



Reflections on the NPL-2013 Estimate of the Boltzmann Constant

Michael de Podesta

Fundamental Constants
February 2015

EMRP
European Metrology Research Programme
► Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries
within EURAMET and the European Union



EURAMET
European Association of National Metrology Institutes



Also my wonderful NPL colleagues

**Gavin Sutton, Robin Underwood,
Gordon Edwards, Graham Machin,
Richard Rusby, David Flack,
Andrew Lewis, Michael Perkin,
Stuart Davidson, Kevin Douglas,
Rob Ferguson, David Putland,
Anthony Evenden, Louise Wright,
Eric Bennett, Alan Turnbull,
Gareth Hinds, Phil Cooling,
Gergely Vargha, Martin Milton,
Michael Parfitt, Peter Harris, Leigh Stanger
and others**

Also my colleagues outside NPL

Paul Morantz, Cranfield

Darren Mark and Fin Stuart, SUERC

Laurent Pitre, LNE-CNAM

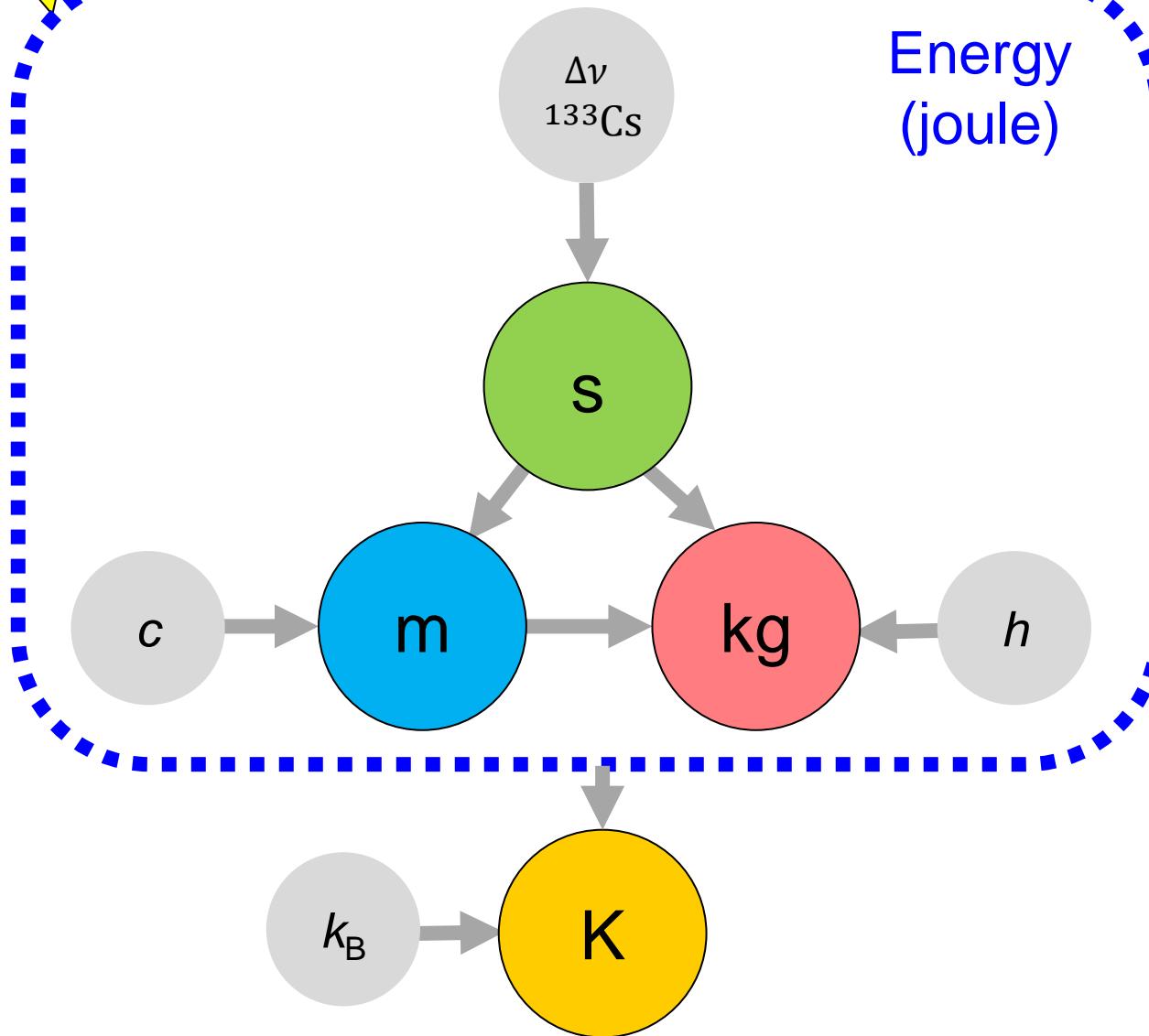
Roberto Gavioso, INRiM

Inseok Yang, KRISS

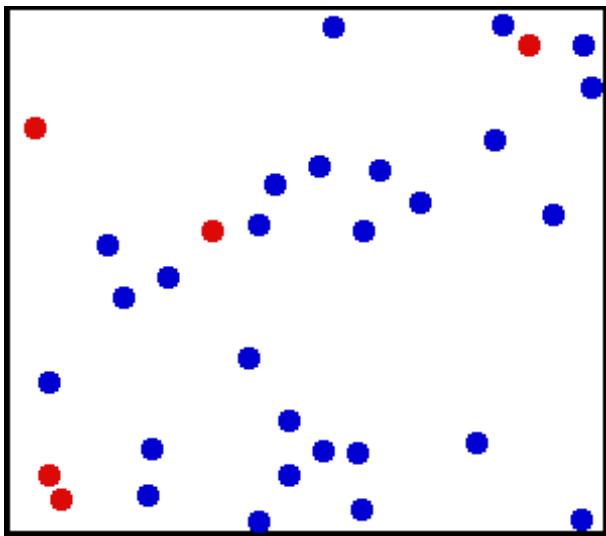
Reflections on the NPL-2013 Estimate of the Boltzmann Constant

- 1. Background**
- 2. History**
- 3. The NPL uncertainty estimate**
- 4. NPL Update February 2015**
- 5. The NPL Analysis**
- 6. Summary**

The NEW International System of Units



The Challenge



Molecular Motion

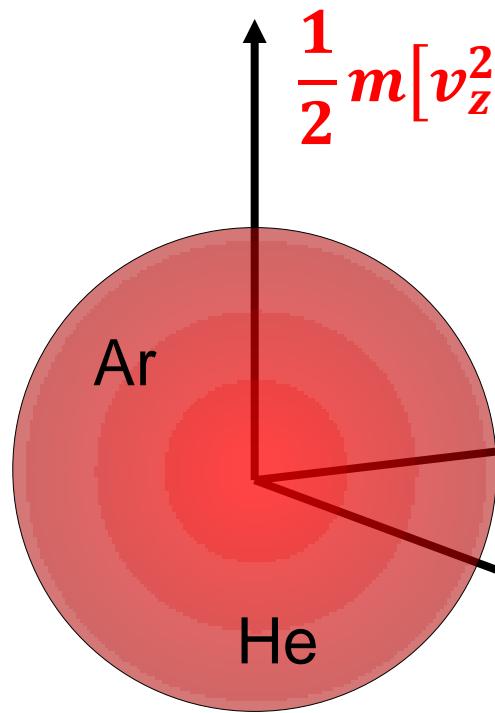


Thermometer

How do we relate the number produced by a thermometer (e.g. 20 °C) to the basic physics describing the jiggling of molecules?

Primary thermometers are based on gases

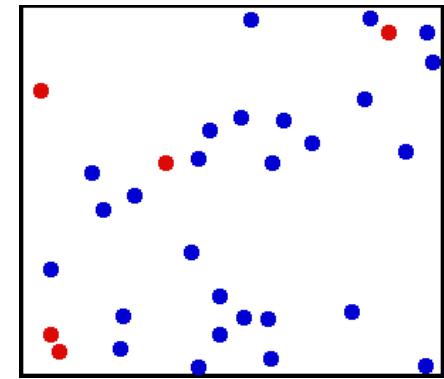
- Molecular motions are simple
- We can approach ‘ideal gas’ conditions at low pressure
- In an ideal gas the internal energy is just the kinetic energy of the molecules



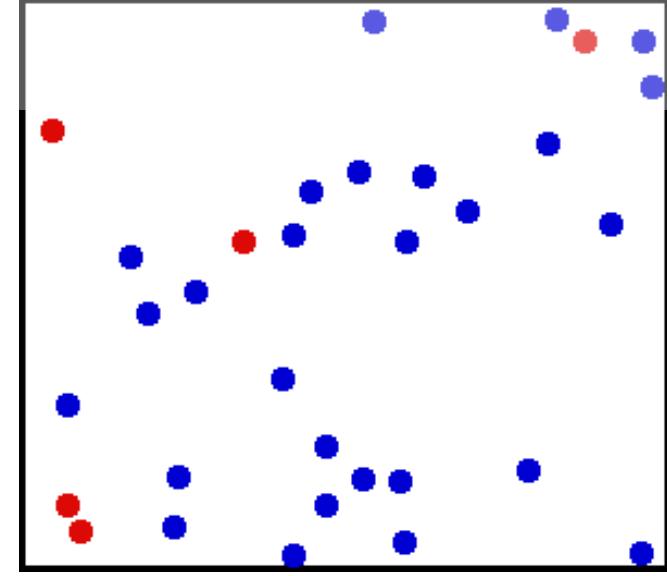
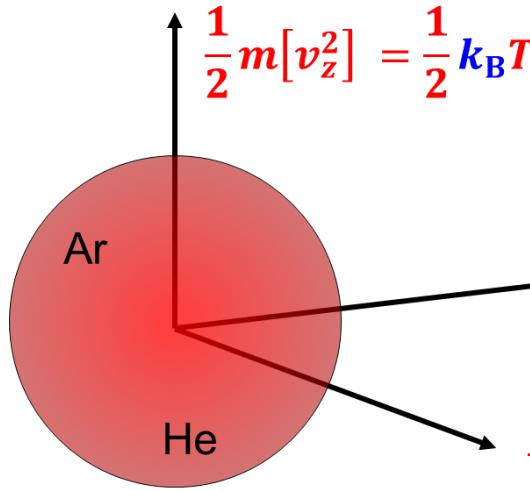
$$\frac{1}{2} m[v_z^2] = \frac{1}{2} k_B T$$

$$\frac{1}{2} m[v_y^2] = \frac{1}{2} k_B T$$

$$\frac{1}{2} m[v_x^2] = \frac{1}{2} k_B T$$



The big idea...



Find mass of molecule

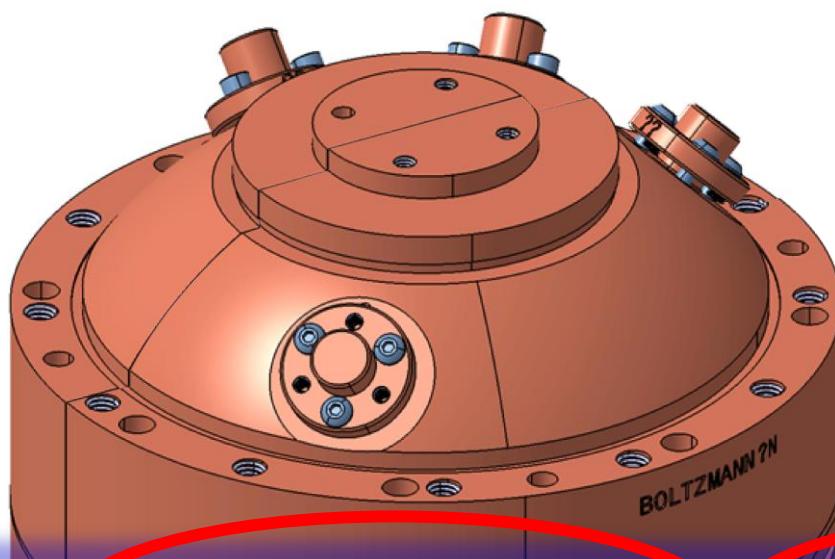
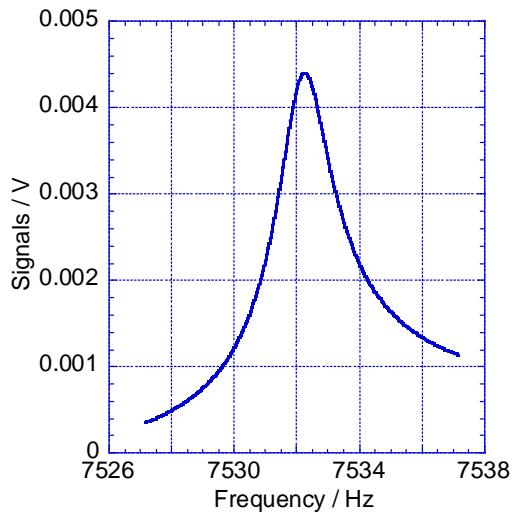
$$k_B = \frac{3m}{5T} [\text{speed of sound}]^2$$

Carry out experiment at T_{TPW}

$$\frac{9}{5} (\text{speed of sound})^2$$

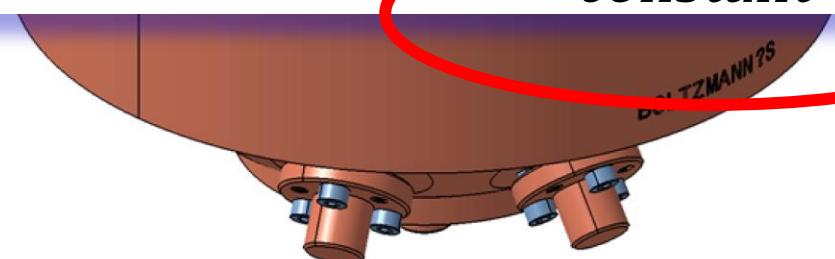
Measure the speed of sound

Measure the speed of sound in a spherical resonator

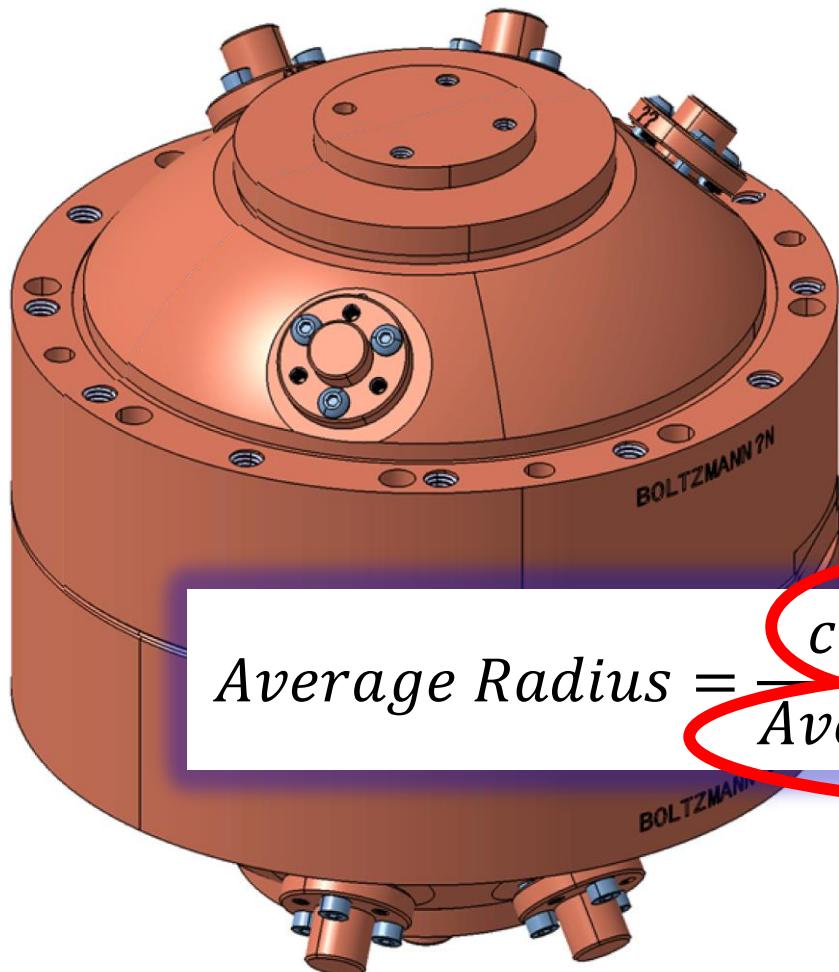


?

$$\text{Speed of Sound} = \frac{\text{Resonant Frequency} \times \text{Average Radius}}{\text{constant}}$$

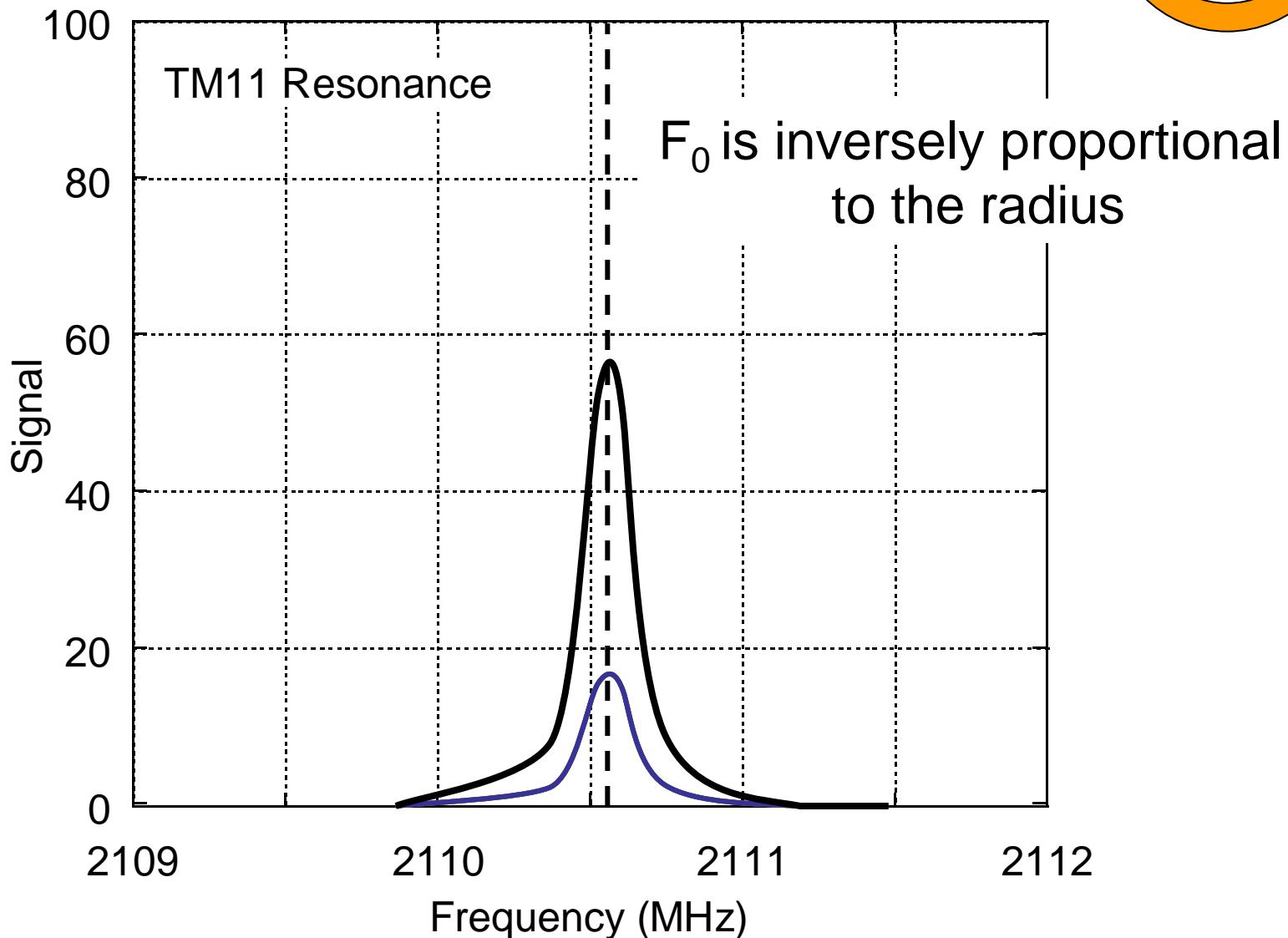
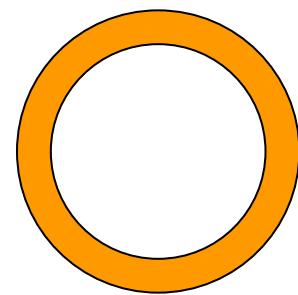


Measure the Average Radius using Microwaves

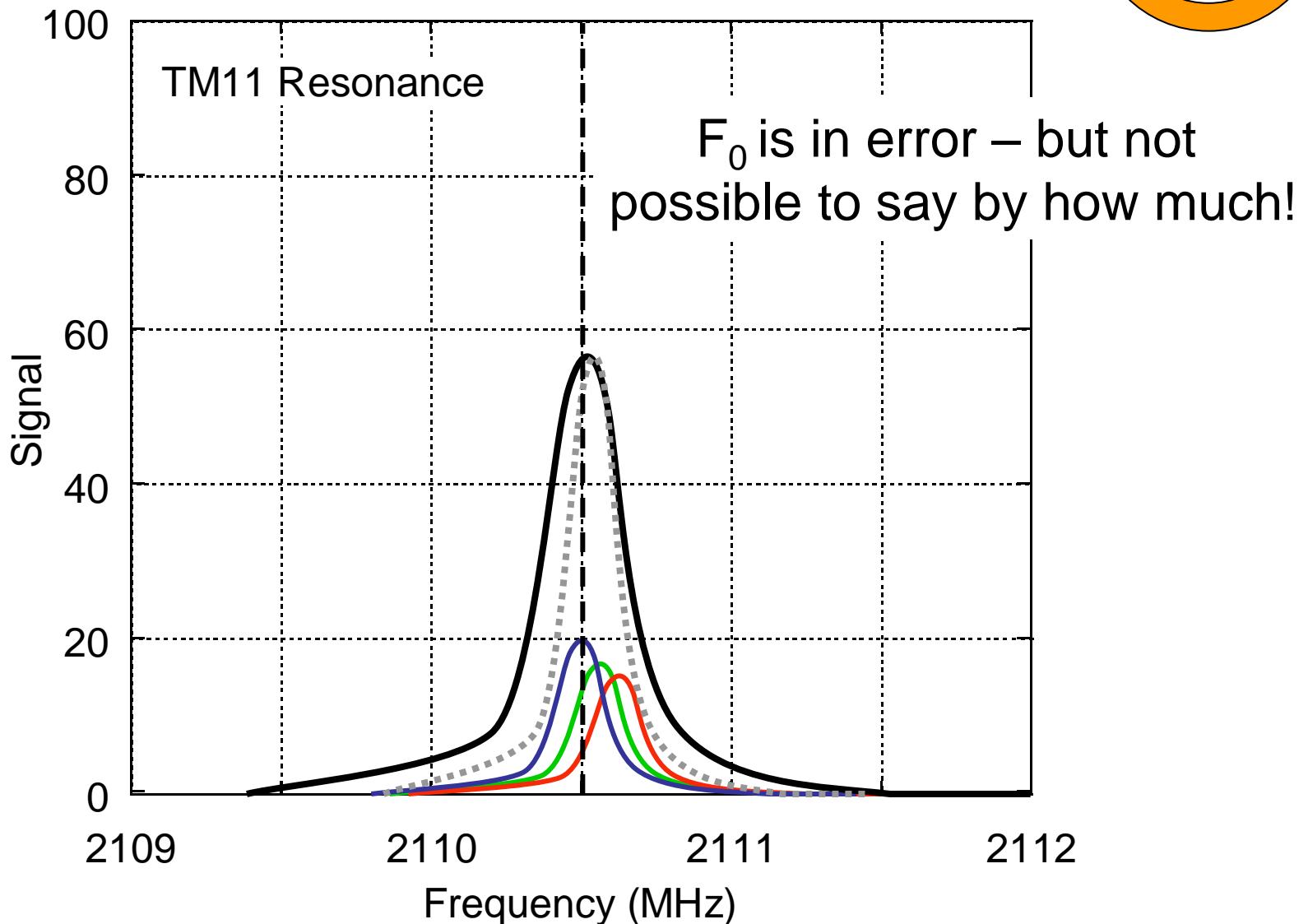
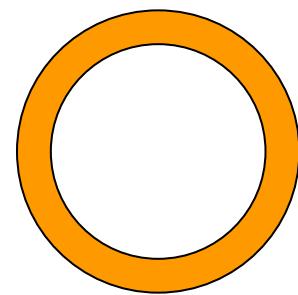


$$\text{Average Radius} = \frac{\text{constant} \times \text{speed of light}}{\text{Average Resonant Frequency}}$$

Microwave resonance in a perfect sphere

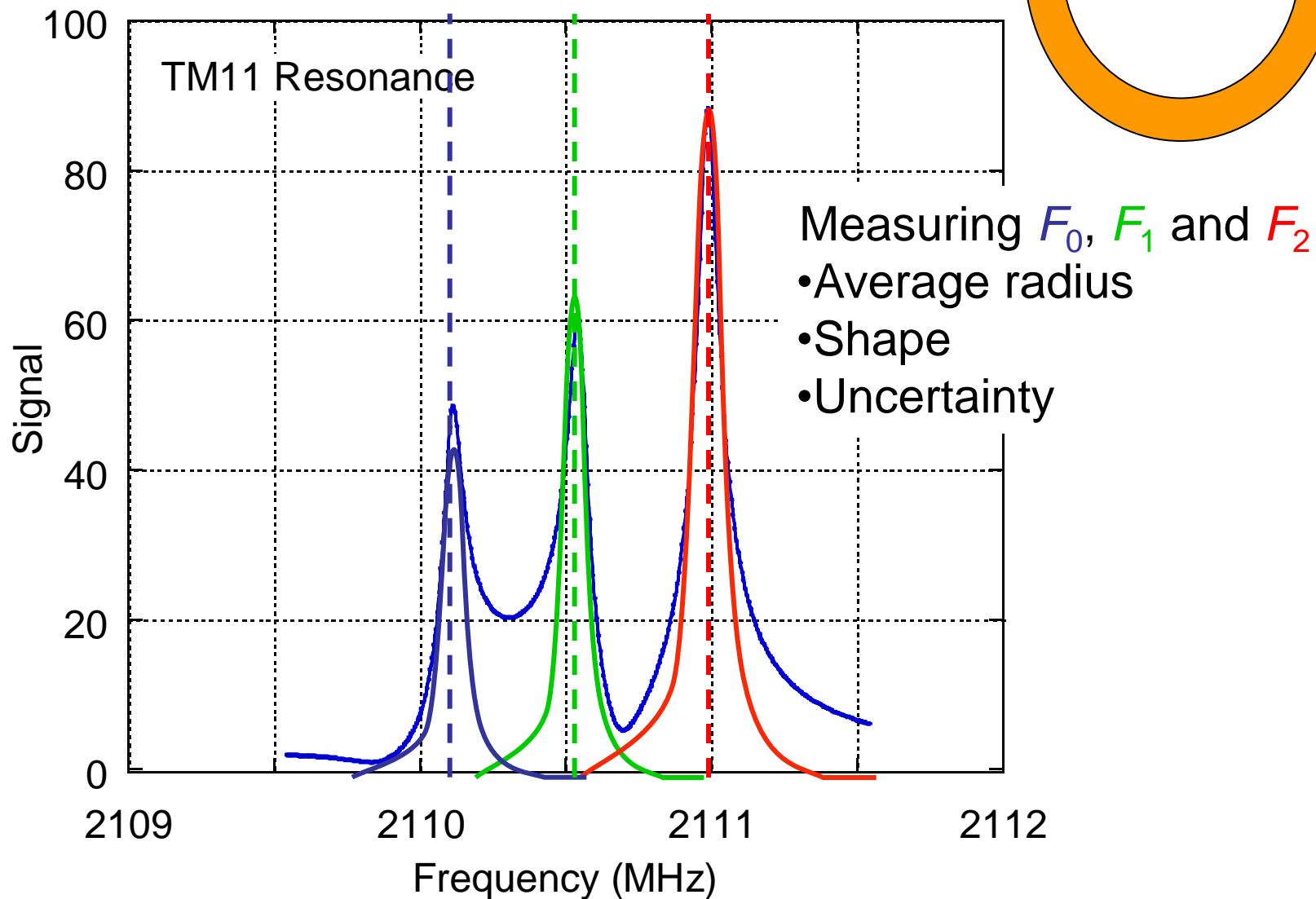
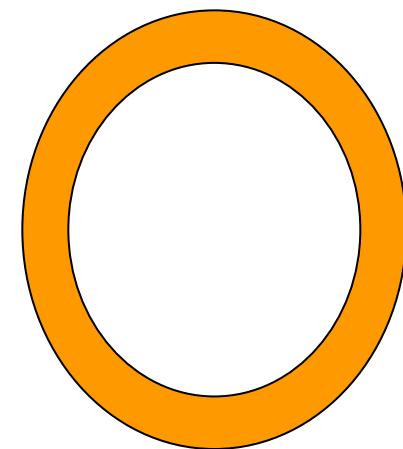


Microwave resonance in a nearly perfect sphere



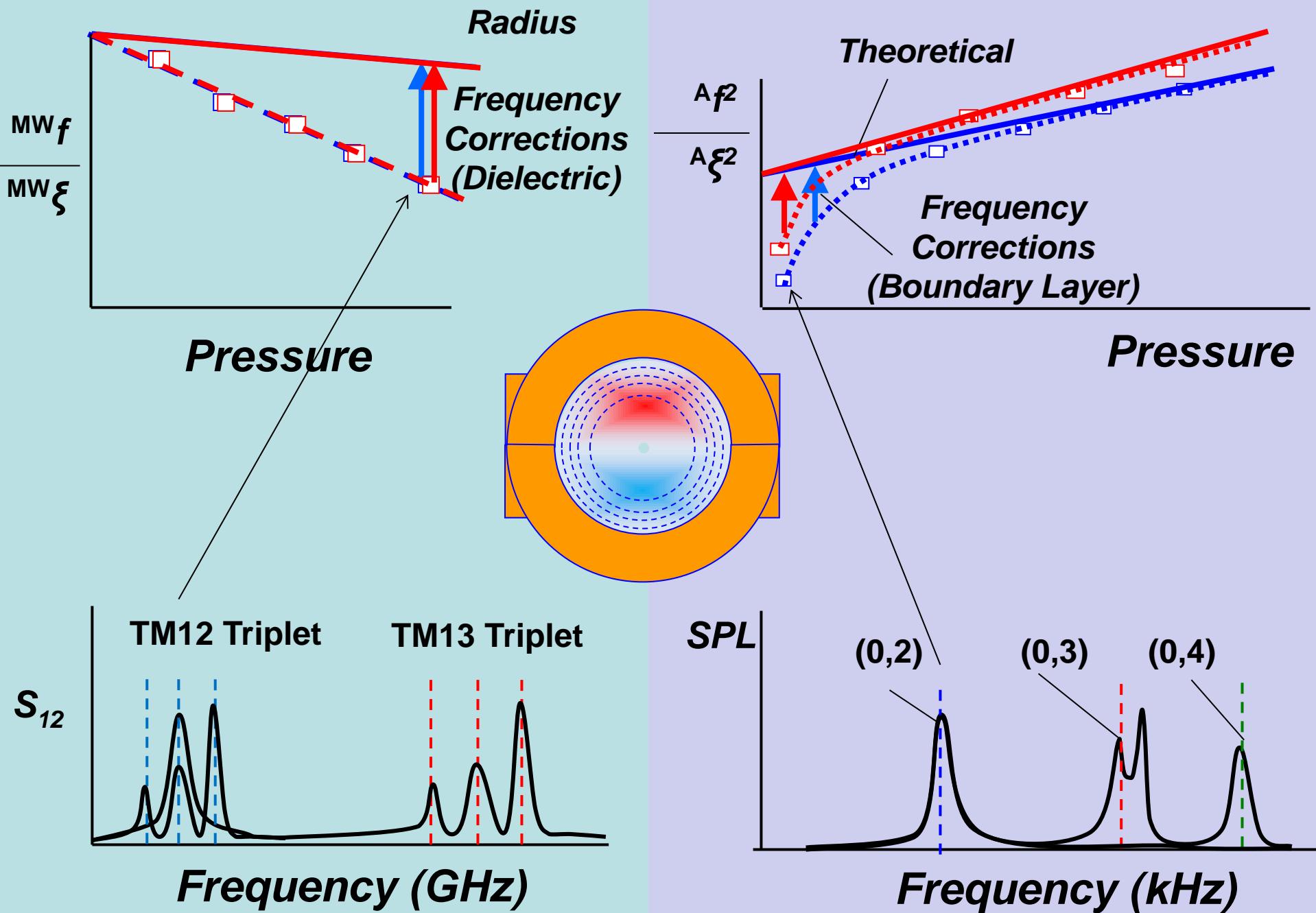
Microwave resonance in a triaxial ellipsoid

