Periodic banding in crystallization from rotating supersaturated solutions

2001 J. Phys.: Condens. Matter 13 5001

(http://iopscience.iop.org/0953-8984/13/21/324)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 5001–5008 www.iop.org/Journals/cm PII: S0953-8984(01)19838-3

Periodic banding in crystallization from rotating supersaturated solutions

S G Lipson

Physics Department, Technion—Israel Institute of Technology, 32000, Haifa, Israel

Received 6 December 2000

Abstract

A supersaturated solution of NH_4Cl cools while rotating in a horizontal drum. When crystals nucleate, they accumulate in well-defined periodic bands, normal to the axis of rotation. The mechanism responsible for this periodic pattern is not understood, but some ideas are proposed.

1. Introduction

In this paper, I should like to present a new and unexplained phenomenon, which may involve both interface physics and hydrodynamics. The approach I have used here was first to do a number of experiments to see how reproducible the effect is, and to collect a certain amount of potentially significant data to indicate its dependence on some obvious parameters. Then I discussed these data with several well-informed colleagues who might be able to contribute to understanding the phenomenon. After all, there is always a chance that there is an obvious explanation which I had overlooked, or that the phenomenon is already known and has been explained elsewhere. Since from these discussions it appeared that there is no simple explanation, I am taking this opportunity to present to a wider audience the incomplete data that I have obtained together with some possible routes to an explanation.

Several years ago, as part of a study of the influence of anisotropy on the character of dendritic crystals [1], we developed a technique for studying the growth of crystals from supersaturated solution in three dimensions without any interaction with a substrate. We wanted to levitate the crystal in the solution during its growth, at a distance much greater than the diffusion length $d_D = D/2v$ from any wall, substrate etc, where D is the diffusion constant and v the crystal growth velocity. The true growth form should then be observed. Growth of crystals under microgravity conditions in space has been reported by Glicksman *et al* [2]. After considering several possible methods of achieving levitation in the laboratory, we decided on a system using a rotating fluid. The supersaturated solution was contained in a glass tube, 17 mm in diameter, closed at both ends and immersed in a large water bath (aquarium) whose temperature was controlled. We rotated the tube about its axis at a fixed rate of rotation Ω. The crystals levitated at a position where the upwards Stokes force due to the fluid flow balanced gravity, and were photographed during their growth. The aquarium had two purposes. The first was to provide a controlled-temperature environment; the second was to allow distortionless imaging of the crystals through the tube, which would otherwise act

0953-8984/01/215001+08$30.00

as a cylindrical lens. Figure 1 shows an example of a single large dendritic crystal of NH_4Cl grown in this way. One observes the delicate dendritic structure, within an envelope which can be described as a cube with somewhat concave facets. NH_4Cl grown with some additives resulted in octahedral envelopes [3].

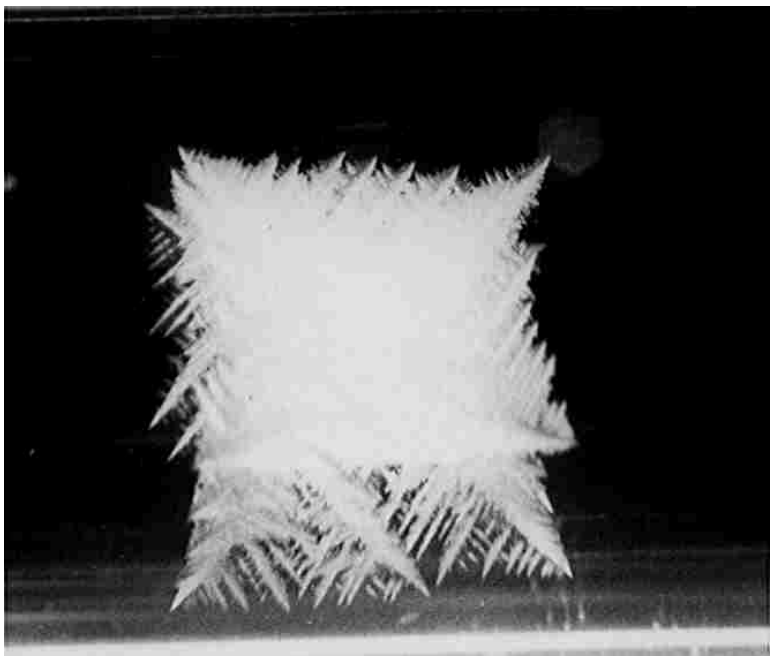

Figure 1. A dendritic single crystal of NH_4Cl growing while levitating. The crystal is approximately a cube with 6 mm edges.

