Bistable Heat Transfer in a Nanofluid

Gea Donzelli, Roberto Cerbino,* and Alberto Vailati†

CNISM and Dipartimento di Fisica, Università degli Studi di Milano, via Celoria 16, 20133 Milano, Italy

(Received 18 November 2008; published 13 March 2009)

Heat convection in water can be suppressed by adding a small amount of highly thermophilic nanoparticles. We show that such suppression is not effective when a suspension with uniform concentration of nanoparticles is suddenly heated from below. At Rayleigh numbers smaller than a sample dependent threshold Ra^* we observe transient oscillatory convection. Unexpectedly, the duration of convection diverges at Ra^*. Above Ra^* oscillatory convection becomes permanent and the heat transferred exhibits bistability. Our results are explained only partially and qualitatively by existing theories.

DOI: 10.1103/PhysRevLett.102.104503 PACS numbers: 47.55.P−, 44.35.+c, 65.80.+n

Rayleigh-Bénard (RB) convection represents a fundamental process for heat transfer in fluids. It is of relevance in many natural phenomena, such as circulation in the atmosphere, in the oceans, and inside the Earth's mantle, and for innumerable technological applications where cooling and thermal insulation are involved. Although this is not widely known, adding even a tiny amount of highly thermophilic nanoparticles (NP) to a liquid could prevent the convective heat transfer, irrespective of the magnitude of the temperature difference applied to the fluid [1,2]. Because of the thermal diffusion (TD) effect [1,2], the NP accumulate near the hot (bottom) boundary and give rise to a stabilizing density difference $\Delta\rho_c$ which counteracts the unstable density difference $\Delta\rho_T$ created by the thermal dilation of the liquid. The relative strength of the two contributions is expressed by the separation ratio $\Psi = \Delta\rho_c/\Delta\rho_T$, and for $\Psi \lesssim -1$ the NP suppress the RB instability [1–3]. Recent theoretical work [3–5] suggests that by starting in a configuration where the concentration of NP is uniform and by suddenly imposing a large temperature difference the suspension is brought into a *stationary* convective regime lasting indefinitely.

In this work we investigate experimentally RB convection in a suspension of highly thermophilic NP ($\Psi = -7.5$). We observe a transient oscillatory convective state whose lifetime increases with the Rayleigh number Ra and diverges at a sample dependent threshold Ra^*. Our results confirm that an instability can indeed be triggered, as expected from theories. However, in contrast with them, above Ra^* the instability becomes permanent but remains *oscillatory*. We show that above Ra^* the heat transferred exhibits a bistable behavior. The upper bistability branch is represented by the permanent oscillatory convective regime obtained with an initially uniform concentration of NP, while the lower branch is the conductive regime selected in the presence of a fully developed concentration profile. Beyond its fundamental relevance, the opportunity of controlling the stability of a nanofluid (NF) is of great practical relevance for many industrial processes. As an example, the samples investigated in this work are widely used in the production of industrial paints and coatings. From the technological side, the ability of tuning the heat transfer of a NF represents a first step towards the development of smart cooling materials [6].

As usual, convection is induced in the RB configuration by heating from below a horizontal layer of sample [7]. The thermal driving of the fluid is represented by the Rayleigh number $\mathrm{Ra} = \alpha g \Delta T h^3/(\nu\kappa)$. Here h is the sample thickness, α is the thermal expansion coefficient, ν the kinematic viscosity, κ the thermal diffusivity, ΔT the temperature difference, and g the gravity acceleration. In a simple fluid such as water, convection sets in when Ra exceeds the critical threshold $\mathrm{Ra}_c = 1708$. The heat transferred by the fluid is expressed by using the dimensionless Nusselt number $\mathrm{Nu} = Qh/(\chi\Delta T)$. Nu is defined as the ratio of the actual heat flow Q across the fluid to the heat that would be transferred by conduction only (χ is the fluid thermal conductivity). In the conductive state $\mathrm{Nu} = 1$, while an increase of Nu is observed in the presence of convection. For a simple fluid Nu is characterized by a supercritical bifurcation at Ra_c [7–9]. By adding NP to the fluid the bifurcation scenario becomes more complicated (see, for example, [3], and references therein) because the thermal gradient induces a flow of particles with respect to the carrier liquid by means of the TD effect [2]. In the absence of convection the TD flow generates a steady state concentration difference $\Delta c = -S_T c(1-c)\Delta T$ and in turn a density difference $\Delta\rho_c = \rho\beta\Delta c$. Here S_T is the Soret coefficient, c the weight fraction concentration of the NP, and ρ the mass density of the fluid. S_T (and in turn Ψ) can be either positive (thermophobic NP) or negative (thermophilic NP). The sample under consideration in this work is a suspension of spherical particles made of a copolymer of tetrafluoroethylene and perfluoromethylvinylether (Hyflon® MFA) [10] dispersed in water with a concentration $c = 4\%$ and is characterized by a large negative separation ratio $\Psi = \beta S_T c(1-c)/\alpha = -7.5$. We stress that this implies that the stabilizing effect of $\Delta\rho_c$ prevails on the destabilizing one associated with $\Delta\rho_T$ when the NF is heated from below. On the other side, the growth of $\Delta\rho_T$ is much faster than that of $\Delta\rho_c$. The ratio between the time scales associated with these two growth processes is the Lewis number $\mathrm{Le} = D/\kappa = 8.84 \times 10^{-5}$. The large difference between the time scales is typical of NFs and gives rise to a dynamic competition between $\Delta\rho_T$ and $\Delta\rho_c$ which originates a rich bifurcation scenario [3].