Radius 62 mm
0.031 mm eccentricity

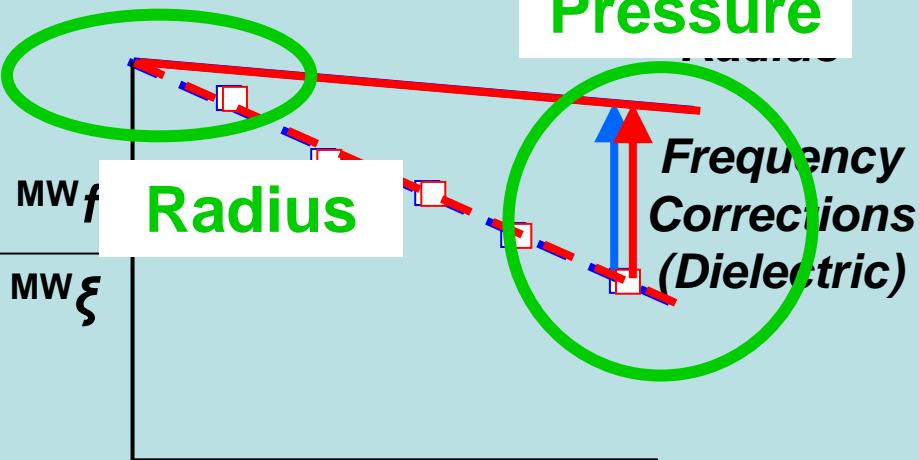


Microwaves

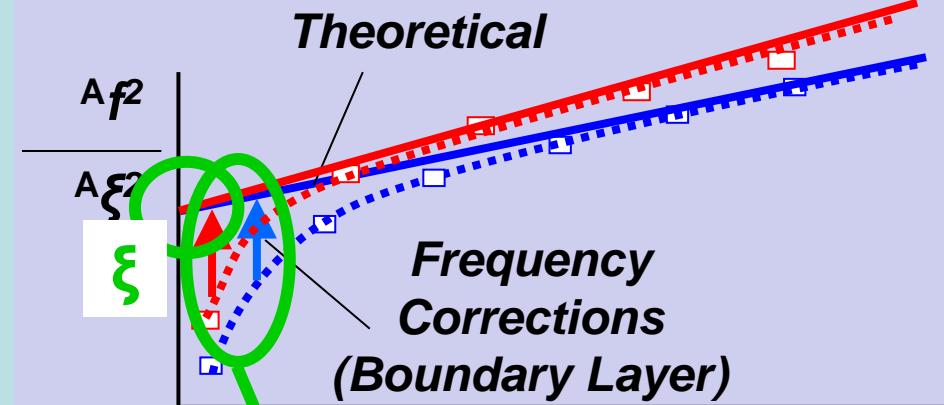
Acoustics



Microwaves

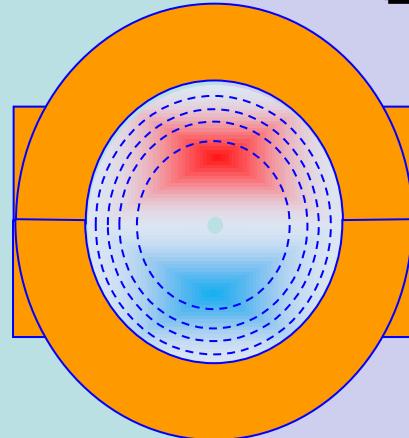


Acoustics

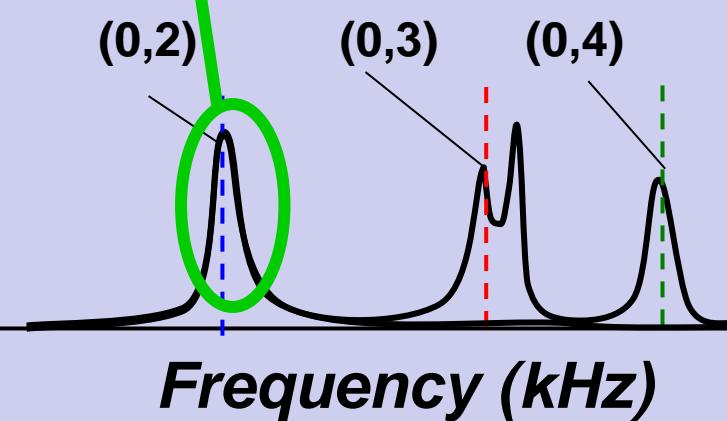
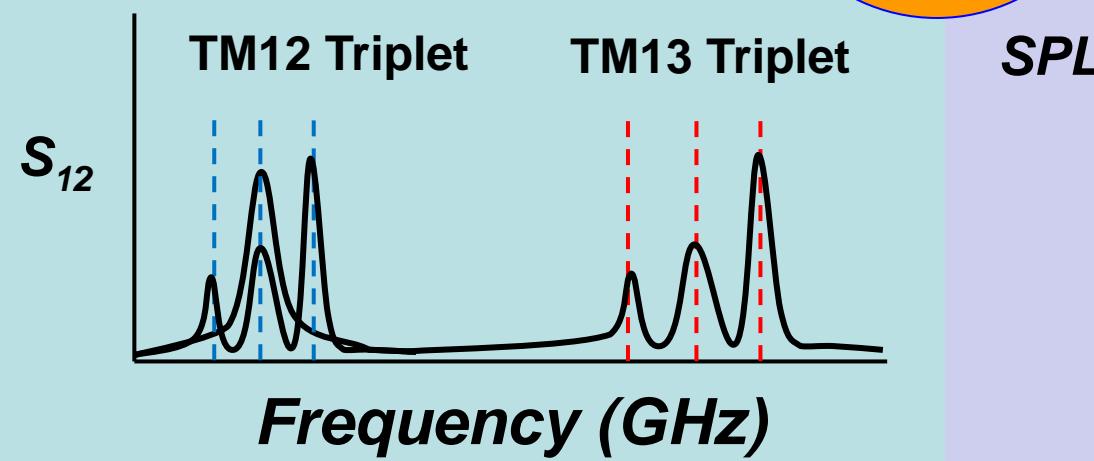


Pressure

Pressure

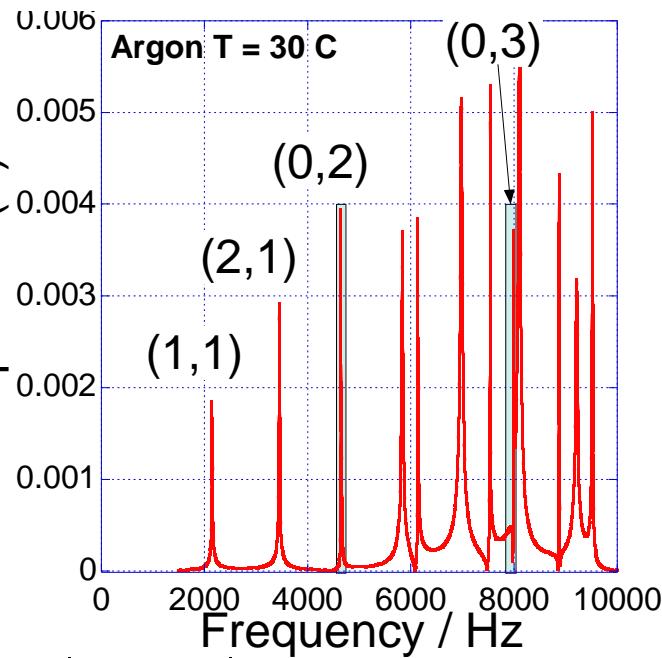
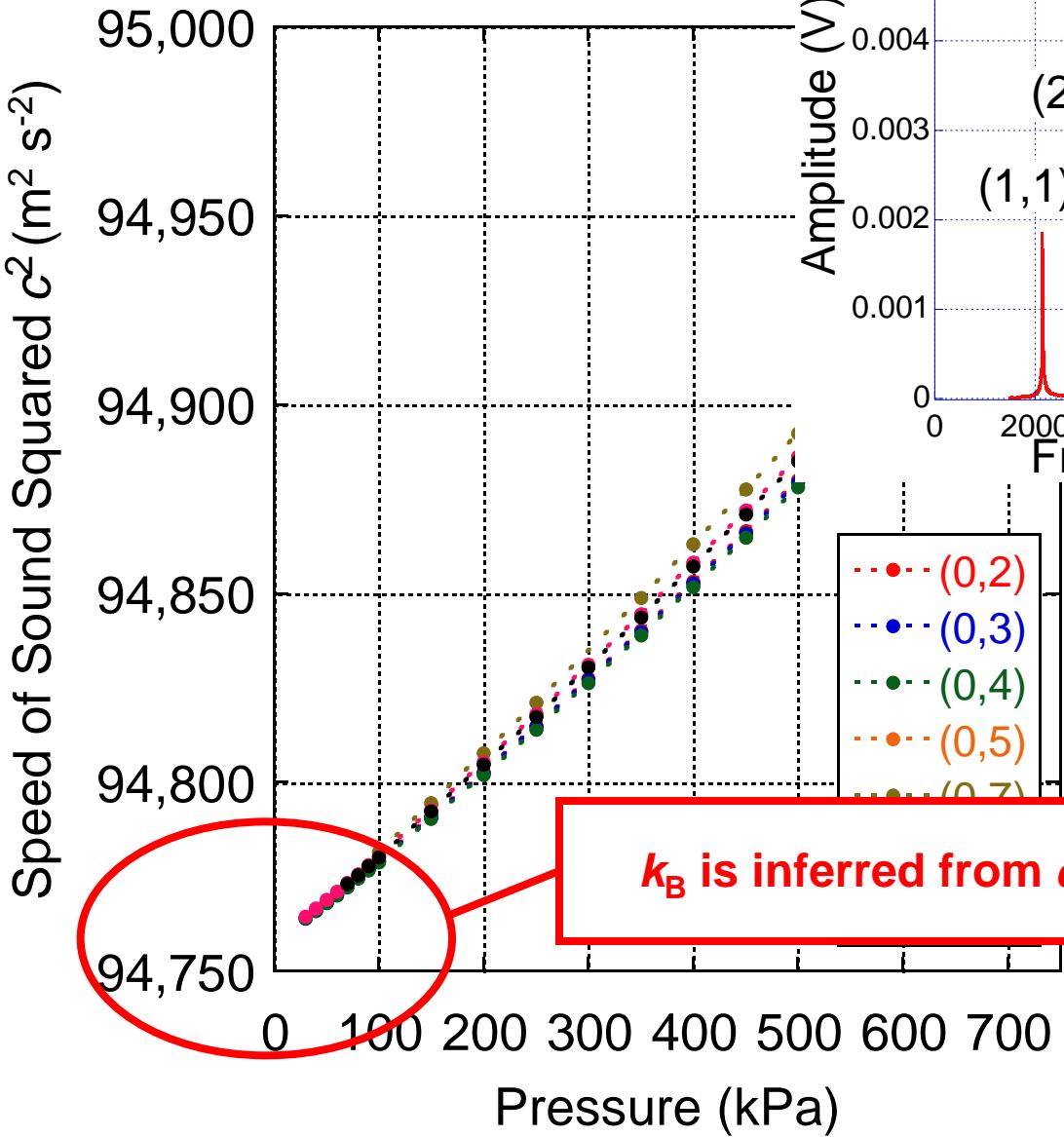


Δf_0



Isothermal data for c^2

c_{EXP}^2



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2005:

NPL REPORT
DEPC TH 006

Review of methods for

3 ANALYSIS OF TECHNIQUES.....	4
3.1 <i>p-v-T</i> GAS THERMOMETRY	4
3.2 ACOUSTIC GAS THERMOMETRY.....	10
3.3 ABSOLUTE RADIOMETRY.....	17
3.4 JOHNSON NOISE THERMOMETRY.....	20

ACOUSTIC GAS THERMOMETRY

A Report for the DII
Quantum Programme

scheduled for 2011.

The change is made.

The need for a better value of the Boltzmann constant was highlighted by B N Taylor of NIST,

New

data was needed for the redefinition of the kelvin, and Dr Taylor considered this to be next in significance to the need for data from watt-balances in supporting the proposed revision of the SI.

R RUSBY, M de PODESTA
and J WILLIAMS

NOT RESTRICTED

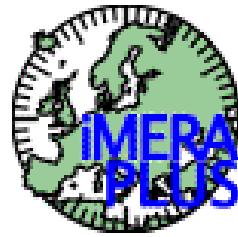
NOVEMBER 2005



European Metrology Research Programme
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The EMRP is jointly funded by the EMRP participating countries
within EURAMET and the European Union

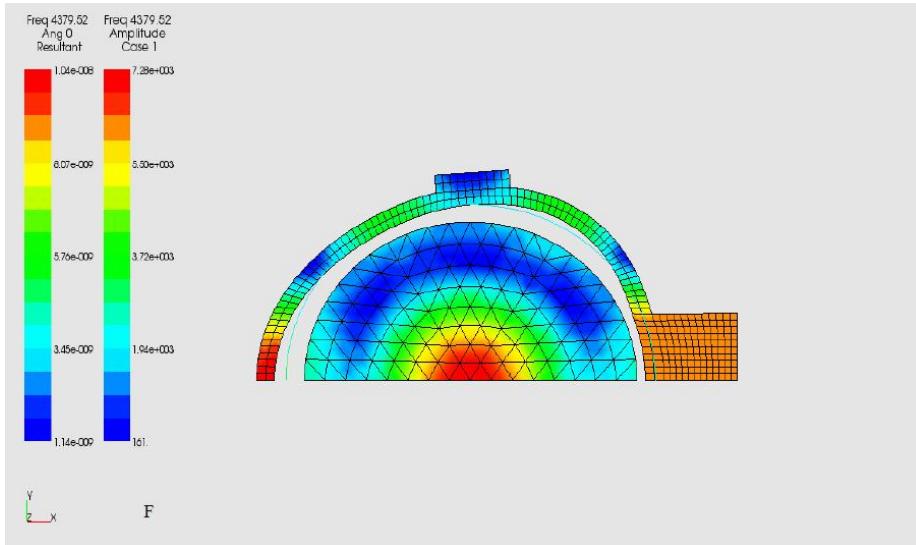


...and just 4 years later...

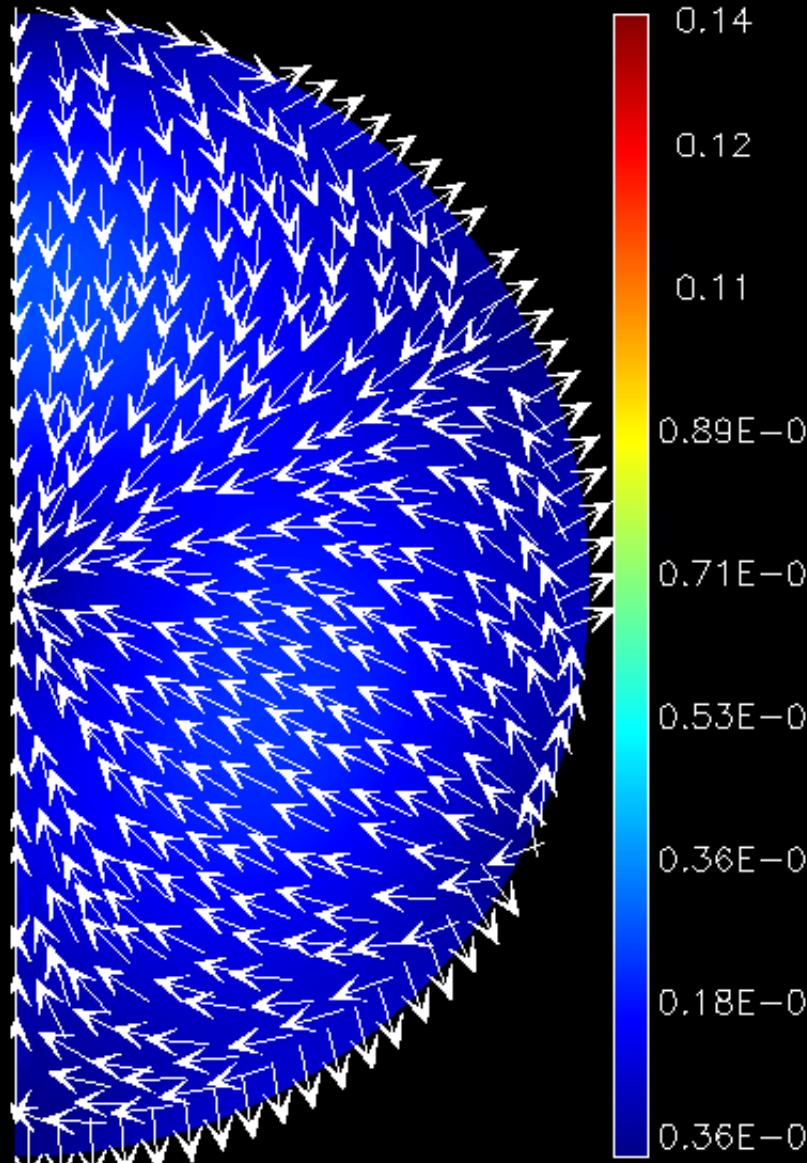


Acoustic modelling in view of a determination of the Boltzmann constant within 1 ppm for the redefinition of the kelvin

Pierre Gélat¹, Nicolas Joly², Michael de Podesta^{1,†}, Gavin Sutton¹, Robin Underwood¹



module de la vitesse 94T/96



Waveguide effects on quasispherical microwave cavity resonators

R J Underwood¹, J B Mehl², L Pitre³, G Edwards¹, G Sutton¹ and M de Podesta¹

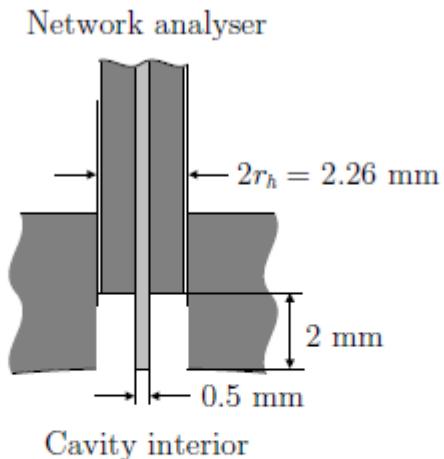


Figure 1. Diagram of a waveguide in TCU2v2, formed from a cylindrical hole and stripped coaxial cable. Although a looped antenna would offer the possibility of additionally detecting the TE_{1n} modes, such antennas are more complex to model and were not considered in this study.

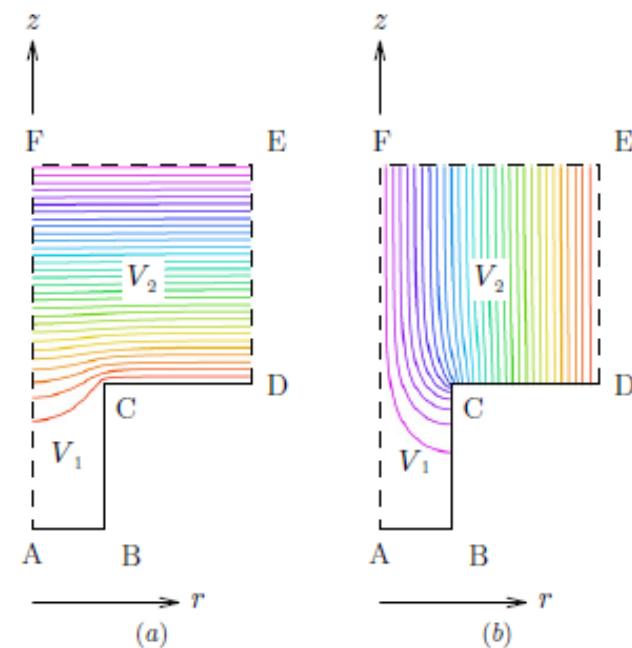


Figure 4. Potential fields (a) Φ_E and (b) Φ_H near the entrance of a cylindrical waveguide of depth $2r_h$. Adjacent contours represent equal increments in Φ .

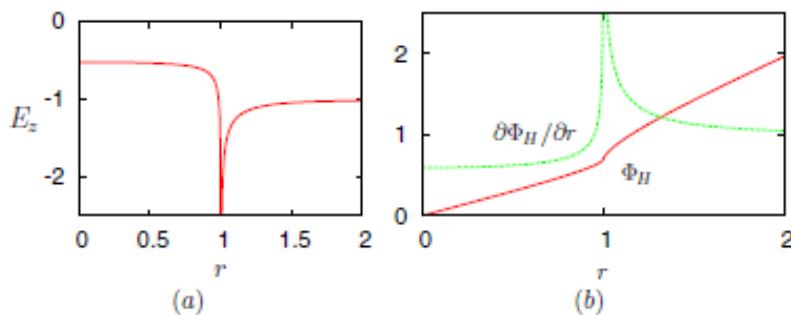


Figure 5. (a) Normal electric field and (b) magnetic potential and its radial derivative near the waveguide entrance in the static limit. The fields and lengths are all dimensionless, and were computed for unit incident values of E_0 and H_0 . The value of $|E_z|$ approaches 0.53 as r is reduced below 1; similarly $|\partial\Phi_H/\partial r|$ approaches 0.59 as r is reduced below 1.

Acoustic Resonator Experiments at the Triple Point of Water: First Results for the Boltzmann Constant and Remaining Challenges

Gavin Sutton · Robin Underwood ·
 Laurent Pitre · Michael de Podesta ·
 Staf Valkiers

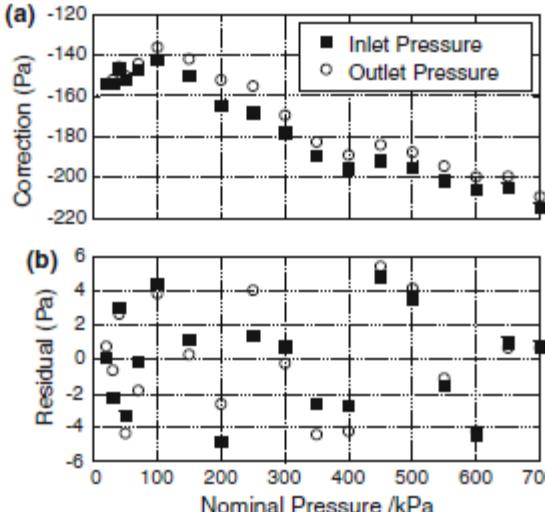


Fig. 5 (a) The calibration correction required for the pressure meters and (b) The residuals of a fit to the calibration data

Table 1 Isotopic composition of the argon gas used in the two isotherms

	Molar mass[Ar] (g · mol ⁻¹)
39.947 706 21	
39.947 857 10	

Highlighted Issues

- Variability of Molar Mass
- Need for precise pressure measurement
- ‘Negative’ Excess Half-Widths
 - *Line narrowing*

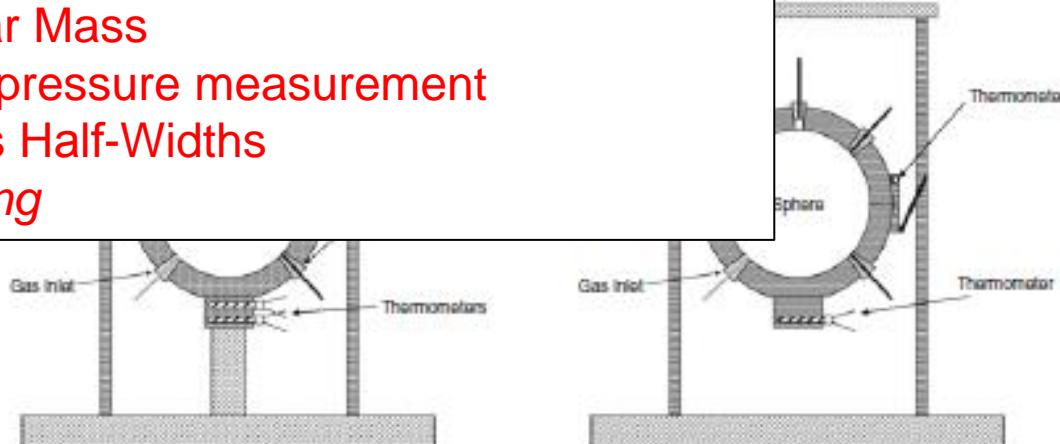


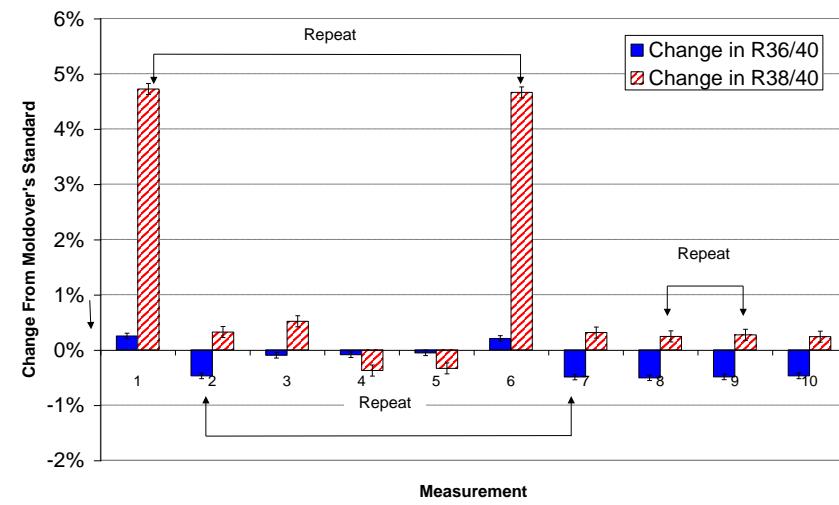
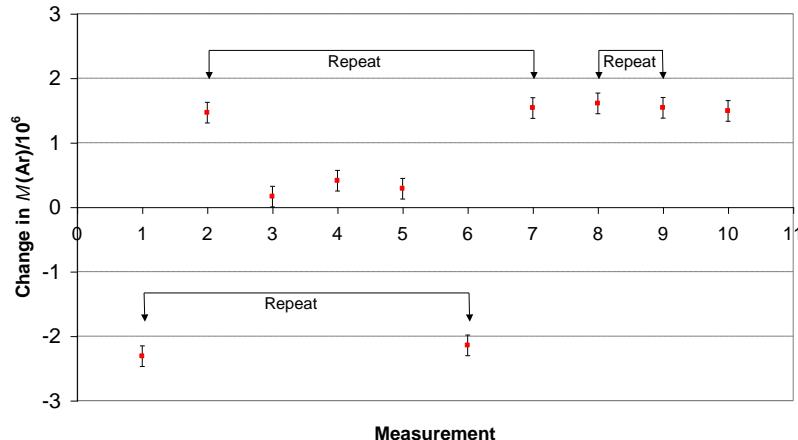
Fig. 2 The sphere in the two measurement configurations ‘Fixed’ and ‘Hung’



Preparation of argon Primary Measurement Standards for the calibration of ion current ratios measured in argon

S. Valkiers^a, , D. Vendelbo^a, M. Berglund^a, M. de Podesta^b

Received 16 December 2009, Revised 7 January 2010, Accepted 8 January 2010, Available online 15 January 2010



2011:

IOP PUBLISHING
Metrologia 46 (2009) 554–559

METROLOGIA
doi:10.1088/0026-1394/46/5/020

Second-order electromagnetic eigenfrequencies of a triaxial ellipsoid

James B Mehl

IOP PUBLISHING
Metrologia 48 (2011) 114–122

METROLOGIA
doi:10.1088/0026-1394/48/3/005

The electromagnetic fields of a triaxial ellipsoid calculated by modal superposition

Gordon Edwards and Robin Underwood

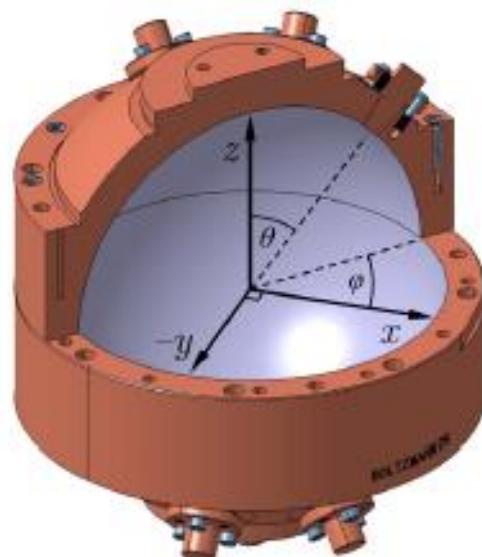


Figure 1. Cut-away diagram of NPL-C2 showing the coordinate axes. Notice the $-y$ -axis is shown. The outer cylinder and inner

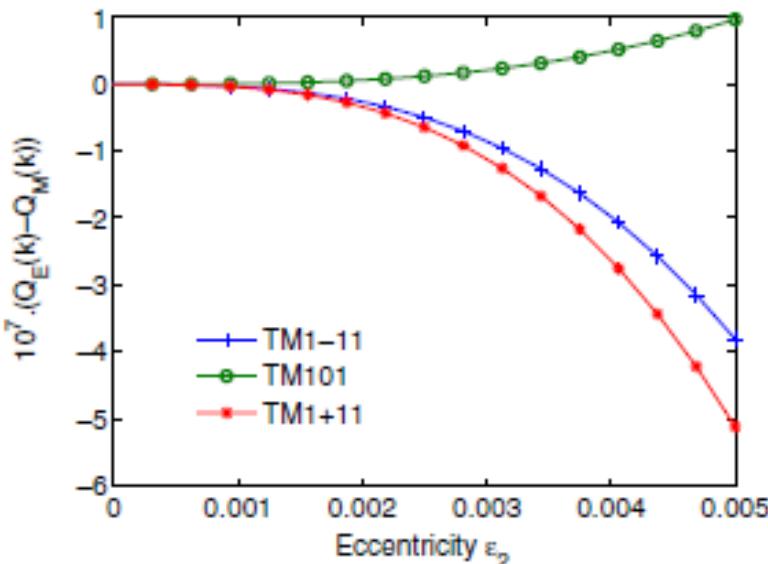


Figure 11. The difference between $Q(k)$ values calculated by modal analysis, $Q_E(k)$, and Mehl's second-order analysis, $Q_M(k)$, for $TM_{1,p,1}$ states.

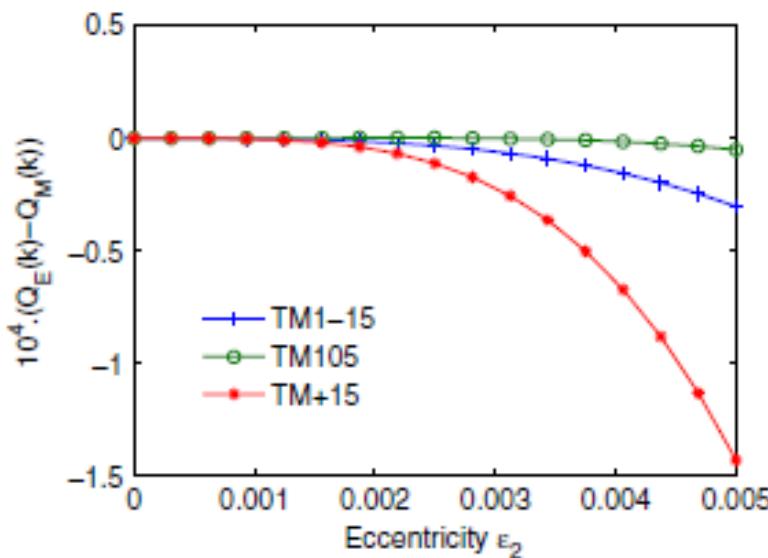


Figure 12. The difference between $Q(k)$ values calculated by modal analysis, $Q_E(k)$, and Mehl's second-order analysis, $Q_M(k)$, for $TM_{1,p,5}$ states.