The levitation mechanism can be described for a general particle of finite size. Consider a particle of radius a and volume V at distance r from the axis of the tube, in the horizontal plane containing the axis. On the side of the axis where the fluid flow is upwards, two opposing forces act on the particle. One is gravitational, of magnitude $F_1 = Vg\,\delta\rho$, where $\delta\rho$ is the difference between the density of the particle and that of the fluid, ρ. The other is the Stokes force from viscosity, $F_2 = 6\pi\nu\rho ua$, where ν is the kinematic viscosity and u the upwards velocity of the fluid; if the particle is not a sphere, this expression is modified by a constant factor [4]; moreover, the proximity of the tube walls also alters the value of the Stokes force considerably [5]. Since the velocity $u = \Omega r$, balance between these two forces is achieved at a size-dependent radius, which is of the order of a few mm for the parameters of the present experiments. It is not immediately obvious that this point is an attractor, but experimentally we observed it to be so. We shall call the line of such points the 'neutral axis'. A levitated crystal will grow as if in an unperturbed environment provided that

$$d_D < d_V \tag{1}$$

where $d_V = \sqrt{\nu/\Omega}$ is the viscous penetration depth. One can also observe that a particle 'trapped' in this position rotates on its own axis since the fluid on the two sides moves at different velocities; it is in shear flow.

The levitation mechanism is not specific to crystals. However, one should note that the density difference $\Delta\rho$ in the case of a crystal such as that shown in figure 1 is quite small,

since the dendritic structure traps a lot of fluid, which one would expect to move rigidly with the crystal mass if (1) is true. Moreover, the crystals grow, so a possibly size-dependent mechanism is scanned over time. In all, the conditions reproduce fairly well those in which the most well-known dendritic crystals, snowflakes, grow while falling at their terminal velocity through water-supersaturated air.

The discussion so far concerns the behaviour of a single levitated particle. When further particles are present, several possibilities occur. We ignore for the moment the thorny problem of interactions between crystals. A second particle of a similar size to the first one might come to equilibrium at another point along the neutral axis. On the other hand, it might enter an orbit around the neutral axis in the same vertical plane as the first crystal. Then, if the second particle has a different size it might come to equilibrium on an axis at a different radius. But the interactions between particles are very strong and complicated, particularly if the particles are rotating (spinning) on their axes.

2. Experimental observations

While using the levitation technique experimentally, we succeeded in growing satisfactory crystals provided that the number nucleated was very small, such that interaction between individual crystals could be ignored. However, we discovered that when many crystals nucleate at the same time, periodic patterns develop, presumably as a result of the interactions between them. We have at present no clear understanding of this phenomenon.

In order to obtain some more complete data on the process, a simple mechanical system (a tumbler) was used to rotate glass tubes about a horizontal axis at a rate between 0.5 and 2 rotations per second (figure 2). The experiments were done in air, without the aquarium. Aqueous solutions of NH_4Cl, both in the pure state and contaminated with small amounts of $CuSO_4$ or urea, were prepared saturated at temperatures about 10 °C above room temperature. Glass tubes between 22 and 11 mm in inner diameter and about 200 mm long were filled with a solution and inserted into the tumbler and the rotation started. After a period of up to half an hour, crystals nucleated spontaneously and their distribution along the tube was observed.

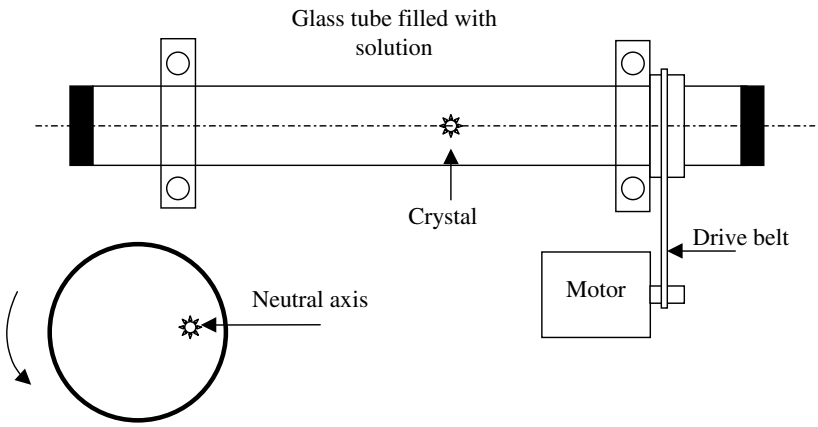

Figure 2. The experimental set-up.

