

distribution law to a new equipartition theorem; but one cannot rely on a restricted equipartition theorem to furnish a guide as to the parameters in a new distribution law. This second and unreliable course appears to lie behind the discussion in refs. 1 and 3.

(F) *Generalized equipartition.* It follows that what is needed is a generalized Boltzmann distribution in  $I$  for the particles of a system of which the centre of mass has velocity  $\mathbf{w}$  when viewed from  $I$ . This is easily obtained from the appendix of ref. 6 as proportional to

$$\exp \left[ -\frac{\beta(w)}{kT} (E - wp_1) \right] \quad (9)$$

One may take  $E = c(p_1^2 + p_2^2 + p_3^2 + m_0^2 c^2)^{1/2}$ . Writing  $\mathbf{p}_i = m_i \mathbf{u}_i$ , where  $\mathbf{u}_i$  is the velocity of the  $i$ th particle in  $I$  and  $m_i = m_0 / \sqrt{1 - \mathbf{u}_i^2/c^2}$  is the inertial mass of the  $i$ th particle in  $I$ , one finds after a short calculation

$$\left\langle \frac{p_{1i}^2}{m_i} - wp_{1i} \right\rangle = \left\langle \frac{p_{1i}^2}{m_i} \right\rangle = \left\langle \frac{p_{1i}^2}{m_i} \right\rangle = \frac{kT}{\beta(w)} \quad (10)$$

This is a generalization of equations (7) and (8).

One may apply to equations (9) and (10) the two hypotheses  $T = T_0/\beta$  and  $T = T_0$ , as was done in the case of the Doppler effect, and one finds that both are compatible with the generalized equipartition theorem. Thus the argument from equipartition does not enable one to discriminate on theoretical grounds between accepted theory and a Lorentz-invariant temperature.

(G) It is well known<sup>9</sup> that the transformation laws of energy and momentum for a free system of particles are different from transformation laws for a confined system. It may be of interest to point out, therefore, that the statistical thermodynamics obtained in refs. 6 and 7 by using the laws for a free system are found to remain largely valid for a confined system. Indeed, K. A. Johns and I have shown that the transformation laws for a free system are identical with those for a confined system if the stresses in the container are included as part of the system. The transformation for heat is  $Q = Q_0/\beta$  (this corrects a remark in ref. 7) and leads to the second law in the form  $T\Delta S \geq \beta\Delta Q$  in frame  $I$ .

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P. T. LANDSBERG

Department of Applied Mathematics and  
Mathematical Physics,  
University College, Cardiff.

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### Hysteresis in the Flow through an Orifice

MCVEIGH<sup>1</sup> has construed my statement concerning the novelty of the hysteresis effect in a circular orifice<sup>2</sup> rather too literally. With the exception of Grace and Lapple<sup>3</sup>, all his references are concerned with liquid flows which do not fall within the terms of the generally accepted definition of a compressible fluid. The effect of compressibility in a gas flowing at a Mach number nearly equal to unity can never be achieved in a liquid under normal laboratory conditions. In a flowing gas it is the compressibility that is responsible for the change in the area of the jet which leads to attachment to the wall surface, the hysteresis itself being due to fluid viscosity. In a liquid, other factors such as cavitation may well be the triggering mechanism.

At the time the note on hysteresis was communicated<sup>2</sup>, the results of experiments with liquid flows in long orifices were known but in no case was there a well

defined hysteresis loop. The result reported by Grace and Lapple may well be the effect of jet attachment on the chamfered downstream face of their long orifice ( $l/d = 1.0$ ). Careful measurements of air flowing through orifices with  $l/d$  ratios between 0.60 and 2.0 and between 0.40 and 0.020 have shown that hysteresis does not occur when the downstream face is plane. The experimental points defining the hysteresis loop in the case of an orifice with an  $l/d$  ratio of 0.5 can scarcely be interpreted as a scatter as implied by McVeigh. The hysteresis loop can be reproduced with the same tolerance in measurement as over any other part of the flow range.

Details of the experimental techniques used in these investigations, and in particular the care taken to avoid uncertainties of the type mentioned by McVeigh, have recently been described<sup>4</sup>. It is possible that in testing similar orifices earlier investigators may have overlooked the existence of a hysteresis phenomenon because of the scatter of their measurements which, as in the report by Grace and Lapple, have been attributed to experimental limitations. The fact that the hysteresis loop can be reproduced accurately each time is evidence that it is a natural phenomenon and does not result from any random effects associated with the experimental technique.

B. E. L. DECKKER

Department of Mechanical Engineering,  
University of Saskatchewan,  
Saskatoon, Canada.

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## THE SOLID STATE

### Conversion of Single Crystals of Chlorapatite into Single Crystals of Hydroxyapatite

SINGLE crystals of synthetic hydroxyapatite with minimum dimensions larger than about 0.1 mm have been required for X-ray and neutron diffraction investigations but they have not been available. The solid state exchange of chloride ions in single crystals of chlorapatite for hydroxyl ions, as reported here, produces suitably large single crystals of hydroxyapatite. The exchange holds additional interest both as a process and for the effects of a partial exchange on crystal properties.

The chemistry and preparation of hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , have been investigated extensively, partly because it is the prototype for the inorganic component of bones and teeth. Hydroxyapatite as normally prepared by precipitation from aqueous solutions, or by solid state reactions at about 1,000° C, has crystals which are at most only a few microns in size. Hydroxyapatite crystals prepared by the hydrothermal bomb method<sup>1-4</sup> have typical dimensions of  $1 \times 0.1 \times 0.1$  mm. Though small, they have been used for X-ray studies, but have not been used in neutron diffraction experiments. Although the bomb product is sufficiently well crystallized to be suitable for thermodynamic experiments, it has the undesirable feature that it is often contaminated by  $\beta$ -tricalcium phosphate and  $\beta$ -calcium pyrophosphate. This necessitates sorting by hand which, because of the small size of the particles, must be done under a microscope. Furthermore, apatites prepared by the hydrothermal bomb method may depart from stoichiometric composition under certain conditions<sup>5-8</sup>.

Polycrystalline hydroxyapatite has been prepared from both mineralogical fluorapatite<sup>9</sup> and synthetic chlorapatite<sup>10</sup> powders heated in steam (1,360° C and 800° C,