Onset of Oscillatory Convection in a Binary Fluid Mixture

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Flow-visualization experiments are described which study the onset of convection in ethanol-water mixtures. It is shown that the conducting state becomes unstable to oscillatory convection, and the onset Rayleigh number, the frequency of oscillation, the linear growth rate of the instability, and the spatial pattern of the flow are studied as functions of the parameters of the fluid mixtures. This oscillatory fluid motion does not stabilize at a finite amplitude but grows exponentially with time until large-amplitude, overturning convection is triggered.

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For a wide range of parameters, convection in binary fluid mixtures is expected to begin with a forward bifurcation to a state in which the velocity oscillates about a state of zero flow in a spatial pattern of parallel rolls. While there have been numerous experimental studies[1–5] and considerable theoretical work[6–8] on this problem spanning more than a decade, many gaps remain between theory and experiment. In this paper, we address these questions by studying the onset of oscillatory convection in a system where we can both control precisely the temperature difference across the convection cell and study the flow pattern directly.

In a homogeneous fluid, convection can be described by two dimensionless parameters: The Rayleigh number R, which is proportional to the temperature difference across the layer, and the Prandtl number P, which is the ratio of the viscosity ν to the thermal diffusivity κ. In a fluid mixture, two additional dimensionless parameters are necessary: The separation ratio Ψ is a measure of the destabilizing effect of concentration gradients caused by the Soret effect, and the Lewis number L is a dimensionless measure of the concentration diffusion time. Specifically,

$$\Psi = c(1-c)(\partial\rho/\partial c)_T(\partial\rho/\partial T)_c^{-1}S_T,$$

where c is the concentration, expressed as a weight fraction, ρ is the density, T is the temperature, and S_T is the Soret coefficient[1] and $L = D/\kappa$, where D is the diffusivity of concentration. For $\Psi < 0$, the Soret effect contributes a stabilizing component to the density gradient, and the onset of flow is suppressed to larger R than that for the onset of convection in the homogeneous fluid mixture. A linear stability analysis, which assumes conducting, permeable, free-slip boundaries and a spatial pattern of stationary parallel rolls, predicts that, for $\Psi < -L^2$, the conducting state is unstable to an oscillatory state in which the circulation within each roll periodically reverses.[1,2,8] With these assumptions, nonlinear calculations predict that this is a forward bifurcation which will lead to a stable oscillatory state just above onset.[7,8] In a laterally infinite system, it has recently been shown that, with the idealized boundary conditions described above, this standing-wave state is unstable to one in which the rolls move laterally as traveling waves.[9] For the more realistic case of rigid, impermeable bondaries, the resuts of the linear analysis are qualitatively the same[1,6]; however, to our knowledge, the nonlinear analysis has not been done.

In this Letter, we report an experimental study of the onset of convection in ethanol-water mixtures for values of Ψ in the range $-0.57 \leq \Psi \lesssim -0.11$. For these mixtures, $L \lesssim 10^{-2}$. We directly observe that convection begins with an oscillatory instability. However, we find that the onset of oscillatory convection is not a forward Hopf bifurcation. For the range of parameters studied, convection continues to grow exponentially with time until finite-amplitude,[3] nearly-steady-state convection is triggered.

In the experiments reported here, the fluid layer is contained in a cell consisting of a copper bottom plate, plastic walls, and a sapphire top plate. The plastic walls ($\kappa = 1.6\times10^{-3}$ cm^2/sec) are much larger in width than the depth of the fluid. The temperature regulation is better than 1 mK, and the entire convection cell is optically accessible from above. The flow pattern is illuminated by a HeNe laser and is visualized by a shadowgraph technique[10]; the light intensity at specific points in the image is also recorded as a function of time.

