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Journal of Supercritical Fluids 24 (2002) 231–237

THE JOURNAL OF Supercritical Fluids

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The characteristics of coherent structures in the rapid expansion flow of the supercritical carbon dioxide

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Received 29 October 2001; received in revised form 1 March 2002; accepted 17 April 2002

Abstract

By the use of a tiny pressure-transferring probe and capacitor-type sensor, the dynamic pressure signals in the jet flow of the rapid expansion of supercritical carbon dioxide are measured, which distinctively shows the characteristics of quasi-periodical coherent structures. After Fast Fourier Transform (FFT) conversion of the time series signals of the dynamic pressure, there exist three dominant frequency bands in the power spectrum, which correlate with the scale of the dominant eddies in the turbulent field. The dominant frequencies change little with the distance from the nozzle exit or the pre-expansion pressure, while the power density of the dominant frequencies, which correlates with the energy of the dominant eddies in the turbulence, attenuates along the axial direction and with the decrease of the pre-expansion pressure. Through analysis, it is inferred that the nozzle structure and initial conditions remarkably affect the coherent structures in the expansion flow which should be the important factors in the particle nucleation and its growth process in ultra-fine particle preparation by rapid expansion of supercritical fluid solution (RESS).

Keywords: Rapid expansion; RESS process; Supercritical fluids; Turbulence; Jet flow

1. Introduction

In the rapid expansion of supercritical fluid solution (RESS) process, the supercritical fluid solution expands rapidly through a narrow throttling structure, e.g. capillary or orifice nozzle, to a low pressure and low temperature state, which leads to a very high supersaturation at an ultra-short time interval of about 10^{-7} s. The steep increase of supersaturation and rapid density drop prompt an outburst of homogeneous nuclei, and ultra-fine particles with a narrow size distribution are expected to form. With mild operational temperature and without organic solvents, the RESS process promises a solvent-free product with high purity in a single process, and has the potential for eliminating the disadvantages of the conventional methods in fine particle preparation in such areas as chemical engineering, pharmaceutical industry, material science and biotechnology etc.

Most experimental and theoretical researches in literature focus on the effects of various parame-

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0896-8446/02/$ - see front matter
PII: S0896-8446(02)00084-0

ters, including pre- and post-expansion temperature, pressure and concentration, nozzle geometry, upon the product characteristics, e.g. size and morphology. But the experimental results are usually available only for the specified conditions. Various solute and solvent systems usually show different characteristics of the process [1–9]. Debenedetti et al. [1,2,9] developed a one-dimensional compressible model of sub-sonic flow to study the dynamics of particle nucleation and growth in the RESS process. Shaub et al. [5] calculated the adiabatic process of the free jet expansion from the nozzle into vacuum with supercritical carbon dioxide (SC-CO_2) as a solvent and phenanthrene as a solute. These calculations are helpful for understanding the qualitative trends, but not able to predict the quantitative results. To produce fine and mono-dispersed particles with a narrow size distribution, the suggested way is preventing the supercritical fluid solution from phase separation until it expands at the nozzle exit [2–7].

Nevertheless, another important factor in the RESS process, i.e. the strong turbulence in the expansion flow, has not been investigated sufficiently. Just like the particle preparation in aqueous solution, the turbulence in the jet flow may remarkably affect the particle nucleation and growth even during ultra-short residence time. The turbulent characteristics of the expansion flow may be the key factor affecting the particle preparation by the RESS process. This paper studies the characteristics of the rapid expansion flow of pure supercritical carbon dioxide. Coherent structures in the expansion flow are shown from the experimental results.

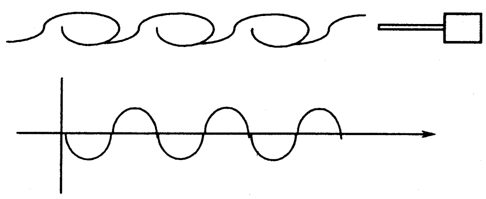

Fig. 1. Formation of dynamic pressure signals from the moving eddy at the probe top.