SHORT COMMUNICATION

Outgassing of water vapour, and its significance in experiments to determine the Boltzmann constant

Michael de Podesta, Gavin Sutton, Robin Underwood, Stephanie Bell,
Mark Stevens, Thomas Byrne and Patrick Josephs-Franks

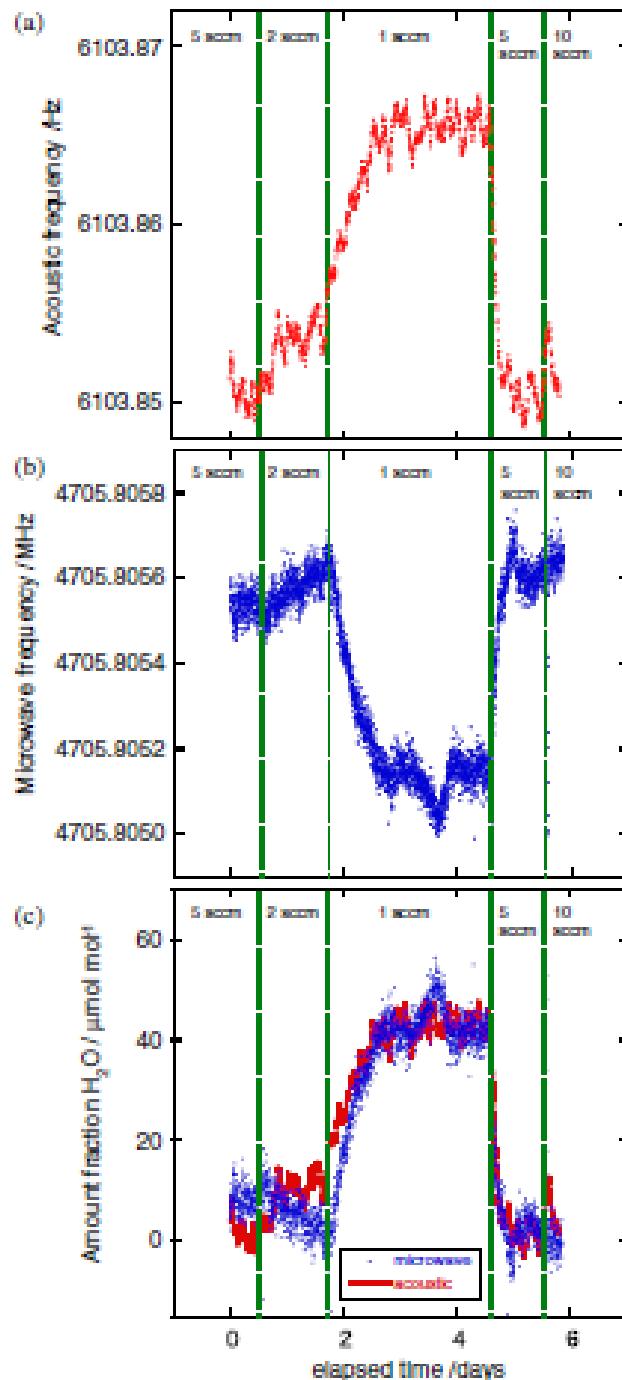


Figure 3. (a) Acoustic resonant frequency of the (0,3) resonance;

Characterization of the volume and shape of quasi-spherical resonators using coordinate measurement machines

M de Podesta¹, E F May², J B Mehl³, L Pitre⁴, R M Gaviosso⁵,
G Benedetto⁵, P A Giuliano Albo⁵, D Truong⁴ and D Flack¹

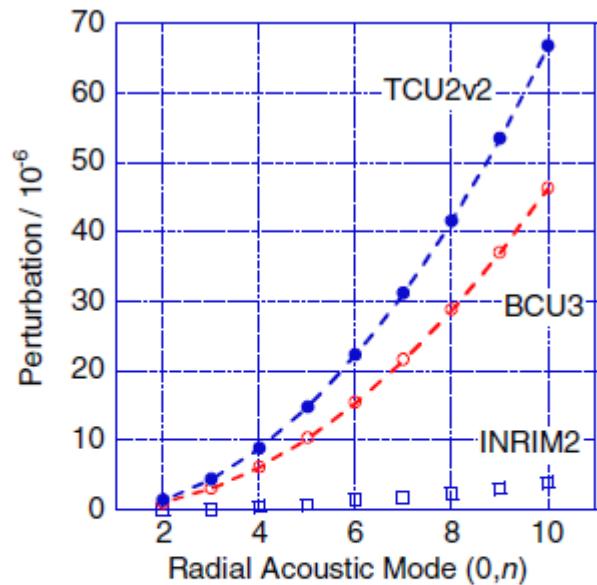
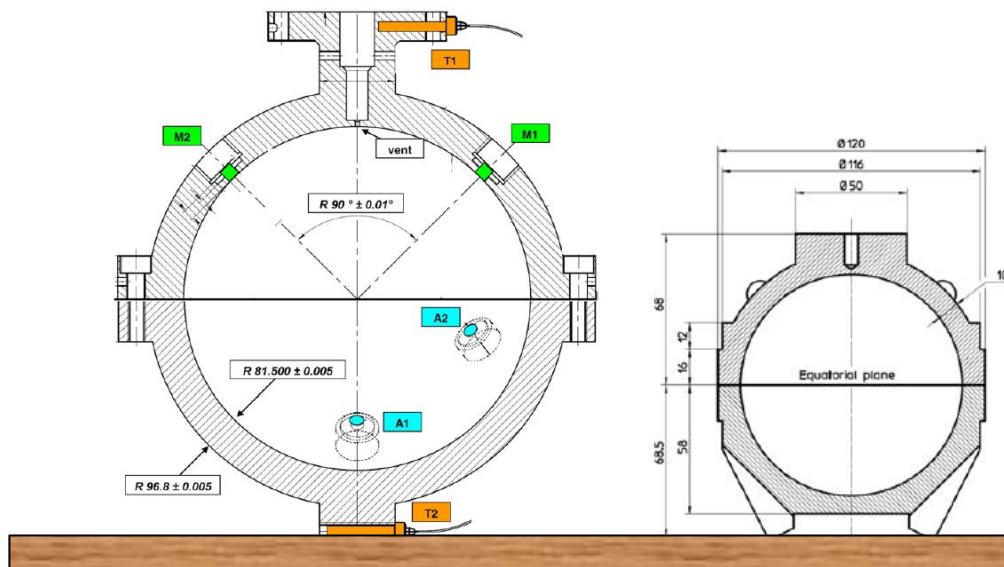


Figure 14. Relative shape perturbations $[(ka)^2 - \xi_{0n}^2]/\xi_{0n}^2 \times 10^6$ to the eigenvalues of the first nine purely radial acoustic modes of INRIM2, BCU3 and TCU2v2; BCU3 and TCU2v2 were alternatively modelled as triaxial ellipsoids (shown as dotted lines) or as more complex shapes, taking into account the complete results of the spherical harmonic expansion.



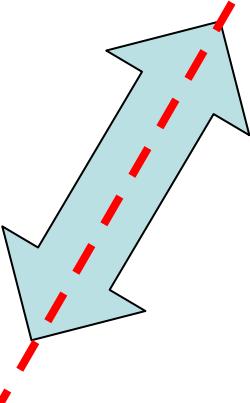
Figure 3. CMM measurements conducted at NPL probing the inner surface of a copper quasi-sphere alongside a spherical density and volume standard. Note the two thermometers (embedded in copper blocks) positioned around the artefacts.



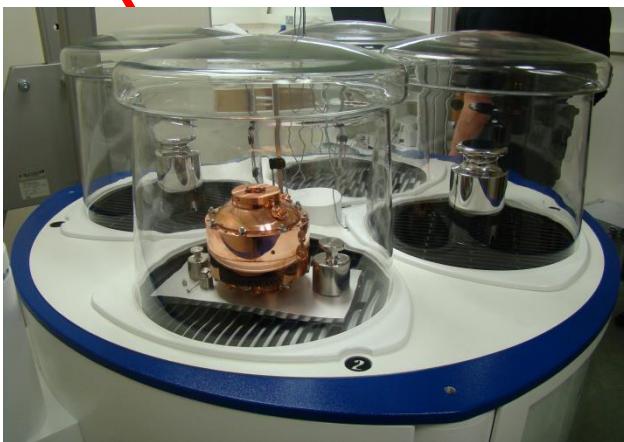
CMM



Microwaves



Pyknometry



Dimensional characterization of a quasispherical resonator by microwave and coordinate measurement techniques

R Underwood¹, D Flack¹, P Morantz², G Sutton¹, P Shore² and M de Podesta¹

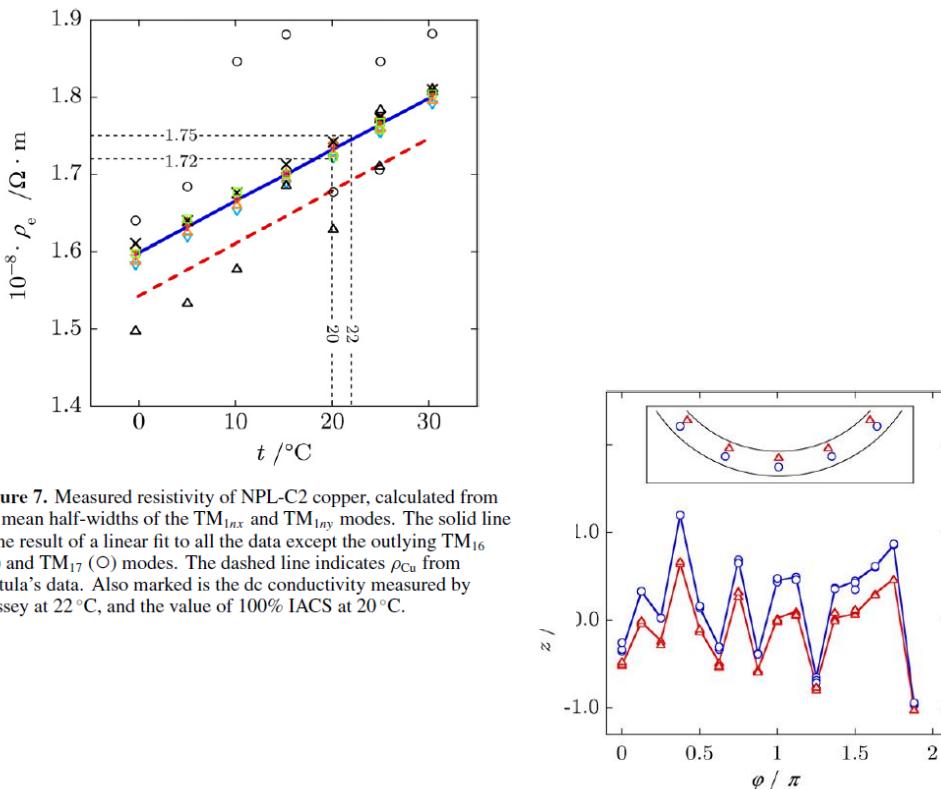


Figure 7. Measured resistivity of NPL-C2 copper, calculated from the mean half-widths of the TM_{1nx} and TM_{1ny} modes. The solid line is the result of a linear fit to all the data except the outlying TM₁₇ (Δ) and TM₁₆ (\circ) modes. The dashed line indicates ρ_{Cu} from Matula's data. Also marked is the dc conductivity measured by Bussey at 22 °C, and the value of 100% IACS at 20 °C.

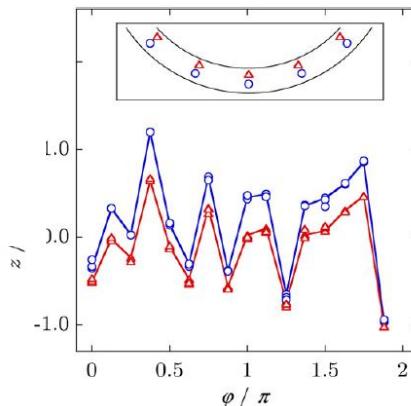


Figure 5. Typical deviations in the height of the equatorial flange from the fitted $z = 0$ plane. The inset shows the position of the probing points relative to the flange. Three data sets are plotted to highlight the repeatability of these measurements.

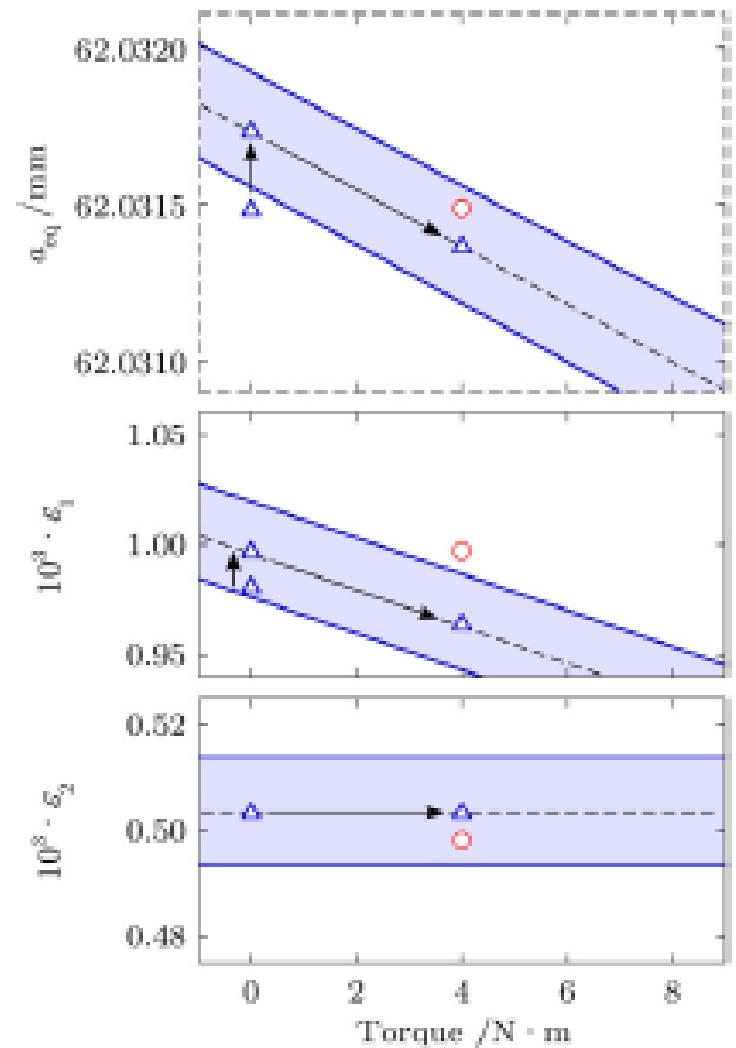


Figure 9. Comparison of CMM (Δ) and microwave (\circ) measurements of a_0 , b_0 and c_0 at 20 °C. The arrows indicate adjustments to the CMM data for a 1 μm equatorial gap and 4 N m bolt torque. The $k = 1$ uncertainty bounds (table 8) are shown as a shaded band. The uncertainty in a_0^{exp} is smaller than the marker itself.

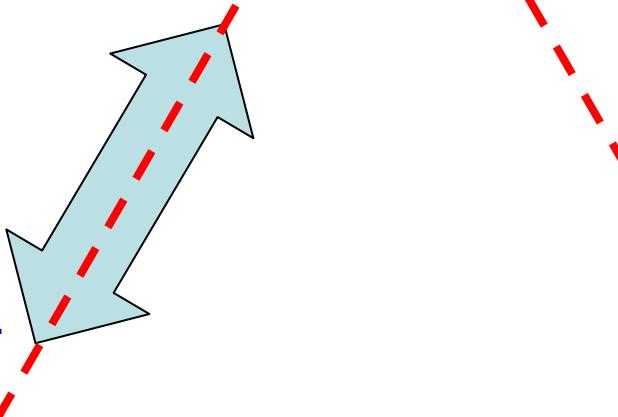
CMM

$u(k = 1) = 114 \text{ nm}$,
 $u_R(k = 1) = 1.8 \times 10^{-6}$.



Microwaves

$u(k = 1) = 11.7 \text{ nm}$,
 $u_R(k = 1) = 0.17 \times 10^{-6}$.



Pyknometry



Pyknometric volume measurement of a quasispherical resonator

R Underwood¹, S Davidson¹, M Perkin¹, P Morantz², G Sutton¹ and M de Podesta¹

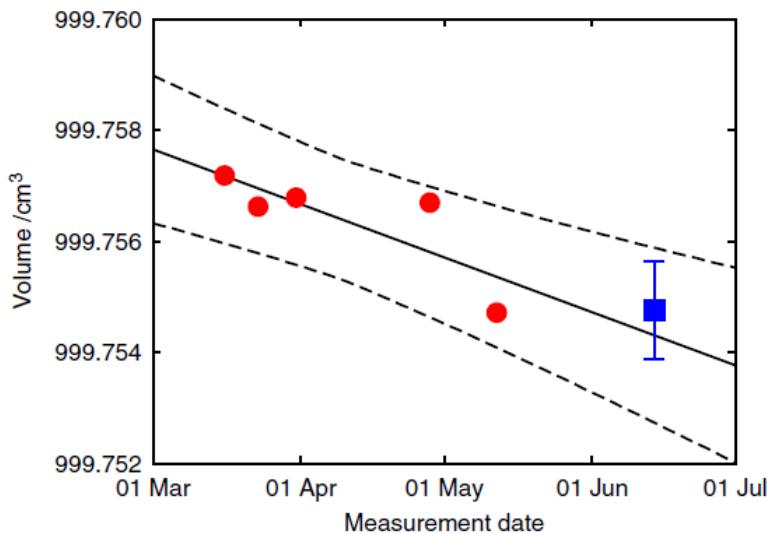


Figure 8. Volume estimates from the pyknometric (●) and microwave (■) measurements, corrected to a reference temperature of 20 °C and pressure of 101 325 Pa. The solid line is a linear fit to the five pyknometric measurements, and the dashed lines indicate the uncertainty in the pyknometric volume. The uncertainty bars indicate the microwave uncertainty. All measurements were performed in the year 2010.

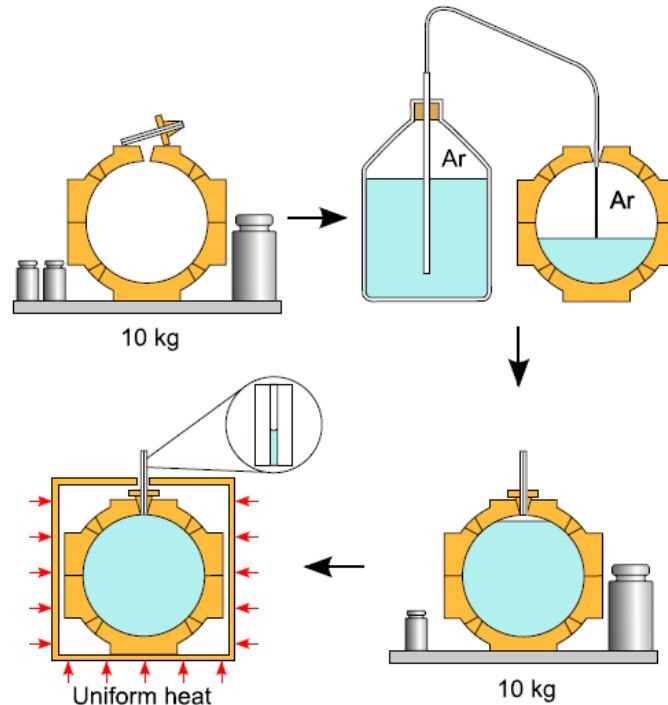


Figure 2. The five-step pyknometry procedure: empty weighing, filling, full weighing and temperature stabilization. The final step (emptying and re-weighing) is not shown.

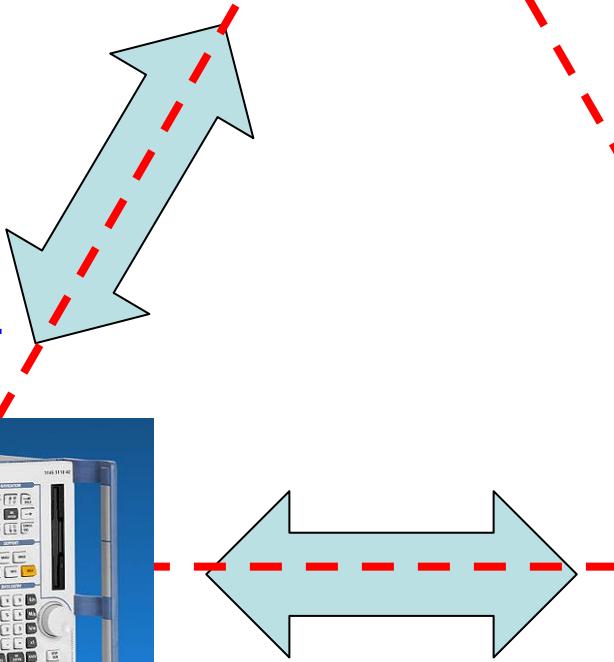
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Microwaves

$u(k = 1) = 11.7 \text{ nm}$,
 $u_R(k = 1) = 0.17 \times 10^{-6}$.



Pyknometry

$u(k = 1) = 37 \text{ nm}$,
 $u_R(k = 1) = 0.60 \times 10^{-6}$.



A low-uncertainty measurement of the Boltzmann constant

Michael de Podesta¹, Robin Underwood¹, Gavin Sutton¹, Paul Morantz², Peter Harris¹, Darren F Mark³, Finlay M Stuart³, Gergely Varga⁴ and Graham Machin¹

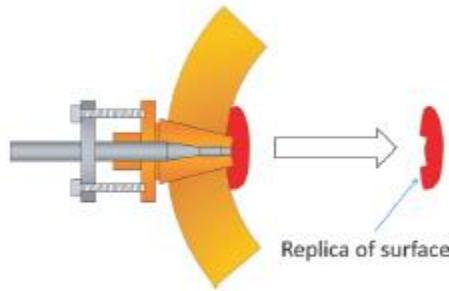
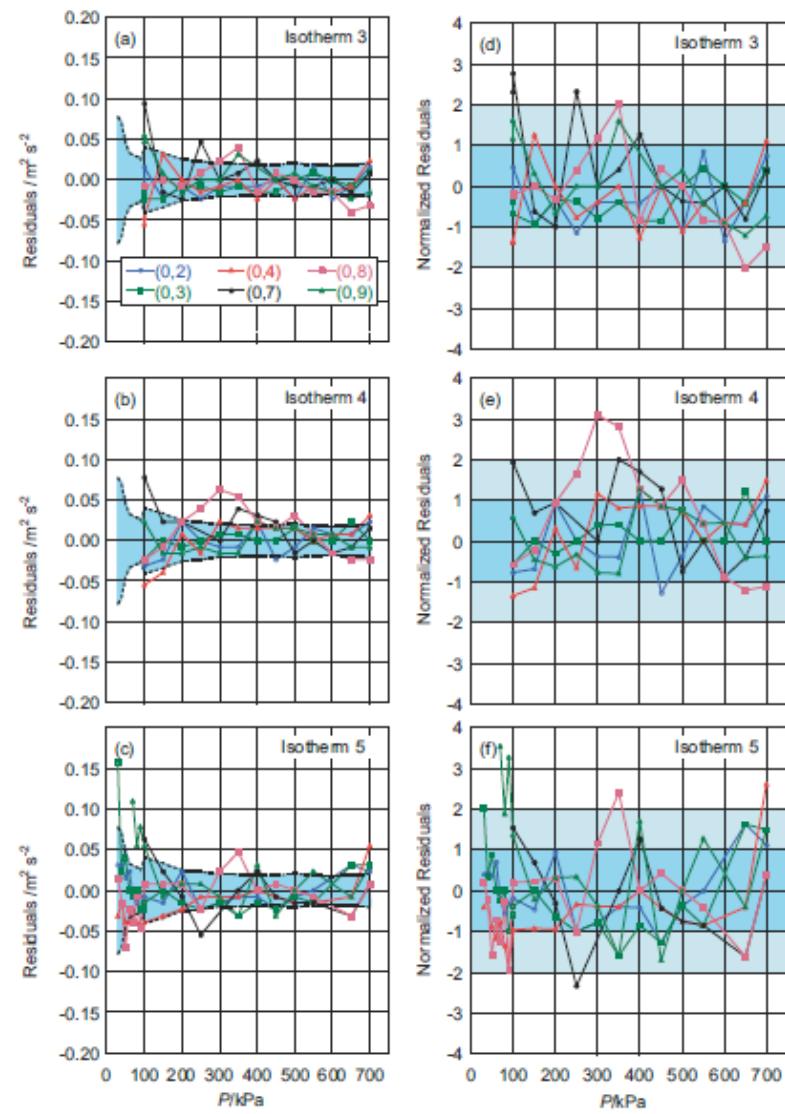
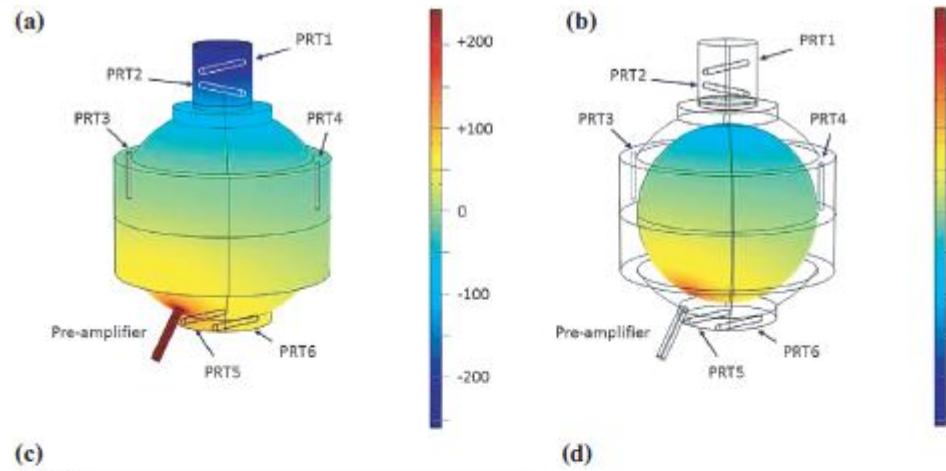
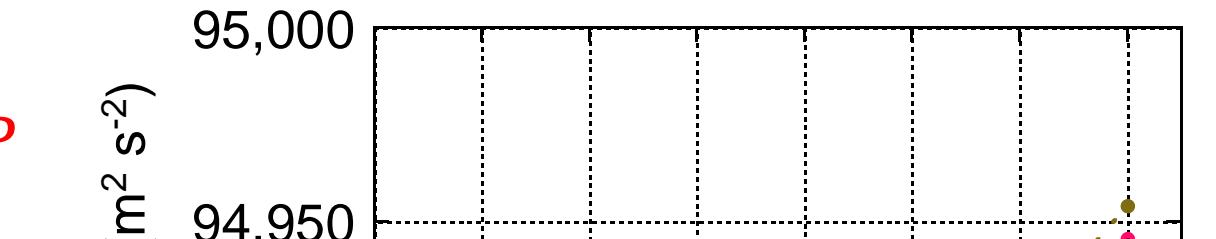


Figure 10. Illustration of how the perturbation caused by protrusion of the acoustic transducers was measured using a quick-setting silicone compound.



Isothermal data for c^2

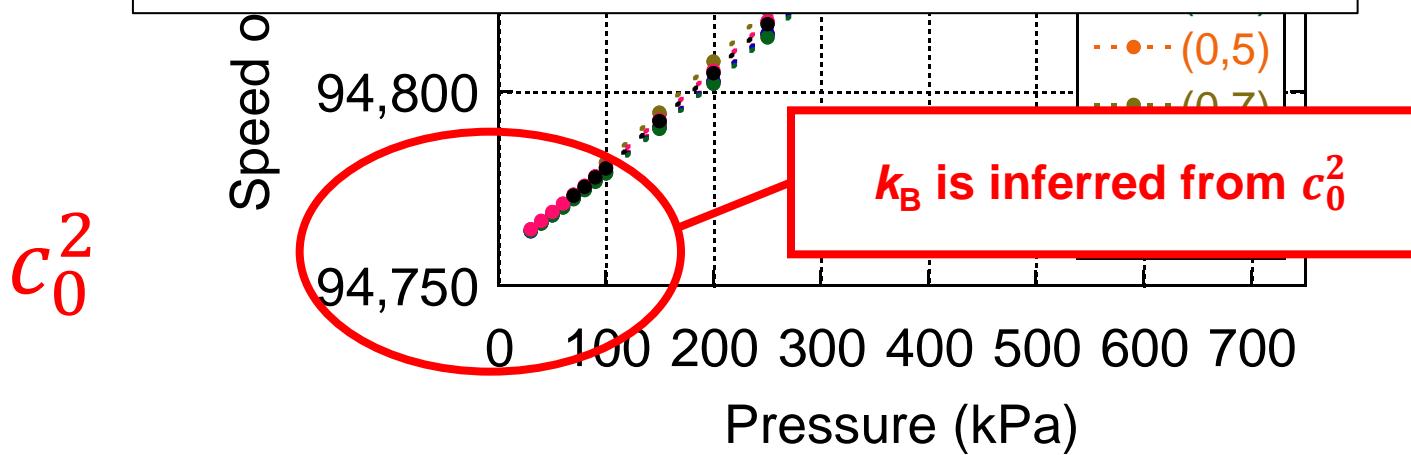
c_{EXP}^2



$$u_R = 0.71 \times 10^{-6}$$

Highlighted Issues

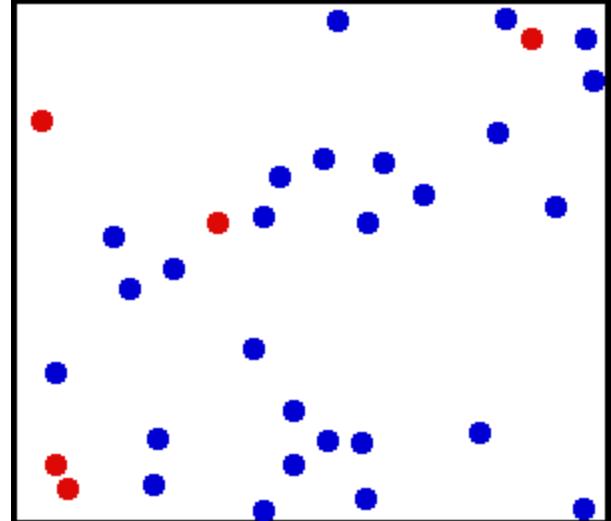
- Variability of Molar Mass
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- 'Negative' Excess Half-Widths
 - *Line narrowing*

