

Convection induced by composition gradients in miscible systems

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Abstract

When two miscible fluids, such as glycerol (glycerin) and water, are brought in contact, a large concentration (and density) gradient exists, which relaxes through diffusion. With a mathematical model based on the Korteweg stress, we show that convection can occur which is analogous to surface-tension induced convection (STIC) or Marangoni convection. Specifically, we show that with realistic parameters significant flows can occur with plane interfaces and that drops of miscible fluids can act like their immiscible counterparts. Regarding plane interfaces, an experimental confirmation of this phenomenon is planned for the International Space Station. *To cite this article: V.A. Volpert et al., C. R. Mecanique 330 (2002) 353–358.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

fluid mechanics / computational fluid dynamics / convection / miscible fluid / diffuse interface / microgravity / interfacial tension

Convection induite par des gradients de composition dans les systèmes miscibles

Résumé

Quand deux fluides miscibles, tels le glycérol (glycérine) et l'eau, sont mis en contact, un fort gradient de concentration se crée, qui décroît au cours du temps du fait de la diffusion. Avec un modèle mathématique basé sur le tenseur des contraintes de Korteweg, nous montrons qu'il peut se produire un phénomène de convection analogue à la convection due à la tension de surface, ou convection de Marangoni. En particulier, nous montrons qu'avec des paramètres réalistes on peut obtenir des courants significatifs avec des interfaces planes, et que des gouttes de liquides miscibles peuvent se comporter comme leurs analogues non miscibles. Pour les interfaces planes, une confirmation expérimentale de ce phénomène est prévue dans la Station Spatiale Internationale. *Pour citer cet article: V.A. Volpert et al., C. R. Mecanique 330 (2002) 353–358.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

mécanique des fluides / mécanique des fluides numérique / convection / fluides miscibles / interface diffuse / microgravité / tension superficielle

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Version française abrégée

Korteweg [1] fut le premier, en 1901, à proposer que des gradients de densité dans un fluide pouvaient engendrer des forces, analogues à la tension de surface entre fluides non miscibles, mais qui décroissent avec le temps du fait de la diffusion. En 1949, Zeldovich [2] s'intéressa à l'existence d'une tension interfaciale transitoire, et proposa pour cette tension l'expression (1), où ΔC est la variation de fraction massique à travers la zone de transition, et δ est la largeur de cette zone. Cette relation fut généralisée par Rousar et Nauman [3] à des systèmes loin de l'équilibre, pour des gradients de concentration linéaires, et retrouvée également par Cahn et Hilliard [4] dans le cadre de leur théorie sur l'énergie libre des fluides non-uniformes.

D'autres travaux ont été consacrés à différents aspects de ce phénomène [7,8], notamment à la mesure de cette tension suivant une méthode proposée par Vonnegut [5] et reprise par Petitjeans pour des fluides miscibles [6]. Cependant nous n'avons pas connaissance de travaux sur des courants causés par des gradients de concentration ou de température, en l'absence de convection naturelle.

Nous montrons ici par des simulations numériques que lorsque deux fluides miscibles sont mis en contact, les gradients de concentration peuvent générer des courants de convection. Ces courants ont des effets analogues à ceux de la tension de surface pour des liquides non miscibles. Deux cas sont étudiés : les gouttes de fluides miscibles et les interfaces planes.

Dans l'hypothèse où les fluides sont incompressibles, ont même densité ρ , même viscosité μ , on obtient le système décrit à la Section 2.1, où C désigne la concentration, v la vitesse du fluide, p la pression, et D le coefficient de diffusion, supposé indépendant de C . Enfin, $T = (T_{ij})_{i,j=1,2}$ est le tenseur de contraintes de type Korteweg, où k est un paramètre que nous estimons par des mesures expérimentales de tension de surface. Ce système est considéré dans un domaine rectangulaire, avec des conditions au bord de flux nul pour la concentration, et de non-glissement pour la vitesse. Il est discrétisé par différences finies et résolu par directions alternées.

