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THERMODYNAMIC EFFECTS IN A GAS MODULATED INVAR-BASED DUAL FABRY-PÉROT CAVITY REFRACTOMETER ADDRESSING 100 KPA OF NITROGEN

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Abstract:
An Invar-based dual Fabry-Pérot cavity refractometer used for assessments of pressure by the gas modulation refractometry (GAMOR) methodology has been scrutinized with respect to the influence of thermodynamic effects (*pV*-work) that originates from the gas exchange process when 100 kPa of nitrogen is addressed. It is shown that the actual temperature variation of the cavity spacer solely is a fraction of the previously assessed upper limits (0.5 mK/100 kPa), limited to sub-parts-per-million (ppm) levels. This finding additionally supports the conclusion that the thermodynamic effects will not be a limiting factor when the system is used for assessments of pressure.

Keywords: pressure; *pV*-work; refractometry; gas modulation; Fabry-Perot cavity.

1. INTRODUCTION

By measuring the refractivity, $n-1$, where n is the index of refraction, and the temperature, T, of a gas, its pressure can be assessed from fundamental principles, viz. by the use of the Lorentz-Lorenz equation and an equation of state [1].

The highest performing optical instruments for pressure assessment are based on Fabry-Perot cavities (FPC). This technique has demonstrated assessment of pressures with both high precision and good accuracy over large dynamic ranges [2]-[4]. Recent works have indicated that the methodology has the potential to replace current pressure standards, in particular in the 1 Pa to 100 kPa range [5].

To be able to assess pressure with highest accuracy, which is of particular importance when such a system is to be used as a primary standard, it is of importance to verify that the assessments are taken under adequate conditions; in particular to assess whether (and if so, to which extent) the gas exchange process affects the assessment of the gas temperature. Hence, to allow for high accuracy assessments, it is of importance to assess the uncertainty contribution from the thermodynamic effects that are associated with the gas exchange process in the cavity in the system used (here referred to as *pV*-work).

Until recently, the best characterized system was the FLOC system at NIST [6]. It was found that that system is adequate for assessment of pressure under the condition that it is given enough time to equilibrate after a gas filling (in the order of 3000 s to reach an uncertainty level of 0.5 mK).

We have since then performed a detailed scrutiny of the influence of the gas exchange process on the assessment of gas temperature on an Invar-based dual-FPC (DFPC) instrumentation used for the gas modulation refractometry (GAMOR) methodology [7]. It was shown, by the use of simulations, that, by virtue of a combination of a number of carefully selected design entities (a small cavity volume with a bore radius of 3 mm, a spacer material with high heat capacitance, large thermal conductivity, and no regions that are connected with low thermal conductance, i.e. no heat islands), and a continuous assessment of temperature of the cavity spacer, the assessment of pressure is not significantly affected by *pV*-work when pressures up to 100 kPa are addressed by the use of gas modulation cycles of 100 or 200 s [7].

The system was scrutinized in terms of three separate processes, viz.

i. gas dynamics,
ii. gas-to-cavity-wall transfer of heat, and

iii. thermalization of the cavity spacer.

It was shown, regarding the former of these, that the pressure in the cavity equilibrates on a time scale of some tens of ms. The gas thereafter rapidly adopts the temperature of the cavity walls. For the case with 30 kPa of N_2, it was found that the decay is exponential with a time constant of 0.07 s, while, for 100 kPa, it is 0.14 s. This implies that the average temperature of the centre part of the cavity will quickly (within 1 – 2 s) equalize to temperatures well within sub-mK of that of the cavity wall [7].

Regarding the second concept, due to the small dimensions of the system, the gas volume of which is less than 5 cm^3, when 100 kPa of gas are addressed, solely < 0.5 J of energy is let into the system. This is only 3% of the energy that is let into the system in the NIST FLOC system (172 cm^3 of gas, representing 17 J of energy) [6]. Moreover, since Invar has a three times larger volumetric heat capacity than glass (in fact, it has a more than three orders of magnitude larger volumetric heat capacity than the gas), it was concluded that the initial heating of the cavity walls will be at least two orders of magnitude smaller than that of the FLOC system. It was then also found that the increased gas temperature decays exponentially towards the cavity wall temperature with a time constant of 0.14 s and that it is within 1 mK of the temperature of the wall already after 1.5 s [7].