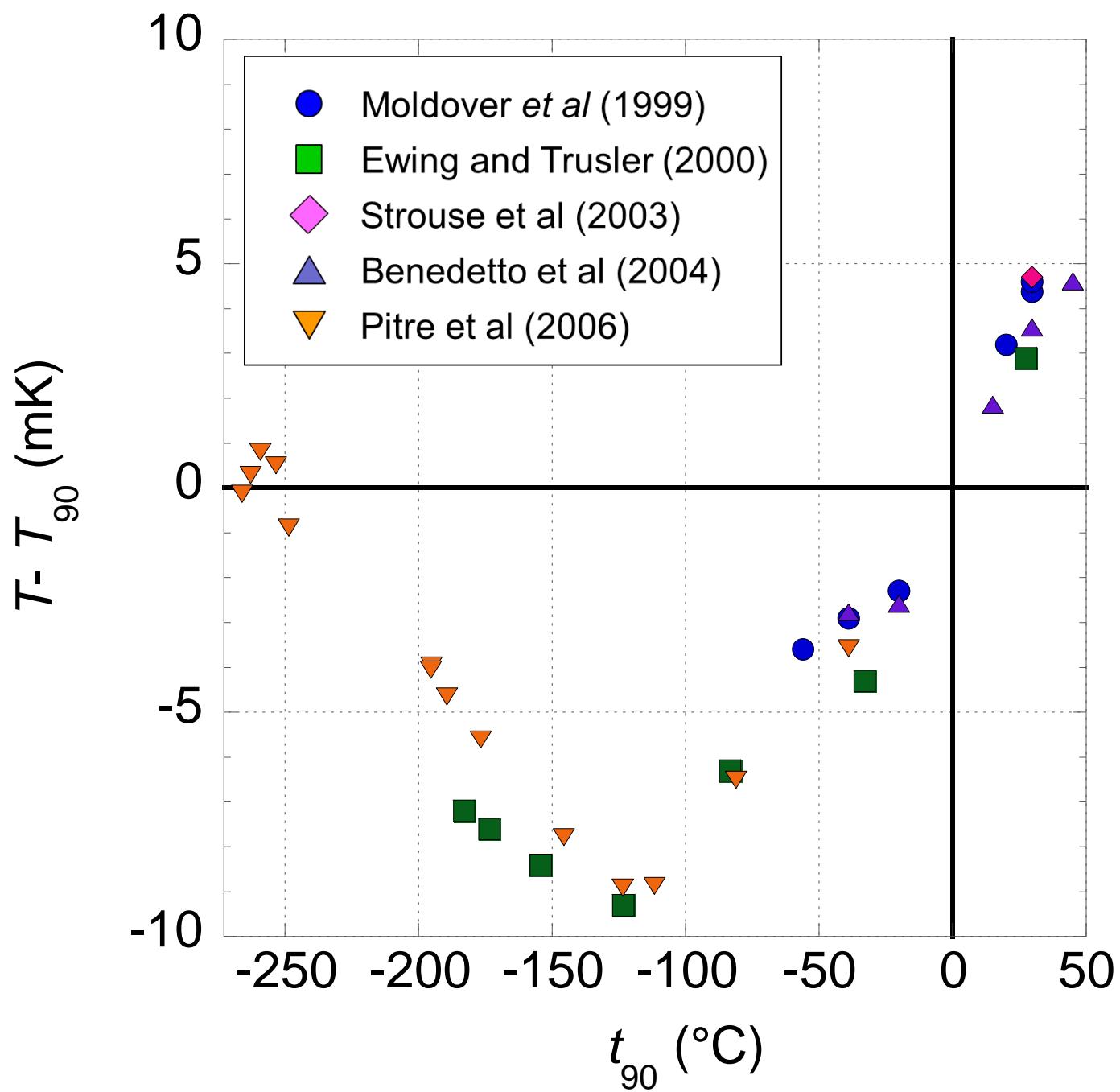


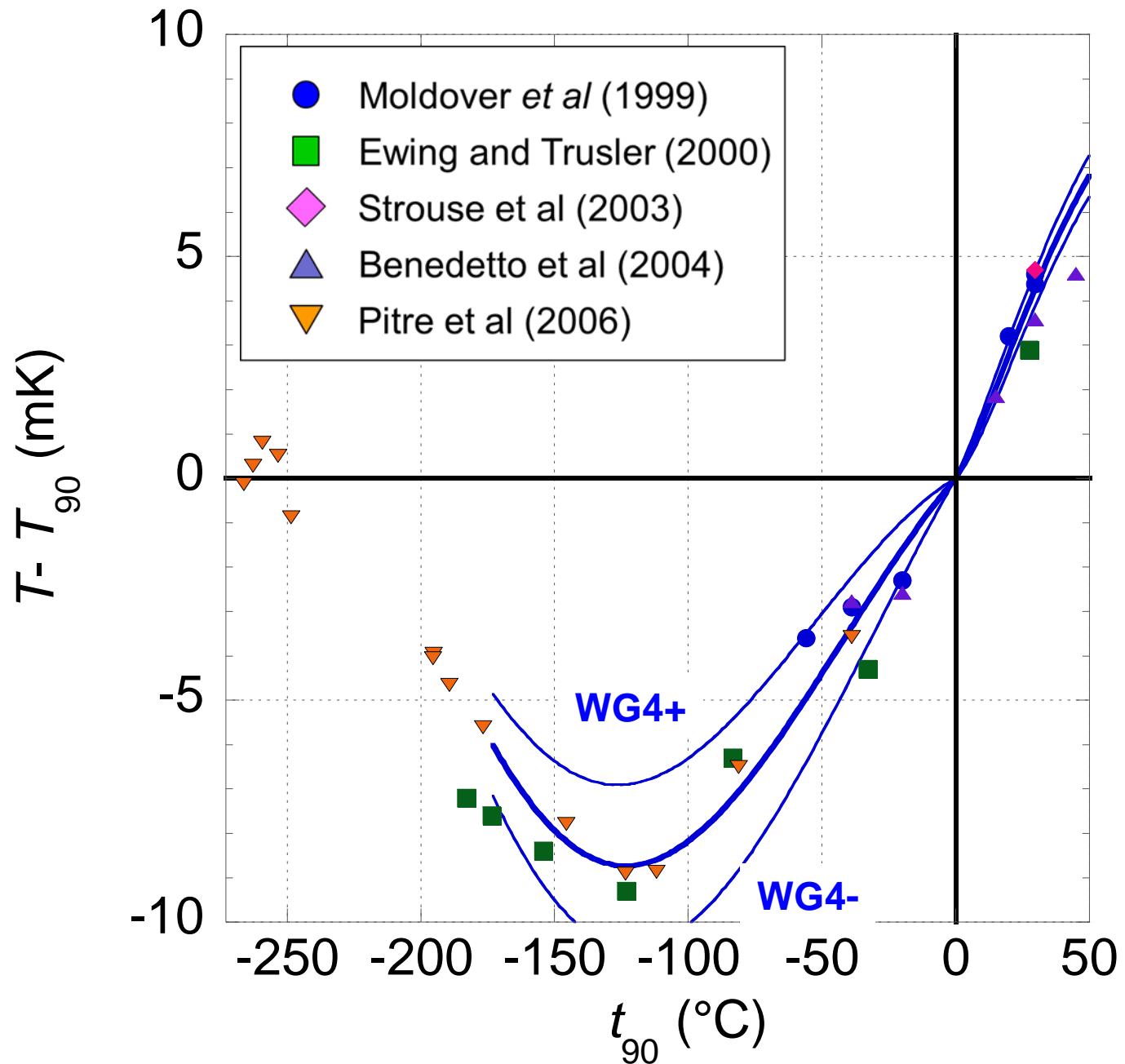
Since 2013

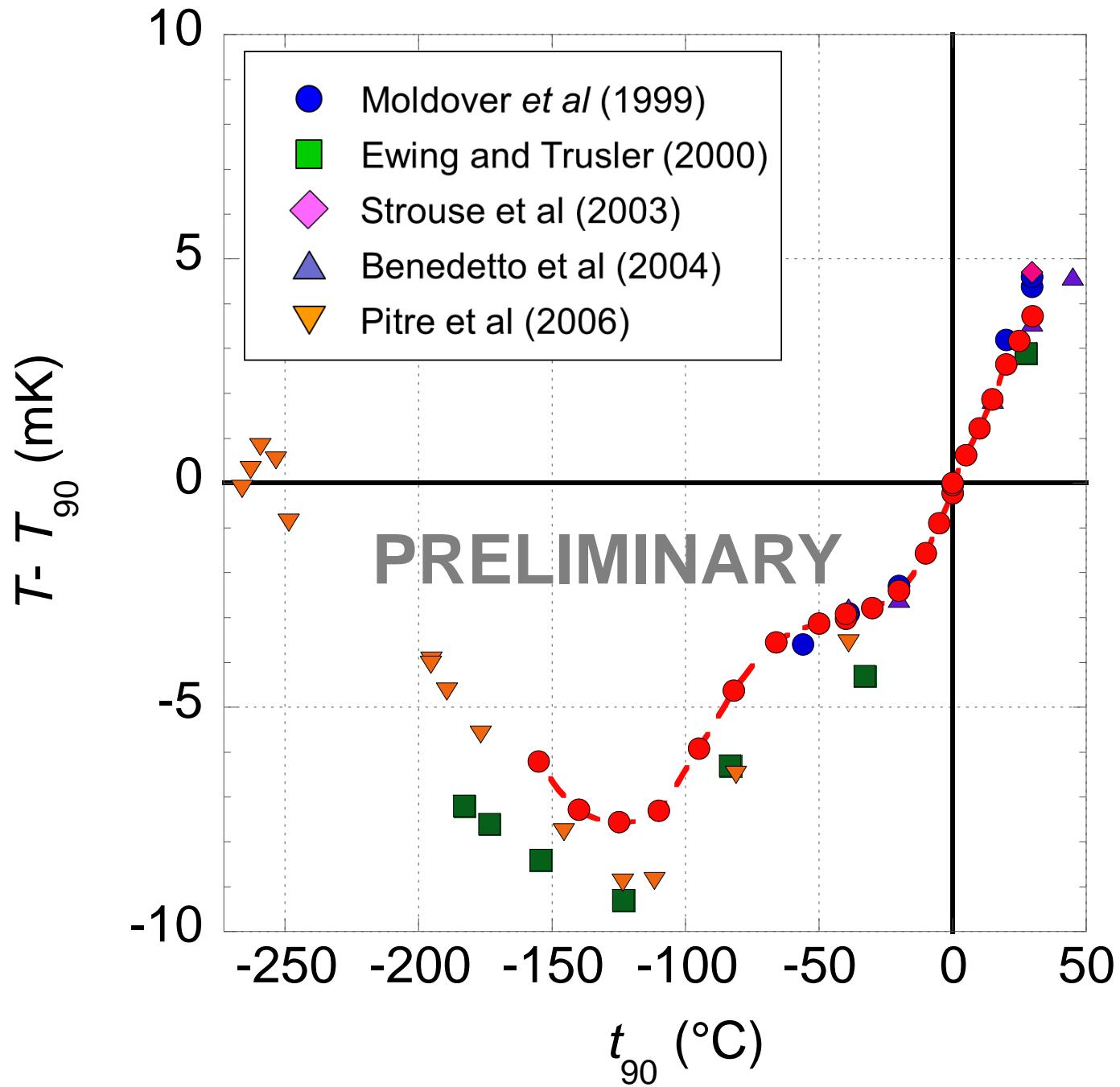
Acoustic Thermometry

$$c^2 = \frac{\gamma k_B N_A T}{M}$$

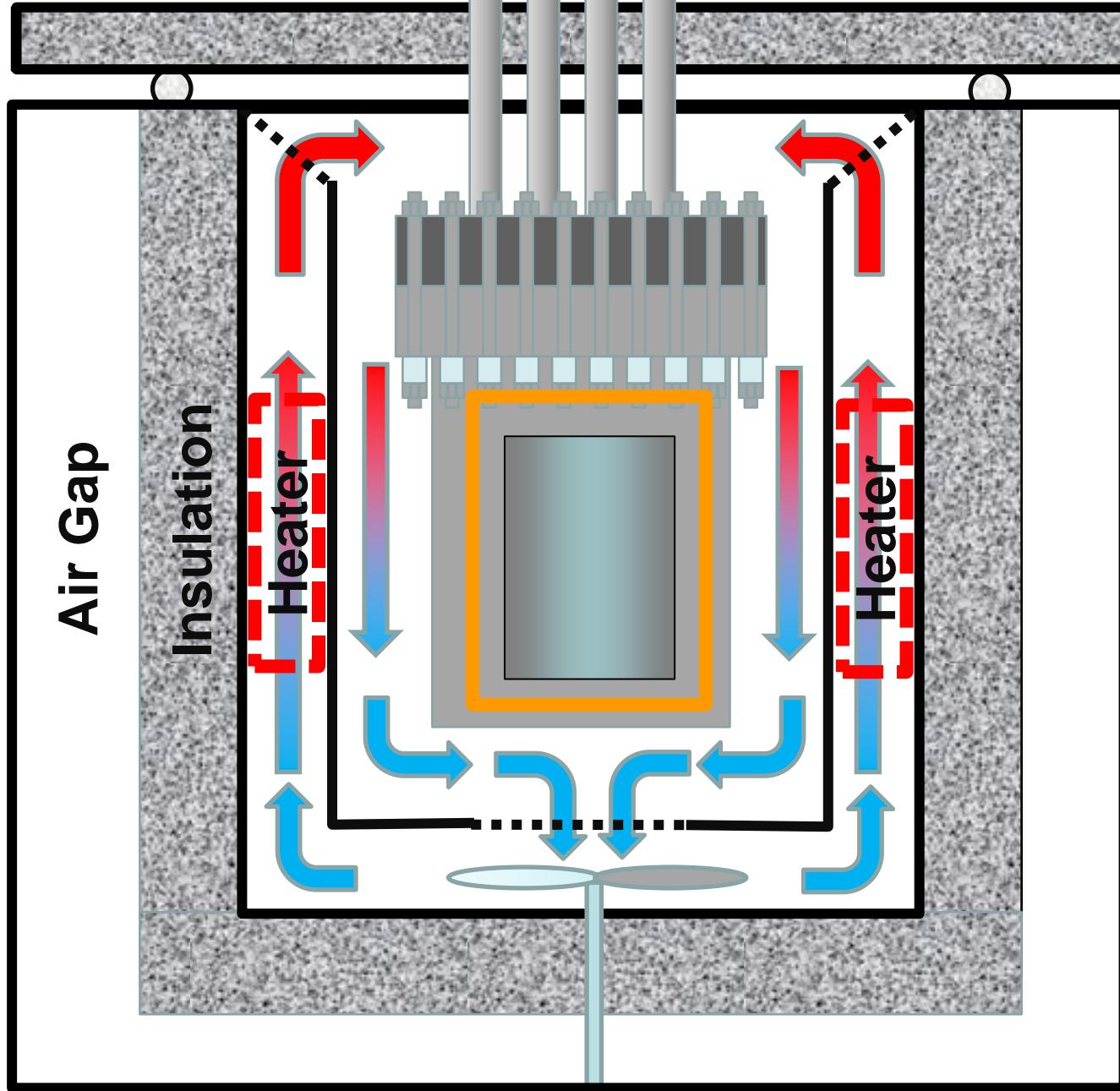








NPL High-Temperature Cylindrical Resonator



Reflections on the NPL-2013 Estimate of the Boltzmann Constant

- 1. Background**
- 2. History**
- 3. The NPL uncertainty estimate**
- 4. NPL Update February 2015**
- 5. The NPL Analysis**
- 6. Summary**

Working Equation

- Measure $f_{(0,n)}$ in the limit of low pressure

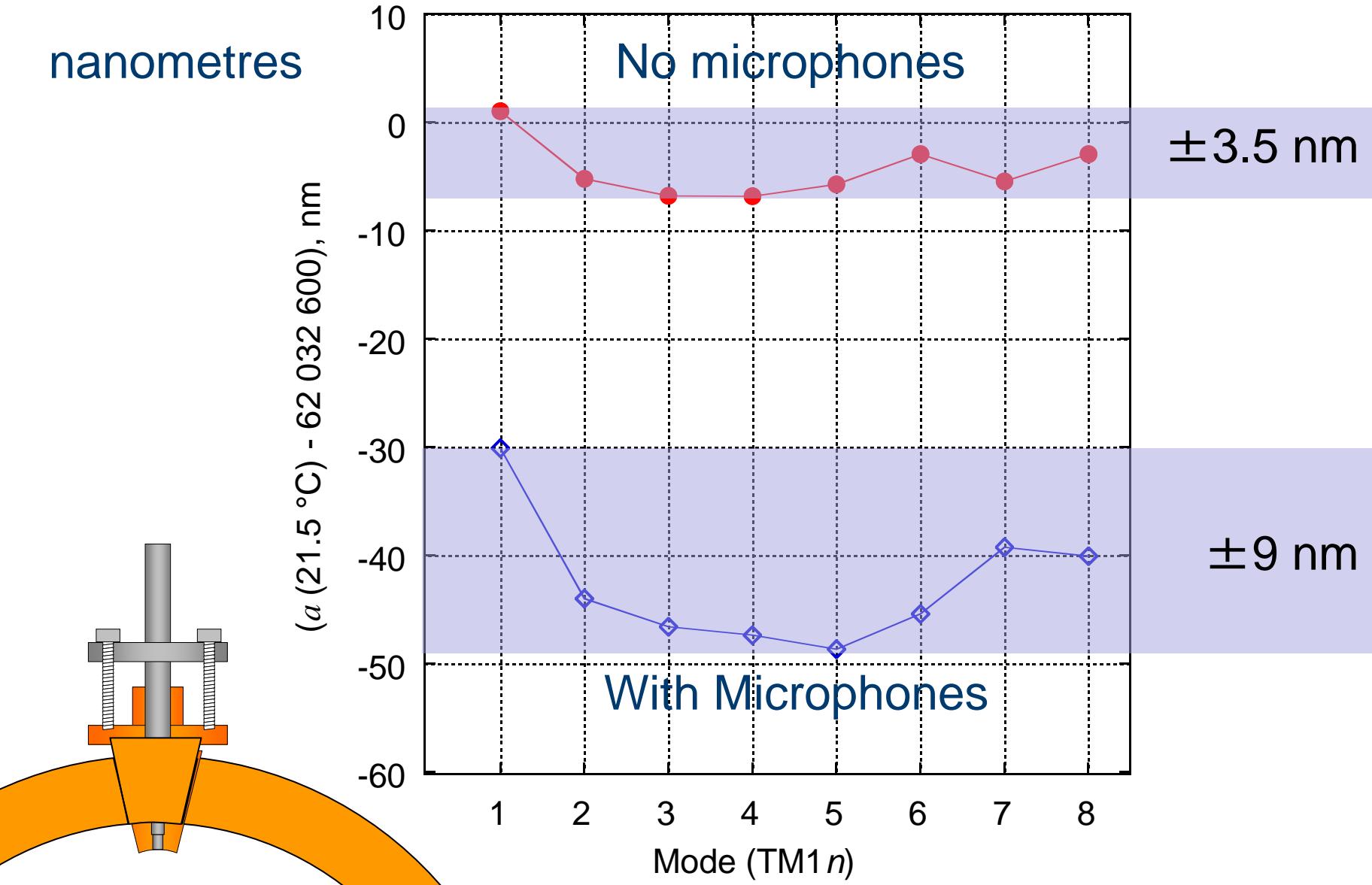
$$k_B = \frac{(M/\gamma)}{N_A T_{\text{TPW}}} \times \left[\frac{2\pi a (f_{(0,n)} + \Delta f_{(0,n)})}{\xi_{(0,n)}} \right]^2$$

1. Resonator radius, a
2. Frequency Corrections $\Delta f_{(0,n)}$
3. Eigenvalues $\xi_{(0,n)}$
4. Pressure
5. Temperature
6. Molar Mass

1: How wrong could the radius estimate be?

1. Resonator radius, a
2. Pressure
3. Eigenvalues $\xi_{(0,n)}$
4. Frequency Corrections $\Delta f_{(0,n)}$
5. Temperature
6. Molar Mass

Microwave Radius Estimates *in Vacuum*



2: How wrong could the pressure be?

$u(k=1)$

11.7 nm

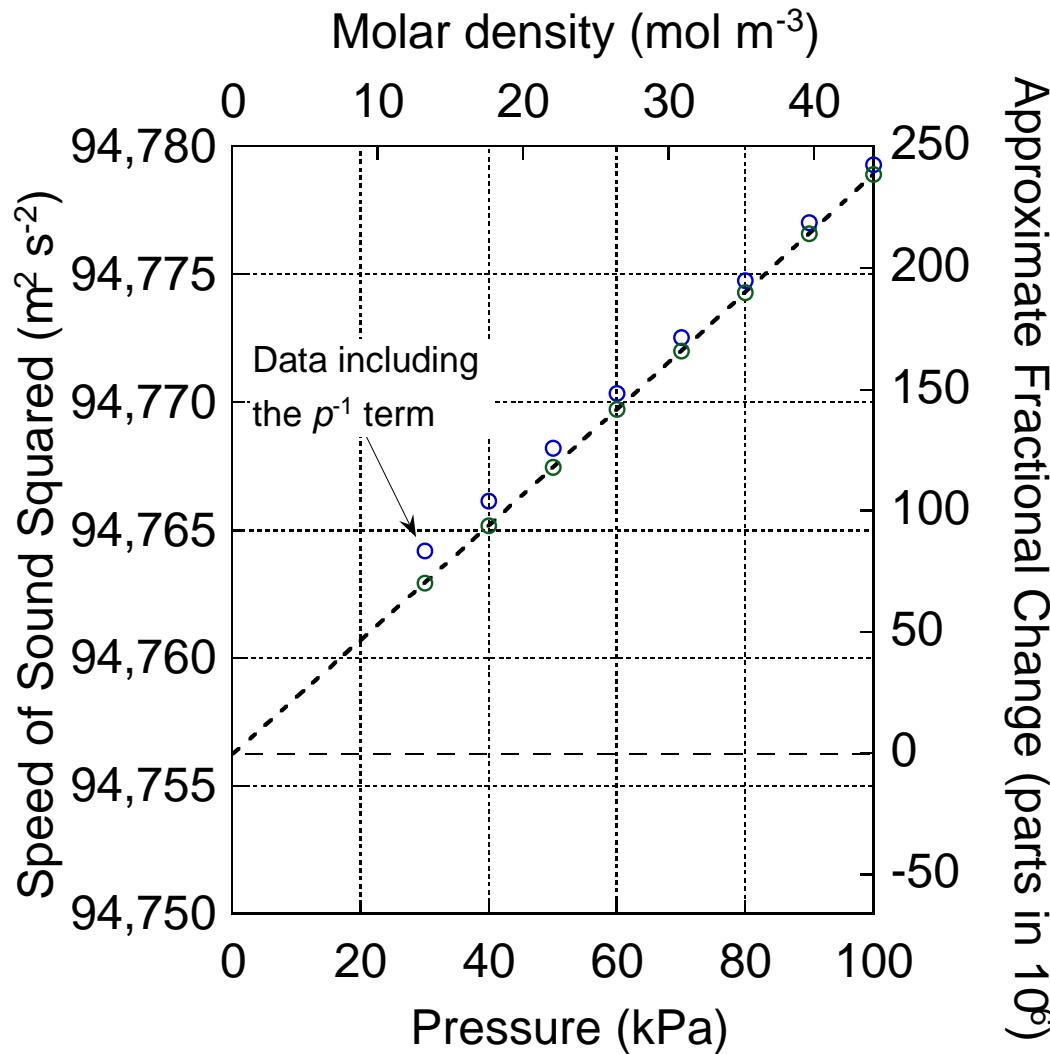
1. Resonator radius, a
2. **Pressure**
3. Eigenvalues $\xi_{(0,n)}$
4. Frequency Corrections $\Delta f_{(0,n)}$
5. Temperature
6. Molar Mass

$u(k_B)$

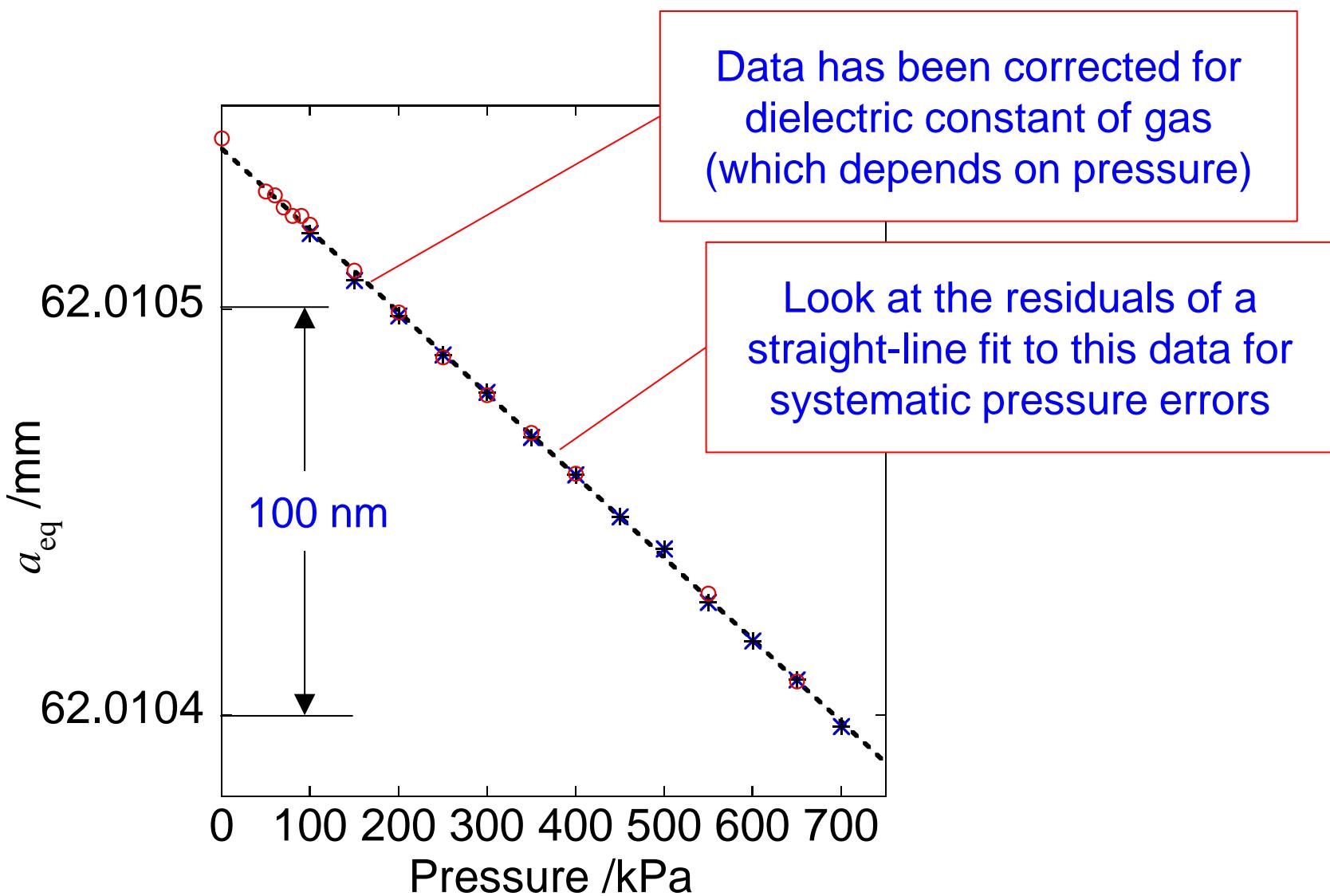
0.38 ppm

Low Pressure Measurements

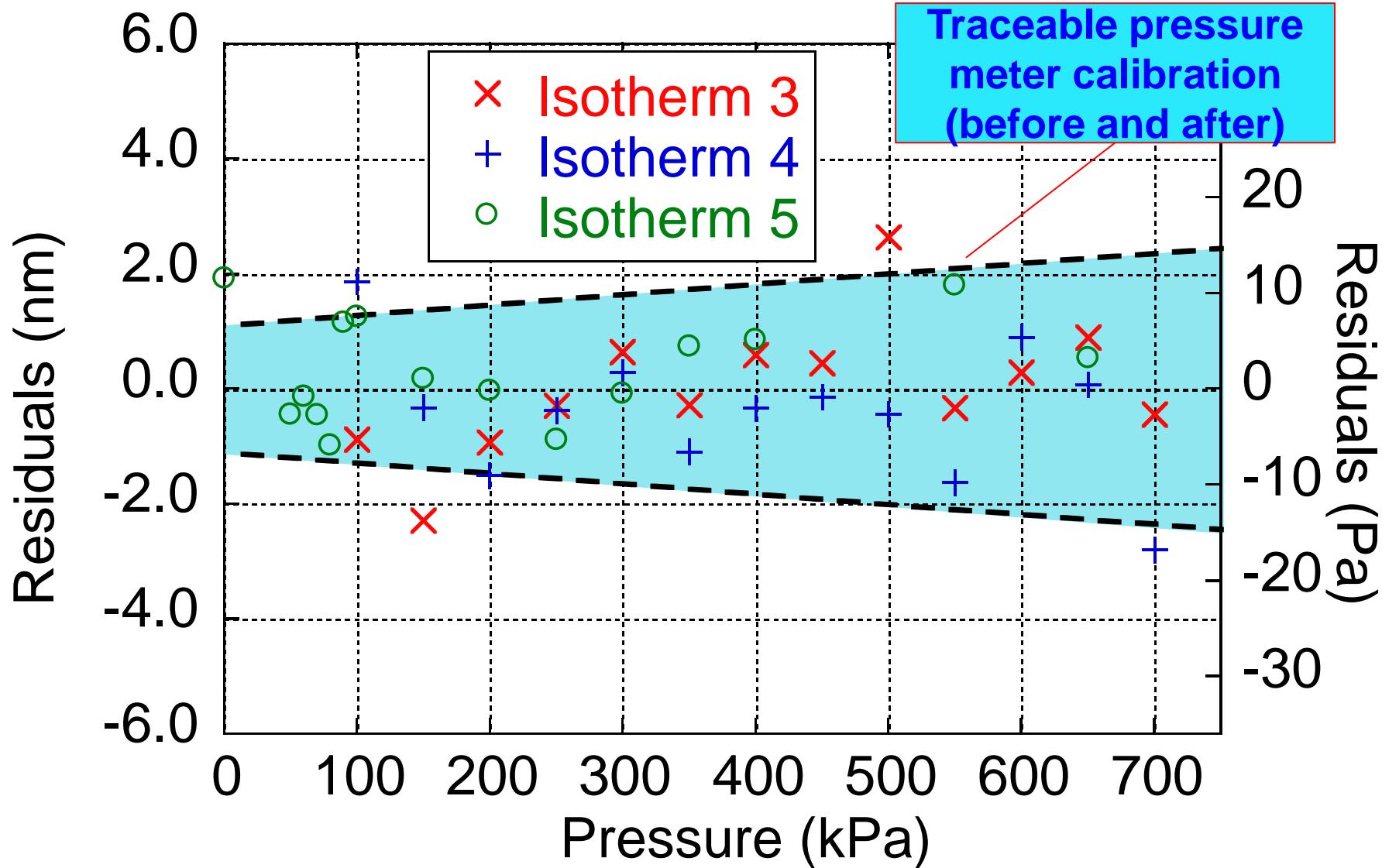
- *Affects thermal boundary layer correction*
- Affects estimate of p^{-1} term



Microwave Radius Estimates at Pressure



Pressure



3: How wrong could the eigenvalues be?

