

# PREFACE

If the gas contained in a vessel at a constant temperature and pressure (reservoir) is left to expand in the vacuum through a sonic nozzle, a supersonic jet is generated. A relevant part of thermal energy, initially existing in the stagnating gas, is converted to kinetic energy of the directional mass flow, and the various degrees of freedom of the molecules are cooled to different extents.

In monatomic gases two different temperatures, which characterise the distributions of the velocity components parallel and orthogonal to the jet axis, are observed. In polyatomic gases, the molecular anelastic collisions inside the jet transfer energy from the internal motions, (i.e. vibrations and rotations), to the external ones (i.e. translations). Hence a cooling of the internal motions results, although to a smaller extent. The jet emitted from the nozzle heats again colliding with the walls of the discharge chamber or with the residual gas contained in it. Nevertheless, there is always an interval of space–time conditions in which a sample is available in a gas phase appreciably super-cooled under the condensation temperature and with a density greater than that of the saturated vapour corresponding to the low achieved temperature. This advantage can be utilised in a number of cases.

Among various applications of molecular beams in the research area, we remember:

- i) Spectroscopy of molecules and Van der Waals clusters;
- ii) Information on the intermolecular potentials by molecular beams scattering experiments;
- iii) Study of the excitation of surface phonons by the scattering of a monatomic beam from the surface of a crystal;
- iv) Study of the onset of the condensation of a gas.

In molecular spectroscopy, the interest in supersonic jets follows from the fact that the cooling of the internal degrees of freedom allows a simplification of the roto-vibrational absorption spectra, which at room temperature appear to be very complicated because of the presence of a very large number of spectral lines. The latter are due to transitions starting from states, which are excited by the molecular collisions (*hot states*). The gas cooling, by reducing the average kinetic energy of the molecules and consequently the energy delivered in the collisions, reduces the number of the excited states. During the expansion the jet evolves through different gas-dynamic regimes, each of them being characterised by the values of the ratio

*molecular mean free path / characteristic dimension of the flow field*

This ratio, which is known as the “*Knudsen number*”, changes between large limits during the jet expansion. However, in the initial phase of the expansion the jet is practically always in the continuous supersonic regime; moreover many of its final characteristics are determined in this phase.

Now, the researcher who has little or no experience in the supersonic gas-dynamics and must deal with the task of planning or utilising a molecular beam is faced with phenomena that are rather unusual for him. Nevertheless, he will find very little help in the scarce, sometimes extended, review articles published on this topic in the past. These articles generally assume as known the ideas and the equations of the continuous supersonic gas-dynamics. Therefore, before analysing the behaviour of a molecular beam in the regime of almost complete absence of collisions, we think that treating those parts of the above-mentioned gas-dynamics will be useful to our aims.

The book is structured in 12 Chapters. Some results of equilibrium thermodynamics and the kinetic theory of gases are recalled in Chap. 1, while Chap. 2 is devoted to the non-equilibrium equations, that is, the Boltzmann, Wang Chang–Uhlenbeck and Master equations. The Boltzmann equation successively (see Chap. 9) will be applied to the expansion of a monatomic gas, while the Master equations will be applied to the vibrational and rotational relaxations of polyatomic molecules. In Chap. 3 the dynamics of compressible and viscous fluids is developed and the basic equations for them are established. Some concepts as the “*Reynold number*” and the “*boundary layer*” are introduced. In Chap. 4 the “*isoentropic flow*” is considered in detail and concepts such as “*characteristic lines*” and “*compression and expansion waves*” are introduced. The general theory of the characteristic lines is developed in Chap. 5. The method for the calculation of the flow field (*method of characteristics*), which is founded on the properties of the forenamed lines, is described. Chap. 6 is devoted to discontinuities in the flow field, and in particular, to the “*shock waves*”. Also the reflections and the intersection of such waves are considered. The results obtained in Chaps. 3, 4, 5 and 6 are utilised in Chap. 7 to interpret the behaviour of the gas flow in two kinds of nozzle (i.e. the convergent-divergent and the convergent). The remaining Chapters (8, 9, 10, 11, 12) are devoted to the characterisation of the axisymmetric under-expanded jet emitted from a converging nozzle (*free jet*). In Chap. 8 the axial dependence of the Mach number determined by the method of characteristics as well as the analogous dependence of the flow variables introduced in Chap. 4 are reported. Moreover, the condition of “*translational non-equilibrium*” and “*thermal conduction model*” are described. The non-equilibrium cooling of vibrations and rotations with respect to the translations in polyatomic gases as well as the effect of the relaxation of the internal degrees of freedom on the flow variables are also considered. In Chap. 9 the Boltzmann equation is applied to the spherically symmetric expansion of a monatomic gas and the results of these calculations are compared with the

corresponding results of the “*thermal conduction model*”. Chap. 10 refers to the characterisation of a particle source and the concept of “*virtual source*” is introduced. We will show that the observed distribution of the orthogonal component of the velocity is non-Maxwellian and an explanation of the phenomenon is given. Then, the effects produced by the introduction of a “*skimmer*” in the jet for the extraction of a collimated beam are considered. Chap. 11 is devoted to the possible presence of Van der Waals clusters in a jet of atoms or molecules and the mechanism of clusters formation is analysed. Finally, Chap. 12 is a miscellanea of different arguments such as the energy conservation in a free jet, the jets of binary mixtures and the expressions of the beam intensity in different points of the jet axis. The complex deductions and the detailed calculations are to be found in the Appendices. Appendices referring to the same Chapter are countersigned by the same letters. An asterisk has marked the sections that can be omitted in a first reading.

The authors are willing to consider or accept new ideas, other people’s suggestions and criticism, and will be gratified if their effort helps to overcome some of the difficulties met by those who have an elementary knowledge of this complex matter. The authors also hope that the reading of this book will enable the reader to assimilate the wide specialised literature on the subject.

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