The experimental investigation of the heat transfer in a NF requires the application of a carefully controlled temperature difference. At the same time, it is desirable to guarantee an optical clearance to the sample for the observation of the convective pattern. For this reason the sample is sandwiched between two 8 mm thick sapphire plates with a diameter of 7 cm acting at the same time as optical windows and thermalizing plates. The sample thickness is $h = 0.29$ cm, the diameter is $\phi = 4.7$ cm, and the aspect ratio is $L = \phi/(2h) = 8.14$. The plates are in contact with toroidal thermoelectric devices (TED), controlled by a proportional integral servo control. Each TED is also in contact with a toroidal flange connected to a water loop, which keeps the sample at an average temperature of 25 °C. The thermal stability at steady state is of the order of 1 mK/24 h for the average temperature and of the order of 3 mK/24 h for the applied temperature difference. The convective patterns are visualized by means of the shadowgraph technique [11].

The time resolved determination of the actual heat Q_S transferred by the sample and of the actual temperature difference ΔT_S applied to it requires a careful calibration of the cell. The first step of the calibration involves the determination of the power Q_T pumped by the TEDs. This has been achieved by monitoring the supply current, the voltage, and the temperatures at both sides of the TED and by calculating Q_T by using a mathematical model of the TEDs [12]. The second step involves the careful assessment of the heat losses in the thermal gradient cell by using a calibration sample. This has been achieved by modeling the cell by a suitable network of thermal resistances and performing calibration measurements by using disks made of Macor ceramics instead of the sample. In order to check the reliability of the calibration procedure we have performed measurements of the convective heat transfer in water and compared them with reference data [7–9]. Figure 1 shows a plot of Nu as a function of Ra. Upward pointing triangles represent our measurements on water. Squares represent seminal measurements on water by Chandrasekhar and Silveston ($10 \leq L \leq 66$) [7,8] and downward pointing triangles are high precision results obtained by Behringer and Ahlers on a large aspect ratio sample ($L = 57$) of liquid helium [9]. Our results are in good agreement with reference data.

We investigate convection in a NF by starting in a homogeneous concentration condition [3–5]. This condition is not trivial to obtain, due to the sedimentation process which produces an accumulation of particles at the bottom of the cell. We found that, even by using small

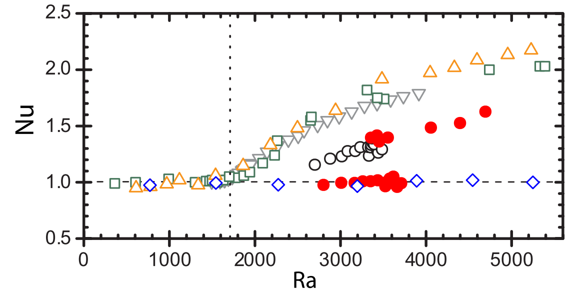

FIG. 1 (color online). Nusselt number plotted as a function of Ra. Squares and downward pointing triangles represent reference data on water [8] and liquid helium [9], respectively. Upward pointing triangles represent data for water taken by us. The vertical dotted line marks the threshold for RB convection Ra_c. Circles represent measurements on the MFA NF performed by starting with a uniform concentration of NP; open circles represent data taken during transient convection, while solid circles represent measurements taken at steady state. The data clearly show a discrete jump of Nu in correspondence of the transition from transient to permanent convection at $\mathrm{Ra}^* \approx 3400$. Diamonds represent measurements on the MFA NF performed by starting in the presence of a fully developed concentration profile. At variance with a simple fluid, above Ra_c the conductive branch is stable for a highly thermophilic NF heated from below [1–3]. The horizontal dashed line represents the conductive regime $\mathrm{Nu} = 1$.