2. Fundamental

Before 1980s, it was considered that the coherent structures of the eddy only exist in the flow with low Reynolds number, and in the fully developed turbulence the periodical signals should not exist. Afterwards, more and more experimental results showed that the coherent structures exist in almost all kinds of turbulent fields, even in the flow with high Reynolds number of 10^7 [10]. The formation of the structures is not random but correlates with the initial conditions and inner non-linear specialities of the turbulence [10–18]. The coherent structures in turbulent flow can be analyzed theoretically [13] [17] or experimentally [11,12] [14–16]. The scale and energy information of eddies in the turbulence can be analyzed from the power spectrum of the dynamic pressure or velocity signals. The frequency band where the eddy energy concentrates densely reflects the characteristics of the dominant eddy in the turbulence. The characteristics of the turbulent flow can be modified through the control of the coherent structures, which can be intensified by the periodical stimulations upon the flow [10] or weakened by the addition of small polymer particles into the flow [18].

The rapid expansion of supercritical fluids, considered as a supersonic or at least subsonic free jet, brings out tempestuous turbulence, which forms a large number of eddies in different scales. When a series of eddies pass through the probe set in the jet flow, time series signals of dynamic pressure will be detected, which are converted from the eddy momentum. Smaller eddy size or faster change of the velocity in the eddy reflects higher frequency in detected signals. Thus the eddy parameters in the turbulent flow can be evaluated from the pressure signals of time series, as shown in Fig. 1.

Based on the acoustic scattering principle, Baudet et al. [12] set up an experimental technique allowing the direct probing of the vorticity field in a turbulent flow. The spatial correlation length of discrete vorticity events was measured to reveal the time continuous transfer of energy from the largest scales towards smaller scales. It is claimed that the recourse to time–frequency distributions

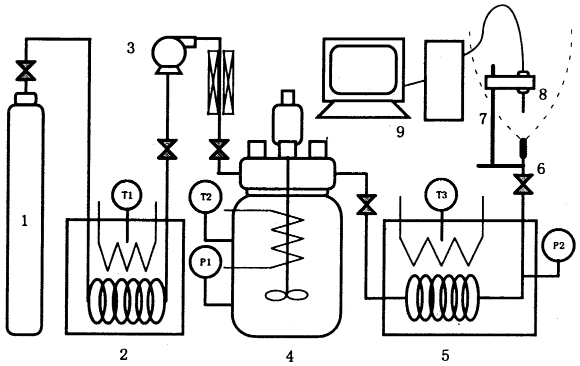

Fig. 2. Schematic diagram of the experimental apparatus and flow sheet of the RESS system. (1) CO_2 bomb, (2) cooler, (3) high pressure pump, (4) extracting tank, (5) constant temperature bath, (6) nozzle, (7) fixed micrometer caliper, (8) probe and sensor, (9) data sampling computer.

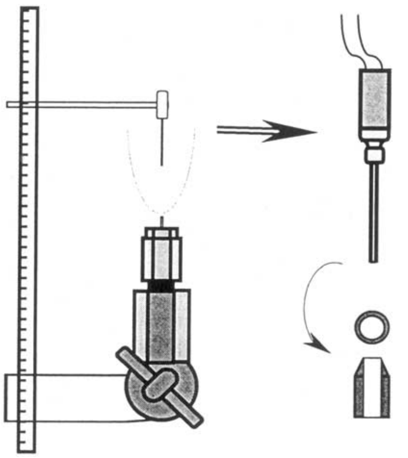

Fig. 3. The structure and position of the sensor and probe in the expansion flow.

(TFD) leads to an operational definition of coherent structures associated with phase stationarity in the time–frequency plane.

The experimental results in the following text will show that the expansion flow in the RESS process obviously contains coherent structures, which should be one of the important factors affecting the particle nucleation and growth in fine particle preparation. Although the residence time of the nuclei is as short as 10^{-7} s, the report of simulated growth rate of the nuclei is as high as 10^{26} m/s [9], which indicates that the expansion turbulence may remarkably affects the particle size and morphology. It is supposed that stronger and more uniform turbulence in microscopic scale has advantages on the formation of super-fine particles with a narrow size distribution.