The working fluid is a mixture of ethanol and water, and the quantity Ψ can be changed by variation of the concentration c or the mean temperature of the fluid. For example, the data described below for $\Psi - = 0.57$ and $\Psi = -0.28$ were obtained with an 8% solution by weight of ethanol in water with top-plate temperatures of 10 °C and 25 °C, respectively. The Prandtl numbers of these fluids are 14.9 and 9.7, and the Lewis numbers are 5×10^{-3} and 6.8×10^{-3}, respectively.

For $\Psi < -L^2$, a linear stability analysis, with free-slip boundary conditions, predicts that oscillatory convection will begin when the reduced Rayleigh number $r = R/R_c$ is raised above

$$r_{c0} = 1 - \Psi(1+\Psi+1/P)^{-1}, \quad (1)$$

where R_c is the onset of convection in the homogeneous fluid, and we have neglected terms of order $L \ll 1$.[1,8] The assumption of rigid boundary condi-

tions increases the quantity $r_{c0}-1$ given by Eq. (1) by about 5%.[1] The oscillatory convection is predicted to be

$$\tau_0=(4/3\pi)\tau_v[(1+\Psi+1/P)/(-\Psi)]^{1/2}, \quad (2)$$

where $\tau_v=d^2/\kappa$ is the vertical thermal diffusion time with d the height of the convection cell.[1,8] The assumption of rigid, impervious boundaries decreases the value of τ_0 given by Eq. (2) by about 30%.[1]

For the mixtures studied here, convection is observed to begin at a value of r in agreement with Eq. (1) and with values of Ψ obtained from previous measurements[11] of S_T and the known physical parameters[12] of the fluid mixtures. However, the values of Ψ extrapolated from existing data for S_T are accurate to only $\pm 50\%$ for the range of parameters studied here. We will present evidence that our experimental data on the onset of oscillatory convection and Eqs. (1) and (2) determine Ψ to within $\pm 5\%$.

For an 8% mixture of ethanol in water at 10 °C, flow begins at Rayleigh number $R=2.215R_c$, where R_c is the onset Rayleigh number for steady convection in a pure fluid, as calculated from the thermal properties of the homogeneous fluid mixture. Although the calculation of R_c is accurate to only 0.5%, our precision in measuring changes in $r=R/R_c$ is approximately 1×10^{-4}. If r is stepped from 2.208 to Rayleigh numbers greater than 2.238, then the expected oscillatory instability is not observed. Instead, we obtain a sudden transition to a finite-amplitude state of "traveling waves" (i.e., a state in which the rolls translate slowly in the hroizontal direction perpendicular to their axes), which has been discussed previously.[3] In contrast to the fluid motion in the oscillatory state, this is a state of "overturning" convection, in which fluid motion within a roll never reverses. The time dependence observed in this finite-amplitude state (whose period is $\gg\tau_0$) is due solely to the translation of the rolls and appears to be unrelated to the oscillatory instability. However, if r is stepped to just above 2.215, we observe a transient composed of exponentially growing oscillations. Figure 1(a) shows the intensity measured at one point in the shadowgraph after r was increased to 2.217. This signal consists of oscillations whose period τ is 50.3 ± 0.1 sec. As shown by the upper curve in Fig. 1, the amplitude A of oscillations increases exponentially with time at early times. During this phase, the observed frequency is constant to within $\pm0.2\%$. Defining $\gamma=d[\ln(A)]/dt$, we find $\gamma=1.16\times10^{-4}$ sec^{-1} for the data shown in Fig. 1.

With the measured value of the onset of convection, Eq. (1) predicts that $\Psi=-0.57$, if the correction for rigid boundary conditions is included. From Eq. (2) and with inclusion of the 30% correction for rigid boundaries, the period of the oscillations is predicted to be $\tau_0=49.9$ sec. This agrees quite well with the observed value of 50.3 sec and confirms that this procedure for measuring Ψ is correct. Hereafter, we will associate the onset of convection with r_{c0} and use Eqs. (1) and (2), with the corrections for rigid boundaries described above, to determine Ψ and τ_0.

