

over the capillary method that no direct observations of the liquid helium level are necessary, difficulties inherent in an optical cryostat.

The obtained onset temperatures are: for sample A 1.57 K and for sample B 1.72 K. Applying the well-known expressions<sup>3</sup> of Ginzburg and Pitaevskii and of Mamaladze, the values for the gap width were obtained, respectively: for sample A, 36 Å and 24 Å and for sample B, 42 Å and 29 Å. Note that for superleaks made of natural materials the values of the onset temperatures are only approximate since they vary from different samples of the same material because of the non-uniformity of the diameters of the pores or gap widths. Also, with these measurements, there is a real doubt that the superleak is really a superleak. For instance, the way in which the superleak is fixed to the system, whether it is soldered to the glass of a cell or fixed with an indium wire gasket, might present microscopic leaks. Also it is impossible to apply any kind of reliable leak detection to a superleak. It is, however, possible to overcome that doubt with a reasonable number of observations and, as far as possible, mounting and dismounting the same sample to observe the reproducibility of the measurements.

The search for magnetic superleaks had its origin in the anisotropic magnetic superfluid phases of liquid <sup>3</sup>He recently found. The application of magnetic superleaks to the peculiar anisotropic magnetic superfluid phases of liquid <sup>3</sup>He at very low temperatures<sup>4,5</sup> might be relevant. However, to check magnetic superleaks in the anisotropic superfluid phases of <sup>3</sup>He will not be easy. In that physical situation those phases would be influenced by an adequately magnetised finite geometry medium, not necessarily those described here, which they filled, since below the transition temperatures the liquid has the properties of a superfluid and has magnetic properties, compared with those of nematic liquid crystals.

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## Towards a theory of stochastic vorticity-augmentation

THE mechanism of genesis of atmospheric tornado-like vortices is not yet known, although the hydrodynamic mechanism of a mature tornado is reasonably well understood thanks to recent research efforts. This lack of understanding of the physics of tornado genesis has been a great handicap in attempts to avert tornado occurrences. I present here a new hypothesis to account for the formation of tornadoes.

The hypothesis is based on the observation that thunderstorm associated tornadoes almost invariably occur in the environment of an intensely (vertically) sheared horizontal wind, say  $V_x(z)$  which is penetrated by a vertical columnar jet-draught along the  $z$ -axis. It is easily recognised that the vertically sheared wind field could serve as an abundant source of

ambient vorticity; nonetheless a casual theoretical consideration<sup>1</sup> of such a wind-jet interaction does not lead to a net gain of axial vorticity ( $\omega_z$ ) for the vertical jet at the expense of the horizontal vorticity ( $\omega_y = -\partial V_x/\partial z$ ) according to the Helmholtz vorticity transport equation:

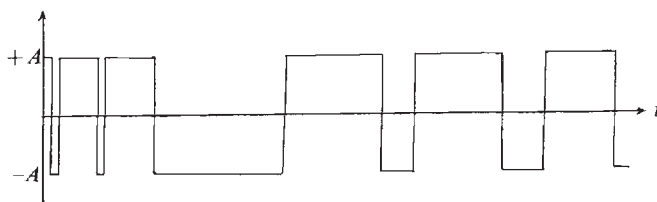
$$\frac{d\omega_z}{dt} = \omega_x \frac{\partial V_z}{\partial x} + \omega_y \frac{\partial V_z}{\partial y} + \omega_z \frac{\partial V_z}{\partial z} \approx \omega_y \frac{\partial V_z}{\partial y} \quad (1)$$

assuming  $\partial/\partial z \ll \partial/\partial y$ . A closer examination of the present wind-jet interaction, taking into account the resulting random lateral deflections of the jet caused by the alternating vortex sheddings in the wake of the cross-wind over the jet<sup>2,3</sup>, shows that random sharp velocity gradients ( $\partial V_z/\partial y$ ) are induced at the boundary of the random impulsively oscillating jet. This random input ( $\omega_y \partial V_z/\partial y$ ) in equation (1) converts the latter into a stochastic differential equation having the axial vorticity ( $\omega_z$ ) as the output function. It is this stochastic vorticity transfer process that is considered herein as primarily responsible for starting a columnar vortex leading eventually to a mature tornado vortex after the pendant funnel extending down from the cloud base to the ground.