3. Experimental

The experimental apparatus and flow sheet are schematically shown in Fig. 2. The CO_2 from a bomb is cooled in a cooler with the setting temperature of 263 K, then fed into a tank with the volume of 1.5 l through a high-pressure pump. The temperature of the CO_2 in the tank can be controlled from room temperature to 573 K within 1 K, and the pressure can be controlled from 0 to 40 MPa within 0.1 MPa. After the temperature and pressure of the CO_2 in the tank are stabilized at the scheduled values, the CO_2 fluid is let out to a coil pipe in a second constant temperature bath, in which more accurate pre-expansion temperature is controlled within 0.1 K. A stainless steel capillary, which is 15 mm long and 100 μm in inner diameter, is used as jet nozzle. Another stainless steel capillary 15 mm long and 600 μm in inner diameter is also used to explain influence of the nozzle structure on the coherent structure in the jet flow. This paper mainly deals with the experimental results of the former nozzle. A probe is axially set in the expansion flow to detect the dynamic pressure signals, which is fixed on the movable part of a fixed micrometer caliper to locate the exact position along the axis.

The probe is 1 mm in inner diameter, 1.5 mm in outer diameter and 13 mm long, the top of which is designed to reduce the influence on the flow field due to its existence, as shown in Fig. 3. The circular and sharp shape of the probe can also lighten the shock wave caused by the speedy flow. The probe is connected with the sensor. The capacitor-type sensor (64–170 dB, 0.98 mV/Pa, inherent frequency: 70 kHz) with high accuracy is employed to detect the pressure signals. Even so, some very small turbulence could possibly not be measured due to the capillary filtration on high frequency signals and the limitation of the sensor inherent frequency or the sampling frequency of the computer. The dynamic pressure signals propagate by the elastic gas in the probe to the sensor. They are converted to electric signals through the sensor, then magnified and sampled by the computer. The sampling frequency is 16 000 points at each interval of 0.33 s. The sampled signals of time series are converted into power spectrum for analysis through the Fast Fourier Transform (FFT) method.

Before measurements the noise from the background is detected in order to exclude possible disturbance from the environment variables. When the pressure and temperature in the extraction tank reach the setting value and are stable, the exit valve is opened to the maximum, starting the rapid expansion. When the jet flow is stable, the pressure signals are sampled, and then the jet flow is shut for next measurement. The conditions in steady state are insured in the measurements. The measurement process lasts about 10 s. The pressure decrease ($\sim$ 0.5 MPa) in the extraction tank in each measurement are recovered through the high-pressure pump and the temperature controller. Parallel experiments are carried at each condition to insure the measurement result available.

The dynamic pressure signals are detected along the axis of the expansion flow of pure solvent CO_2 under certain thermodynamic conditions. The axial distance between the probe top and the nozzle exit ranges from 0 to 50 mm. Considering the

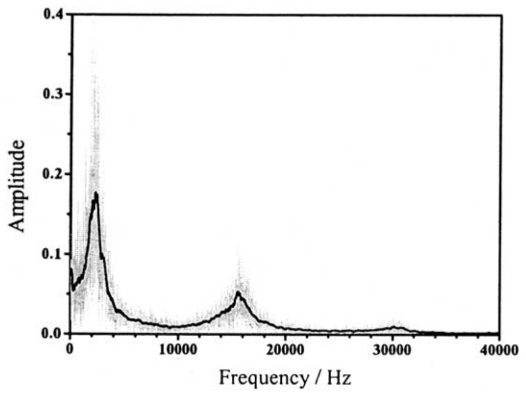

Fig. 4. Power spectrum of the coherent structure with capillary nozzle inner diameter of 100 μm ($L/d = 150$, $z = 19$ mm, 373 K, 20 MPa).

influence of the probe on the expansion flow and the accuracy of the measurement, the nearest axial distance is limited to 2 mm. The experiments reflecting the influence of the pre-expansion pressure ranged from 5 to 20 MPa are carried out at intervals of 0.5 MPa, with the pre-expansion temperature controlled at 323 and 373 K, respectively.

When the pre-expansion pressure is 20 MPa, and pre-expansion temperature is 373 K, the mass flow through the nozzle of 100 μm is calculated through the pressure drop during a certain time and the Reynold number of the flow in the nozzle is estimated at about 10^4. In the rapid expansion of supercritical carbon dioxide, there should be Joule–Thompson effect in the process. In the experimental conditions, dry ice does not form in the experimental process.

4. Results and discussion

4.1. The inherent characteristics of the turbulent flow

The detected signals of dynamic pressure remarkably show quasi-periodical characteristics of coherent structures. The power spectrum from FFT conversion contains three frequency bands, the energy of which concentrates on each peak value respectively. In order to easily characterize the coherent structures and compare the difference under various conditions, the power spectrum in gray line is smoothed by taking the average of every 50 adjacent points into a black line, as shown in Fig. 4. Three dominant frequency peaks are at 2300, 15 500 and 30 000 Hz, respectively. The half width of the dominant frequency bands is about 1000–2000 Hz. The low frequency band has the most of the turbulent energy and the high frequency band has the least.