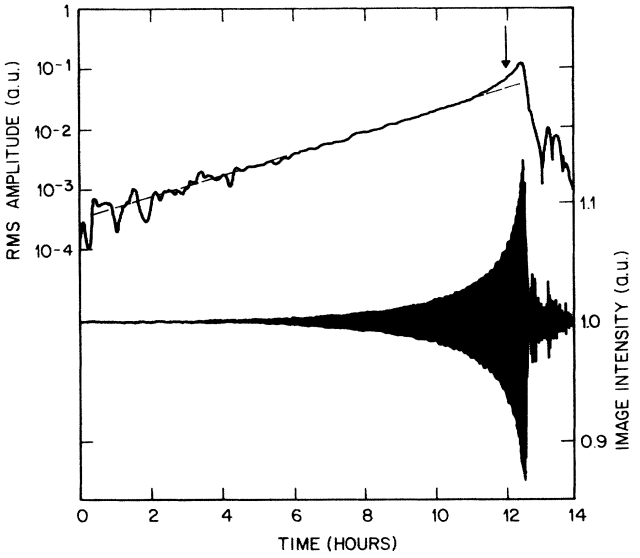

FIG. 1. The intensity at a point in the image as a function of time for $\Psi=-0.57$, after the Rayleigh number r was stepped from $0.9997r_{c0}$ to $1.0009r_{c0}$. For noise reduction, this signal has been passed through a narrow-band filter, with a Q of 40, tuned to $\tau=50.4$ sec. Thus, at $t=12.5$ h, when overturning convection is triggered, the oscillation period increases, and the filter output rapidly drops. Upper curve: The logarithm of the rms amplitude. The dashed straight line corresponds to a growth rate of $\gamma=1.16\times10^{-4}$ sec^{-1}. The arrow indicates the time at which the spatial scans shown in Fig. 3 were taken.

Shown in Fig. 2 is the growth rate γ of the oscillations as a function of reduced Rayleigh number. Data for $\gamma<0$ were obtained by allowing the oscillations to grow to some amplitude, then stepping r to $r-r_{c0}<0$ and measuring the decay of the oscillations. (Here r_{c0} is the experimentally determined value of r at which the growth rate is measured to be zero.) The slope of the solid line in Fig. 2 yields a value of $r_{c0}\,\partial\gamma/\partial r$ of 0.129 ± 0.004 sec^{-1}. In the context of an amplitude equation, the amplitude A is expected to be governed by

$$\dot{A}=\gamma A-g|A|^2A, \quad (3)$$

where $\gamma\propto r-r_{c0}$.[8] For free-free boundary conditions, $r_{c0}\,\partial\gamma/\partial r=\pi^2/\tau_v$,[8] yielding $r_{c0}\,\partial\gamma/\partial r=0.055$ sec^{-1} for the data shown in Fig. 2. To our knowledge, the corresponding calculations for rigid boundaries have not been done.

The spatial pattern of the flow during the oscillatory phase is observed to be a set of straight parallel rolls oriented perpendicular to the long side of the cell. Figure 3 shows the image intensity as a function of position along a line parallel to the long dimension of the