particles, an initial concentration difference as small as about 2% between the top and bottom of the cell is enough to completely inhibit any convective motion. Therefore, to attain an initially uniform concentration of the sample we balanced the barodiffusive flow of the particles by applying a small temperature difference ΔT_g, by heating from above. The temperature difference was chosen so that it induces a TD flow that exactly counterbalances the barodiffusive one. This condition was checked experimentally by carefully inspecting the shadowgraph images for the presence of convective motions induced by a solutal convective instability. In fact, the threshold for the solutal instability when heating from above corresponds to a temperature difference about 50 mK larger than ΔT_g [1]. Therefore, we chose a value $\Delta T_g = -3.33$ K, slightly smaller than the theoretical one so to avoid going beyond the solutal convective threshold. Before starting any measurement the sample was kept under the action of ΔT_g for 2.5×10^5 s (about 3 days), roughly 4 times the characteristic time associated with the slowest diffusive mode $\tau_D = h^2/(D\pi^2)$. In this way its concentration became uniform up to about 0.2%.

By starting from a homogeneous density profile and by applying abruptly a thermal gradient such that $\mathrm{Ra} > \mathrm{Ra}_c$, heating from below, convection sets in. The initial patterns are stationary and the structures are very similar to those obtained with water [13]. This is due to the fact that the initial stages of convection are dominated by the destabilizing effect of thermal dilation due to the very small Le of the sample, in agreement with recent theoretical predictions [5]. However, after a few minutes the convective pattern starts to move. Looking at the shadowgraph images, acquired in sequence at a rate of one image every 4 s, we observe traveling waves in the form of parallel rolls, zippers, reticular patterns, and chaotic patterns. All these different behaviors occur at every difference of temperature imposed, and at any moment during the evolution of the instability. The rise of traveling waves is the sign that the role of concentration becomes relevant [14]. Thermal diffusion and sedimentation determine an accumulation of NP near the bottom plate and a depletion near the upper one, giving rise to boundary layers of concentration. In this regime the evolution of the system depends on the dynamic competition between the stabilizing action of the concentration profile near the boundaries and the remixing of the concentration due to convective motions.

Figure 2(a) shows a typical evolution of the power Q_S transferred by the NF after the sudden imposition of a temperature difference of 9.82 K. Q_S exhibits a transient convective phase, where it remains stable at $Q_S \approx 6.76$ W. After about 55 000 s convection stops suddenly, Q_S decreases abruptly and stabilizes to the conductive value $Q_S = 5.39$ W. Together with Q_S we have simultaneously determined the root mean square (rms) average $I_{\rm rms}$ of shadowgraph images of the convective pattern. $I_{\rm rms}$ provides a quantitative characterization of the lack of homogeneity in a shadowgraph image due to the presence of the instability. The behavior of $I_{\rm rms}$, shown in Fig. 2(b), qualitatively mirrors that of Q_S. However, in this case pronounced fluctuations of $I_{\rm rms}$ are apparent during the transient convective regime. During the drop to steady state $I_{\rm rms}$ exhibits intermittency. The analysis of the shadowgraph images shows that intermittency corresponds to the convective pattern being temporally confined only in a portion of the cell, a behavior known as transient localized states [15].

By performing measurements at many temperature differences we found that the time t_e needed by the transient instability to come to an end increases as Ra is increased and diverges to infinity close to $\mathrm{Ra}^* \approx 3400 \pm 60$. This behavior is shown by the open circles in Fig. 3. The value of t_e has been determined by estimating the time, starting from the imposition of the temperature difference, needed for Q_S to fall down to steady state. Above Ra^* we observed that the oscillatory instability survived indefinitely (full circles in Fig. 3) and it was stopped by shutting down the temperature difference after one week. The sudden drop of the convective flow shown in Fig. 2, together with the scattering of the data in Fig. 3 near Ra^*, suggests that the end of convection is a catastrophic process, rather than a deterministic one.