To examine the possible error from the probe, experimental measurements with different probes in varied shape, length and inner diameter are carried out. It is found that the power spectrum of the measured pressure signals does not change with the shape of the probe. The inherent frequency of the sensor is 70 kHz, which is much

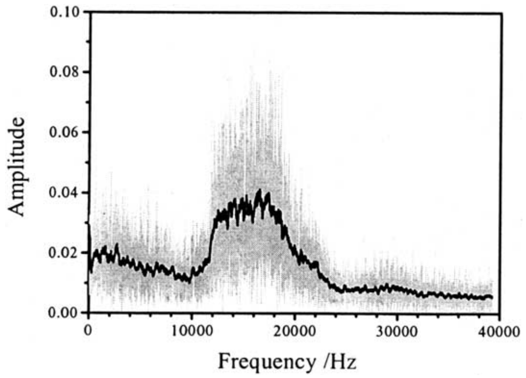

Fig. 5. Power spectrum of the coherent structure with capillary nozzle inner diameter of 600 μm ($L/d = 25$, $z = 10$ mm, 373 K, 20 MPa).

higher than the dominant frequencies. The resonant frequencies of the probe can be calculated from the equation [19]

$$f_{\text{resonent}} = n\frac{U_{\text{sound}}}{4L} \approx 4800n \text{ (Hz)} \quad (1)$$

where U_{sound} is the in-situ sound velocity and L is the pipe length of the probe. The resonant frequencies of $4.8 \times n$ kHz ($n = 1, 2, 3...$) are also different from the dominant frequencies. Therefore, it can be confirmed that the dominant frequencies reflect the inherent characteristics of the expansion flow, instead of coming from the measurement errors.

The results of measurement show that there exist eddies in various scales in the jet flow, and the turbulent energy mainly concentrates on the eddies of the three group scales. The large eddies correspond to the low frequencies and the small eddies correspond to the high frequencies. The formation and composition of the eddies should be affected by the turbulence and flow field at the nozzle exit, i.e. affected by the thermodynamic and flow conditions of the supercritical fluid, and the nozzle structure etc. The disturbance due to the shear between the peripheral layer of the jet and the ambient atmosphere may also contribute to the pressure signals of measured.

4.2. Influence of factors

4.2.1. Influence of the nozzle structure

In the RESS process, the initial and boundary conditions of the expansion flow are the key factors affecting the formation of coherent structures. Besides fluid velocity in the expansion flow, the most important boundary condition is the nozzle structure. In this research, the coherent structures of the expansion flow with the capillary nozzle of 600 μm in inner diameter and 15 mm long are measured. The result in Fig. 5 shows that there is only one dominant frequency band ranging from 10 000 to 20 000 Hz, and the energy of the coherent structures in the turbulence is much weaker than that with the capillary nozzle of 100 μm inner diameter shown in Fig. 4. It is inferred that the coherent structures can be obviously changed by the change of the boundary condition of the nozzle.

4.2.2. Coherent structures along the axis

The axial measurements are carried out under the conditions with pre-expansion temperature of 323 and 373 K, pre-expansion pressure of 10 and 20 MPa, respectively, using the capillary with inner diameter of 100 μm and 15 mm long as nozzle. The power spectrum of the measured pressure signals indicates that there exist three dominant frequency bands, which reflect three kinds of coherent structures in the expansion flow. The dominant frequency and their power density change along the axis under pre-expansion thermodynamic conditions of 20 MPa and 373 K, as shown in Fig. 6. The higher frequency bands becomes obvious at certain positions, and the dominant frequency bands change little along the axis, while the power density gradually decreases along the axis. Similar results can be obtained under other pre-expansion thermodynamic conditions.

Therefore, it can be inferred that the coherent structure scale of the eddy in the jet flow do not change much, while the eddy energy decreases along the axis. The eddy energy in the jet flow mainly concentrates on the fore part of the jet flow close to the nozzle exit, which is similar to the reported result in the incompressible free jet, that the energy of the jet flow in the vicinity of the nozzle accounts for 50% of the energy in the total flow region [10].