$u(k=1)$

11.7 nm

6.3 Pa

$u(k_B)$

0.38 ppm

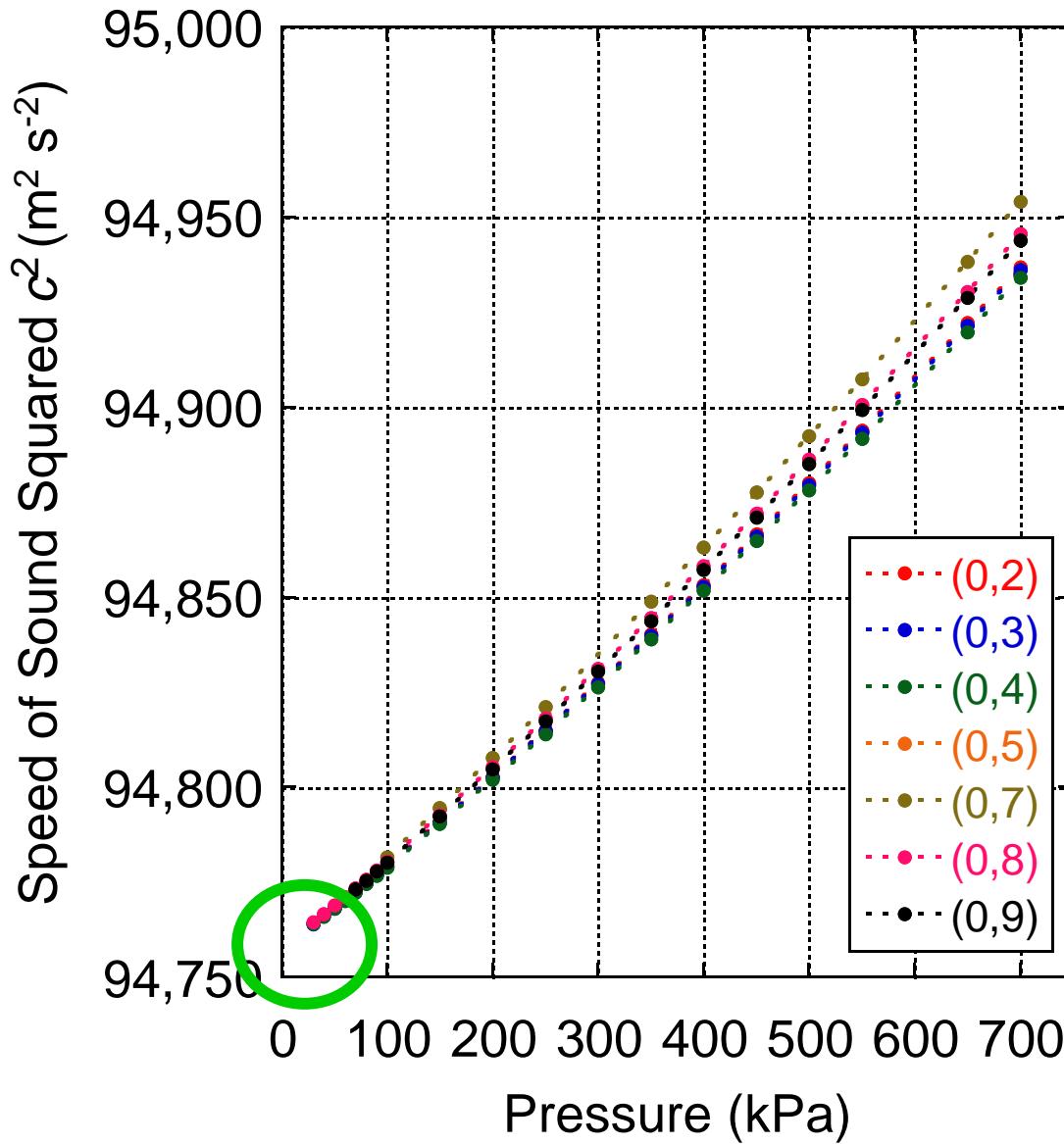
0.11 ppm

1. Resonator radius, a
2. Pressure
3. **Eigenvalues** $\xi_{(0,n)}$
4. Frequency Corrections $\Delta f_{(0,n)}$
5. Temperature
6. Molar Mass

Data for c^2

c_{EXP}^2

c_0^2



Data Model

After correction for Boundary Layer

From high pressure
studies

Common to all modes

$$c_{EXP}^2 - A_3 P^3 = c_0^2 + A_{-1} P^{-1}$$

Experimental
Estimates
Function of
pressure P
and mode, n

Low Pressure Speed of
Sound Squared

Common to all modes

Virial Correction
Common to all modes

$$+ A_1^n P + A_2 P^2$$

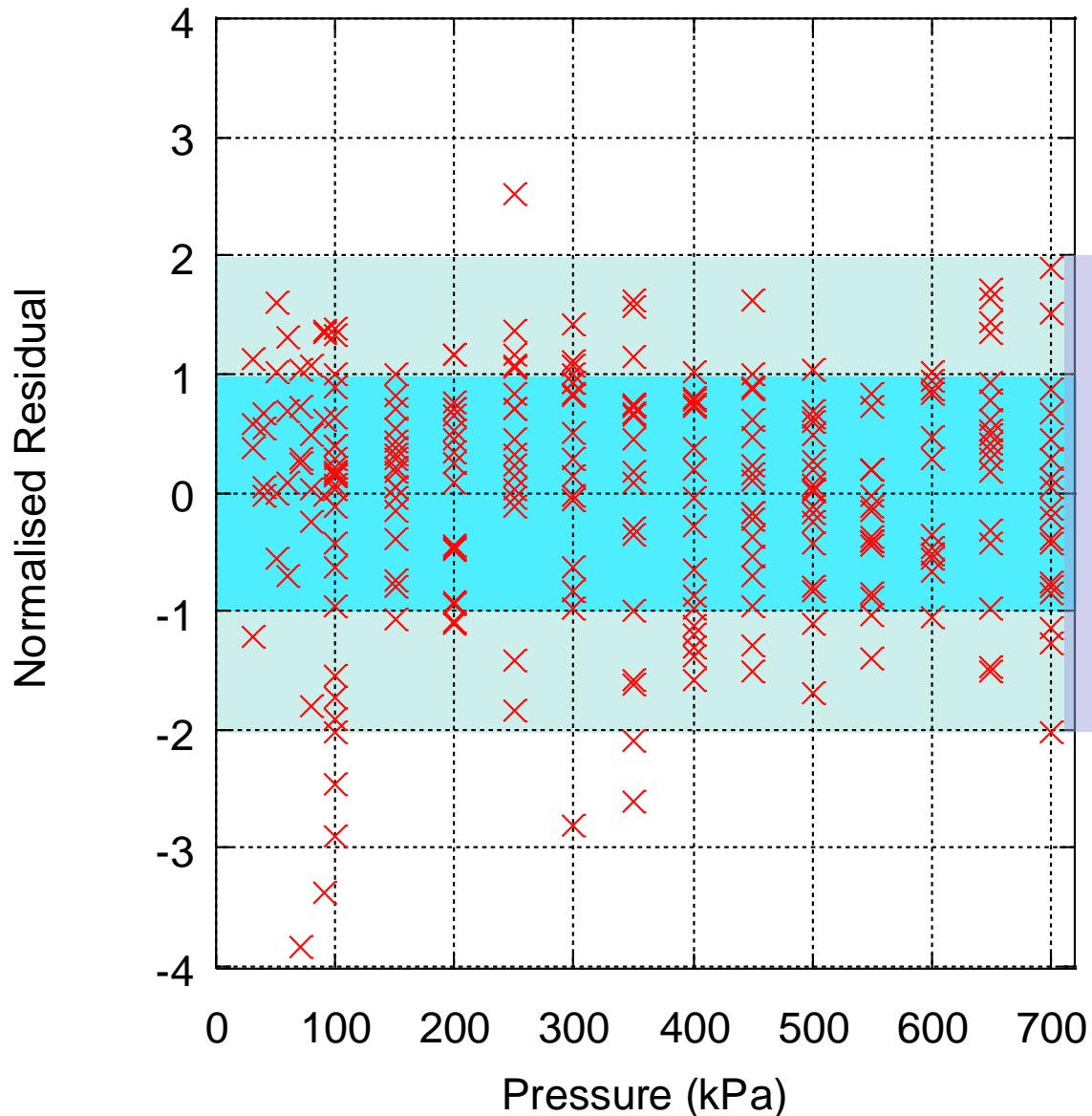
'Accommodation'
Correction to Boundary
Layer

Common to all modes

Virial Correction
Common to all modes
'Shell' Correction
Varies with mode

Residuals of all data to fits

expressed in terms of standard uncertainty



96% of data
within $\pm 2u_R$

Data Model

Low Pressure Speed of
Sound Squared
Common to all modes

$$c_{EXP}^2 - A_3 P^3 = c_0^2 + A_{-1} P^{-1} + A_1^n P + A_2 P^2$$

$$u(c_0^2) = 0.017 \text{ m}^2 \text{s}^{-2}$$

$$u_R(c_0^2) = 0.18 \times 10^{-6}$$

4: How wrong could the Frequency Corrections be?

$u(k=1)$

11.7 nm

6.3 Pa

1. Resonator radius, a
2. Pressure
3. Eigenvalues $\xi_{(0,n)}$
- 4. Frequency Corrections $\Delta f_{(0,n)}$**
5. Temperature
6. Molar Mass

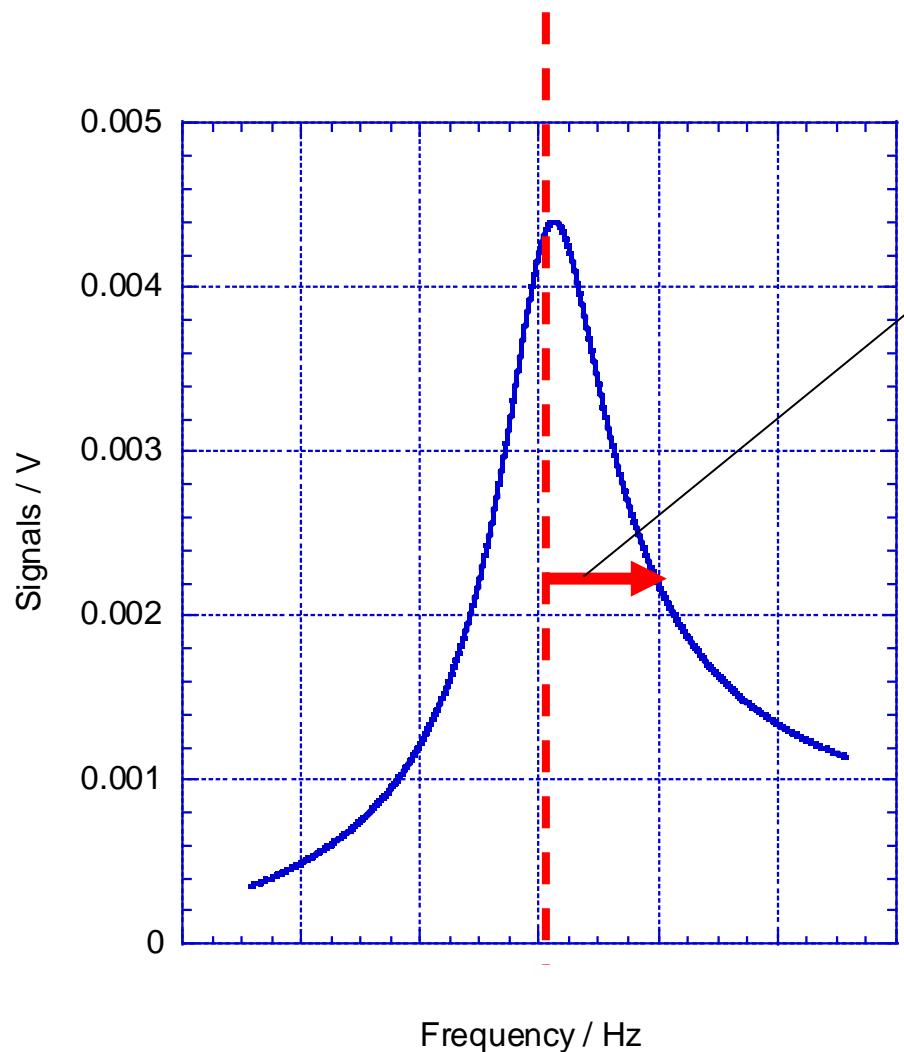
$u(k_B)$

0.38 ppm

0.11 ppm

0.18 ppm

Central frequency



Half-Width should be
exactly what we expect

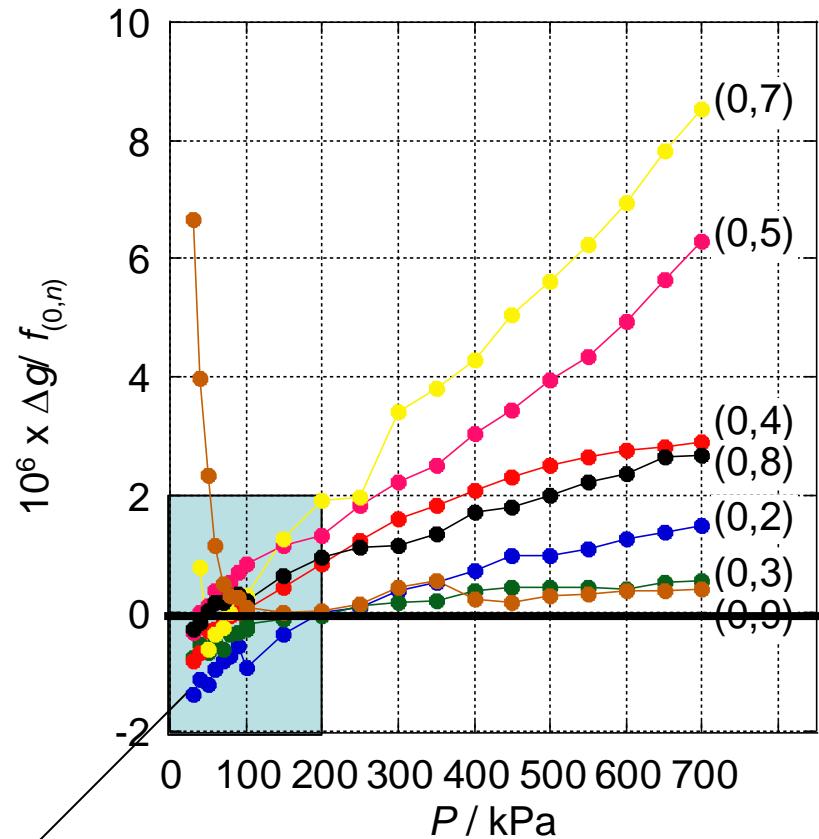
When $f_0 = 3548.8095$ Hz

expected width = 2.864 Hz

measured width = 2.858 Hz

Half-Width (*Experiment – Theory*)

Parts per million of resonance frequency

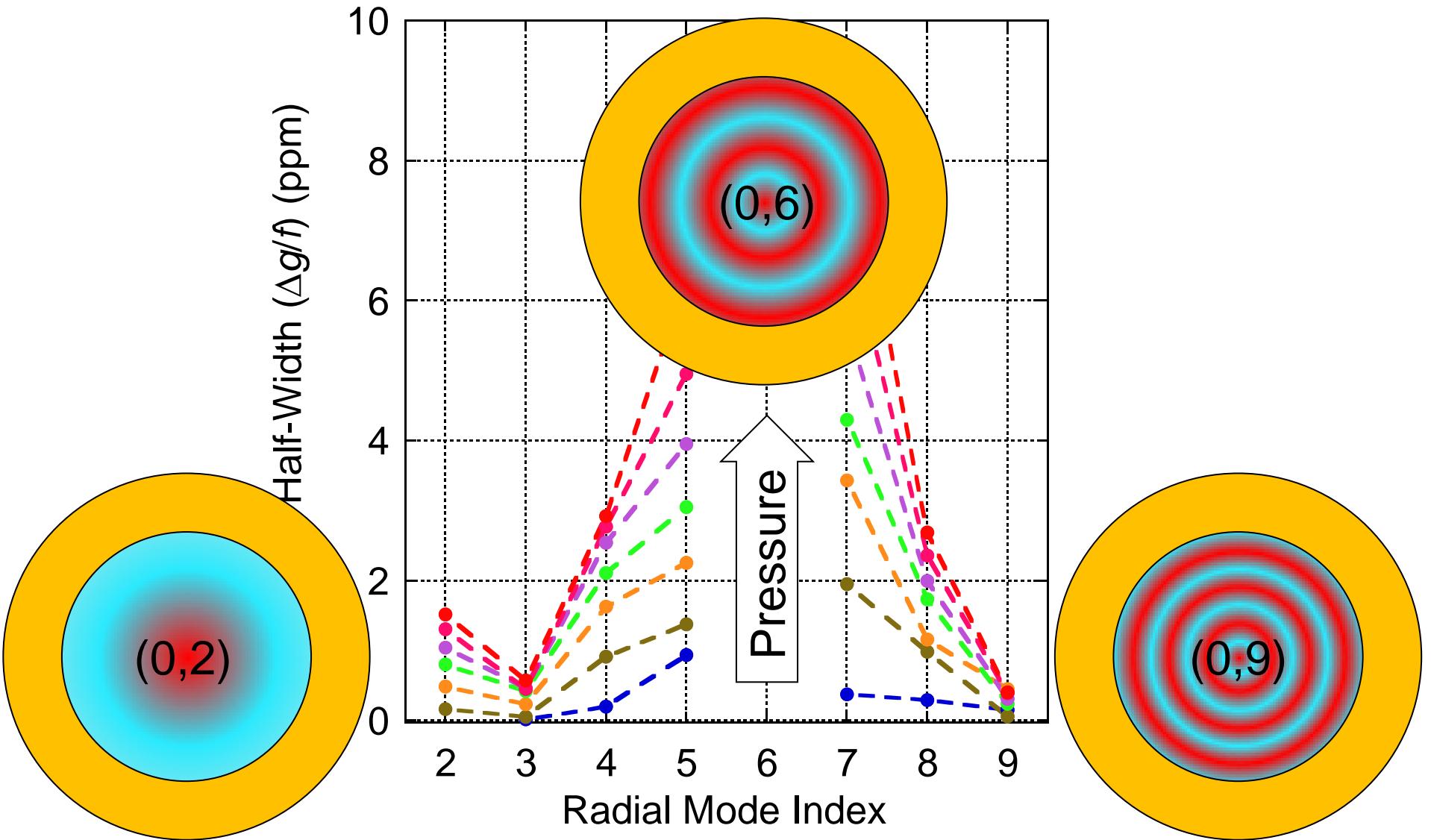


$f_0 = 3548.8095$ Hz
expected width = 2.864 Hz
measured width = 2.858 Hz

Half-Width (*Experiment – Theory*)

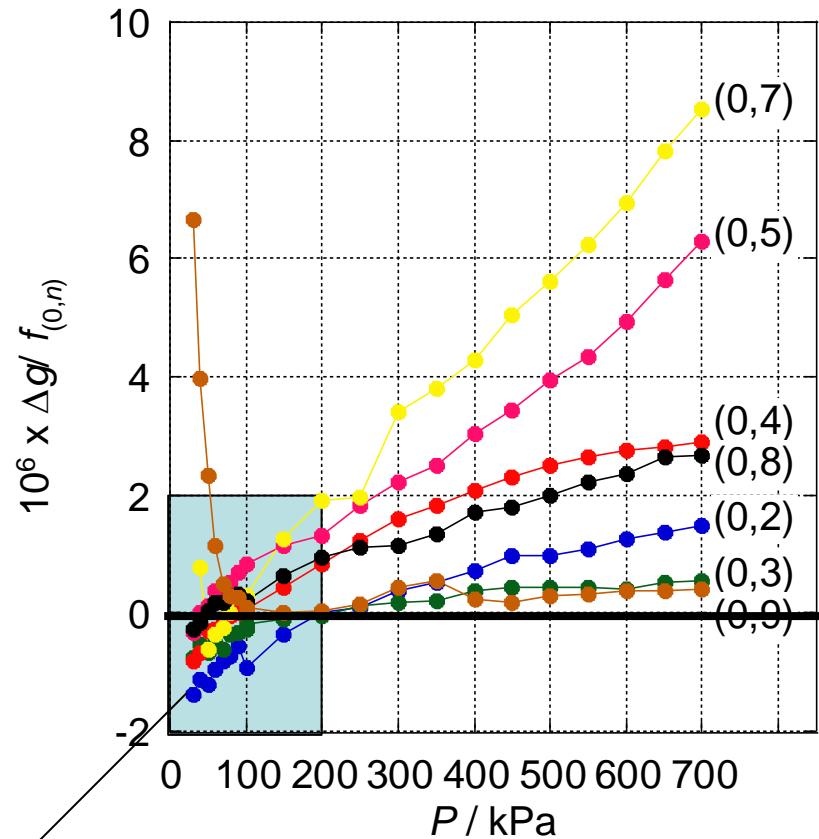
Shell Interaction

Shows the effect of mode and pressure



Half-Width (*Experiment – Theory*)

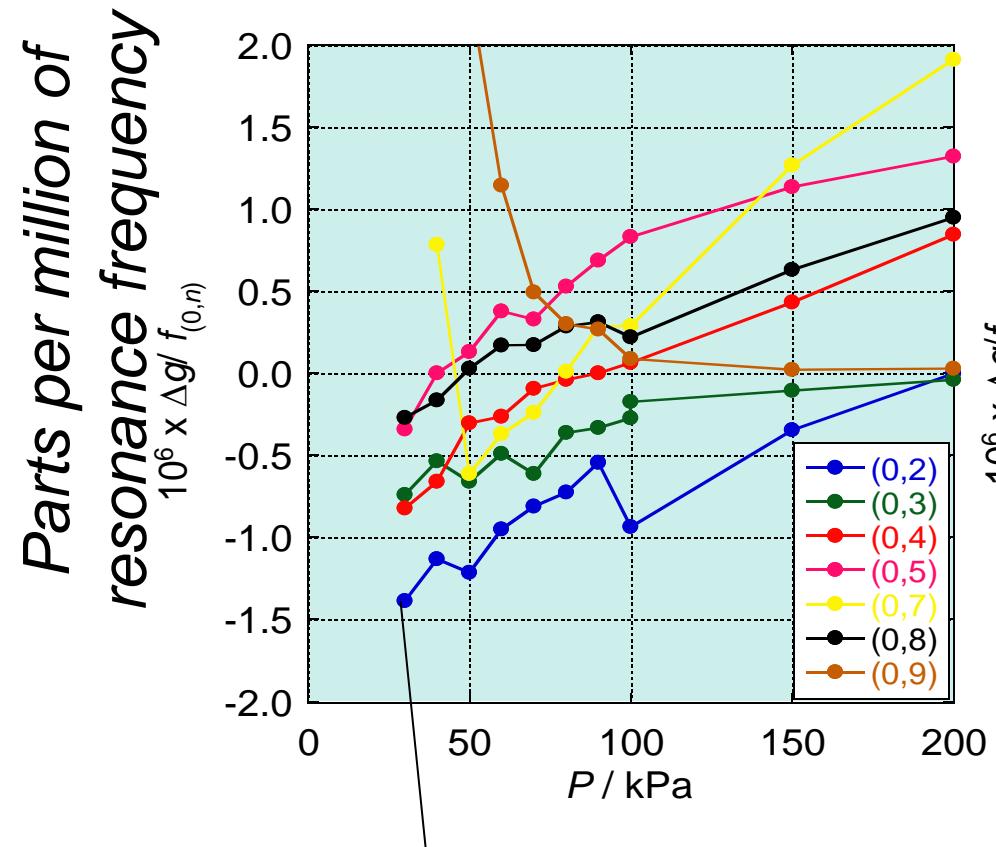
Parts per million of resonance frequency



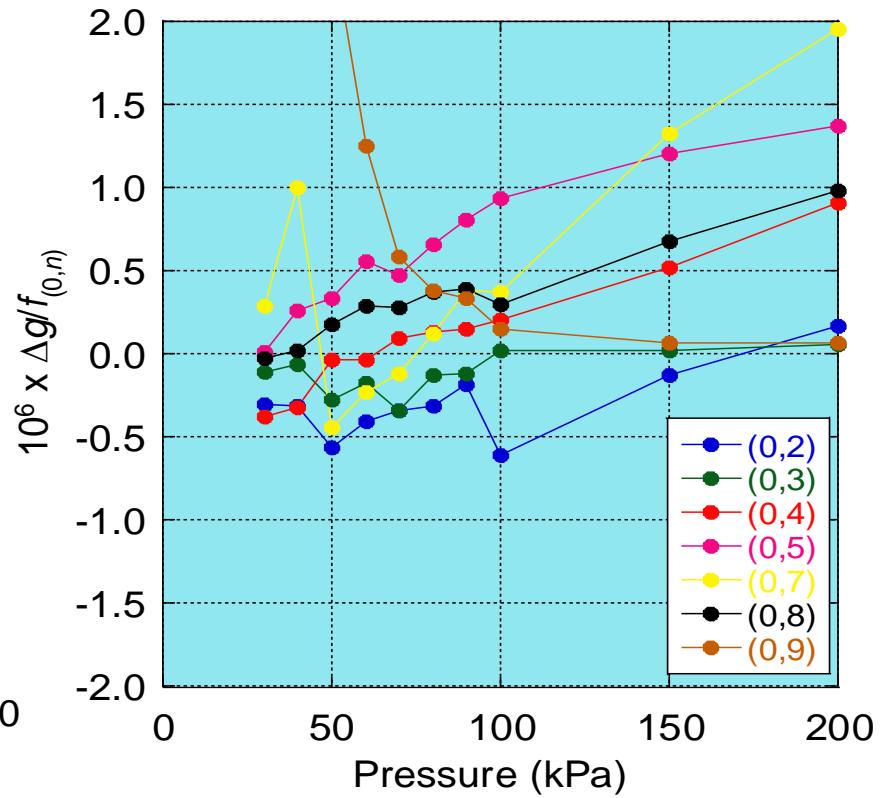
$f_0 = 3548.8095$ Hz
expected width = 2.864 Hz
measured width = 2.858 Hz

Half-Width

Experiment – Theory



Experiment – New Theory



$f_0 = 3548.8095$ Hz
expected width = 2.864 Hz
measured width = 2.858 Hz

5: How wrong could the Temperature be?

$u(k=1)$

$u(k_B)$

11.7 nm

1. Resonator radius, a

0.38 ppm

6.3 Pa

2. Pressure

0.11 ppm

3. Eigenvalues $\xi_{(0,n)}$

0.18 ppm

~0

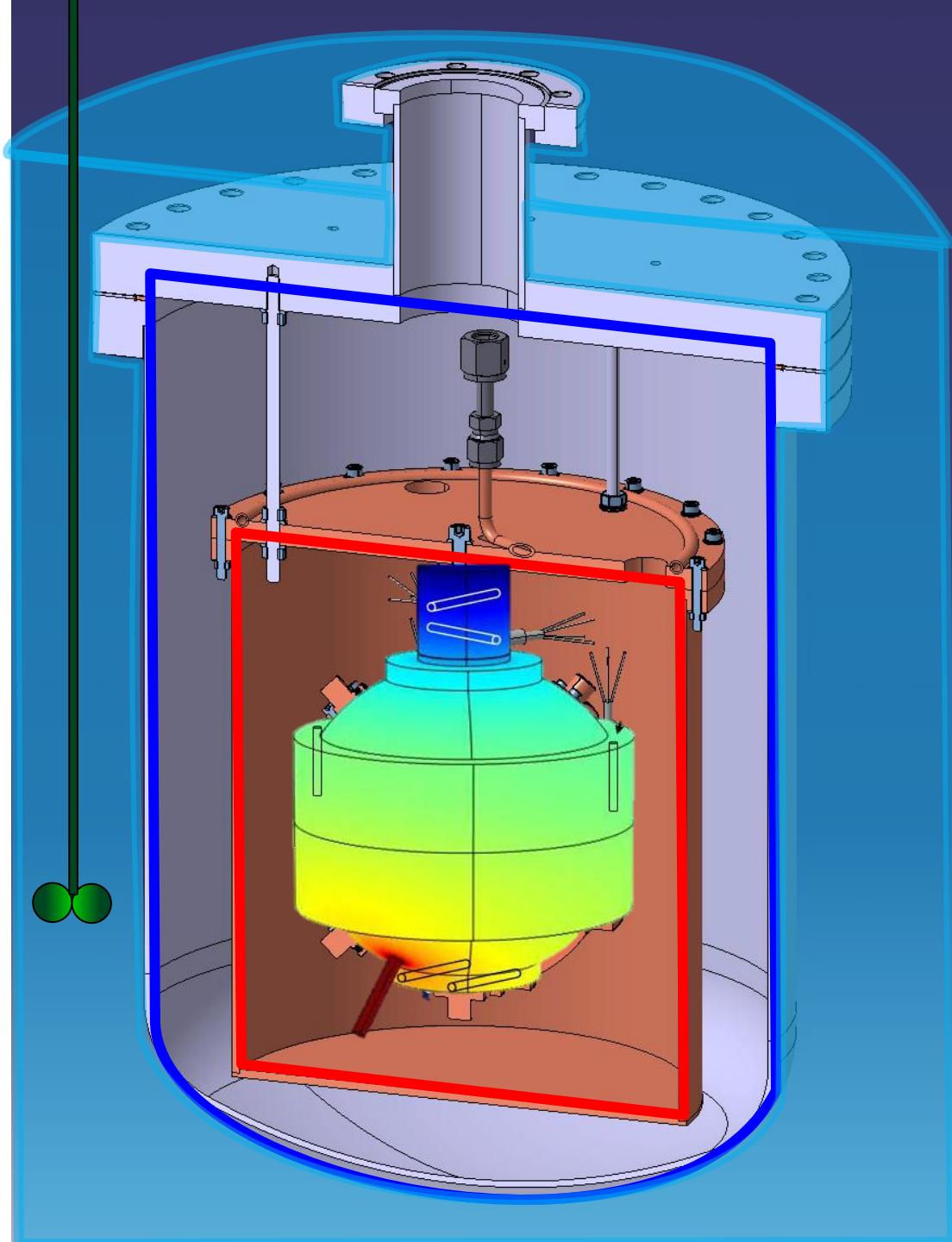
4. Frequency Corrections $\Delta f_{(0,n)}$

5. Temperature

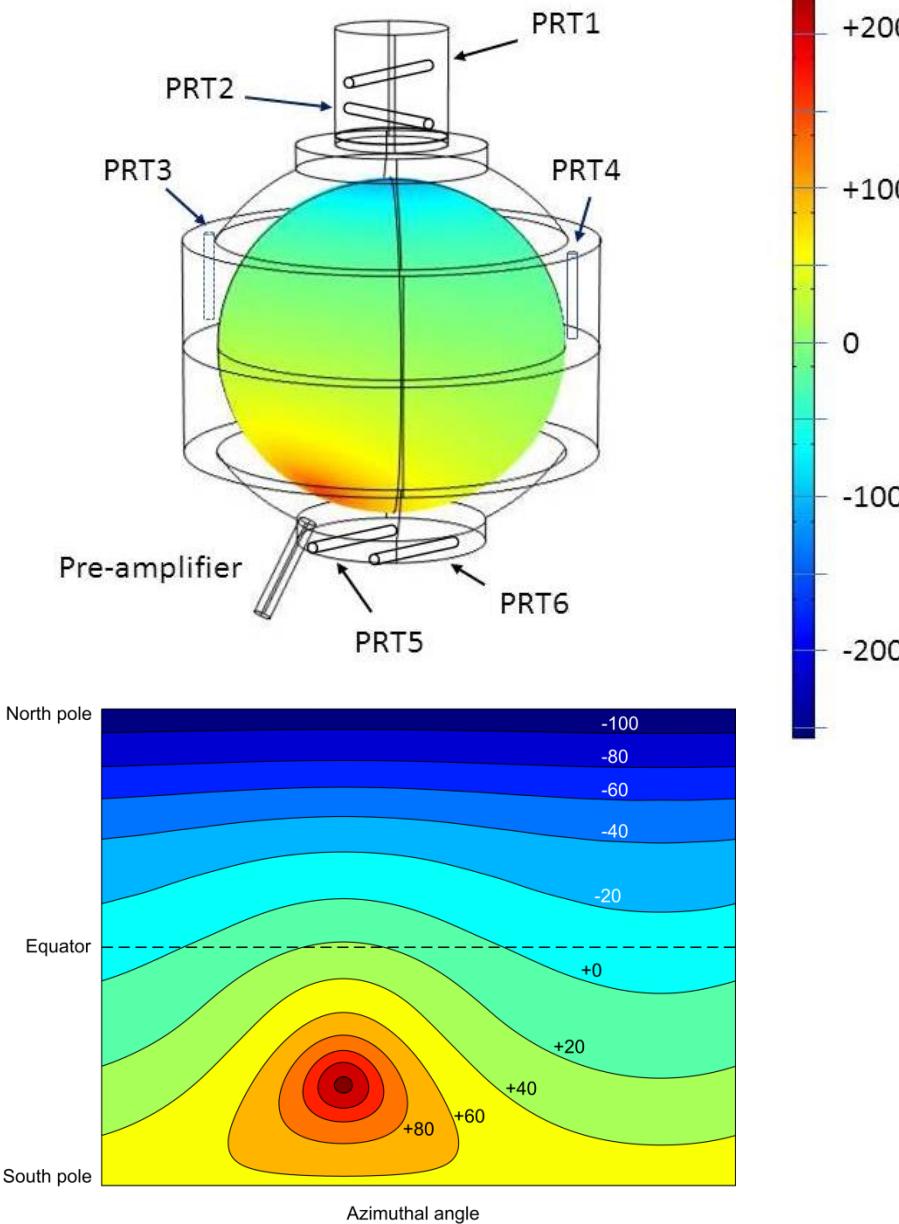
6. Molar Mass

Temperature Gradient

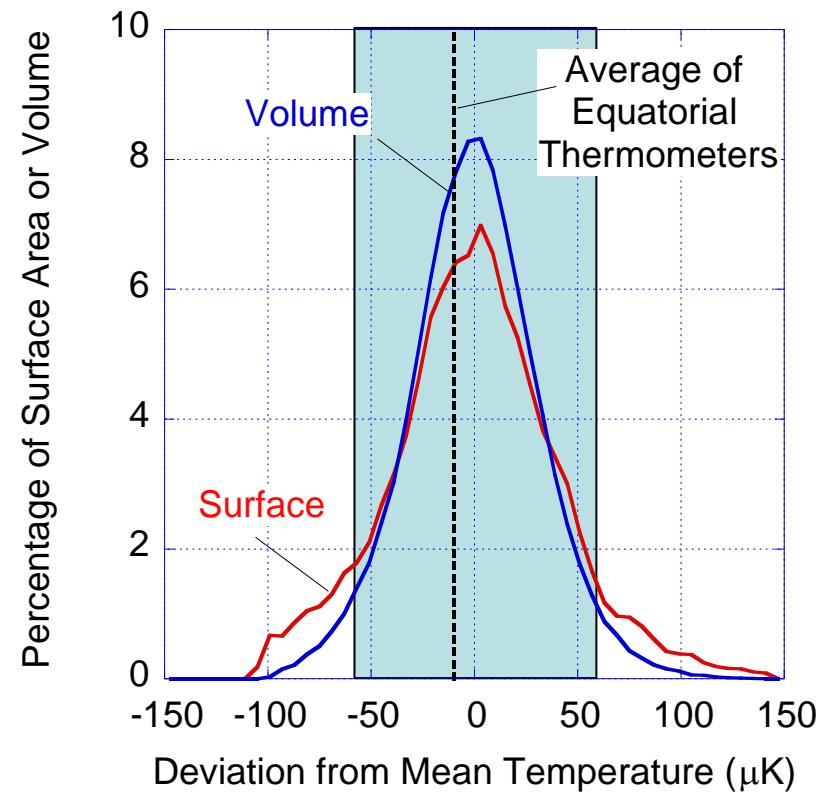
Temperature gradient was
 $\pm 91 \mu\text{K}$ about equator



Temperature



We modelled the temperature at the *inner* surface of the sphere, and then in the gas.