Les simulations numériques de ce modèle, réalisées avec des paramètres réalistes, donnent les résultats suivants : une goutte elliptique, miscible dans le fluide environnant, prend une forme sphérique du fait des courants de convection (Fig. 1). Par contre, une goutte très allongée a d'abord tendance à se scinder en petites gouttes (Fig. 2), mais elle finit par se contracter en une seule goutte également sphérique. Enfin, dans le cas d'interfaces planes, des gradients de température, des gradients de concentration parallèles à l'interface, ou des gradients de la largeur de la zone de transition peuvent générer des courants de convection (Fig. 3).

Une série d'expériences en microgravité est prévue pour vérifier les résultats concernant les interfaces planes entre un monomère et son polymère. La microgravité doit permettre d'éliminer les phénomènes de convection naturelle.

1. Introduction

Korteweg proposed in 1901 that a nonuniform density (concentration or temperature) distribution leads to stresses in a fluid [1]. He was the first to propose a model how miscible fluids could behave like immiscible fluids. When two miscible fluids, such as a glycerol (glycerin) and water, are brought in contact, a large concentration (and density) gradient exists, which relaxes through diffusion. He supposed that stresses caused by the density gradient acted like a surface tension that would also relax with time. Zeldovich considered the problem of an effective interfacial tension (EIT) for such systems in 1949 and derived an expression for this tension [2].

$$\sigma = k \frac{\Delta C^2}{\delta} \quad (1)$$

where k is a system-specific parameter, ΔC is the variation of mass fraction through the mixing zone, and δ is the width of that zone.

By assuming a linear concentration gradient, Rousar and Nauman demonstrated that an interfacial tension can be found without assuming that the system is at equilibrium and arrived at the same relationship as Zeldovich [3]. Cahn and Hilliard considered diffuse interfaces of immiscible fluids [4]. They treated the free energy of a nonuniform fluid by including a term proportional to the square of the concentration gradient. Their theory predicts that for a linear gradient the interfacial tension has the same form as Eq. (1). The interfacial tension between two fluids can be measured using spinning drop tensiometry, which was developed by B. Vonnegut [5]. Petitjeans was the first to apply this technique to miscible fluids [6]. Petitjeans measured the EIT for glycerol/water and found that the drop diameter reached a quasi-steady value after 100 seconds with a value of 0.6 mN/m.

Petitjeans [7] and Joseph and Renardy reviewed many aspects of interfacial phenomena in miscible fluids [8]. However, we know of no works on the problem of convection caused by concentration or temperature gradients in miscible fluids that is not caused by buoyancy-driven flows. We propose that convection can occur that is analogous to surface-tension induced convection (STIC) or Marangoni convection. Specifically, we show that with realistic parameters significant flows can occur with plane interfaces and that drops of miscible fluids can act like their immiscible counterparts. Experimental confirmation will require weightlessness to eliminate the buoyancy-driven flows that would necessarily occur.

2. Mathematical formulation

2.1. A Korteweg-like stress

In our model, we assume that thermal and diffusive fluxes are small; the fluids are incompressible and have the same density and viscosity. The last assumption is made to simplify the model and to separate the influence of several factors that would complicate the interpretation of the results. With these assumptions the Korteweg-like stress takes the form [9]:

$$T_{11} = k \left(\frac{\partial C}{\partial y} \right)^2, \quad T_{12} = T_{21} = -k \frac{\partial C}{\partial x} \frac{\partial C}{\partial y}, \quad T_{22} = k \left(\frac{\partial C}{\partial x} \right)^2$$

where C is the mass fraction of the first liquid, and where k is system-specific and depends on temperature. We emphasize that k is the constant arising in the square gradient energy term in the Cahn–Hilliard theory [4] ($e = e_0 + k|\nabla C|^2$).

Writing the mass and momentum conservation equations, we obtain the following system of equations:

$$\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C = D \nabla^2 C \quad (2)$$

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{v} + \frac{1}{\rho} \nabla \cdot T \quad (3)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (4)$$

Here D is the coefficient of mass diffusion, \mathbf{v} is the velocity, p is the pressure, ν the kinematic viscosity, and ρ the density. ∇^2 denotes the Laplacian operator. We recall that ν , ρ and D are supposed to be independent of the concentration C .