Initially the few crystals which nucleated moved randomly around the neutral axis on the up-flowing side as described above. However, within a few minutes, as the crystals grew in both size and number, they organized into planes normal to the rotation axis at periodic

intervals along the tube (figure 3). Within the planes, the crystals orbited around the off-centre neutral axis. The planar regions then thickened into bands (figures 4 and 5), retaining the original periodic separation, until most of the tube was full of crystallites. Observation from the top showed the crystals to be grouped on the up-flowing side of the tube. The banding period was somewhat larger than the inner diameter of the tube.

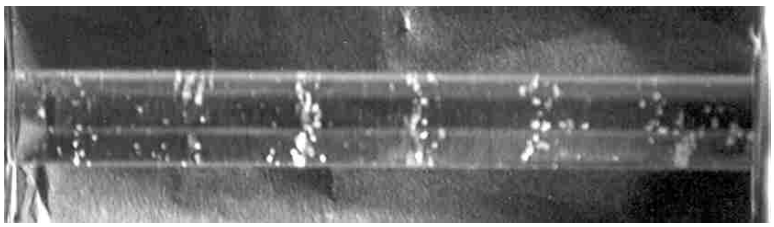

Figure 3. Initial stages of banding in $NH_4Cl(CuSO_4)$ crystal growth.

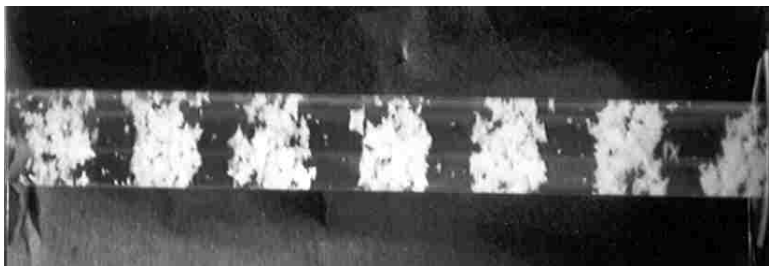

Figure 4. Developed bands in NH_4Cl in a 16 mm ID tube rotating at 42 rpm.

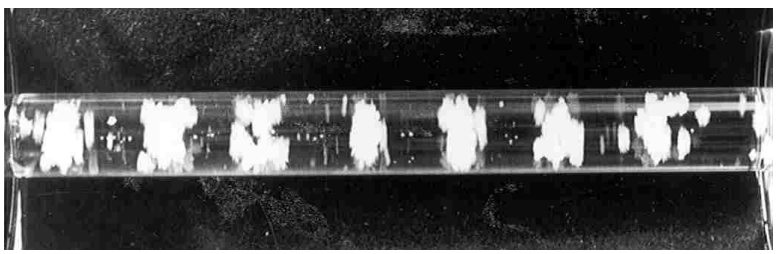

Figure 5. Developed bands in NH_4Cl in an 11 mm ID tube rotating at 54 rpm.

The effect was observed at rates of rotation Ω between 0.5 and 1.3 s^{-1}. For each size of tube the range of Ω through which it persisted spanned a factor of about 2, with lower Ω for larger tubes. The spatial period of the banding was between 1.2 and 1.7 times the tube diameter and seemed to be independent of Ω within the range for which banding occurred, although there was some evidence for a shorter banding period very close to the lower cut-off of Ω (but this may be a transient). No systematic relationship between the positions of the terminal bands and the ends of the tube was observed.

