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THE DIELECTRIC POLARIZABILITY OF FLUID PARAHYDROGEN

John W. Stewart*
Cryogenic Engineering Laboratory, National Bureau of Standards
Boulder, Colorado

Introduction

In the case of nonpolar substances such as hydrogen, the macroscopic polarizability (induced dipole moment per unit mass per unit electric field) P is related to the dielectric constant ε and the density ρ through the Clausius–Mossotti equation:

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{1}{\rho} \tag{1}$$

Elementary theory predicts that the righthand side of equation (1), often called the Clausius–Mossotti function, should be a constant independent of density. Detailed verification of this requires accurate measurements of both ε and ρ over as wide a range of conditions as possible. Sufficiently accurate measurements of ρ have previously been available for *normal* hydrogen, but a really meaningful investigation of the constancy of P for fluid parahydrogen over a wide range of density in both the gaseous and liquid states has been made possible only recently by the high-precision density measurements in this laboratory by Goodwin and his co-workers.[1] Their values of ρ are estimated to have an absolute precision of better than 0.1%. They are internally consistent to 0.02%. For corresponding precision in the calculated values of P, the dielectric constant must be determined to considerably higher accuracy.

Experimental Technique

In the present investigation, the dielectric constant of fluid parahydrogen was measured by the capacitance ratio method over the density, pressure, and temperature ranges 0.0024 to 0.0796 g/cm^3, 2.6 to 326 atm, and 24° to 100°K, respectively. The measuring capacitor (nominal vacuum capacitance C_0, 60 pF) was wholly contained within a copper pressure bomb capable of withstanding 5000 psi internal pressure. A General Radio Type 1615-A capacitance bridge was employed to measure the capacitance to 1 or 2 parts in 6×10^5 at 1 and 10 kc. Shielded leads were used so that no correction for lead capacitance was necessary. Only ratios of capacitances were needed in the final results, since $\varepsilon = C/C_0$.

The pressure and temperature of the hydrogen within the cell were determined at the same time as the capacitance. A calibrated platinum resistance thermometer was mounted at atmospheric pressure in a well on the outside of the pressure chamber. When the temperature was changed, thermal equilibrium with the samples was attained in a short time through the copper walls. A thermocouple monitored

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* National Academy of Sciences—National Research Council Post Doctoral Research Associate, 1962–63. Permanent address: Department of Physics, University of Virginia, Charlottesville, Virginia.

the temperature gradient along the length of the pressure bomb. A sensitive deadweight piston gauge was used to measure the pressure. The special electronically controlled regulating system designed and built by Goodwin[2] for the density measurements maintained the temperature of the system constant to $\pm 10^{-3}$ °K for as long as desired.

The presence of parahydrogen was verified by continuous sampling during filling of the stream of gas downstream from the catalyst in a differential thermal conductivity comparison instrument,[3] and by occasional vapor pressure measurements of the sample itself.

A total of 205 (P, T) points on twenty-two isotherms was investigated. The density corresponding to each measured pressure and temperature was determined through a computer program in accordance with the earlier measurements.[1] Small corrections were made for variations in density caused by the observed thermal gradients along the length of the pressure bomb and for the change of volume of the copper in the capacitor resulting from the hydrostatic pressure.

Results and Discussion

The resultant values of the Clausius–Mossotti function were calculated from (1). They do not appear to depend explicitly upon temperature. The results were fitted by least squares to a quadratic function of density:

$$\frac{1}{P} = A + B\rho + C\rho^2 \tag{2}$$

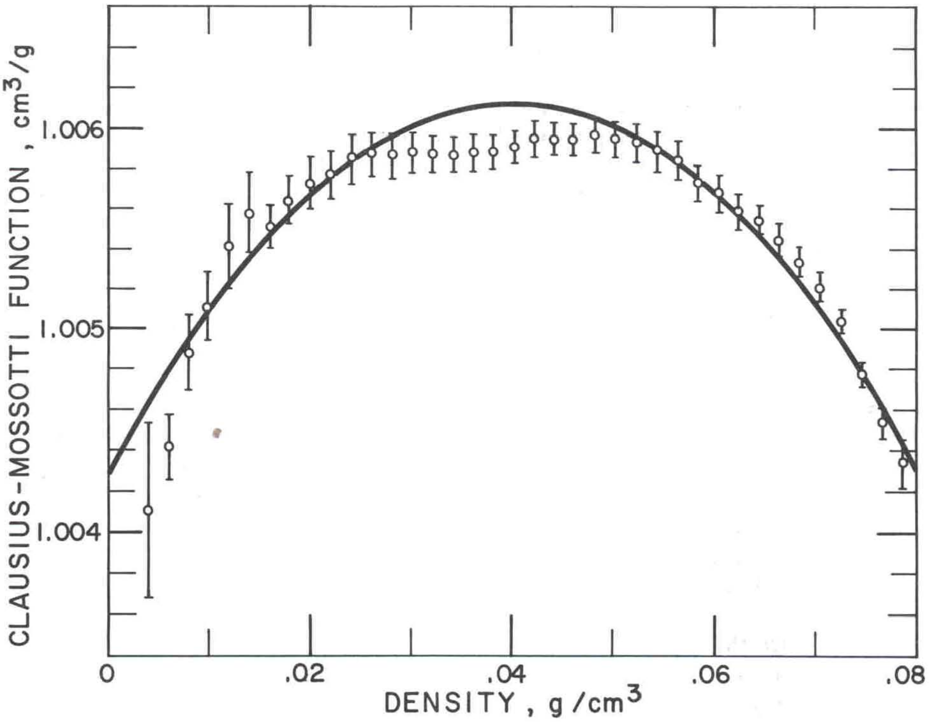

Fig. 1

The constants A, B, and C have the values: $A = (0.99575 \pm 0.00132)$ g/cm^3, $B = (-0.09069 \pm 0.02463)$, and $C = (1.1227 \pm 0.2895)$ g/cm^3. The maximum value of P occurs at $\rho = 0.040$ g/cm^3, and is 0.2% above the value at $\rho = 0$.

This fitted curve for the Clausius–Mossotti function is shown in Fig. 1. The points on this plot are interpolated and averaged values of the actual experimental observations. The deviations from the means at each density are shown as error bars.

The observed departure from constancy of P is believed to be a real effect. The reproducibility of the data for the same density at different temperatures and with separate fillings of the sample holder was of the order of 0.05%, except for the points close to the critical density (0.031 g/cm^3). It is impossible to achieve high precision PVT measurements near the critical point by these techniques because $(\partial\rho/\partial T)_P$ becomes infinite. The corrections to the calculated density for thermal gradient were much larger in this vicinity.

The initial rise of the Clausius–Mossotti function followed by a decrease is qualitatively similar to the behavior reported for other nonpolar gases,[4] including argon[5,6] and carbon dioxide.[7,8] Hamann[9] comments that the maximum of the Clausius–Mossotti function for these two and for ethylene all fall in the vicinity of the critical density. Here it is seen that parahydrogen, with a critical density only 1/15th that of carbon dioxide, shows the same behavior.

In view of the simplifying assumptions made in its derivation, it is quite remarkable that the Clausius–Mossotti equation holds as well as it does. For real substances, one can make qualitative estimates of the effect of deviations from these assumptions. For example, fluctuations of the induced molecular dipole moments should increase in proportion to density, and lead to the initial increase of the Clausius–Mossotti function with ρ. This might also be expected to lead to an inverse temperature effect, which, however, was not observed in the case of parahydrogen. At higher densities, short-range interactions between the molecules would assume increasing importance, leading to a subsequent decrease in the polarizability. The magnitude of the effect in the case of parahydrogen is too small to make quantitative correlation with existing theories of polarizability feasible.

A more detailed description of this work has been published elsewhere.[10]

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