In order to check whether the observed transition is universal we have performed parallel measurements by using a suspension of spherical silica NP [16] dispersed in water at a weight fraction concentration $c = 4.1\%$ (separation ratio $\Psi = -3.5$). The silica sample exhibits the same qualitative behavior shown in Fig. 3 for MFA: a transient oscillatory convective regime becoming permanent above the threshold $\mathrm{Ra}^* = 2200 \pm 80$. A tentative linear fit of Ra^* as a function of Ψ yields $\mathrm{Ra}^* = \mathrm{Ra}_c[1 - (0.12 \pm 0.01)\Psi]$, where we have taken into account that for a simple fluid $\Psi = 0$ and $\mathrm{Ra}^* = \mathrm{Ra}_c$ and we have neglected any dependence from the Lewis and Prandtl numbers. Our results are not compatible with the theoretical model in Ref. [4], which predicts the existence of a transition from transient oscillatory convection to permanent stationary convection at $\mathrm{Ra}^* = 1805$, irrespective of the separation ratio of the NF. We think that this discrepancy is most likely due to the fact that available models fail to provide a reasonable description of the nonlinear cou-

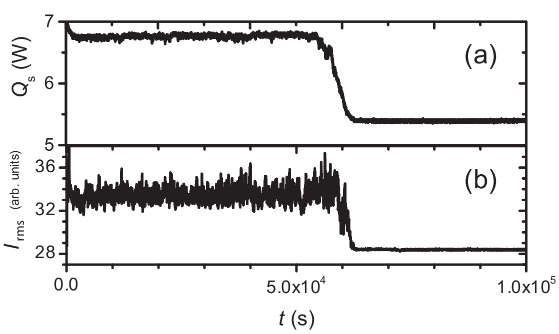

FIG. 2. (a) Power Q_S transferred by the sample as a function of the time elapsed from the imposition of the temperature difference. Q_S remains stable at 6.76 W for about 5.5×10^4 s. After this transient the convective heat transfer stops suddenly and Q_S drops to 5.39 W. (b) Time evolution of the rms average of shadowgraph images. During the oscillating convective regime $I_{\rm rms}$ exhibits large fluctuations generated by the propagating convective patterns.

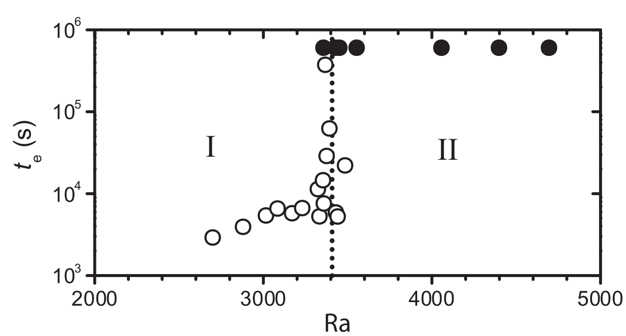

FIG. 3. Open circles represent the time t_e needed for transient oscillatory convection to end as a function of Ra. The time t_e diverges as $\mathrm{Ra}^* \approx 3400$ (vertical dotted line) is approached from below. Full circles represent experimental runs where oscillatory convection survived indefinitely, until it was stopped after 1 week. Regions I and II mark the transient and permanent oscillatory convective regimes.

pling between the convective flow and the concentration boundary layers.

As a further characterization of the transition from transient to permanent convection we have studied the dependence of Nu from Ra. Experimental results for MFA are shown by the circles and diamonds data points in Fig. 1, together with the results obtained for water. Circles represent transient (open circles) and steady state (solid circles) measurements of Nu taken by imposing a temperature difference to a NF with a uniform concentration of NP, while diamonds represent measurement taken by starting with a fully developed concentration profile. The dispersion of the data shows that the uncertainty of Nu is typically of the order of 10%. Quite interestingly, at $Ra^* \approx 3400$ the Nusselt number exhibits a discrete jump [17]. Above Ra^* the Nusselt number has a bistable behavior: an upper permanent oscillatory convection branch (solid circles) and a lower conduction branch (diamonds) separated by a forbidden gap. The selection of the branch is attained by changing the initial concentration profile. Whenever the initial concentration of NP is homogeneous the system bifurcates into the upper branch, while in the presence of a fully developed concentration profile the lower branch is selected. By exploiting the TD effect the initial state can be switched easily simply by imposing a suitable conditioning temperature difference to the sample. We think that the reported bistable heat transfer is very promising for the development of a smart heat transfer medium that can be switched at will between two high-low conductance states. This kind of bistable behavior has been recently predicted to occur for convection in NFs with large negative separation ratio [3,4]. However, these models predict a transition to a permanent *stationary* convective state which is not compatible with our results. Indeed we observe an *oscillatory* convective state which can be either permanent or not (see Fig. 3), depending on the value of Ra. Moreover, Fig. 1 shows that the Nusselt number of the NF is significantly smaller than that of the carrier liquid, at every value of Ra above Ra_c. This result and the oscillatory nature of permanent convection suggest that strong concentration differences can develop within the cell irrespective of the convective mixing generated by thermal convection. We believe that this surprising finding might represent a challenging task for future theoretical work.

