significant reductions in density gradients in the cell must be achieved. Because these experiments are done extremely close to the critical point, a microgravity environment is essential.

The specific plan will be to operate two or more cells of sulfur hexafluoride in the Critical Point Facility (CPF) under microgravity. The ground-based program consists of preparation and testing of the sample cells, improvement of the sample cell to minimize temperature gradients in the fluid, and numerical simulation of the phenomena including hydrodynamics.

REFERENCES

1. J. D. Gunton, M. San Miguel and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, vol 8, edited by C. Domb and J. L. Lebowitz (Academic Press, 1983), p.269 and references therein.
2. N. C. Wong and C. M. Knobler, *Phys. Rev. A* **24**, 3205 (1981).
3. Y. Jayalakshmi, B. Khalil and D. Beysens, *Phys. Rev. Lett.* **69**, 3088 (1992).
4. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Clarendon Press, 1971).
5. M. R. Moldover, J. V. Sengers, R. W. Gammon and R. J. Hocken, *Rev. Mod. Phys.* **51**, 79 (1979).
6. D. Beysens, P. Guenoun and F. Perrot, *Phys. Rev. A* **38**, 4173 (1988).
7. see e.g. A. Onuki and R. A. Ferrel, *Physica A* **164**, 245 (1990); P. Guenoun, D. Beysens, Y. Garrabos, F. Kammoun, B. Le Neindre and B. Zappoli, *Phys. Rev. E* **47**, 1531 (1993).
8. Y. Garrabos, B. Le Neindre, P. Guenoun, B. Khalil and D. Beysens, *Europhys. Lett.* **19**, 491 (1992) and refs. therein.
9. A. Cumming, P. Wiltzius, F. S. Bates and J. H. Rosedale, *Phys. Rev. A* **45**, 885 (1992); T. Baumberger, F. Perrot and D. Beysens, *Phys. Rev. A* **45**, 7636 (1992).
10. I. M. Lifschitz and V. V. Sloyosov, *J. Phys. Chem. Solids* **19**, 35 (1961).
11. F. Perrot, P. Guenoun, T. Baumberger, D. Beysens, Y. Garrabos and B. Le Neindre, *Phys. Rev. Lett.* **73**, 688 (1994).
12. H. Tanaka, *Phys. Rev. Lett.* **72**, 1702 (1994).
13. E. D. Siggia, *Phys. Rev. A* **20**, 595 (1979).
14. S. Puri and B. Dünweg, *Phys. Rev. A* **45**, R6977 (1992).
15. F. J. Alexander, S. Chen, and D. W. Grunau, *Phys. Rev. B* **48**, 634 (1993).
16. A. Shinozaki and Y. Oono, *Phys. Rev. E* **48**, 2622 (1993).
17. O. T. Valls and J. E. Farrel, *Phys. Rev. E* **47**, R36 (1993).
18. K. Kawasaki, T. Ohta, *Physica A* **118**, 175 (1983); T. Koga, K. Kawasaki, M. Takenaka and T. Hashimoto, *Physica A* **198**, 473 (1993).

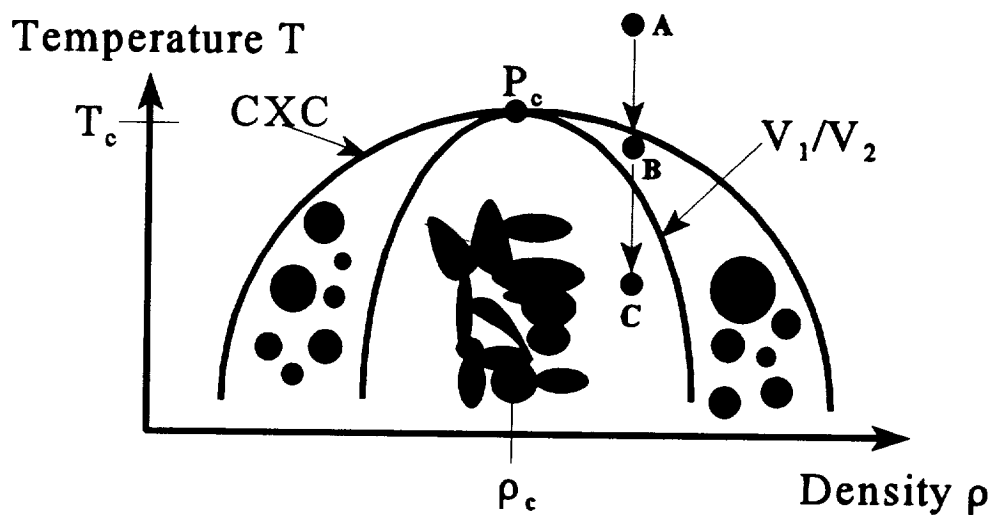


Figure 1.—Morphology and growth. A phase diagram (schematic) of SF_6 that shows the critical point P_c , the critical temperature T_c (45.55°C), the critical density ρ_c (0.737 g/cm^3), and the coexistence curve CXC. When the supercritical fluid (point A, density off-critical by $+0.5\%$) is quenched below CXC, droplets of vapor (volume V_1) and liquid (volume V_2) nucleate and grow. The experiments in IML2 show that the curve $V_1/V_2 \approx 50\%$ separates a region of “slow” growth (A \rightarrow B quench $50 \mu\text{K}$ below CXC) where the droplets are disconnected and grow as $(\text{time})^{1/3}$, from a region of “fast” growth (A \rightarrow C quench 3 mK below CXC), where the droplets are interconnected and grow as $(\text{time})^1$.