Regarding the third concept, since the Invar system is constructed without heat islands (i.e., with no internal isolation layers) and since Invar has a ten times higher thermal conductivity than many types of glass, it was found that any temperature gradient will dissipate more than one order of magnitude faster than it will in a glass-based system. This reduces the temperature gradients in the spacer and thereby the time it takes for a given temperature disturbance to level off to its steady state value [7].

Moreover, since the system incessantly assesses temperature (either by the use of sensors placed in the holes bored in the cavity spacer or a thermocouple wrapped tightly around the spacer), any possible homogeneous heating of the cavity spacer affecting the gas temperature will be measured and thereby automatically accounted for by the data evaluation process. The pressure assessments are therefore only influenced by any possible *difference* between the temperature of the cavity walls and that of the cavity spacer at the position(s) of the sensors. Simulations showed that 10 s after the filling of 30 kPa of nitrogen, all temperature gradients in the system are well into the sub-mK range [7].

An analysis of the simulations indicated that an upper limit for the uncertainty in the assessment of temperature due to the influence of *pV*-work in the Invar-based DFPC system using 100 s long gas modulation cycles when 100 kPa of nitrogen is addressed is 0.5 mK [corresponding to an uncertainty in the assessment of pressure of 1.8 parts-per-million (ppm)]. The corresponding numbers when 200 s long cycles are employed are even lower, 0.4 mK and 1.3 ppm, respectively [7].

Experiments performed at pressures up to 30 kPa supported the assumption that refractivity assessments are not markedly affected by the *pV*-work; cycle-resolved assessments did not show any variation in pressure or temperature that could be attributed to the gas exchange process. We interpreted this as, when 30 kPa of nitrogen are addressed, there is no significant (detectable) influence of *pV*-work on the temperature of the gas, and thereby the assessment of pressure, at the time in the modulation cycle when the refractivity assessments are made (which is after either 40 or 90 s, depending on mode of operation) [7].

Although the experiments performed could verify that the actual thermodynamic effects are not above the upper limits estimated by the simulations, they could not clearly assess the true influence of *pV*-work on the system. Since the simulations were performed for a simplified system neglecting, among other things, the thermal contact of the gas supply and evacuation tubing to the cavity spacer (i.e., the thermal influence of the gas tubing on the cavity spacer), which implies that they assumed that all energy carried by the gas was delivered to the walls of the cavity, it is likely that the actual thermal effects are smaller than the aforementioned estimated upper limits.

In order to assess the true influence of *pV*-work on the system, the instrumentation has, since the previous work was performed, been modified so as to be able to handle 100 kPa of nitrogen (to increase any possible thermodynamic effect with respect to those investigated in that work) and incorporate an improved temperature assessment system (to improve on the signal-to-noise of the temperature assessment).

By these two alterations, it became possible to assess the true gas modulation induced temperature variations of the cavity spacer, resulting in the conclusion that the actual influence truly is a fraction of the previously reported upper limits.

2. EXPERIMENTAL

The Invar-based DFPC-refractometer used is, to a large extent, identical to the one presented in detail in some other publications [8], [9]. The heart of the system is the cavity spacer, machined from a rod of Invar (see Figure 1). The spacer comprises two through-going holes for the measurement and reference cavities and three for temperature sensors.

Each cavity is supplied with gas (and evacuated) through a tube connected on the side. The cavity temperature is assessed with either 3 Pt-100 sensors or by a thermocouple that is wound around the cavity block and referred to a Ga fix point cell [9].