In this present study of the wind-jet interaction, I have constructed an extremely simplified model with only bare essential physics. For instance the entrainment which accounts for the incorporation of the ambient air into the jet is not taken into account. The hydrodynamic problem here is the determination of the probable increments of the jet axial vorticity due to the induced random input ( $\omega_y \partial V_z/\partial y$ ) as a consequence of the random lateral displacement of the jet which can be viewed as a beam in Brownian motion<sup>4</sup>. Recognising the filamentary structure in a vortex jet<sup>5</sup> and even in the fine scales of turbulent flows<sup>6</sup>, we envisage the jet as a bundle of vortex filaments along the jet axis ( $z$ ) which faces a vertically sheared horizontal wind along the  $x$ -axis thus shedding alternating vortices on each side and, in so doing, inducing alternating hydrodynamic Magnus forces (along  $y$ -axis) on the jet. It can be shown that this many-filament system constitutes essentially a system of coupled nonlinear oscillators<sup>7</sup>, under the influence of a high-frequency harmonic forces, which therefore oscillates as though a random force were acting on it<sup>7,8</sup>. The present many-body system is subdivided into a subsystem, namely a filament, and its environment. The influence of the environment on the subsystem is treated in a way similar that of a heat bath of statistical mechanics except that instead of a random force<sup>9</sup> we have random vorticity impulse with stochastic properties supposedly given. In this way the equation governing the growth of axial vorticity for the total system is reduced to that for the subsystem alone with the quantity  $\omega_z$  in equation (1) representing an unnormalised axial vorticity at a sample point (o) of the test filament; the quantity  $(\omega_y \partial V_z/\partial y)_o$  an effective random vorticity impulses at the point o. We have thus a one-dimensional model neglecting the feedback and damping of the vortex-jet disturbances.

Consider a surface velocity gradient  $(\partial V_z/\partial y)_o$  depicted by the simplest plausible stationary function known as the random telegraphic signals with values  $+A$  and  $-A$  alternately as shown in Fig. 1 where  $A\alpha(t) = \omega_y(\partial V_z/\partial y)_o$  and  $|\alpha(t)| = 1$ . The probability of switching over the signal from one value to its

Fig. 1 Sample function of the  $(+A, -A)$  random telegraph signal  $A\alpha(t), t > 0$



opposite is assumed to be governed by a Poisson distribution at a mean rate of  $\mu \text{ s}^{-1}$ .

The incremental axial vorticity can be obtained from equation (1):

$$\Delta\omega_z(\tau) = \omega_z(\tau) - \omega_z(0) = A \int_0^\tau \alpha(t) dt \quad (2)$$

The ensemble average of the squared incremental axial vorticity is given by<sup>10</sup>

$$\langle [\Delta\omega_z(\tau)]^2 \rangle = A^2 \tau \int_{-\infty}^{\infty} \langle \alpha(o)\alpha(s) \rangle ds \quad (3)$$

the integrand  $\langle \alpha(o)\alpha(s) \rangle$  denotes the correlation function of the stationary random function  $\alpha(t)$  and is equal to  $\exp(-2\mu|s|)$ . Thus:

$$\langle [\Delta\omega_z(\tau)]^2 \rangle = \omega_y^2 (\partial V_z / \partial y)_0^2 \tau \mu^{-1} \quad (4)$$

which gives the important parameter depicting the stochastic growth rate of the columnar axial vorticity of a vortex filament of the jet.

The more detailed probabilistic information is given by the probability  $P(\Delta\omega_z, t)d(\Delta\omega_z)$  that the increment  $\Delta\omega_z$  at time  $t$  lies between  $\Delta\omega_z$  and  $\Delta\omega_z + d(\Delta\omega_z)$ . Recognising the Markovian nature of the stochastic process herein, we can determine the probability density  $P(\Delta\omega_z, t)$  by solving its governing equation in the form of a driftless Fokker-Planck equation for diffusion<sup>9</sup> and obtain the Gaussian distribution:

$$P(\Delta\omega_z, t) = (4\pi Dt)^{-1/2} \exp[-(\Delta\omega_z)^2/4Dt] \quad (5)$$

where  $D = \langle (\Delta\omega_z)^2 \rangle / 2t$ . If a critical value for  $\Delta\omega_z$  is prescribed, say  $(\Delta\omega_z)^* = \beta \sqrt{\langle (\Delta\omega_z)^2 \rangle}$ , for large  $\beta$ ,

$$P[\Delta\omega_z > (\Delta\omega_z)^*] \simeq (2\pi)^{-1/2} \beta^{-1} \exp(-\beta^2/2) \quad (6)$$

In conclusion, a new cause of vorticity transfer between an ambient sheared-wind and a transverse-penetrating jet is proposed for which an elementary one-dimensional theory is formulated. It points out the relevant quantities to be determined, theoretically or experimentally, in describing the present stochastic mode of vorticity-augmentation.