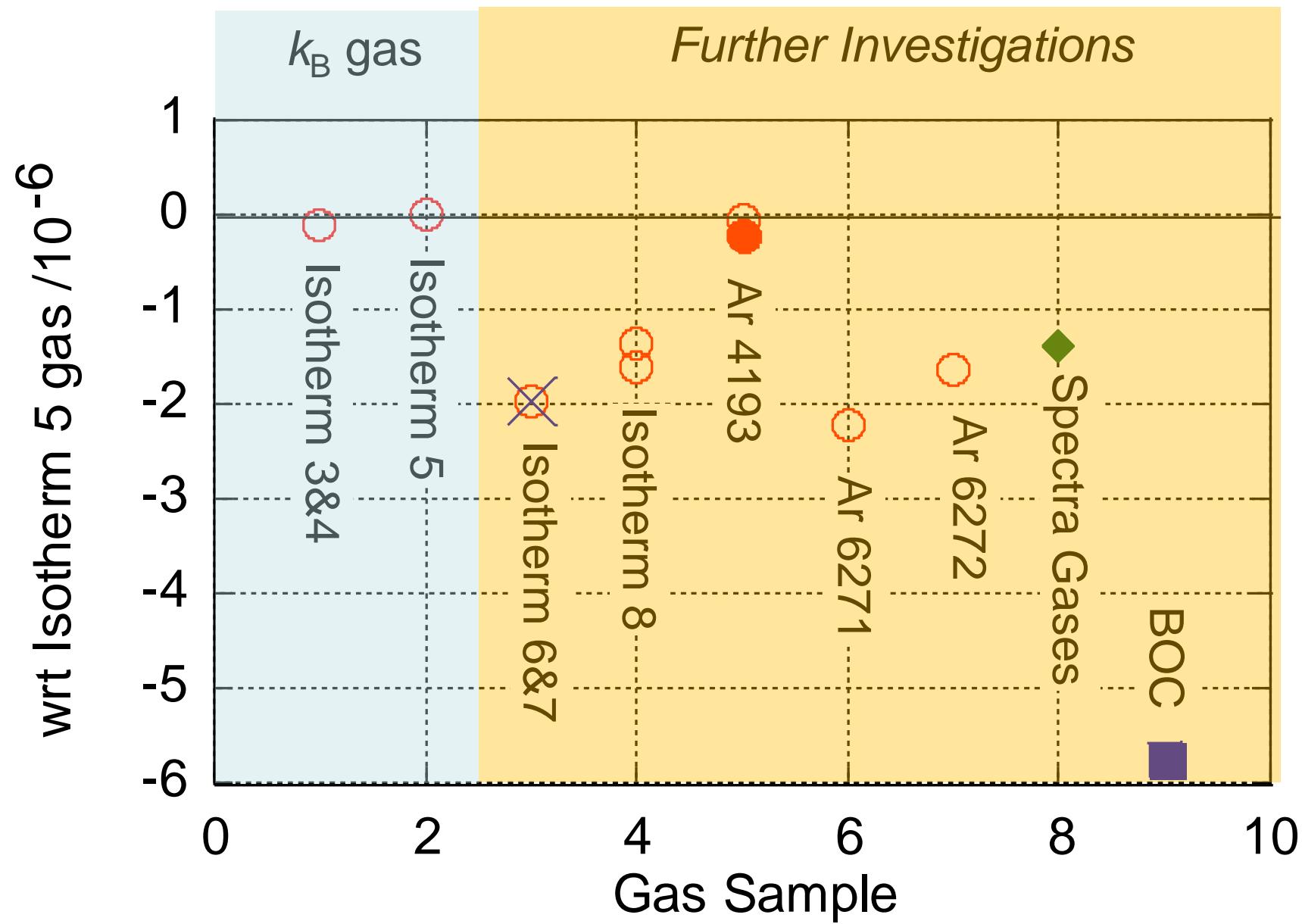
6: How wrong could the Molar Mass be?

$u(k=1)$

$u(k_B)$

11.7 nm	1. Resonator radius, a	0.38 ppm
6.3 Pa	2. Pressure	0.11 ppm
	3. Eigenvalues $\xi_{(0,n)}$	0.18 ppm
~0	4. Frequency Corrections $\Delta f_{(0,n)}$	
0.099 mK	5. Temperature	0.364 ppm
	6. Molar Mass	

Molar Mass Differences from Isotherm 5 Gas



6: How wrong could the Molar Mass be?

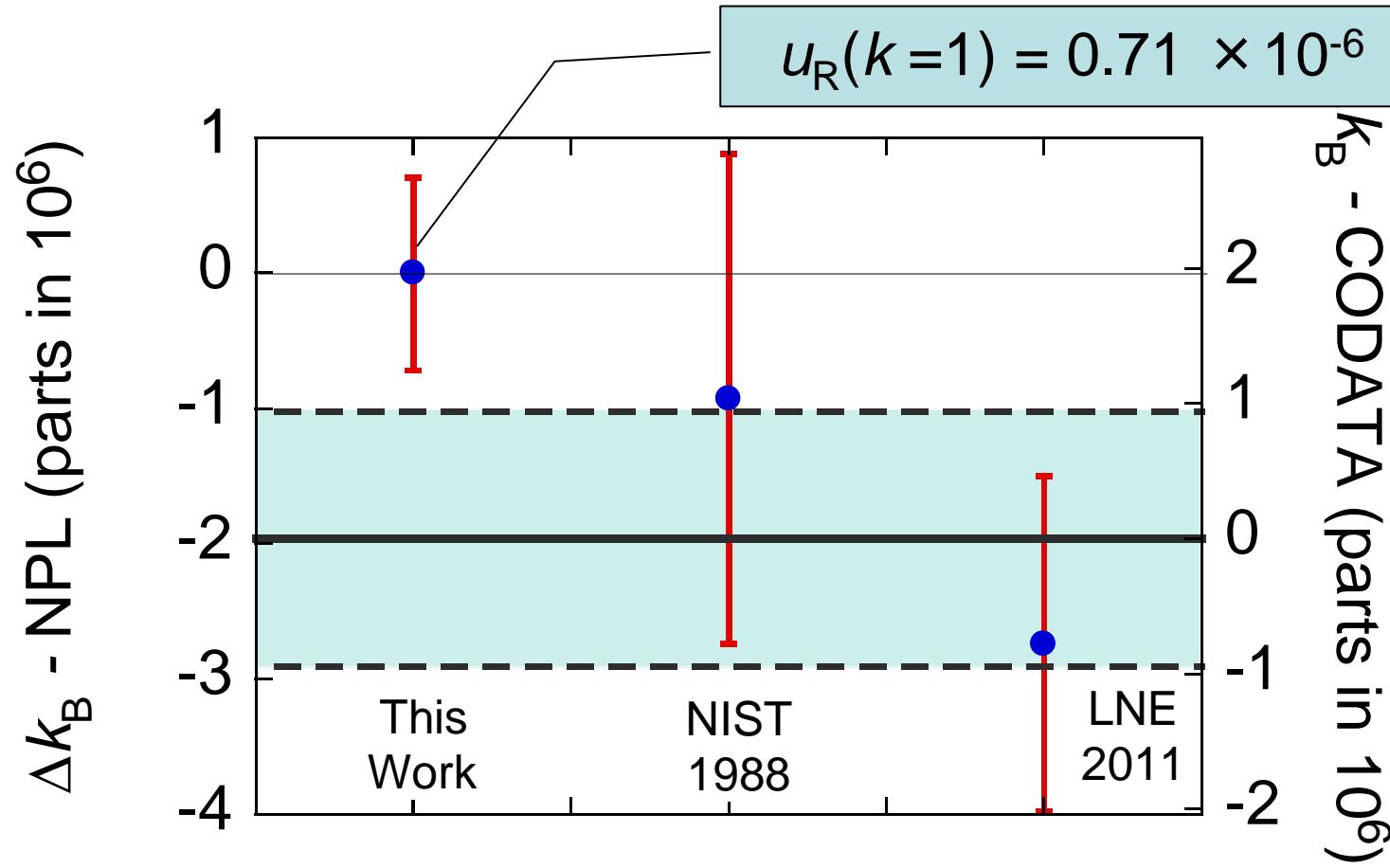
$u(k=1)$

$u(k_B)$

11.7 nm	1. Resonator radius, a	0.38 ppm
6.3 Pa	2. Pressure	0.11 ppm
	3. Eigenvalues $\xi_{(0,n)}$	0.18 ppm
~ 0	4. Frequency Corrections $\Delta f_{(0,n)}$	
0.099 mK	5. Temperature	0.364 ppm
0.390 ppm	6. Molar Mass	0.390 ppm

Traceable to isotopic composition
of atmospheric argon

Uncertainty



Have we learned anything since 2013
that could shed light on the LNE-CNAM-
NPL discrepancy?

Reflections on the NPL-2013 Estimate of the Boltzmann Constant

- 1. Background**
- 2. History**
- 3. The NPL uncertainty estimate**
- 4. NPL Update February 2015**
- 5. The NPL Analysis**
- 6. Summary**

CODATA November 2015

Update on Acoustic Thermometry at NPL

Michael de Podesta

Gavin Sutton, Robin Underwood, Leigh Stanger, Graham Machin

Notes for Joachim Fischer prepared October 2014



NPL update

Change in the best estimate of thermal conductivity of argon

- M R Moldover et al 2014 Metrologia 51 R1 ([doi:10.1088/0026-1394/51/1/R1](https://doi.org/10.1088/0026-1394/51/1/R1))
 - Change in λ (-0.11%) is closer to estimated uncertainty ($u = 0.1\%$) in the NPL paper
 - New uncertainty in λ ($u = 0.02\%$) is a factor 5 lower than we estimated
- Based on this we would expect the NPL estimate for k_s to shift by approximately -0.19 ppm.
- Overall uncertainty would be slightly reduced.
- Excess half-widths would become slightly larger.

Elimination of temperature gradient

- Significant weakness in original paper was the lack of temperature gradient correction.
- Since then we have replaced microphones.
- Two additional thermometers added to the probe.
- Now there is no systematic gradient: $T_s - T_{20}$ measurements involve regular changes.
- No 'change in k_s' observed outside $\sim 0.1\%$.

Molar Mass

- The NPL result is traceable to the estimate of molar mass.
- We await the outcome of measurement.
- If Lee et al estimate revised, or new data available, then the NPL result will change.

NPL strengths

Clear analysis

- Makes significance of fits to data meaningful.
- NPL described their model for the experiment; fitted the model to the data; showed (data - model); and derived uncertainties that were demonstrably statistically self-consistent. We also published our data and analysis scripts.

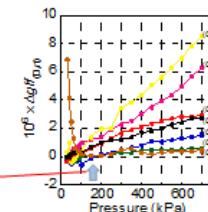
Low pressure measurements

- At low pressure the thermal boundary layer correction is large and strongly pressure-dependent.
- NPL calibrated pressure indicator before and after the experiment and checked consistency in situ using dielectric measurements to give an uncertainty of $u(k=1) = 6.3$ Pa

Excess half-width of acoustic resonances

- Tests for correct estimation of thermal boundary layer and un-anticipated loss mechanisms
- NPL excess half-widths extrapolate to a value barely distinguishable from zero.

- Thermal conductivity revision will increase the low-pressure end of these curves by ~ 0.1 parts in 10^6 .



NPL Update

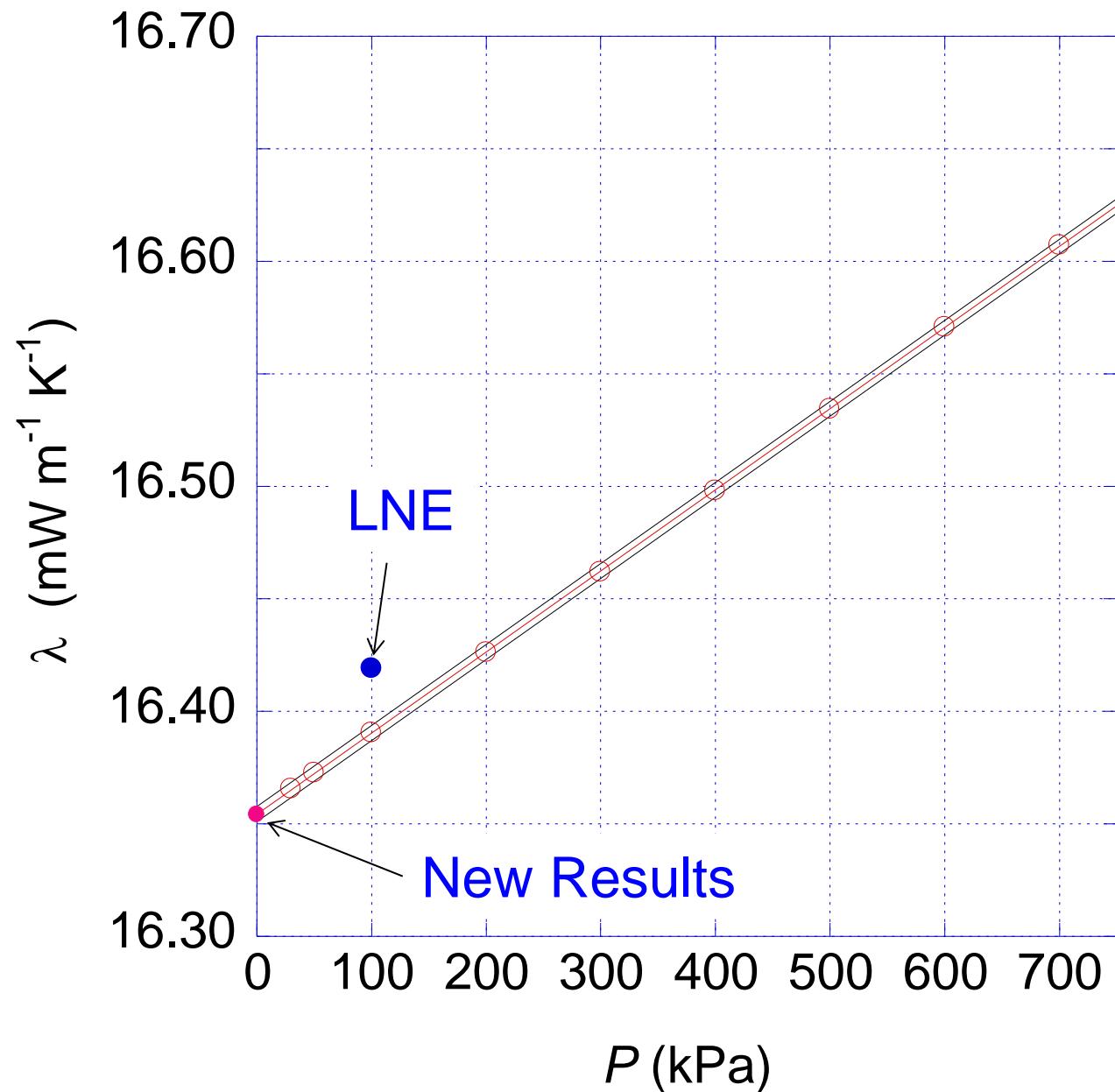
February 2015

1. *New estimate for thermal conductivity*
2. *Temperature Gradients*
3. *Argon Isotopic Molar Mass*

New estimate for thermal conductivity of argon

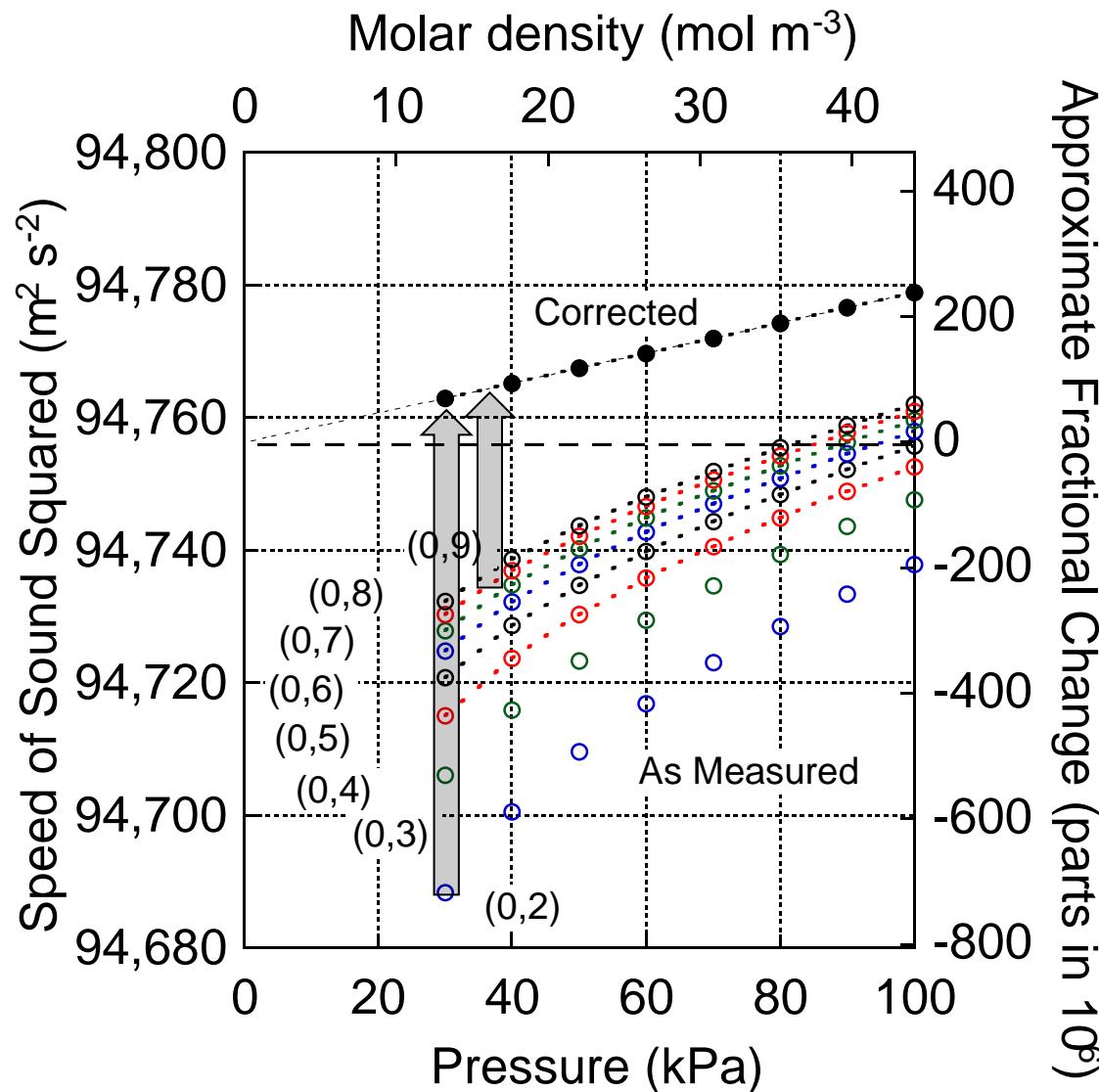
- $\Delta\lambda$ (-0.11%) is close to estimated uncertainty
- ($u = 0.1\%$) NPL paper

New uncertainty in λ
($u = 0.02\%$) is a factor 5
lower than we estimated



New estimate for thermal conductivity of argon

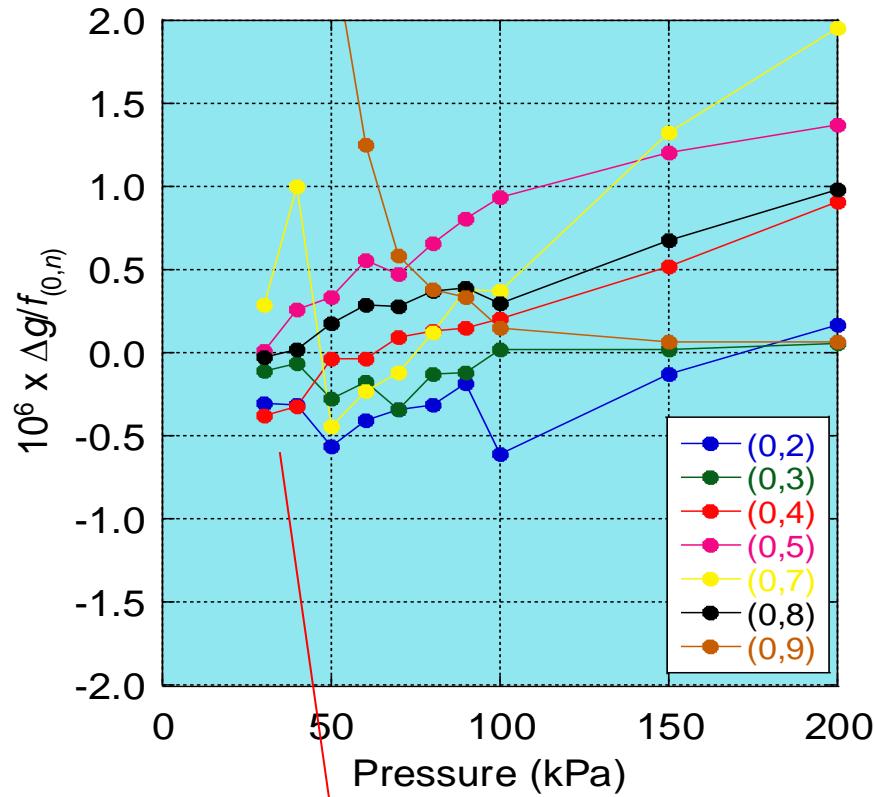
- $\Delta k_B = -0.19 \text{ ppm}$.
- $u_R \sim 0.69 \times 10^{-6}$
- Excess half-widths increased
 - $\Delta g/f \sim + 0.1 \times 10^{-6}$ @ 100 kPa



New estimate for thermal conductivity of argon

Experiment – New Theory

Parts per million of resonance frequency



- Thermal conductivity revision will increase the low-pressure end of these curves by ~0.1 parts in 10^6 .

NPL Update

February 2015

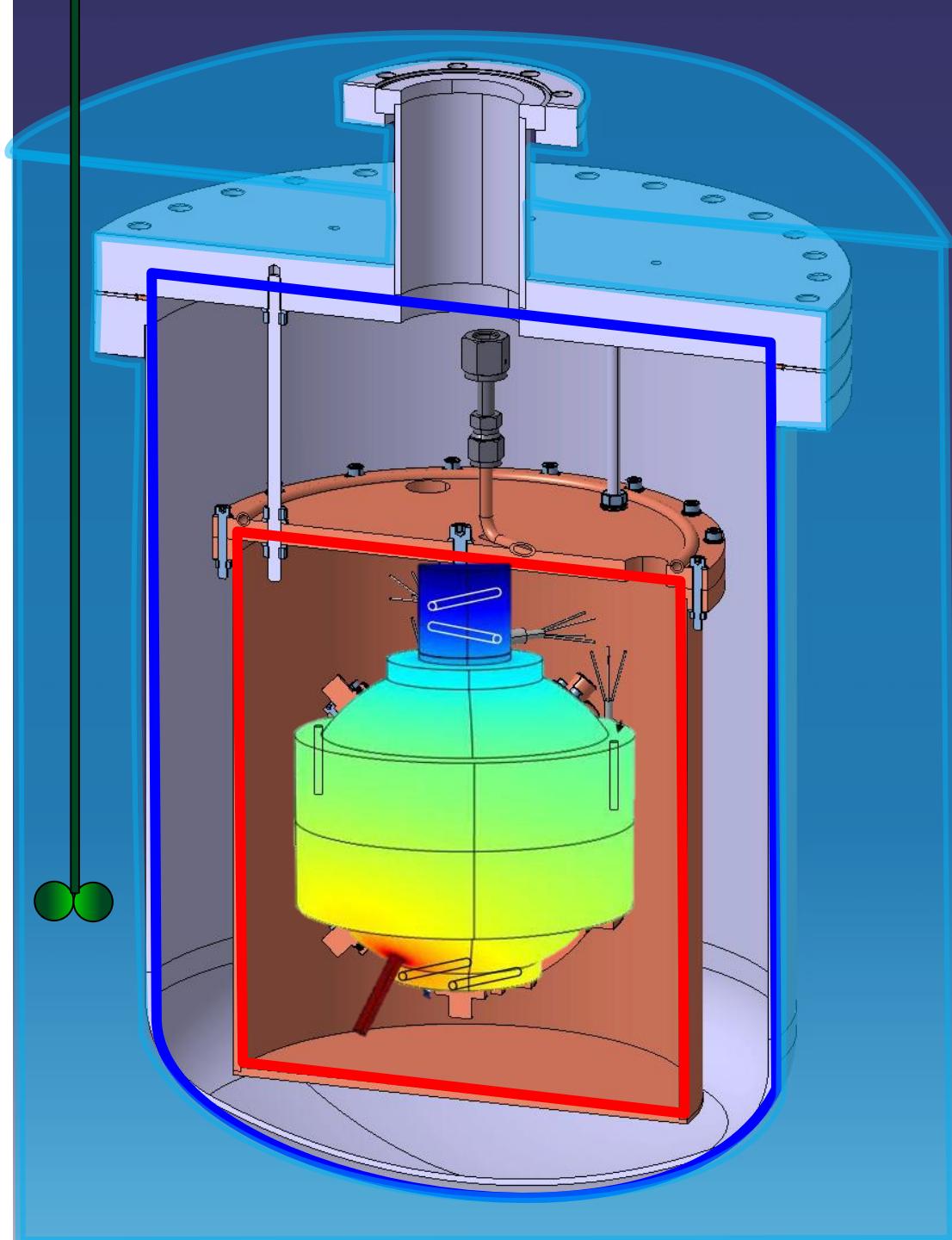
1. *New estimate for thermal conductivity*
2. *Temperature Gradients*
3. *Argon Isotopic Molar Mass*

Temperature Gradient

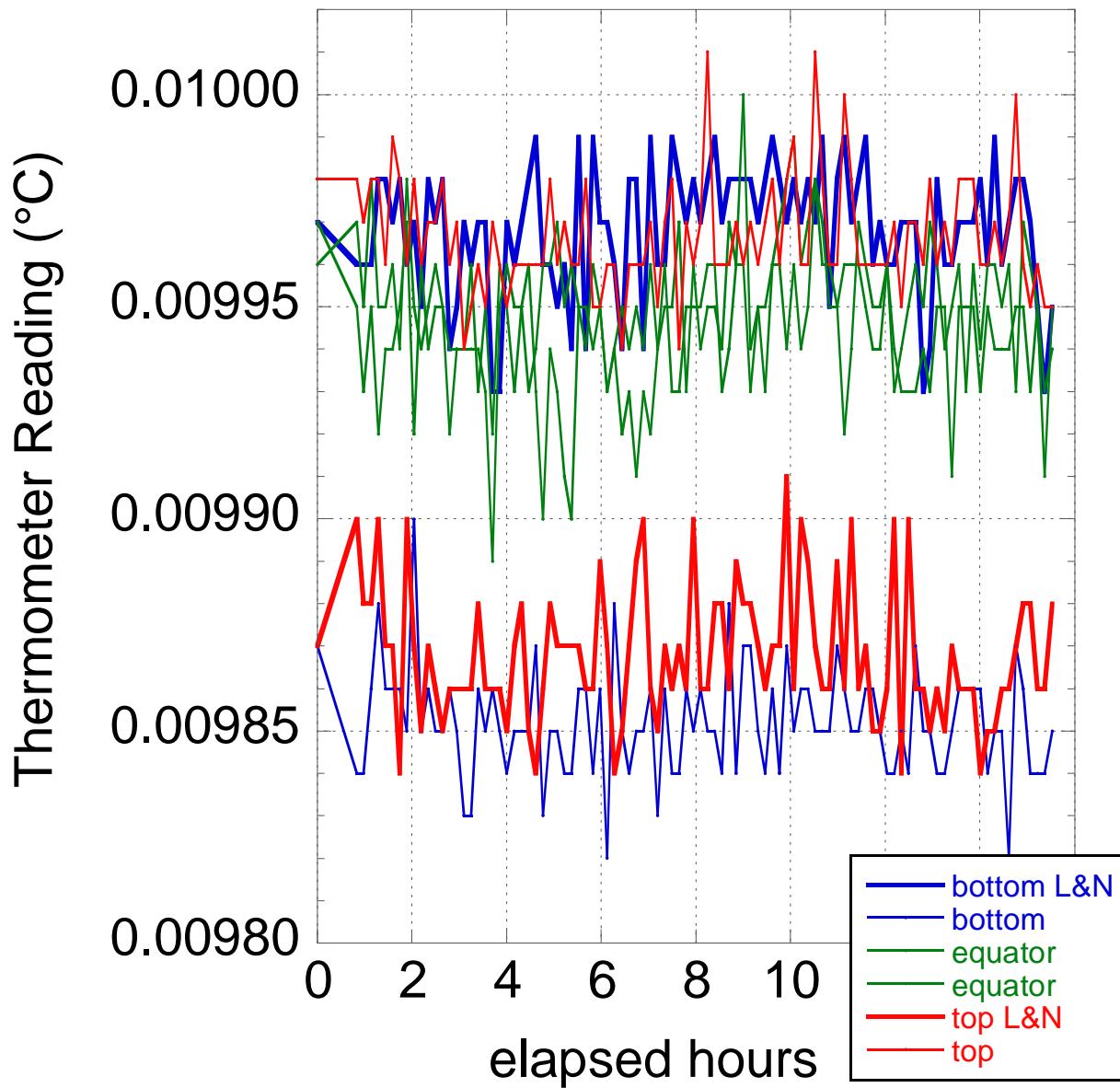
- Temperature gradient was $\pm 91 \mu\text{K}$ about equator

Since 2013

- Replaced microphones
- Moved the pre-amplifier.
- Two additional thermometers added to sphere (6 in all).
- **No systematic gradient: $(\text{max} - \text{min})$ is $\pm 58 \mu\text{K}$**
- **No 'change in k_B ' ($u \sim 0.3 \text{ ppm}$)**.