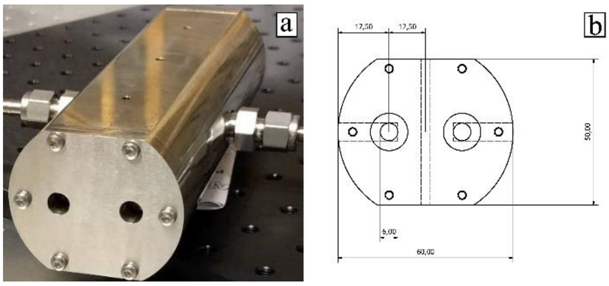

Figure 1: The Invar cavity spacer before placed in a temperature regulated enclosure. Reproduced with permission from [10].

To be able to address gas modulations of 100 kPa of N_2, the turbo-molecular pump used in the original system was exchanged to one with larger capacity, capable of evacuating larger volumes of gas.

To improve on the signal-to-noise conditions of the temperature assessments, the temperature measuring system was improved by the incorporation of a lock-in based temperature assessment system based on a balanced bridge assessing the temperature measured by (in this case) two Pt-100 sensors at the two $\Delta z = \pm$ 50 mm positions.

In the bridge, schematically displayed in Figure 2, the two Pt-100 sensors were balanced by the use of two sets of low temperature drift resistors, R1 and R2, to give zero output voltage ($V_{out} = 0$) at the Gallium melting point.

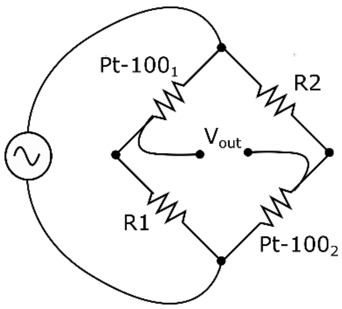

Figure 2: Schematic illustration of the balanced bridge assessing the temperature measured by the Pt-100 sensors. To enhance its performance, it was run with homodyne detection, with the driving voltage sinusoidally modulated a 40 Hz while the V_{out} output voltage of the bridge was assessed by the use of a lock-in amplifier (not in drawing).

To reduce the effect of stray offset voltages (including drifts in such), homodyne detection was used. The bridge was then driven by a sinusoidal voltage with an amplitude of 0.1 V at 40 Hz, generated by the internal frequency generator in a lock-in amplifier. The output signal of the bridge, V_{out}, was then detected by the same lock-in amplifier, the output of which represents the amplitude of the voltage response of the bridge, which in turn is directly related to the resistance of the two Pt-100 sensors: Since the latter is a measure of the temperature, the output of the lock-in amplifier provided, after a calibration, an accurate assessment of the temperature of the sensors.

3. EXPERIMENTAL ASSESSMENTS

By the aforementioned two alterations, it was found possible to assess the true gas modulation induced temperature variations of the cavity spacer in terms of the average of the temperature at the positions of the two Pt-100 sensors.

Referring to the previous scrutiny of the instrumentation by Rubin et al. [7], it was estimated, as was shown in figure 7 in that work, that the maximum temperature deviation of the cavity spacer, assessed in between the two cavities (at the point denoted x_{Pt} in that work, at the $\Delta z = \pm$ 50 mm positions, and displayed by the cyan-colored curve in that figure), for a modulation of 30 kPa of nitrogen, was 0.5 mK (ranging from - 0.2 to + 0.3 mK). Since thermal effects originating from the transfer of gases is proportional to the gas pressure, the corresponding maximum temperature variation of the spacer at these positions for a gas modulation when addressing 100 kPa, represented by the blue "Simulation" curve in Figure 3, can be estimated to be 1.5 mK.

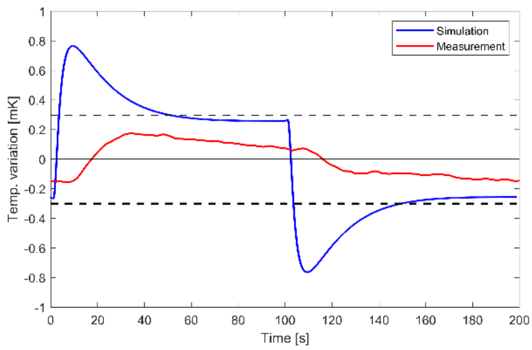

Figure 3: Blue curve: Simulations of the upper limits of the time development of the temperature difference between the wall of the measurement cavity and the time-averaged temperature of the Pt-100 positions (i.e. at $\Delta y = 0$ mm and $\Delta z = \pm$ 50 mm, defined in the work by Rubin et al. [2]) for a 200 s long gas modulation cycle when addressing 100 kPa of nitrogen (comprising 100 s of filling followed by 100 s of evacuation). Red curve: measurement of the temperature at the same two positons of the spacer given in terms of an average of more than 1 900 consecutive 200 s long gas modulation cycles, performed over a continuous period of 4.5 days.