However, the effect was soon seen to be independent of the fact that the crystals were growing. In one experiment, after rotation had been turned off and the system had equilibrated for more than 24 hours, the crystallites were redistributed uniformly by shaking the tube. A

short while after restarting the rotation, the bands reappeared at the same spatial frequency as before. So the crystals appear to be markers of some periodic disturbance in the fluid. Further evidence from bubbles strengthens the case that crystal growth is irrelevant to the banding phenomenon. Before the crystals nucleated, small air bubbles were sometimes released. These bubbles first located along a line (the neutral axis) on the down-flowing side of the tube, and then the smallest ones could be seen to form bands in the same way as the crystals (figure 6). Larger bubbles showed no banding effects.

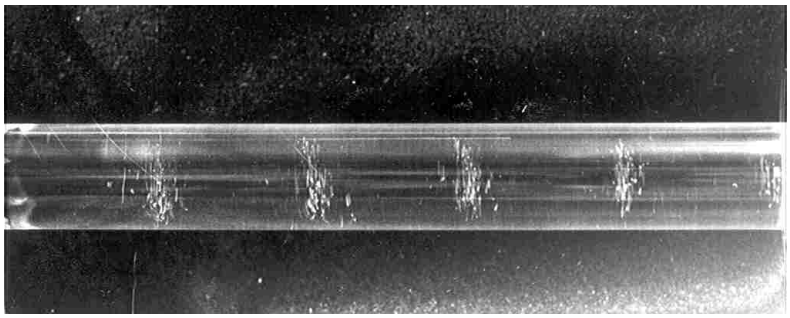

Figure 6. Banding of bubbles in a 16 mm ID tube. Only the smallest bubbles contribute to the band.

3. Discussion

The intention of this article is to promote interest in this banding process, in the hope of obtaining an understanding of its origin. Superficially similar processes have been observed by Zik *et al* [6] in mixed granular media, and by Tirumkudulu *et al* [7] in a viscous fluid containing neutrally buoyant particles. In both of these experiments the fluid within the rotating tube had a free surface, which was shown to be crucial by Zik *et al*, and is probably important in the experiments by Tirumkudulu *et al* also. Moreover, neither of these experiments establishes a well-defined spatial period, even at long times.

In looking for an explanation of the phenomenon described above, we have to take into account the following observations:

(1) The phenomenon has been observed in two very different apparatuses, with similar results as far as they can be compared. In one, the rotating tube was supported at one end only, and was immersed in the aquarium; in the second the tube was supported at two points (not at the ends) and rotated in air. It is therefore unlikely to be an artifact resulting from standing waves set up by some mechanical vibration.
(2) The spatial period of the banding observed is a little larger than the inner diameter of the tube, and is not dependent on the rate of rotation.
(3) The banding starts when the crystals are small, but not microscopic, and the first tendency is to accumulate in planes. After this the regions thicken, but the periodicity persists until there is quite a considerable density of crystallites.
(4) Even after the crystal growth is finished, and equilibrium between a uniform distribution of crystals and the stationary fluid achieved, the periodic banding can be obtained by restarting the rotation. The banding also appears with small bubbles, and with denser crystals only when they are very small, suggesting that near-neutral dynamic buoyancy is required.

Point No 4 suggests that the origin of the observations is hydrodynamic, and that the relevance of the crystals is that their dendritic structure allows very small terminal velocity, because of trapped fluid. It may also be important that during the growth process a variety of crystallite sizes are obtained. Following this theme, we should note that the Reynolds number, calculated on the basis of the crystallite size as a length parameter, is of order 1, whereas on the basis of the tube size it is between 20 and 100. Both of these figures are relatively small, but the second does not preclude the possibility of hydrodynamic inertial effects being important on the scale of the complete tube. Two lines of thought must be pursued concurrently. One is to find a mechanism which results in a hydrodynamic structure with the right periods; the second must provide an origin for the banding, i.e. the tendency for the crystallites to move preferentially towards some part of the periodic structure.

I will first outline some possible approaches to the periodic structure. We assume that the birth of the structure is in a spatial fluctuation in the density of particles. It is clear that, since nucleation of the crystals is homogeneous, there is an initial stage in which only one or two crystals have appeared. This stage often continues for some minutes, and during this period the 'fluctuation' is quite considerable. However, banding is not seen at the stage where there are only a few crystals; it only becomes noticeable when the number is considerable.