Temperature Gradient



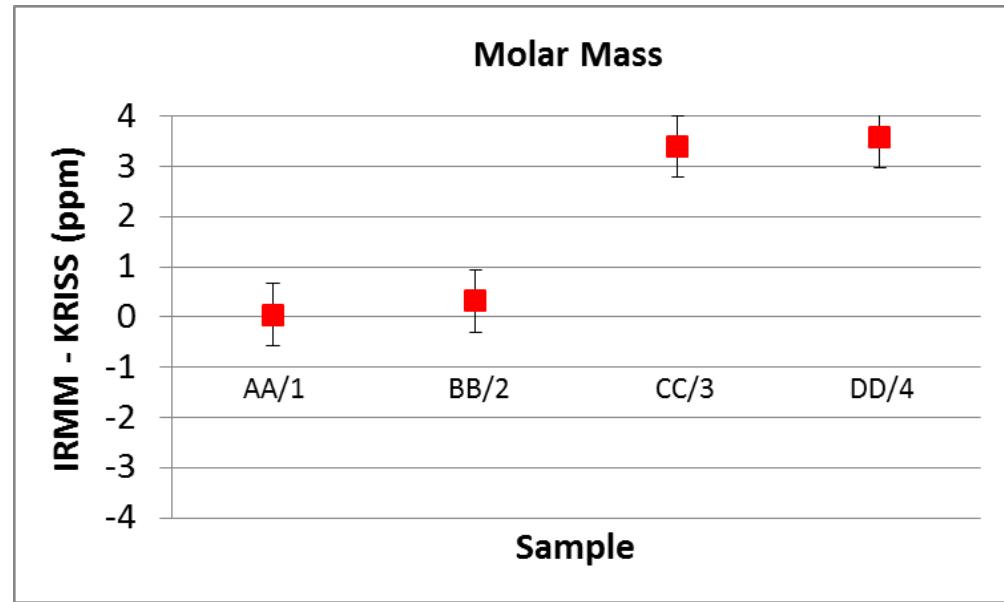
NPL Update

February 2015

- 1. New estimate for thermal conductivity*
- 2. Temperature Gradients*
- 3. Argon Isotopic Molar Mass*

NPL update#3: Molar Mass

- IRMM and KRISS have made gravimetrically traceable isotopic analyses
- Comparison between KRISS (2014) and IRMM (2009) analysis of the same samples



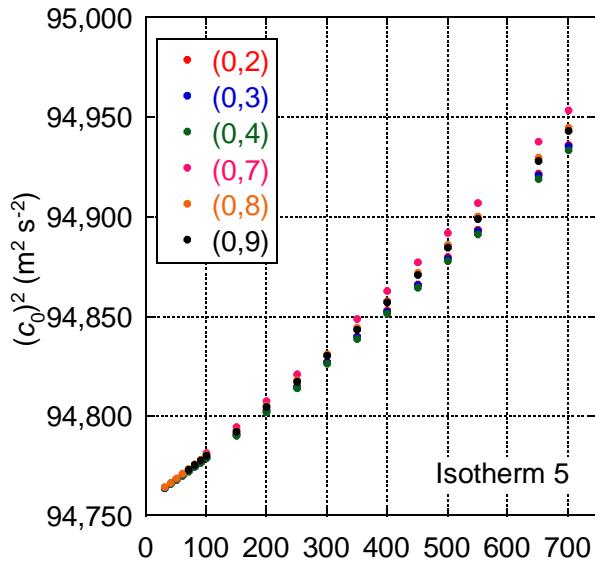
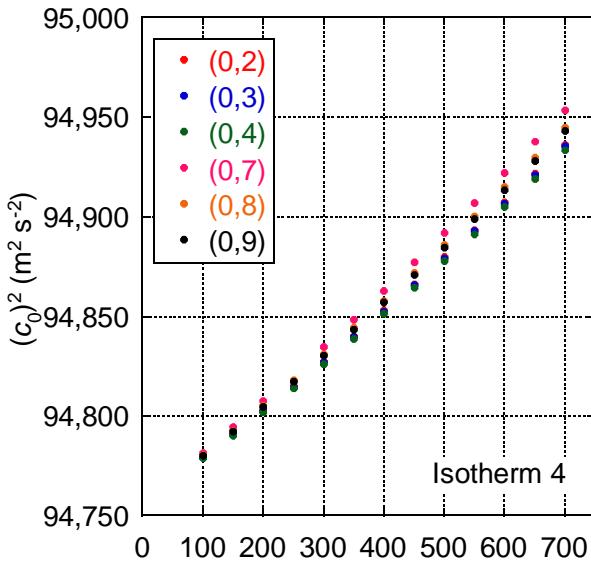
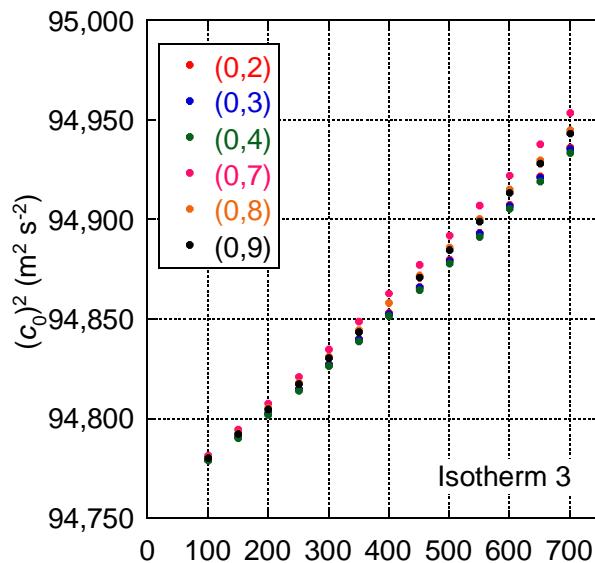
- *No clear pattern of agreement or disagreement between KRISS and IRMM*

Reflections on the NPL-2013 Estimate of the Boltzmann Constant

- 1. Background**
- 2. History**
- 3. The NPL uncertainty estimate**
- 4. NPL Update February 2015**
- 5. The NPL Analysis**
- 6. Summary**

Self-Consistent Analysis

- *Makes the significance of fits to data meaningful.*
 - Data
 - Type A uncertainty of Data
 - Model
 - Fit the model to the data
 - Look at residuals ($\text{data} - \text{model}$)
 - Show data and model are self-consistent
- We published our data and analysis scripts.
- These have been independently checked



From high pressure
studies
Common to all modes

$$c_{EXP}^2 - A_3 P^3 = c_0^2 + A_{-1} P^{-1}$$

Experimental
Estimates
Function of
pressure P
and mode, n

Low Pressure Speed of
Sound Squared
Common to all modes

Virial Correction
Common to all modes

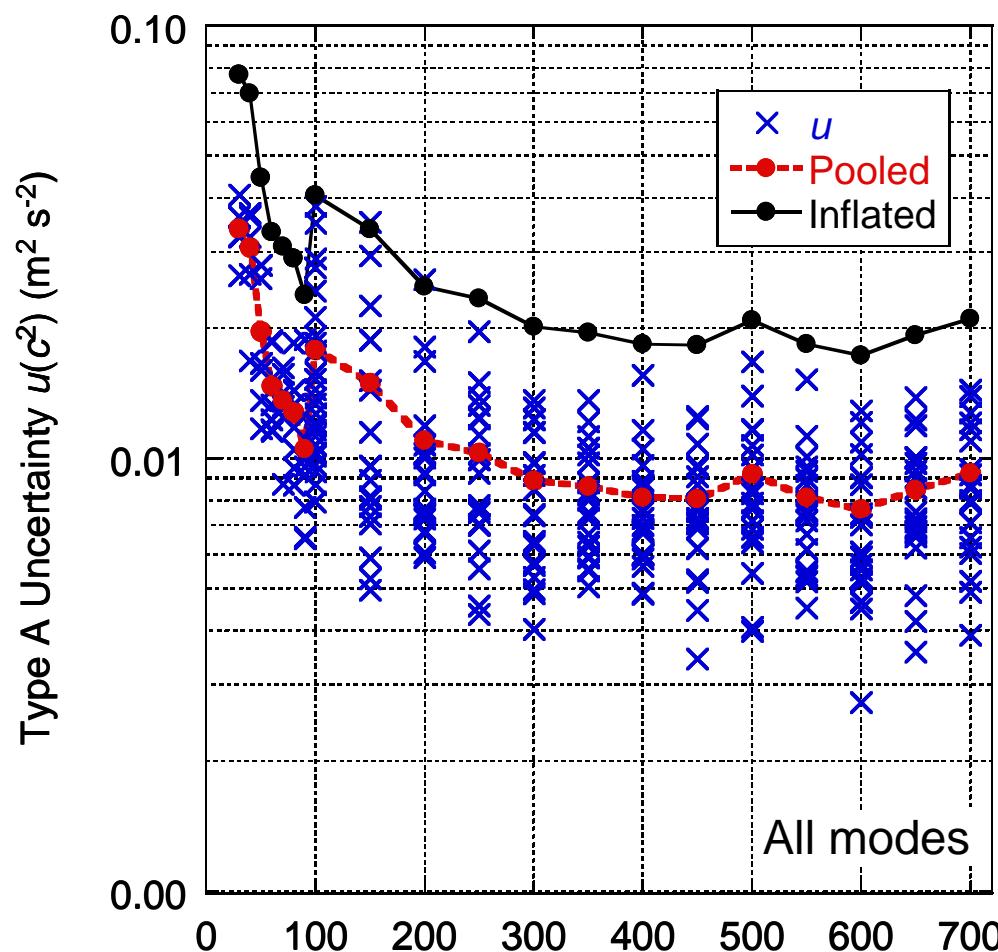
$$+ A_1^n P + A_2 P^2$$

'Accommodation'
Correction to Boundary
Layer
Common to all modes

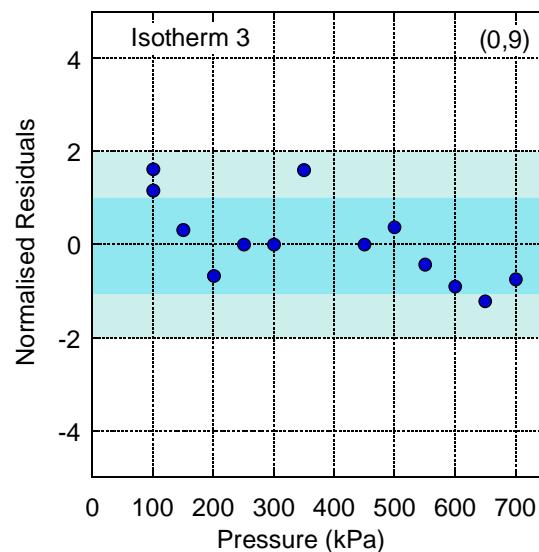
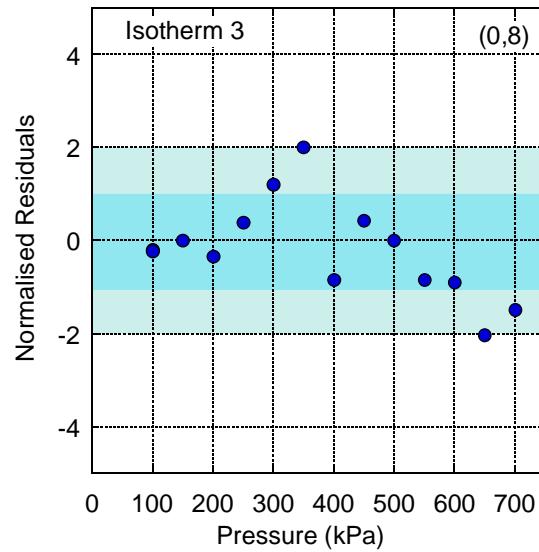
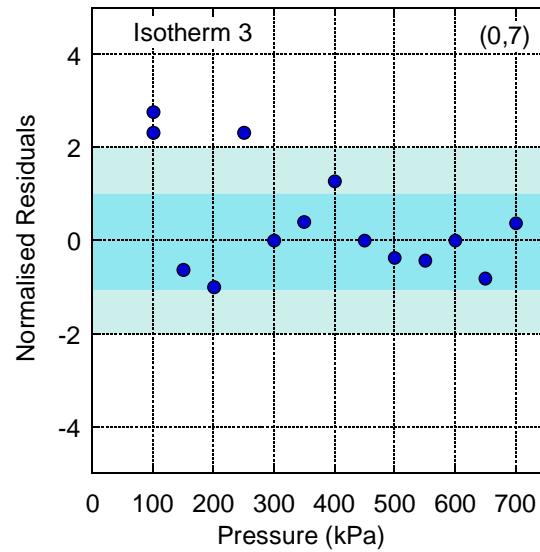
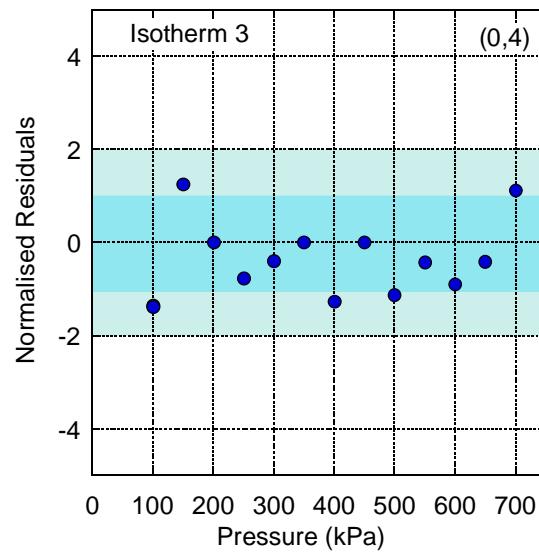
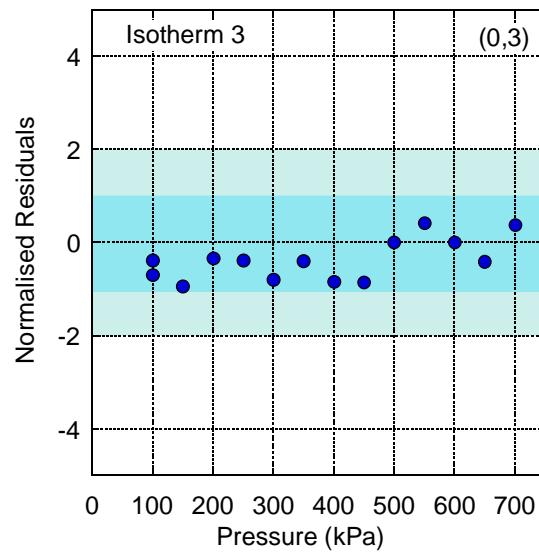
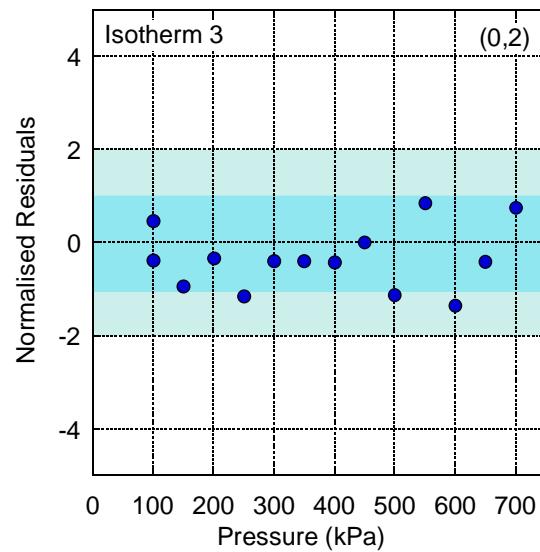
Virial Correction
Common to all modes
'Shell' Correction
Varies with mode

Type A Uncertainty

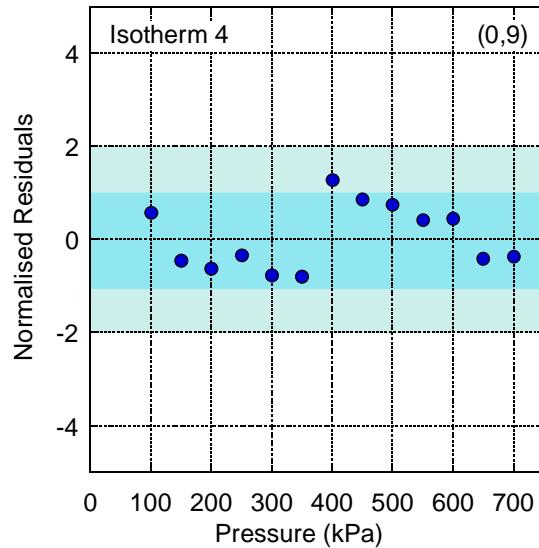
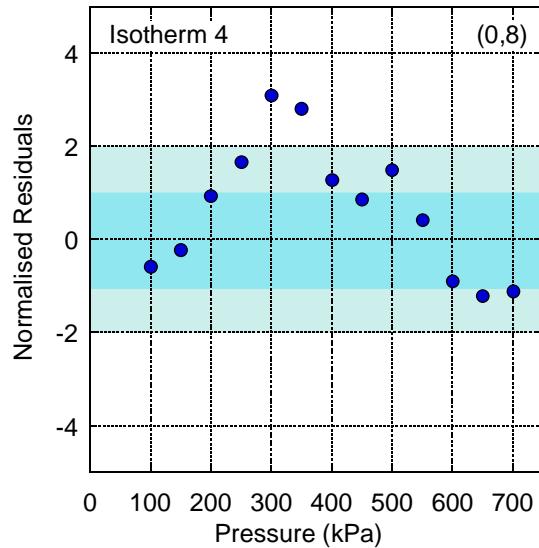
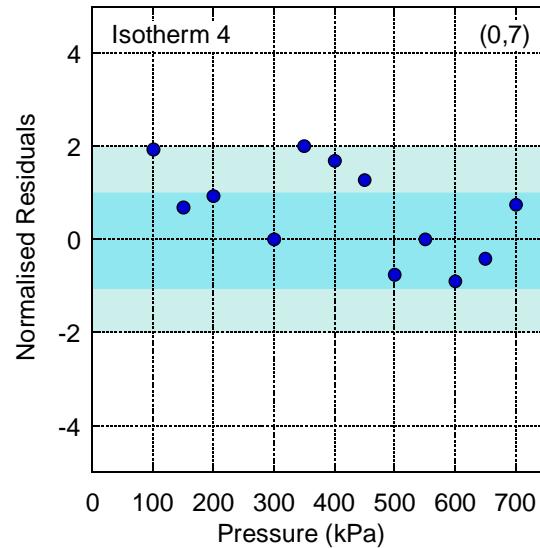
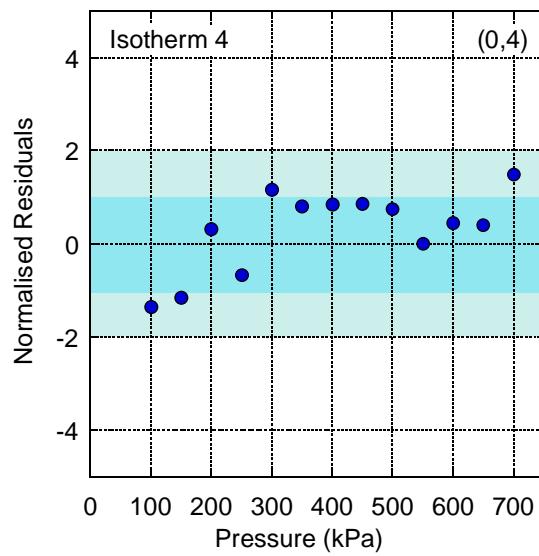
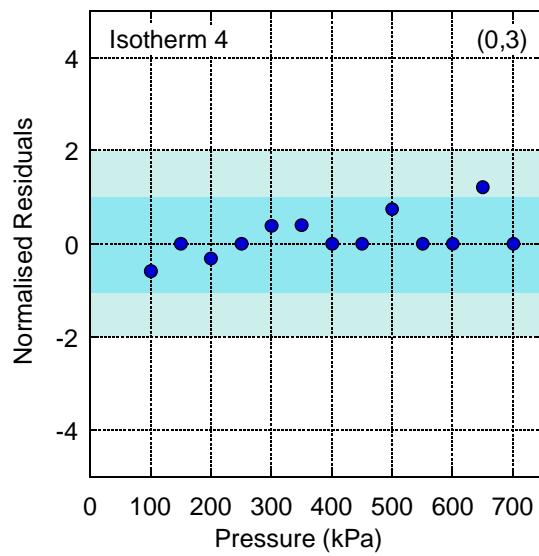
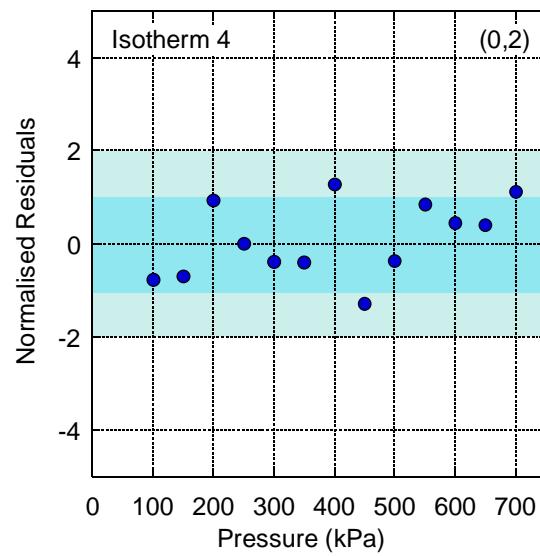
- *Estimated from repeats of a resonance acquisition.*
- *Use pooled uncertainty to weight the data used in the fit.*
- *Inflate uncertainty estimate*



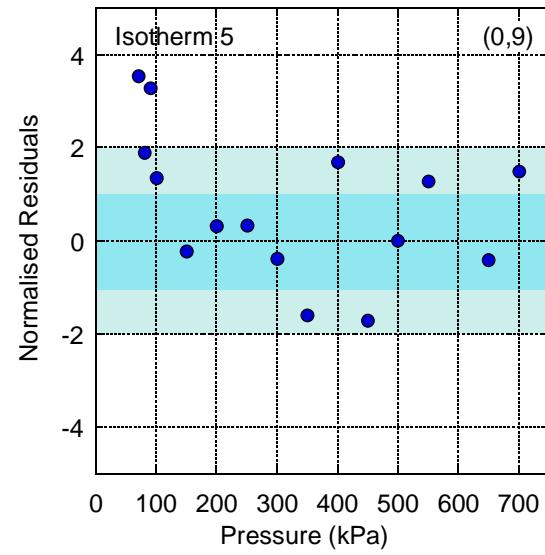
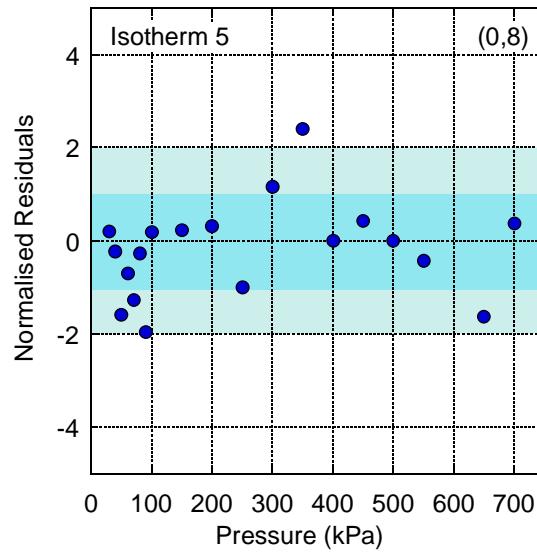
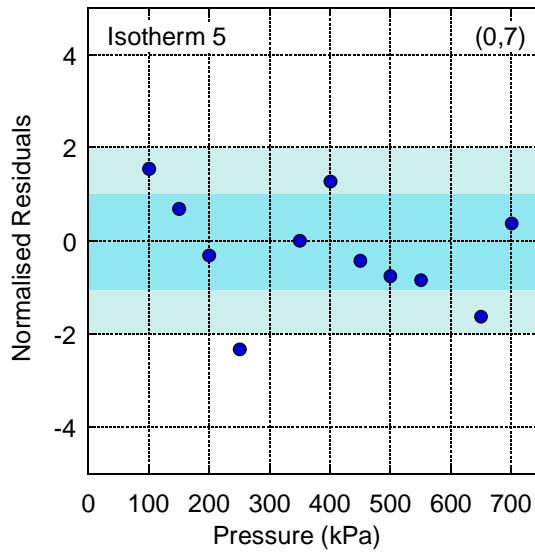
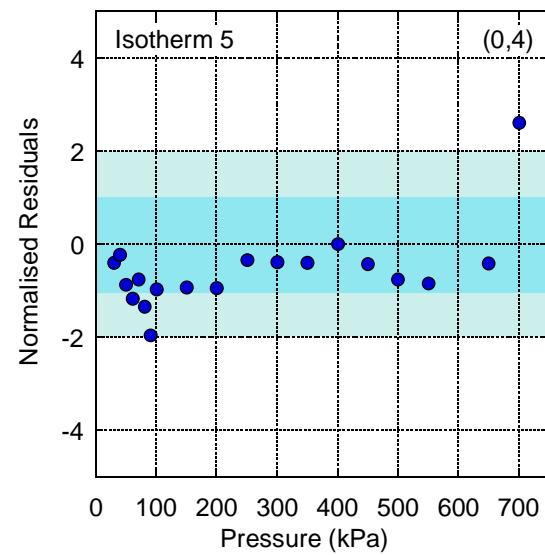
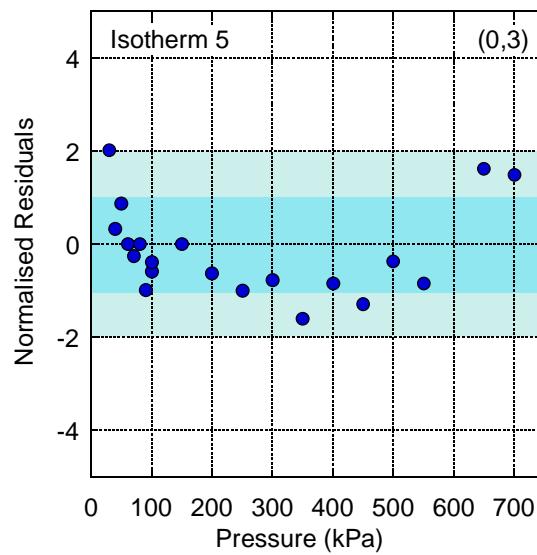
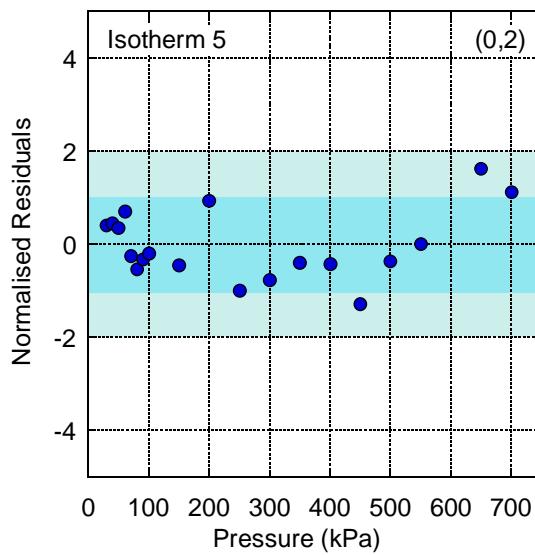
Normalised Residuals from Global Fit: Isotherm 3



Normalised Residuals from Global Fit: Isotherm 4

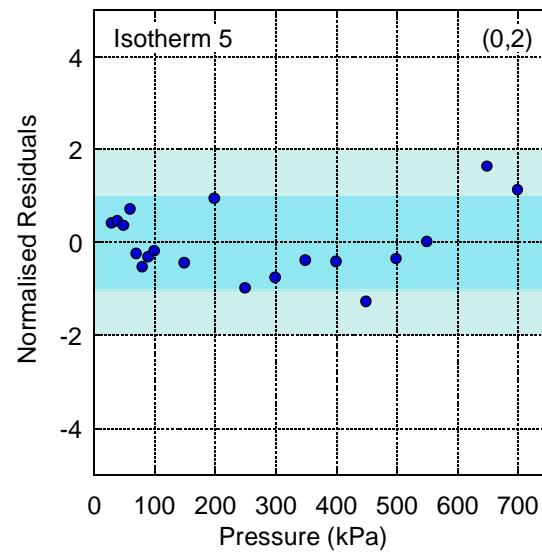
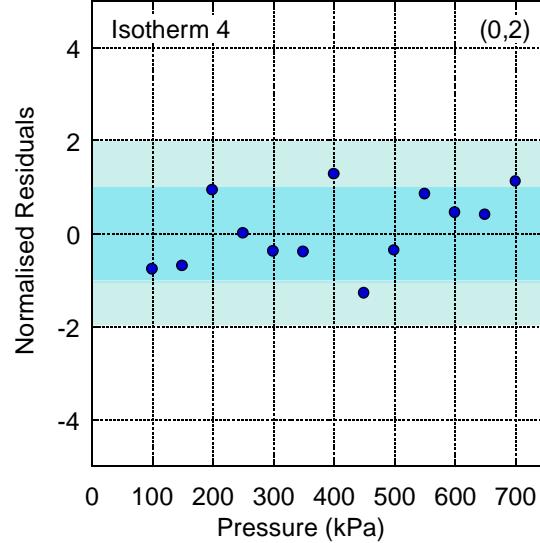
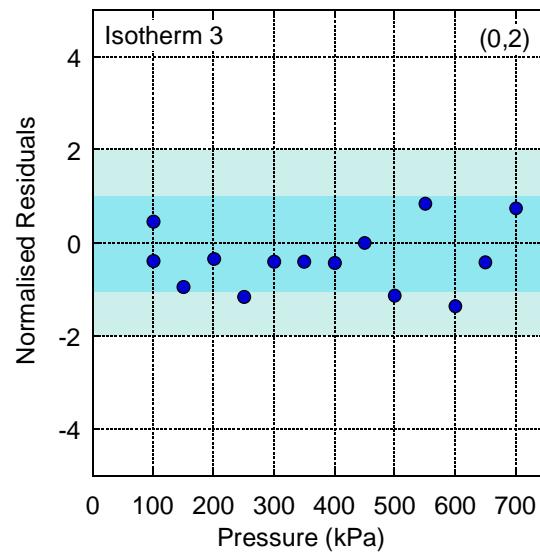


Normalised Residuals from Global Fit: Isotherm 5

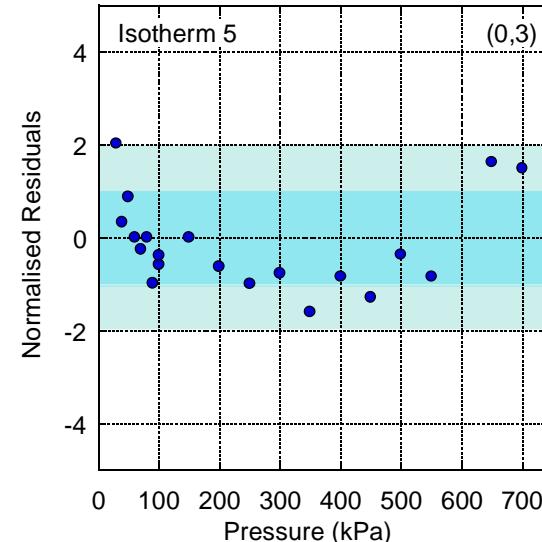
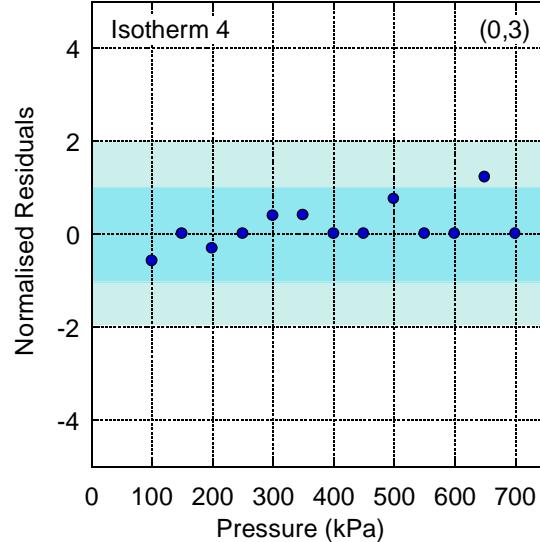
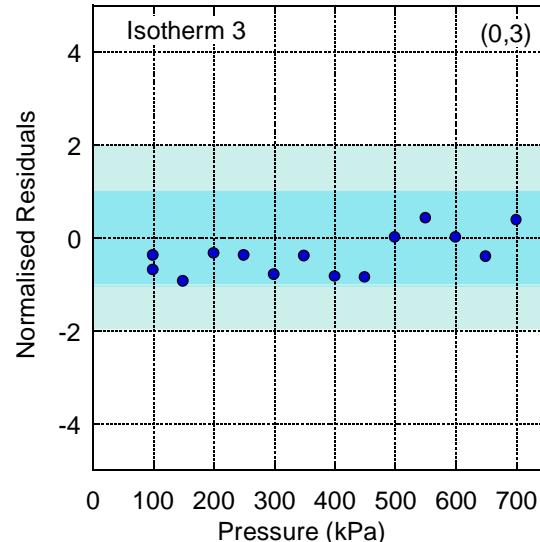