The same figure also shows, by the red curve, the average temperature of the same two Pt-100 positions ($\Delta z = \pm 50$ mm) measured by the instrumentation used in this work while addressing 100 kPa of nitrogen. These data show that the actual maximum (peak-to-peak) variation of the temperature is 0.32 mK, which solely is a fraction (ca. 20%) of the upper limit estimated by the simulations (1.5 mK).

An analysis of the measurement data taken indicates also that the actual increase in temperature of the cavity spacer at the positions of the temperature sensors when the gas is let in (after 0 s in Figure 3) has a less accentuated shape than the simulated one; after a certain delay, it increases less steeply, reaching a maximum value of less than a third of that predicted by the simulations, and decays more slowly. The corresponding decrease in temperature associated with the gas evacuation (after 100 s) is even smaller.

The reason for the delay is attributed to a combination of the finite time it takes for the gas-induced heat wave to propagate to the positions of the sensors and the response time of the sensors.

The cause for the smaller increase in temperature following inlet of gas is attributed to the fact that the gas, after the inlet valve has opened, passes a series of bellows and tubes outside the actual cavity before it enters the cavity. This implies that parts of the energy carried by the gas will be deposited into those devices. We interpret this as that not all of the energy carried by the gas (represented by pV) will be brought into the cavity with the gas and contribute to the heating of the spacer.

Also, the subsequent slower decay of the temperature of the spacer (from 30 to 100 s in Figure 3) can be attributed to the gas supply gadgets (bellows and tubing), since they can successively transfer their excess heat into the cavity by thermal conduction.

It should be noticed that at the time when refractivity measurements are performed, i.e., after 90 s, the measured temperature is about one third of the simulated upper-limit.

The smaller decrease in temperature associated with the evacuation of the gas (displayed in the second part of the gas modulation cycle shown in Figure 3) can be explained by a similar process, viz. that the evacuation process will not only cool the cavity spacer, but also valves and gas tubes connected to the cavity spacer.

Since the construction of the gas inlet (comprising tubing and bellows) is not fully identical to that of the exit, the amplitude and shape of the increase of the temperature associated with the filling differ slightly from those of the decrease of the evacuation. This can be noticed from the data shown in Figure 3; the filling process of the cavity brings in slightly more energy into the cavity than what the evacuation process removes. It is estimated that, when addressing 100 kPa of nitrogen, the temperature of the cavity spacer increases by 0.15 – 0.20 mK per modulation cycle. This implies that, during a series of consecutive gas modulations, the temperature of the cavity spacer will slowly be increased. It is important to note though that, since the temperature of the cavity is incessantly assessed by sensors, any temperature variation of the spacer from this process does not significantly affect the ability to assess pressure.

The increase in the temperature of the cavity spacer will though, due to temperature regulation of the spacer, only take place for a limited time. Under steady state conditions, i.e. after a series of gas modulations that last over a time that is longer than the response time of the temperature regulating system (in the order of an hour), the cycle averaged temperature of the cavity spacer will be equal to the set temperature of the feedback system. This will give rise to a minor temperature gradient in the spacer that will add an additional uncertainty to the difference in temperature between the cavity wall and the sensor positions that is a fraction of the aforementioned temperature increase of the cavity spacer (i.e. a fraction of 0.20 mK). Since this is significantly smaller than many other effects in the system, neither this will significantly affect the ability to assess pressure.