The problem is considered in a rectangular domain $[0, L_1] \times [0, L_2]$ with noflux boundary conditions for the concentration and with the no-slip boundary conditions for the velocity.

2.2. Estimation of the square gradient parameter

We estimated the value of the square gradient parameter from spinning drop tensiometer measurements. Using a Krüss tensiometer and a custom-built high temperature tensiometer, we studied the effective interfacial tension for two miscible systems. For glycerol/water and polymer/monomer (at 200 °C) the values of EIT are approximately 0.6 mN/m. ΔC is the difference in mass fraction, which is one. We needed an estimate of δ , which we obtained from the diffusion distance, $\delta = (Dt)^{1/2}$.

Petitjeans and Maxworthy measured the diffusion coefficient for glycerin/water to be on the order of $10^{-10} \text{ m}^2/\text{s}$. Taking the time on the order of 100 s, we obtain δ of 10^{-4} m . For polymer at 200°C , we estimated the width of the transition zone to be $3 \times 10^{-4} \text{ m}$, which would give $k = 1.8 \times 10^{-7} \text{ N}$.

Although these are only order of magnitude estimates of the square gradient parameter, they allow us to proceed with realistic simulations.

3. Numerical simulations of miscible drops

For the numerical simulations we introduce the stream function and the vorticity. Artificial boundary conditions for the vorticity are used. They are second-order conditions derived from the noslip boundary conditions for the velocity. The problem is discretized with a finite difference scheme and solved by an alternating direction method.

We use the following values for the parameters: $\nu = 10^{-4} \text{ m}^2/\text{s}$; $D = 2.5 \times 10^{-8} \text{ m}^2/\text{s}$; $k = 1.08 \times 10^{-6} \text{ N}$. Note that this value of k is larger than the above estimate. Indeed we use a value of δ ten times as large as the diffusion distance, because we need many points of discretization in the transition area. Therefore we have to raise also the value of k to compensate this. The results of the simulations weakly depend on values of k and δ if the product $k\delta$ is kept constant.

Our simulations show that an initially elliptic drop forms into a circle in 10 seconds (see Fig. 1). If these results are compared with the evolution of the same drop under pure diffusion, it appears clearly that convection is responsible for this evolution.

We also consider a long stream in a rectangular domain. After a few seconds the convection leads to the constriction of the stream, but it does not break into droplets (see Fig. 2). After a long time (90 s), the capillary forces make the drop more circular.

4. Numerical simulations of plane interfaces

We consider a plane interface between two miscible fluids. We found numerically that convection could occur by a temperature gradient or a concentration gradient parallel to the interface, or by a gradient in the transition width δ . Such a gradient in δ could be created by a nonuniform photopolymerization. We

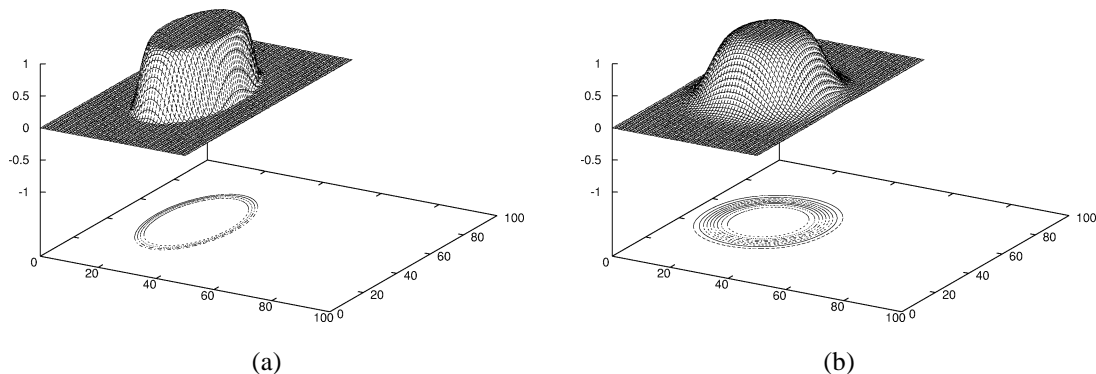


Figure 1. Evolution of an elliptic drop. (a) Initial composition. (b) Composition after 10 seconds. The dimensions of the domain are $L_1 = 0.04 \text{ m}$, $L_2 = 0.02 \text{ m}$. The initial dimensions of the drop (including transition zone) are $0.024 \text{ m} \times 0.012 \text{ m}$.