4.2.3. Influence of pre-expansion pressure

The dominant frequencies and their power densities changing with pre-expansion pressure at pre-expansion temperature of 373 K, 10 mm from the nozzle exit is shown in Fig. 7. The high frequency bands are not very obvious in the experiments. When the pre-expansion pressure is higher than 13 MPa, the high frequency band can be obviously observed. The power densities of the three dominant frequency bands increase remarkably with the increase of pre-expansion pressure. Experimental results also indicate that the pre-expansion temperature has little effect on the dominant frequency bands and their power densities.

The increase of pre-expansion pressure normally results in the increase of the expansion Mach number, and enhances the energy intensity through the disturbance caused by the momentary expansion. It is the phase transformation and supersonic/subsonic expansion flow that make the RESS process different from other free jet flows, and these two factors should be the important conditions to form the coherent structures in the RESS process.

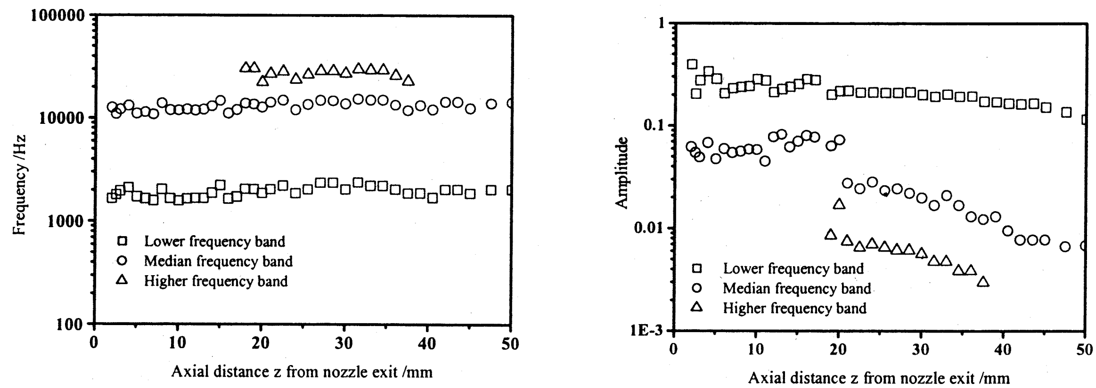

Fig. 6. Power spectrum of the coherent structure changing with the axial distance from nozzle exit ($L/d = 150$, $d = 100$ μm, 373 K, 20 MPa).

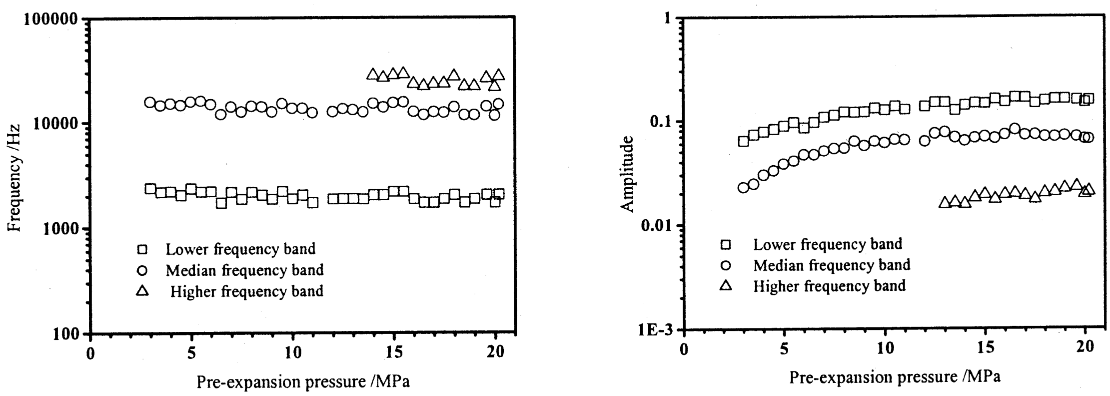

Fig. 7. Power spectrum of the coherent structure changing with the pre-expansion pressure ($L/d = 150$, $d = 100$ μm, $z = 10$ mm, 373 K).