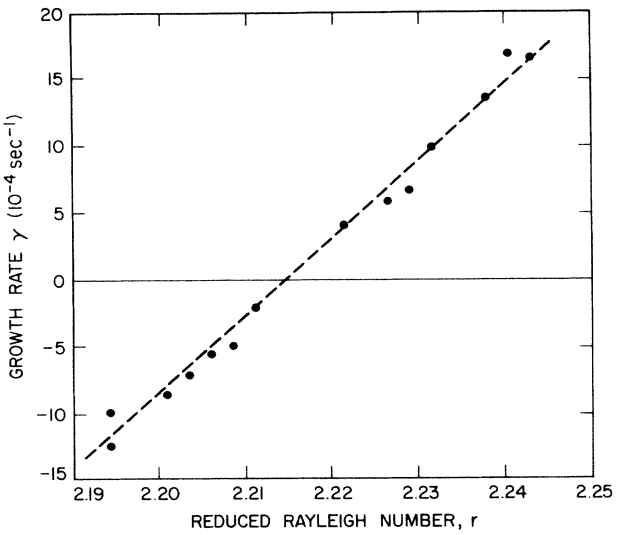

FIG. 2. The growth rate γ as a function of reduced Rayleigh number, r, for $\Psi = -0.57$. The dashed line is a least-squares fit to the data and corresponds to a slope $r_{c0}\,\partial\gamma/\partial r = 0.129 \pm 0.004$ sec^{-1}.

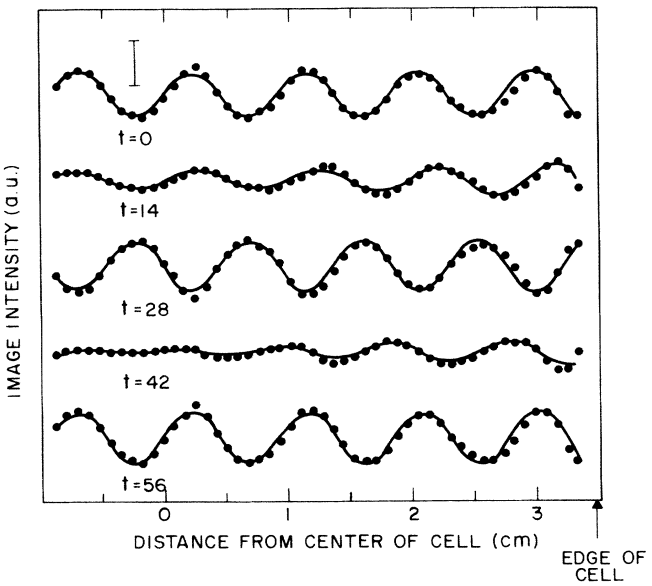

FIG. 3. Measurements of the image intensity (solid circles) as a function of position along a line parallel to the long axis of the cell at several times near 12 h in Fig. 1. The vertical bar represents an intensity modulation of 10%. The solid curves are fits to the data using Eq. (4).

cell, at several times near $t = 12$ h in Fig. 1. Near the center of the cell, the motion is a pure standing wave, but near the edge of the cell, it is not. As shown by the full curves in Fig. 3, the intensity $\tilde{A}(x,t)$ can be represented reasonably accurately by

$$e^{-\gamma t}\tilde{A}(x,t)/\tilde{A}_0 = e^{x/l}\cos(kx-\omega t) - e^{-x/l}\cos(kx+\omega t)$$
$$\equiv 2[\sinh(x/l)\cos(kx)\cos(\omega t) + \cosh(x/l)\sin(kx)\sin(\omega t)], \quad (4)$$

where $\tilde{A}_0$ is a constant, x is the distance from the center of the cell, $\omega = 2\pi/\tau_0$, and k is the wave number of the parallel rolls. For the data shown in Fig. 3, we find $l = 6.0$ cm, as compared with a cell length of 5.9 cm. The first expression in Eq. (4) describes two counter-propagating waves which grow exponentially as they approach the boundaries, while the second expression is written in terms of standing waves. With the same values of γ, ω, and k, Eq. (4) describes the observed flow patterns reasonably accurately down to an amplitude which is two orders of magnitude smaller than shown in Fig. 3. Over this range of amplitude, l is constant to within $\pm 10\%$.