Figure 1. Evolution d'une goutte elliptique. (a) Composition initiale. (b) Composition après 10 secondes. Les dimensions du domaine sont $L_1 = 0,04 \text{ m}$, $L_2 = 0,02 \text{ m}$. Les dimensions initiales de la goutte (zone de transition comprise) sont $0,024 \text{ m} \times 0,012 \text{ m}$.

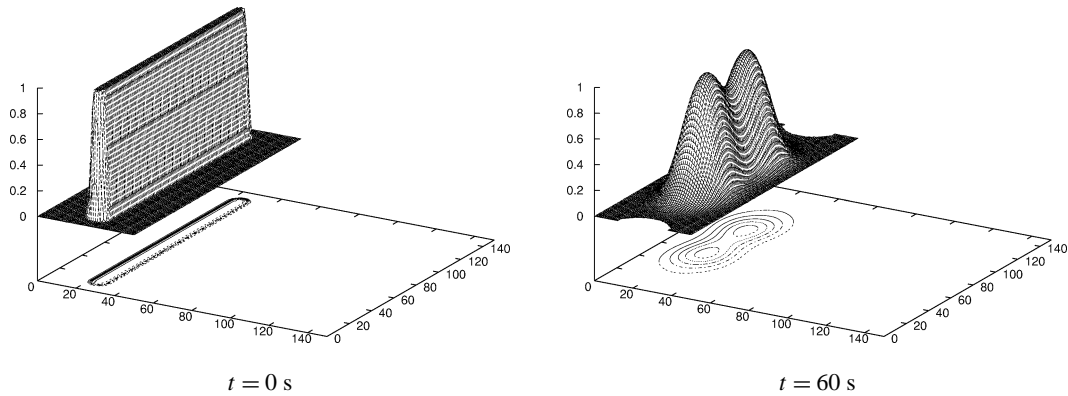


Figure 2. Evolution of composition for a stream. Dimensions of the domain: $L_1 = 0.06$ m, $L_2 = 0.02$ m. Initial dimensions of the stream (including transition zone): 0.05 m \times $2 \cdot 10^{-3}$ m.

Figure 2. Evolution de la composition d'une goutte allongée. Dimensions du domaine : $L_1 = 0,06$ m, $L_2 = 0,02$ m. Dimensions initiales de la goutte (zone de transition comprise): $0,05$ m \times $2 \cdot 10^{-3}$ m.

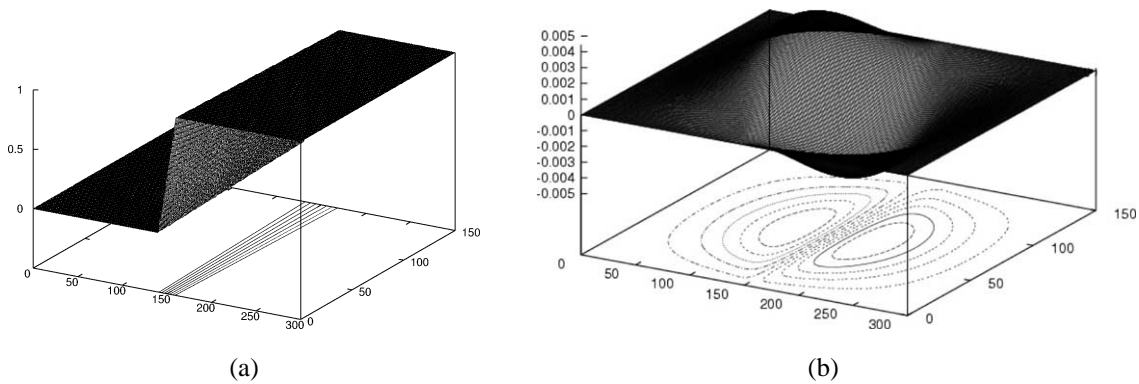


Figure 3. Convection caused by a nonuniform transition width δ . Dimensions of the domain: 0.06 m \times 0.03 m. (a) Initial composition. (b) Stream function after 10 s.