5. Conclusion

Experimental results indicate that there exist coherent structures in the rapid expansion flow of the supercritical carbon dioxide. Three dominant frequency bands were found in the quasi-periodical dynamic pressure signals under the experimental conditions, which correspond to the different eddy scales in the jet flow respectively. The dominant frequencies change little with the axial distance or pre-expansion pressure. The power density that reflects the intensity of the eddy energy attenuates along the axis of the expansion flow and with the decrease of the pre-expansion pressure. The coherent structures should have strong effect on the microscopic environment in which the fine particles nucleate and grow. As one of the boundary conditions, the nozzle structure is an important factor affecting the dominant frequency value and power density of the coherent structures. It is expected that by the design of appropriate nozzle structure and setting suitable initial conditions, the coherent structure of the turbulence field can be controlled.

Acknowledgements

The authors wish to express their appreciation for the financial support of this study by the National Natural Science Foundation of China. The grant number is NSFC No. 29906004.

References

[1] R.S. Mohamed, P.G. Debenedetti, R.K. Prud'homme, Effects of process conditions on crystals obtained from supercritical mixtures, AIChE J. 35 (1989) 325–332.

[2] P.G. Debenedetti, Homogeneous nucleation in supercritical fluids, AIChE J. 36 (1990) 1289–1298.

[3] A.K. Lele, A.D. Shine, Effect of RESS dynamics on polymer morphology, Ind. Eng. Chem. Res. 33 (1994) 1476–1485.

[4] C.J. Chang, A.D. Randolph, Solvent expansion and solute solubility predictions in gas-expanded liquids, AIChE J. 36 (1990) 939–942.

[5] G.R. Shaub, J.F. Brennecke, M.J. McCready, Radial model for panicle formation from the rapid expansion of supercritical solutions, J. Supercrit. Fluids 8 (1995) 318–328.

[6] M. Türk, Formation of small organic particles by RESS: experimental and theoretical investigations, J. Supercrit. Fluids 15 (1999) 79–89.

[7] E. Reverchon, G. DellaPorta, R. Taddeo, P. Pallado, A. Stassi, Solubility and micronization of griseofulvin in supercritical CHF_3, Ind. Eng. Chem. Res. 34 (1995) 4087–4091.

[8] C. Domingo, E. Berends, G.M. vanRosmalen, Precipitation of ultrafine organic crystals from the rapid expansion of supercritical solutions over a capillary and a frit nozzle, J. Supercrit. Fluids 10 (1997) 39–55.

[9] X. Kwauk, P.G. Debenedetti, Mathematical modeling of aerosol formation by rapid expansion of supercritical solutions in a converging nozzle, J. Aerosol. Sci. 24 (1993) 445–469.

[10] J.Z. Lin, The Coherent Structures in Turbulence, China Machine Press, 1995.

[11] J. Dunyak, X. Gilliam, R. Peterson, Coherent gust detection by wavelet transform, J. Wind Eng. Ind. Aerodynam. 77–78 (1998) 467–478.

[12] C. Baudet, O. Michela, W.J. Williams, Detection of coherent vorticity structures using time-scale resolved acoustic spectroscopy, Physica. D. 128 (1999) 1–17.

[13] G. Haller, G. Yuan, Lagrangian coherent structures and mixing in two-dimensional turbulence, Physica D 147 (2000) 352–370.

[14] B.H. Timmerman, D.W. Wat, P.J. Bryanston-Cross, Quantitative visualization of high-speed 3D turbulent flow structures using holographic interferometric tomography, Optics Laser Technol. 31 (1999) 53–65.

[15] Q.L. Fan, H.Q. Zhang, Y.C. Guo, X.L. Wang, W.Y. Lin, Experimental studies of two-phase round turbulent jet coherent structures, Tsinghua Sci. Technol. 5 (2000) 105–108.

[16] H.-L. Zhou, Z.M. Lu, X.-T. Ren, X.-L. Xie, The experimental study of the chaotic phenomena of heated jets, Acta Mechanica Sinica 31 (1999) 603–610.

[17] F. de Souza, J. Delville, J. Lewalle, J.P. Bonnet, Large scale coherent structures in a turbulent boundary layer interacting with a cylinder wake, Exp. Thermal Fluid Sci. 19 (1999) 204–213.

[18] Z.-S. Yu, Interactions of the rigid-rodlike polymer and the coherent structures in a mixing layer, Acta Mechanica Sinica 30 (1998) 743–747.

[19] Nanjing University of Aeronautices and Astronautics, Beijing University of Aeronautices and Astronautics, The principle of sensors. National Defense Industry Press. (In Chinese), 1980.