Over the range of growth rates studied, overturning convection is triggered at an amplitude $\tilde{A}_0(x,t)$, as measured near the center of the cell, which is independent of growth rate to within $\pm 30\%$. If we assume that the observed optical contrast is produced solely by the temperature modulation $\tilde{T}$ of the convection rolls and that $\tilde{T}(x,z,t) = \tilde{T}_0(x,t)\sin(\pi z/d)$, where z is the direction perpendicular to the fluid layer and $\tilde{T}_0(x,t)$ has the form of $\tilde{A}(x,t)$ in Eq. (4), then we estimate that overturning convection is triggered when the maximum amplitude $\tilde{T}_0 \simeq 0.025\Delta T_{c0}$, where $\Delta T_{c0} = 5.2$ K is the temperature difference across the fluid layer at the onset of oscillatory convection. Alternatively, the concentration modulation required to produce the observed optical contrast is $\tilde{c} \simeq 1.4\times 10^{-3} c$, where $c = 0.08$ is the ethanol concentration. The error in these values of $\tilde{T}_0$ and $\tilde{c}$ is estimated to be $\pm 50\%$.

The fact that we did not observe a forward bifurcation at $\Psi = -0.57$ led us to investigate the onset of convection at other values of Ψ. At $\Psi = -0.28$, transient oscillations were also observed which were similar in both space and time to the data for the $\Psi = -0.57$ case. The oscillatory period during the exponential growth phase was measured to be 90.1 sec. This compares well with the value of $\tau_0 = 87.1$ sec, obtained by use of Eqs. (1) and (2) and with the corrections for rigid boundaries. For this value of Ψ, we again find $\gamma \propto r - r_{c0}$, with $r_{c0}\,\partial\gamma/\partial r = 0.064 \pm 0.002$ sec^{-1}. In this case, the prediction is $r_{c0}\,\partial\gamma/\partial r = \pi^2/\tau_v = 0.057$ sec^{-1}. Comparison of the data at $\Psi = -0.57$ and -0.28 indicates a strong dependence of $r_{c0}\,\partial\gamma/\partial r$ on Ψ. This contrasts with the prediction of the theory, assuming free-slip boundary conditions, that $r_{c0}\,\partial\gamma/\partial r$ is independent of Ψ.

Experiments were also conducted with solutions for which $\Psi = -0.13$ and -0.11. For these mixtures, the

oscillation periods at onset are larger, by factors of 1.61 and 1.65, respectively, than those predicted by Eqs. (1) and (2). As in experiments at larger $|\Psi|$, these oscillations exist only as growing transients which trigger finite-amplitude states of overturning convection in the form of traveling waves.

The results presented here confirm previous notions that it is the linear oscillatory instability which triggers convection in ethanol-water mixtures, at least for $\Psi \lesssim -0.11$. We observe that flow begins at a value of r consistent with Eq. (1), in the form of oscillatory convection in a pattern of parallel rolls, with a period and growth rate that are close to those which are expected. The spatial pattern of the oscillatory flow, which is shown in Fig. 2 and described by Eq. (4), gives evidence of a length l which may represent the effect of a finite-sized container. It will be of interest to investigate the scaling of l with the container size.

The most surprising result is that the oscillations do not saturate at a finite amplitude. The oscillations stabilize only if we allow their amplitude to grow to a finite value and then experimentally set $r = r_{c0}$. Thus, we do not observe a forward bifurcation at the onset of oscillatory convection.[13] One possible explanation is that the assumption of "free-slip" boundary conditions is qualitatively incorrect in the case of convection in a binary fluid for $\Psi < 0$. It is also possible that a theoretical treatment of traveling-wave oscillatory states in a system of finite lateral extent will be crucial in the understanding of the nature of this bifurcation.

The results presented here provide insight into several previous experiments.[1-3] Oscillatory convection can easily be missed by stepping too quickly through r_{c0}. When it is observed, it only occurs as a transient in time. However, the oscillatory flow evolves to a finite-amplitude state of overturning convection in a pattern of locally parallel rolls which travel laterally.[3] It is the traveling-wave nature of the finite-amplitude state that gives rise to the time dependence observed in previous experiments[1-3] in alcohol-water mixtures.

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