Figure 3. Convection due à une largeur de transition δ non uniforme. Dimensions du domaine : $0,06$ m \times $0,03$ m. (a) Composition initiale. (b) Fonction de courant après 10 s.

illustrate the latter case in Fig. 3. The total displacement of a liquid particle because of the convection can be up to several millimeters, which would be sufficient to observe it experimentally.

5. Conclusions and future work

Our simulations have shown that using realistic parameters, convection can occur in miscible fluids from composition gradients. Because the composition gradients would also lead to buoyancy-driven convection, experiments must be performed in weightlessness. Preliminary experiments were performed on parabolic flights on NASA's KC-135 airplane in which a drop of water was injected into glycerol and a stream of glycerol was injected into water (Fig. 4). The behavior predicted in the simulations was not observed, probably because quiescent weightlessness conditions available by free-floating the apparatus were only 1 or 2 s in duration.

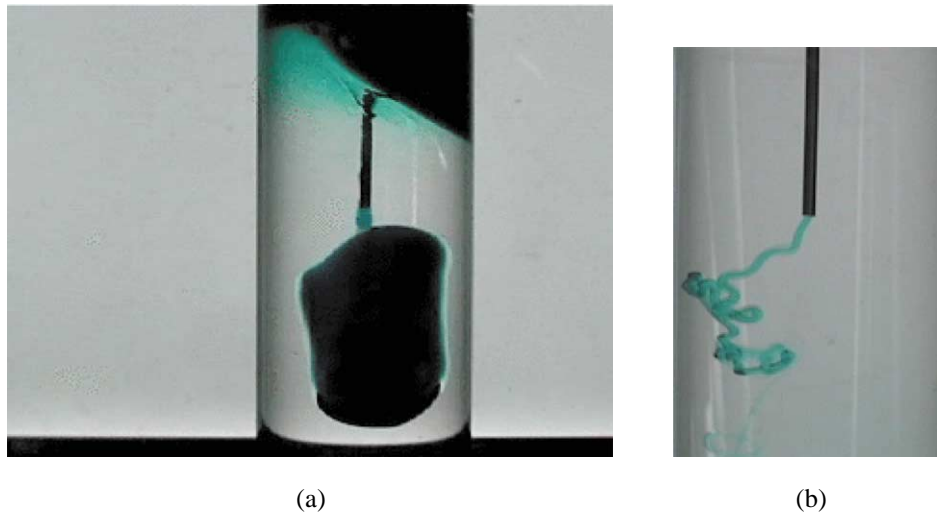


Figure 4. (a) Water (with dye) injected into glycerol in low g . During the short time of the experiment, a few seconds, the drop did not change its shape. (b) A stream of glycerol (with dye) injected into water in low g . The stream did not break during the few seconds of weightlessness. Both experiments were performed in 0.022 m diameter tubes.

Figure 4. (a) *Eau colorée injectée dans la glycérine en faible gravité. Pendant la durée de l'expérience (quelques secondes), la forme de la goutte n'a pas évolué.* (b) *Glycérine (colorée) injectée dans l'eau en faible gravité. La goutte ne s'est pas scindée pendant les quelques secondes de microgravité. Les deux expériences sont réalisées avec des tubes de diamètre 0,022 m.*

Additional experiments are planned with poly(dodecyl acrylate) and its miscible monomer. The Transient Interfacial Phenomena in Miscible Polymer Systems (TIPMPS) experiment will be flown on the International Space Station. Photopolymerization of the monomer will be performed to create known interfacial profiles.

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