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## Theoretical evidence for metastable cyclic ozone

OZONE is a vital component of the atmosphere. Knowledge of its properties is important to the understanding of its involvement in chemical and photo-induced reactions which can affect the stability of the ozone concentration in the upper atmosphere. The reactivity of ozone and its unusually low thermochemical stability with respect to partial dissociation are difficult to reconcile with an apparently multiply bonded

symmetric bent structure. This has led to speculation<sup>1,2</sup> concerning alternative forms of ozone such as the equilateral triangular cyclic form (isoelectronic with cyclopropane) from which facile partial dissociation could be envisioned. To have an important role such a form would presumably need to be thermally accessible from the ground state and bound with respect to partial dissociation. The spectroscopic structure determination of the symmetric bent ground state<sup>3-10</sup> has been finalised<sup>10</sup> ( $r_e$  (O-O) 127.1 pm, angle 116.8°), and there was recently experimental confirmation<sup>11,12</sup> of excited states of this species<sup>13-16,22</sup> which are bound with respect to dissociation, including the predicted <sup>3</sup>B<sub>2</sub> state<sup>13-17,22</sup>. Investigations of bound excited states which are stable to partial dissociation have been stimulated by the sequential observation during O<sub>2</sub> radiolysis experiments<sup>12,18,19</sup> of two short-lived 'ozone precursors' O<sub>3</sub><sup>a</sup> and O<sub>3</sub><sup>b</sup> following recombination of ground state O<sub>2</sub> and O. O<sub>3</sub><sup>b</sup> may be vibrationally excited ground state ozone<sup>20</sup>, whereas the O<sub>3</sub><sup>a</sup> precursor which shows absorption<sup>12</sup> at ~ 315 nm in the ultraviolet (and possibly<sup>21</sup> the emission observed at 1500 cm<sup>-1</sup> in the infrared) has not yet been given an identity beyond an apparent lifetime of 5 μs. The species showing the single infrared emission<sup>21</sup> is interesting as D<sub>3h</sub> cyclic ozone is expected to show one (degenerate) infrared active fundamental, fewer than any alternative structure. Theoretical evidence for the stability of cyclic ozone has been conflicting. In 1973 Wright<sup>1</sup> calculated it to be 26 kJ mol<sup>-1</sup> more stable than the ground state; in 1972 and 1975 Hay *et al.*<sup>13,22</sup> calculated it to be less stable by ~ 150 kJ mol<sup>-1</sup> (that is, above partial dissociation energy  $\Delta H^\circ = 101$  kJ mol<sup>-1</sup>) and in 1974 Shih *et al.*<sup>14</sup> have concluded it is 63 kJ mol<sup>-1</sup> above the ground state. Shih *et al.*<sup>14</sup> have recognised that considerable uncertainty still exists in their computation on total and relative energies, and their calculated ground state structural parameters differ significantly from experiment. We have reinvestigated the relative stability of cyclic ozone and symmetric bent ozone and have obtained a total energy for the ground state of -224.7710 hartree which is 471 kJ mol<sup>-1</sup> lower than the previous best model wavefunction of Hay *et al.*<sup>13</sup> who predicted cyclic ozone to be above dissociation. In other words, the relative shortcoming in total energy in all previous computations on each conformer has been around five times the key energy difference between ground state ozone and the partial dissociation products,  $\Delta H^\circ = 101$  kJ mol<sup>-1</sup>. The computed optimum geometric parameters (bond length  $r_e = 126.4$  pm and bond angle  $\alpha_e = 117.3^\circ$ ) are sufficiently close to the experimental values to lend some confidence to our model wavefunctions in regard to structural predictions. The corresponding wavefunction for cyclic ozone has an energy expectation of -224.7637 hartree at an optimum bond length of  $r_e = 143.5$  pm (bond angle 60°). On this evidence the difference in the energy of the local minima on the ozone ground state conformation hypersurface is less than one fifth of the partial dissociation energy. We, therefore, confidently predict the existence of a bound species of ozone having an equilateral triangle conformation. We believe this species may be the O<sub>3</sub><sup>a</sup> precursor, which in the experiments referred to<sup>18,19</sup> is presumably vibrationally excited.

Our disagreement with Hay *et al.*<sup>13</sup> regarding the stability of the cyclic conformer has a number of origins. Hay *et al.* seem not to have optimised molecular geometries using their best bases and their best correlated wavefunctions, and have apparently omitted polarisation basis functions in any study of the cyclic conformer. The basis sets we used are comparable to the best previously used at the Hartree Fock level  $E_{HF}$  (bent, SCF optimised geometry) -224.314 hartree,  $E_{HF}$  (bent, CEPA optimised geometry) -224.3058 hartree and  $E_{HF}$  (cyclic, CEPA optimised geometry) -224.3011 hartree. The significantly lower final conformational energies we have obtained despite the fact that our basis is not designed to obtain inner 'atomic' correlation effects is due to the use of a pair natural orbital (PNO) basis which is designed to optimise the configuration expansion convergence. We used ~ 750 PNO con-