We have shown that by adding a small amount of NP to water the RB convective process changes drastically. The stationary convective patterns are transformed into a traveling wave scenario. Even in the presence of a strong stabilizing action due to the concentration profile induced by the TD effect, the large time scale needed for this profile to develop in a NF with uniform concentration allows the emergence of a convective instability. The instability exhibits an unforeseen transition between transient and permanent oscillatory convection, characterized by a jump bifurcation of Nu. The bifurcation exhibits two stable branches: an upper convective branch and a lower conductive one. The selection of the two branches depends on whether the initial concentration profile is uniform or fully developed.

We thank M. Giglio and R. Piazza for discussion and support. We thank Grace Davison for the supply of the silica sample. Work partially supported by the Italian Ministry of University and Research (MIUR).

*Current address: Dipartimento di Chimica, Biochimica e Biotecnologie per la Medicina, Università degli Studi di Milano, via Fratelli Cervi 93, 20090 Segrate (Milano), Italy.
†Corresponding author.
alberto.vailati@unimi.it

[1] J. K. Platten and J. C. Legros, *Convection in Liquids* (Springer, Berlin, 1984).
[2] T. E. Faber, *Fluid Dynamics for Physicists* (Cambridge University, Cambridge, England, 1995).
[3] B. Huke, H. Pleiner, and M. Lücke, Phys. Rev. E **75**, 036203 (2007).
[4] A. Ryskin and H. Pleiner, Phys. Rev. E **71**, 056303 (2005).
[5] M. I. Shliomis and B. L. Smorodin, Phys. Rev. E **71**, 036312 (2005).
[6] P. Keblinski, J. A. Eastman, and D. G. Cahill, Mater. Today **8**, 36 (2005).
[7] S. Chandrasekhar, *Hydrodynamic and Hydromagnetic Stability* (Dover, New York, 1981).
[8] P. L. Silveston, Forsch. Ingenieurwes. **24**, 59 (1958).
[9] R. P. Behringer and G. Ahlers, J. Fluid Mech. **125**, 219 (1982).
[10] Hyflon®MFA, Solvay-Solexis. The particles have a diameter of 44 nm. Other properties of the sample at 25 °C are $D = 1.30 \times 10^{-7}$ cm^2/s, $\kappa = 1.47 \times 10^{-3}$ cm^2/s, $\alpha = 2.52 \times 10^{-4}$ K^{-1}, $\nu = 8.96 \times 10^{-3}$ cm^2/s, $\beta = 0.54$, and $S_T = -9.0 \times 10^{-2}$ K^{-1}.
[11] G. S. Settles, *Schlieren and Shadowgraph Techniques: Visualizing Phenomena in Transparent Media* (Springer, Berlin, 2001).
[12] See, for example, http://ferrotec.com/technology/thermoelectric/thermalRef01.php
[13] V. Croquette, M. Mory, and F. Schosseler, J. Phys. (Paris) **44**, 293 (1983).
[14] D. Jung, P. Matura, and M. Lücke, Eur. Phys. J. E **15**, 293 (2004).
[15] K. Lerman, E. Bodenschatz, D. S. Cannell, and G. Ahlers, Phys. Rev. Lett. **70**, 3572 (1993).
[16] Ludox®TMA, Grace Davison. The particles have a diameter of 32 nm. Other properties of the sample at 30 °C are $D = 2.2 \times 10^{-7}$ cm^2/s, $\kappa = 1.52 \times 10^{-3}$ cm^2/s, $\alpha = 2.97 \times 10^{-4}$ K^{-1}, $\nu = 8.18 \times 10^{-3}$ cm^2/s, $\beta = 0.57$, $S_T = -4.7 \times 10^{-2}$ K^{-1}, and $Le = 1.46 \times 10^{-4}$.
[17] The seeming hysteresis of the MFA data in Fig. 1 is an artifact due to the finite thermal conductivity of the sapphire plates that determines a small variation of Ra at the end of convection.