Once a volume of the fluid is perturbed by the presence of crystals, we might imagine that this region has an 'effective viscosity' which is larger than that of the clear fluid. We can then search for periodic solutions of the Navier–Stokes equations in which the kinematic viscosity ν is spatially varying. In the frame of reference rotating with the fluid, the Navier–Stokes equation will be written as (see p 216 in [5])

$$\frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u} \cdot \boldsymbol{\nabla} \boldsymbol{u} = -\rho^{-1} \boldsymbol{\nabla} p' - 2\boldsymbol{\Omega} \times \boldsymbol{u} + \boldsymbol{\nabla} \cdot [\nu(\boldsymbol{r}) \boldsymbol{\nabla} \boldsymbol{u}] \tag{2}$$

where $\boldsymbol{u}$ is the fluid velocity vector, $\boldsymbol{\Omega}$ is the angular rotation vector and p' is the pressure, including the centrifugal term generated by the rotation, $p' = p - \rho\Omega^2 r^2/2$. For small Ω, a steady state in this frame is achieved when

$$2\boldsymbol{\Omega} \times \boldsymbol{u} + \boldsymbol{u} \cdot \boldsymbol{\nabla} \boldsymbol{u} = \boldsymbol{\nabla} \cdot [\nu(\boldsymbol{r}) \boldsymbol{\nabla} \boldsymbol{u}]. \tag{3}$$

This equation should be solved, looking for solutions in which $\boldsymbol{u}$ and ν have the same period, and satisfy appropriate boundary conditions on the tube wall, although it is not obvious that such solutions exist.

A second hydrodynamic approach involves the stimulation of inertial waves in the rotating fluid (see p 51 ff in [8]). To excite inertial waves, it is necessary to have a source at a frequency $\omega < 2\Omega$ oscillating in the rotating frame. Inertial waves then propagate at ω in a direction at an angle θ to $\boldsymbol{\Omega}$ where

$$\omega = 2\Omega|\cos\theta|. \tag{4}$$

These waves have the interesting property that their energy flow is normal to the wave-vector (see p 231 in [5]). The oscillating source in our experiment would be a levitating crystal. If the crystal is situated exactly on the neutral axis, it will appear in the rotating frame as a particle orbiting at frequency $\omega = \Omega$; if it is orbiting around the axis, it will still have fundamental frequency Ω, so in either case $|\cos\theta| = 1/2$. A mechanism is required to ensure that the crystallites accumulate at the nodes, which will be discussed below. One should note that the excitation of a standing wave can be at the node (for example in vibrations of a stretched string).

A third hydrodynamic mechanism supposes that the effective density of the fluid is modified locally by the crystallites. During crystal growth, this would happen as a result of water ejected from the growth front, but even without growth one could suppose that the mean local density is modified by the presence of crystallites. In that case, centrifugal force

(included in p' in (2)) is responsible for an outflow of fluid in the region of the bands, which must be compensated by an inflow between them. Since the particles remain in the bands and do not follow the flow, the effective density returns to its clear value in the return stream. Conceptually, this is analogous to Rayleigh–Bénard convection, albeit in an unusual geometry, and can therefore be treated similarly [9]. For this process to be applicable, we require the effective Rayleigh number to be above a critical value for the mode involved. I could not find a specific solution for the cylindrical geometry. However, for axial symmetry it would be similar to the second mode, rather than the first one, which is generally observed in thermal experiments in a plane-parallel geometry with vertical gravity. The suggested flow pattern is shown in figure 7. The Rayleigh number is defined as

$$Ra = \frac{g\alpha\beta d^4}{\kappa\nu} \tag{5}$$

in which g is gravity, α is the thermal expansion, β is the thermal gradient and κ the thermal diffusivity. In the analogy, d is replaced by the radius r, $r\alpha\beta$ by the fractional effective density difference $\delta\rho/\rho$ and g by the equivalent gravity $r\Omega^2/2$. The thermal diffusivity is replaced by the mass diffusion, although I cannot really justify this. For $\delta\rho/\rho = 0.01$ we find $Ra = 1400$. The proposed instability mode has a critical $Ra = 1101$ and spatial period $2.34r$, so the orders of magnitude are correct.

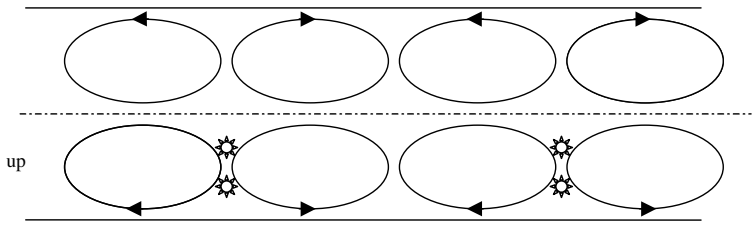

Figure 7. The flow pattern suggested for density-driven convection.