4. SUMMARY AND CONCLUSIONS

A recent scrutiny of an Invar-based dual-FPC (DFPC) instrumentation used for the gas modulation refractometry (GAMOR) methodology, mainly based on simulations, performed by Rubin et al. [7] has indicated that an upper limit for the influence of pV-work on the system when 100 kPa of nitrogen is addressed using 100 s long gas modulation cycles is 0.5 mK (corresponding to an uncertainty in the assessment of pressure of 1.8 ppm). The corresponding numbers when 200 s long cycles are employed were found to be even lower, 0.4 mK and 1.3 ppm, respectively. This indicates that the system is significantly less affected by pV-work than other systems, e.g., the NIST-FLOC system [6].

The reason for these advantageous properties are primarily due to a combination of a number of carefully selected design entities: a small cavity volume with a bore radius of 3 mm, a spacer material with high heat capacitance and large thermal conductivity, no regions that are connected with low thermal conductance, i.e. no heat islands, and a continuous assessment of temperature of the cavity spacer.

We have in this work shown, by temperature measurements of the cavity spacer when 100 kPa of nitrogen is addressed, that the actual influence of the *pV*-work on the system is smaller than these upper limits [7]. The cause for this is attributed to the fact that the gas, after the inlet valve has opened, before it enters the cavity, passes a series of bellows and tubes that will absorb some of the energy carried by the gas (represented by *pV*). Hence, not all of this energy will be brought into the cavity and contribute to the heating of the spacer (as was assumed by the simulations performed in our previous study [7]).

In that work, it was estimated, from the simulations, that the difference between the temperature of the wall of the measurement cavity and the time averaged temperature of the sensor positions when 30 kPa of nitrogen was addressed, 50 or 100 s into the supply-and-filling section, are 0.16 and 0.12 mK, respectively. Since, as was alluded to above, it was estimated that, after 90 s, the measured temperature deviation is about one third of the simulated one, it can be assumed that, in reality, when three times as high pressure (i.e., 100 kPa) is addressed, a deviation similar to that obtained by the simulations, i.e. 0.16 and 0.12 mK respectively, will prevail. This implies that it is possible to conclude that the influence of thermodynamic effects in a gas modulated Invar-based DFPC refractometer addressing 100 kPa of nitrogen is clearly limited to sub-ppm levels when the refractivity assessments are performed, i.e., 50 and 100 s into the supply-and-filling section, respectively.

It was also found that, due to the construction of the system, the system might experience a minor heat pumping effect; the filling part of the gas modulation cycle will bring in slightly more energy than what the evacuation part of the cycle carries out, slowly heating the spacer (estimated to 0.15 – 0.20 mK per modulation cycle). The temperature regulating system of the spacer will though, within its response time (in the order of an hour), regulate the temperature of the spacer to its set temperature. Despite this, it was concluded that, irrespective of whether the temperature regulation feedback system has regulated the spacer temperature to the set-value or not, since the temperature of the cavity is incessantly assessed by sensors, any temperature variation of the spacer from this process will not markedly (only on sub-ppm levels) affect the ability to assess pressure on time scales of the gas modulation time.

It should additionally be noticed that the main processes not considered in the simulations (e.g., the influence of bellows and tubes), in fact, are beneficial for the instrumentation since the actual *pV*-work caused by the filling and evacuation of the cavity will cause less temperature variations of the cavity spacer than what the previous simulations predicted.

Since the instrumentation scrutinized in this work has been assessed to have an extended uncertainty of $[(10\,\text{mPa})^2 + (10 \times 10^{-6}\,\text{P})]^{1/2}$ [3], this scrutiny, which has concluded that the influence of thermodynamic effects on the assessment of pressure when 100 kPa of nitrogen is addressed is in the sub-ppm level, has indicated that, despite the use of gas modulation cycle times of 200 s, as can be used when the GAMOR method is utilized, the Invar-based DFPC system is not significantly affected by thermodynamic effects related to the gas exchange process. Hence, this work further strengthens the conclusion that thermodynamic effects (*pV*-work) will not be a limiting factor when the Invar-based DFPC GAMOR system is used for assessments of pressure or as a primary pressure standard for pressures up to 100 kPa.

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