I now turn to the question of the banding mechanism. This can be either an attraction between the crystallites, mediated by the fluid, or a movement of the crystallites in response to the velocity field. In either case the coupling of the crystallites to the field is required in order to create the standing wave in the first place.

One suggested mechanism is 'acoustic streaming'; this is a second-order effect (see pp 358–62 in [10]) in which a particle situated in an oscillating field experiences a steady force component in the direction given by the gradient of field intensity. Generally this is towards the weakest field (Batchelor [10] uses it to explain the movement of the marker particles to the nodes in the Kundt tube experiment) but at short ranges it may be attractive [11]. At the frequencies involved in this experiment, it seems to me that the range of this force, which is the viscous penetration depth $(\nu/\Omega)^{1/2}$ and comes out to be of the order of millimetres here, is too short to be relevant.

A second mechanism by which the particles interact with the field is Saffman lift [12]. This applies to a macroscopic particle close to buoyancy situated in a shear flow. The shear, measured across the diameter of a particle, causes it to spin (this can be seen in our experiments, too) and as a result the particle was shown to cross streamlines in a direction which depends on its deviation from neutral buoyancy. My interpretation of the source of this is a differential Bernoulli pressure across the particle. For particles travelling faster than the fluid, the movement is in the direction of the minimum fluid velocity. This movement across streamlines can result

in the banding; one must confirm that it would operate in the same way for both bubbles and crystallites.

It is also necessary to consider mechanisms of interaction between the particles themselves, mediated by the fluid, since these will play a part in maintaining the integrity of a band.

4. Further experiments

The value of a theoretical discussion at this point, where there are very few experimental data, is to stimulate significant experiments. The macroscopic aspects are obvious: the dependence on banding wavelength, tube diameter, rotation frequency and particle buoyancy must be determined more completely. In particular, insoluble markers of similar size and buoyancy should be used—if only to confirm the irrelevance of the crystal growth process. It will also be useful to change the viscosity of the solutions, which will affect the hydrodynamics directly. Microscopic investigations, using tracer particles much smaller than the crystallites which would follow streamlines, will be most valuable in distinguishing between different models, although in a rotating geometry it will not be easy to follow the particle motion.

Acknowledgments

I should like to thank David Tannhauser for a critical reading of this manuscript. As mentioned at the beginning, the ideas discussed above originated in discussions with many people. I should particularly like to acknowledge those with Dave Weitz, Michael Brenner, Howard Stone, Victor Steinberg, Oded Regev and Amos Ori. I am particularly grateful to Dave Weitz for his hospitality at Harvard University, where the recent experiments were initiated. I also thank the Minerva Foundation for Nonlinear Science for support.

References

[1] Ben-Jacob E 1993 *Contemp. Phys.* **34** 247
[2] Glicksman M E, Koss M B and Winsa E A 1994 *Phys. Rev. Lett.* **73** 573
[3] Raz E, Lipson S G and Ben-Jacob E 1991 *J. Cryst. Growth* **108** 637
[4] Berg H 1993 *Random Walks in Biology* (Princeton, NJ: Princeton University Press)
[5] Tritton D 1988 *Physical Fluid Dynamics* (Oxford: Clarendon)
[6] Zik O, Levine D, Lipson S G, Shtrikman S and Stavans J 1994 *Phys. Rev. Lett.* **73** 644
[7] Tirumkudulu M, Tripathi A and Acrivos A 1999 *Phys. Fluids* **11** 507
[8] Greenspan H P 1980 *The Theory of Rotating Fluids* (Cambridge: Cambridge University Press)
[9] Drazin P G and Reid W H 1981 *Hydrodynamic Stability* (Cambridge: Cambridge University Press)
[10] Batchelor G K 1967 *An Introduction to Fluid Dynamics* (Cambridge: Cambridge University Press)
[11] van Dyke J 1982 *An Album of Fluid Motion* (Stanford, CA: The Parabolic Press)
[12] Stone H A 2000 *J. Fluid Mech.* **409** 165