Residuals by Mode

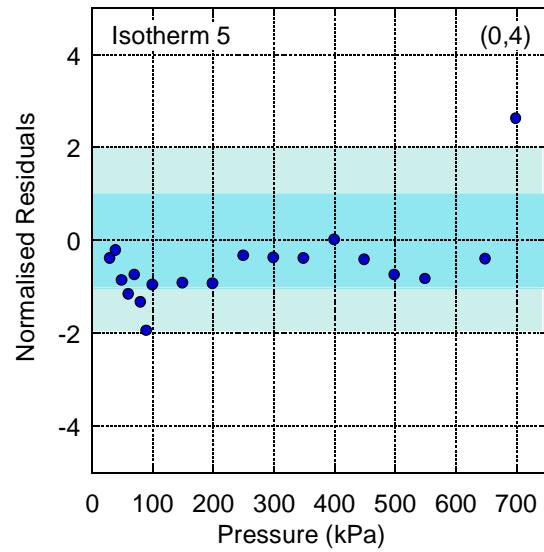
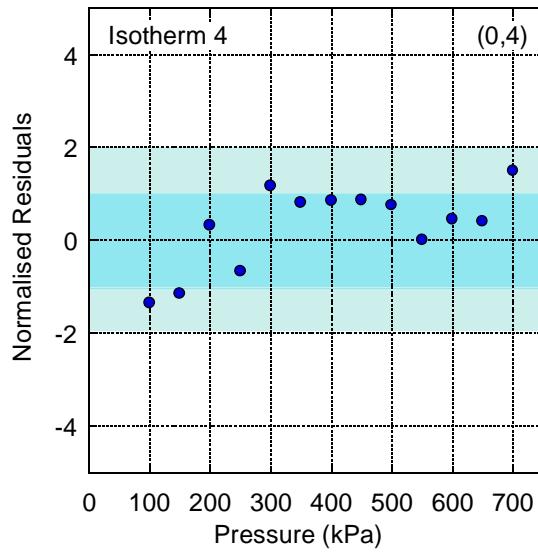
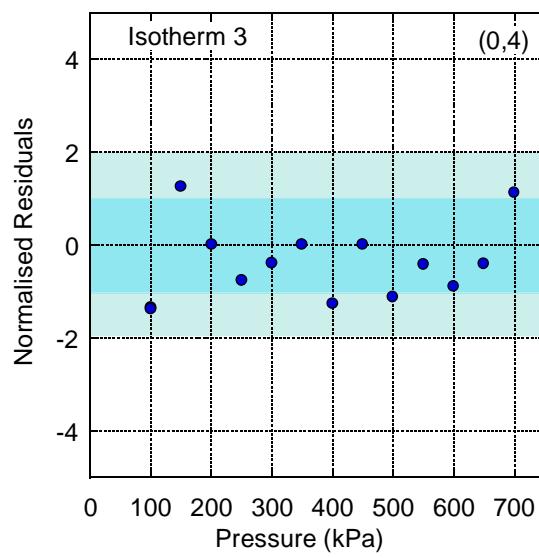
Normalised Residuals from Global Fit: (0,2)



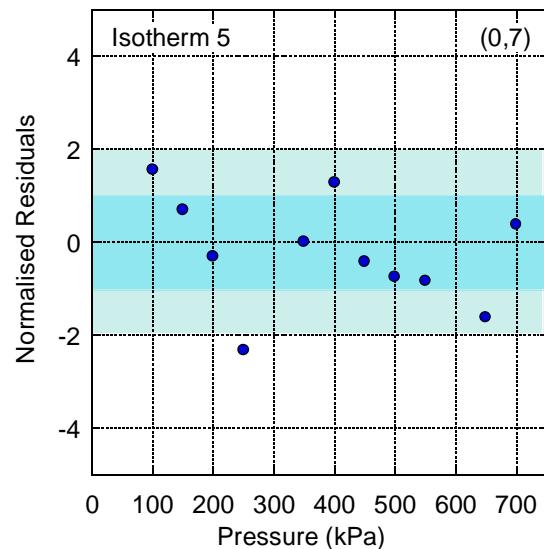
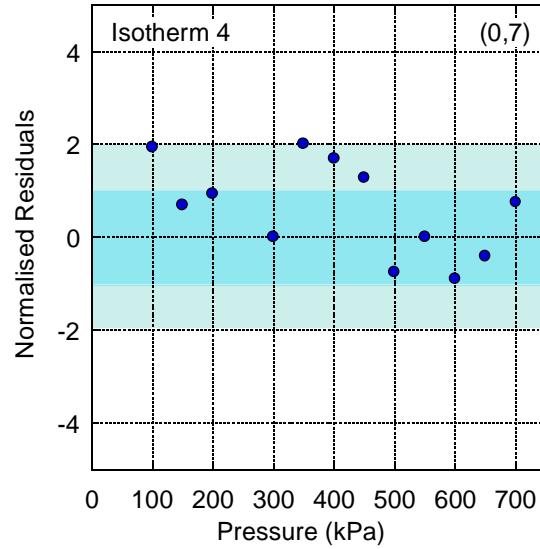
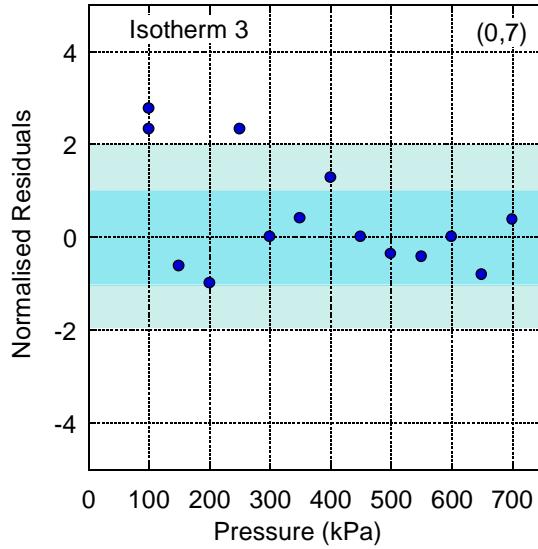
Normalised Residuals from Global Fit: (0,3)



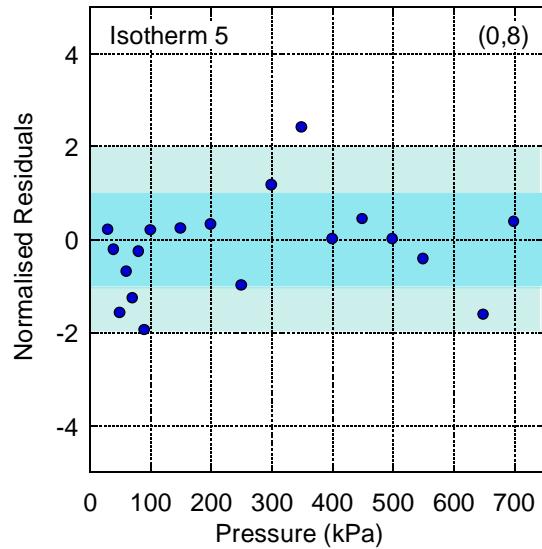
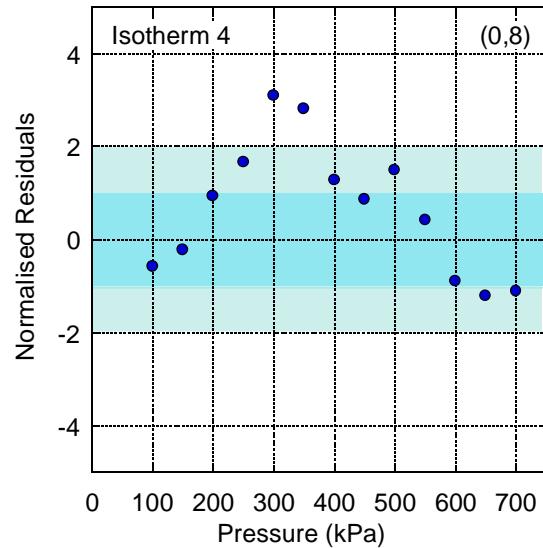
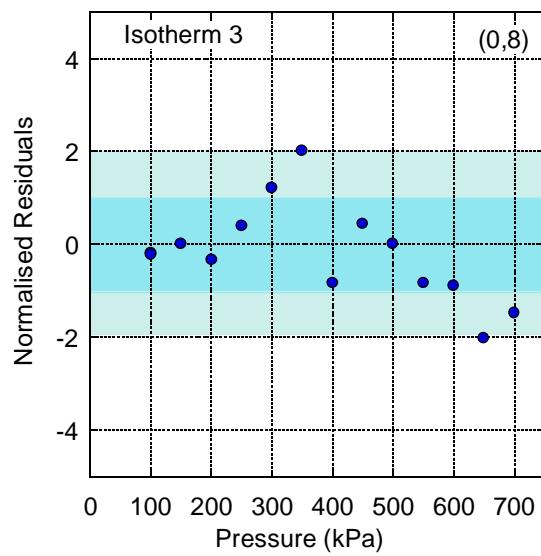
Normalised Residuals from Global Fit: (0,4)



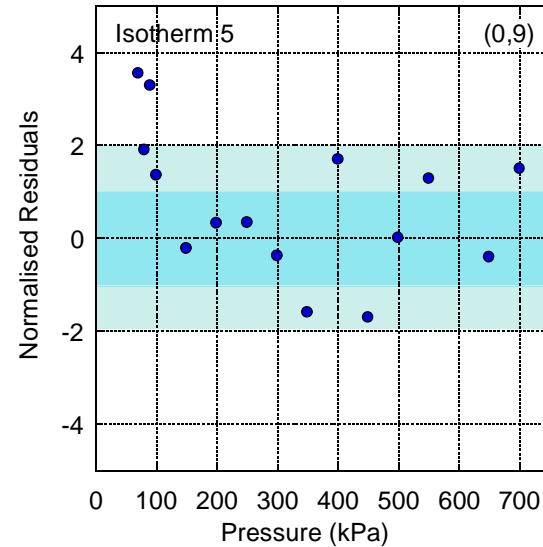
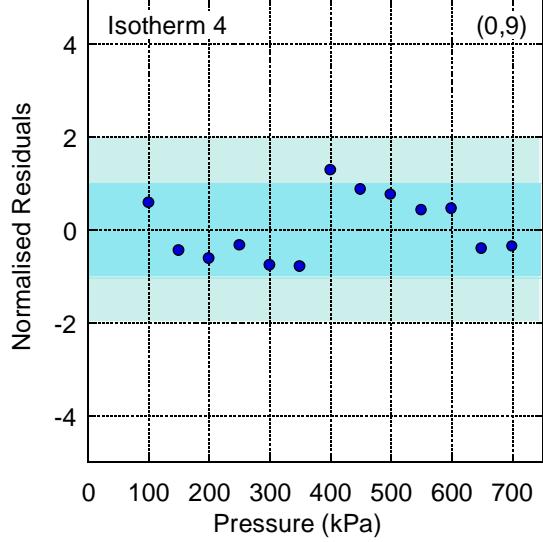
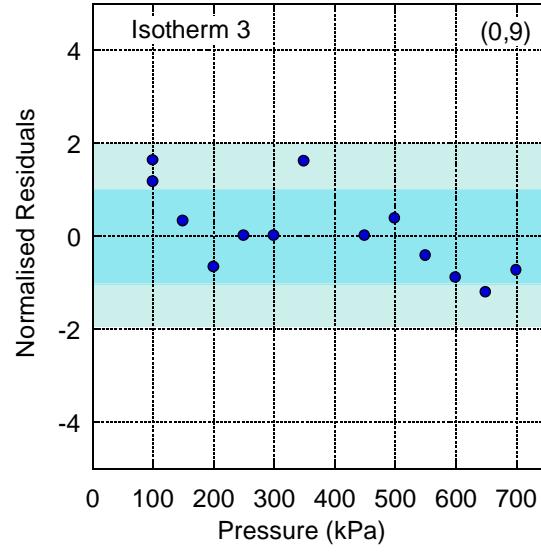
Normalised Residuals from Global Fit: (0,7)



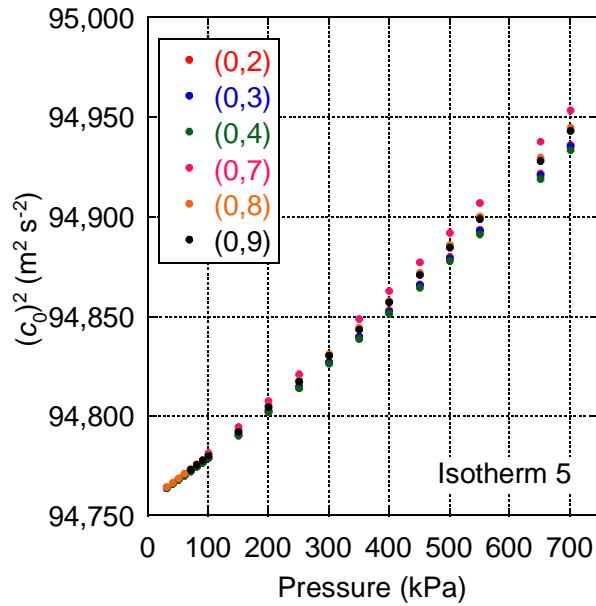
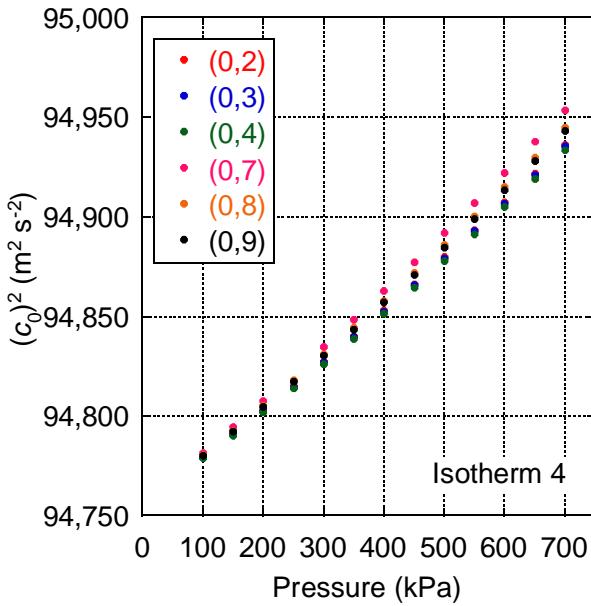
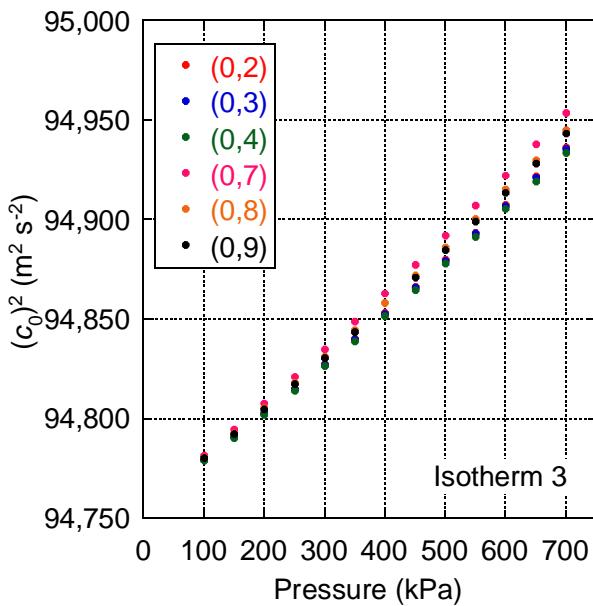
Normalised Residuals from Global Fit: (0,8)



Normalised Residuals from Global Fit: (0,9)



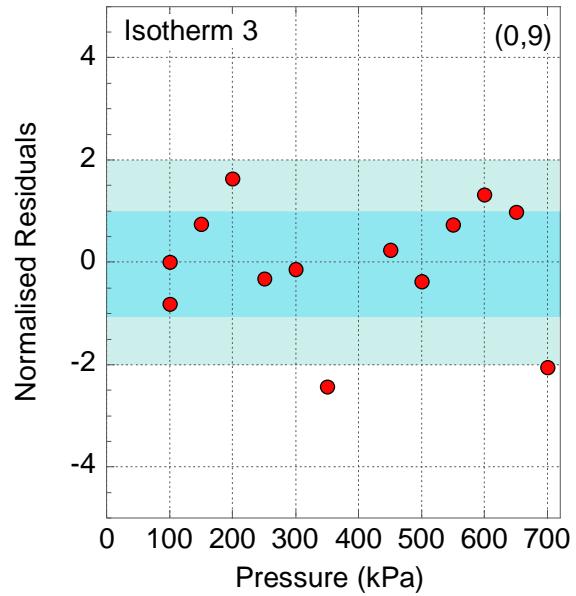
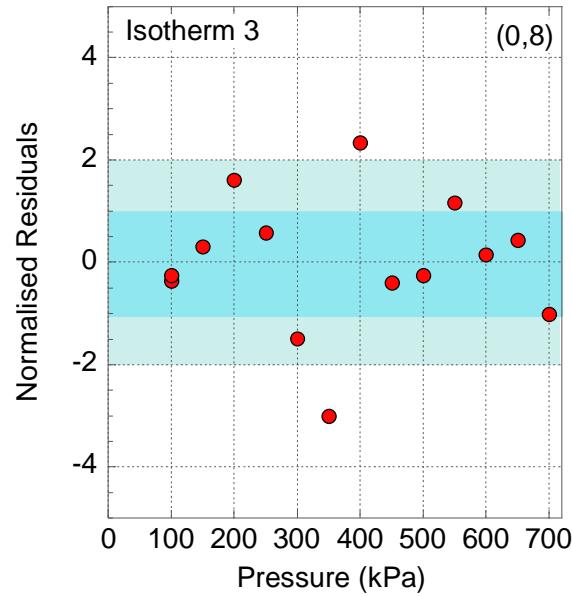
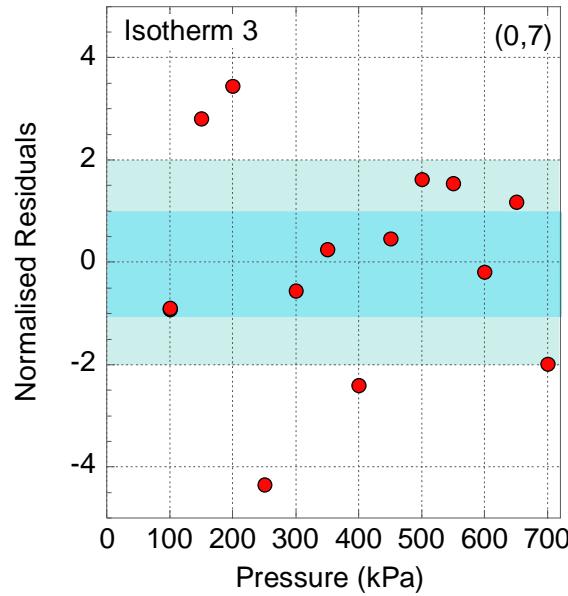
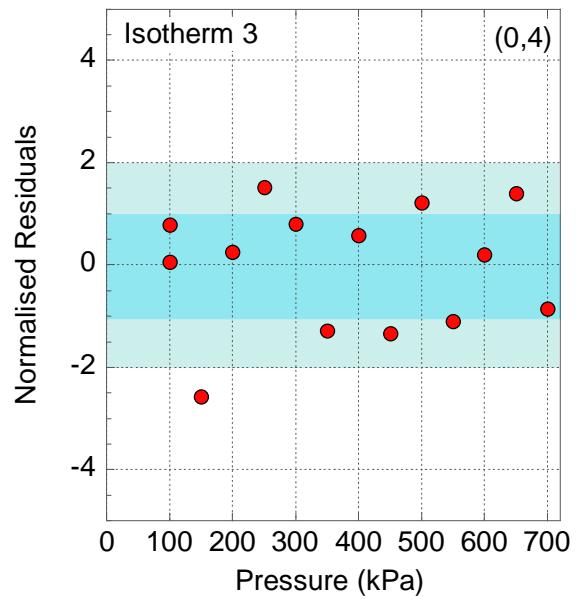
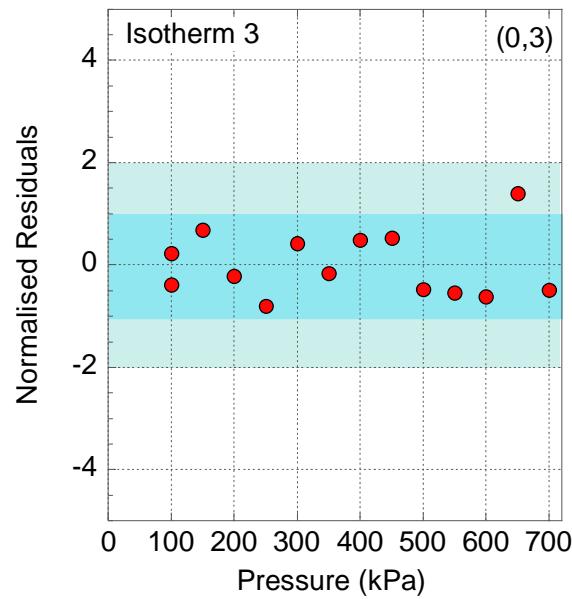
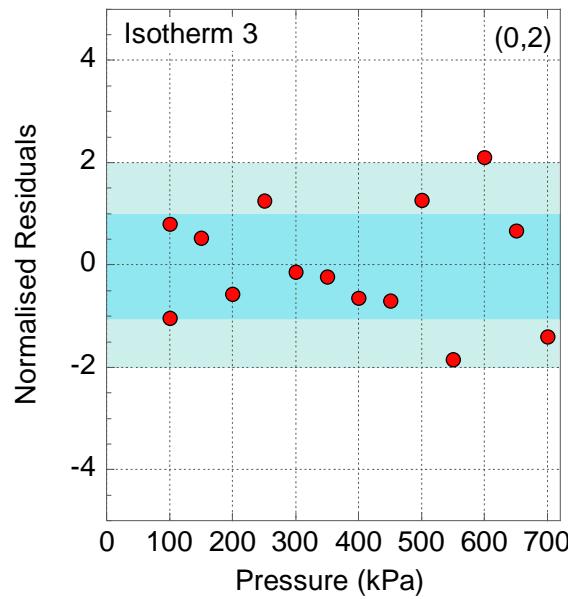
Alternative Analysis



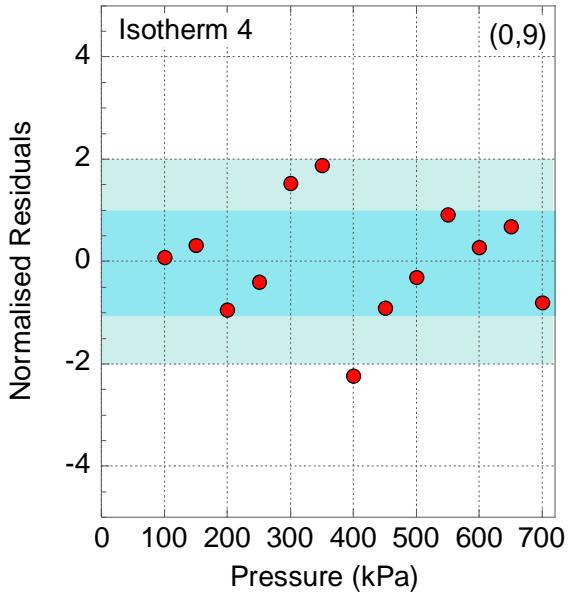
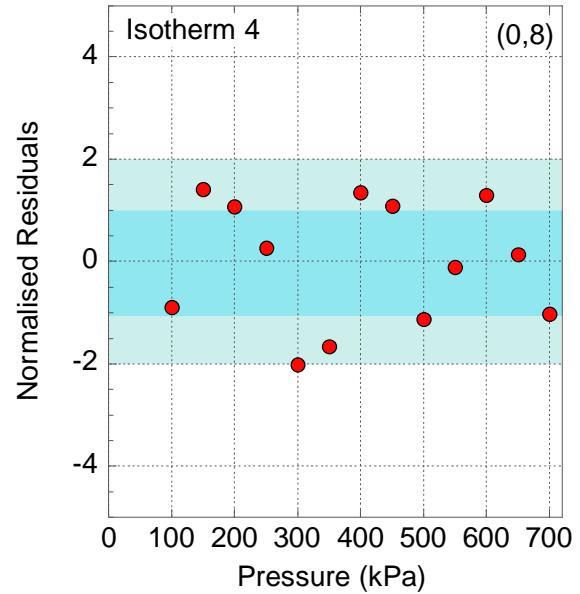
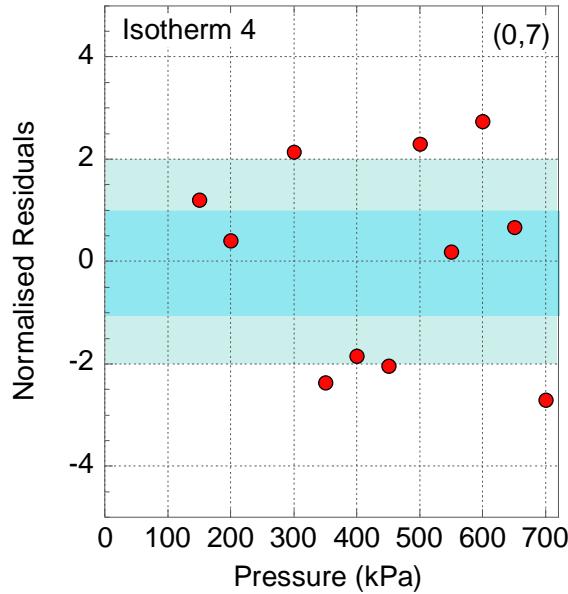
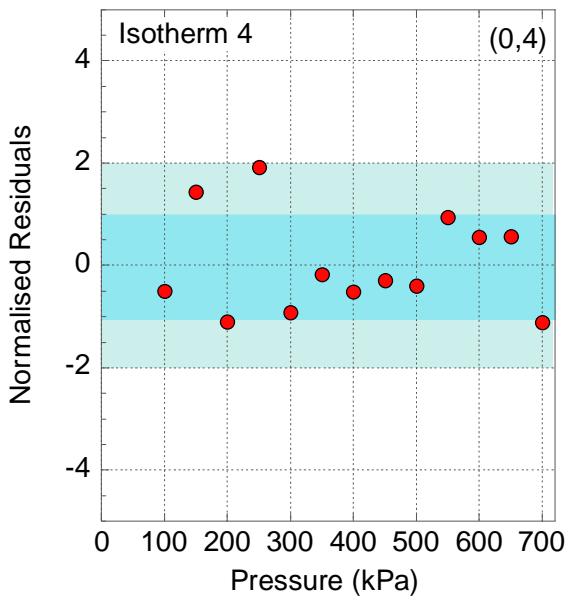
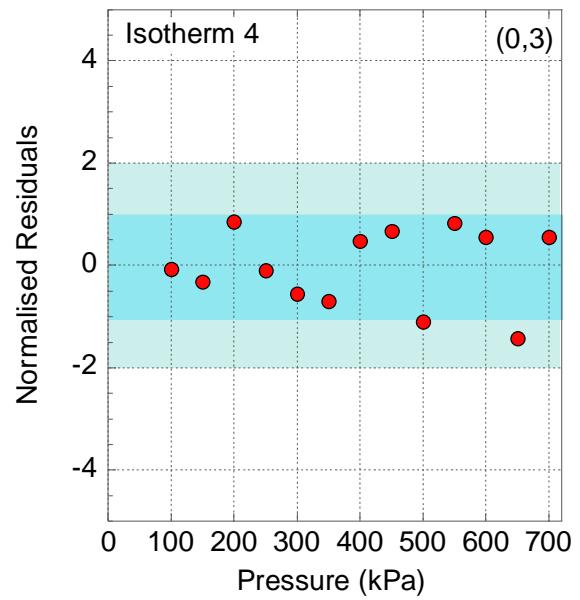
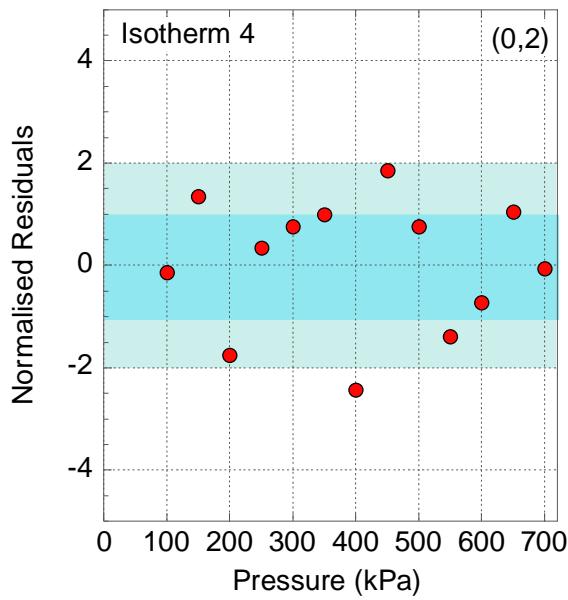
$$c_{EXP}^2 - A_3 P^3 = c_0^2 + A_{-1} P^{-1} + A_1 P + A_2 P^2$$

- Treat each of 18 isotherm/modes independently
- Gives 18 estimates for c_0^2 instead of 1
- Gives 18 estimates for A_1 instead of 6
- Gives 18 estimates for A_2 instead of 1

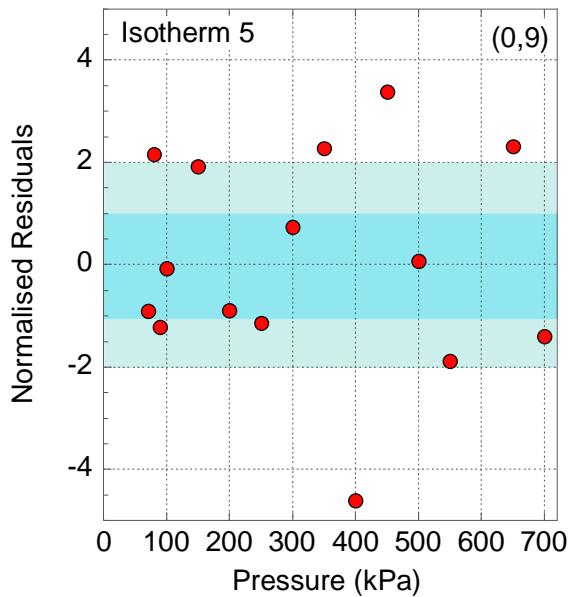
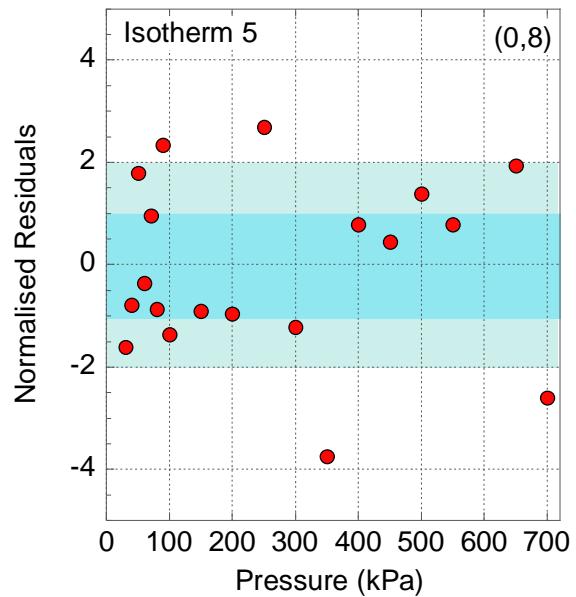
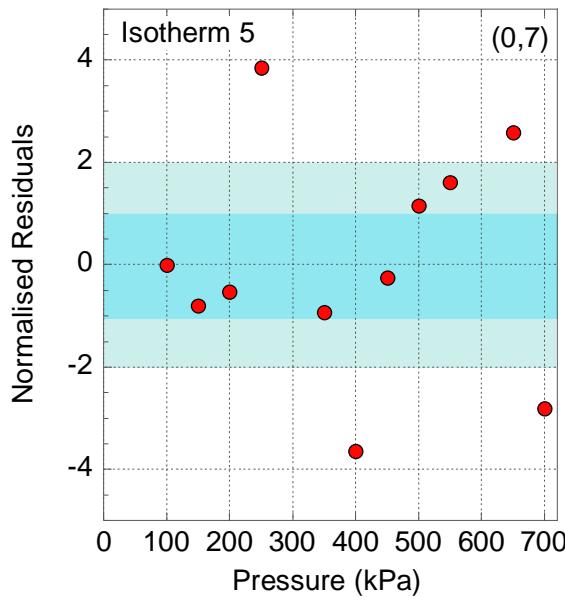
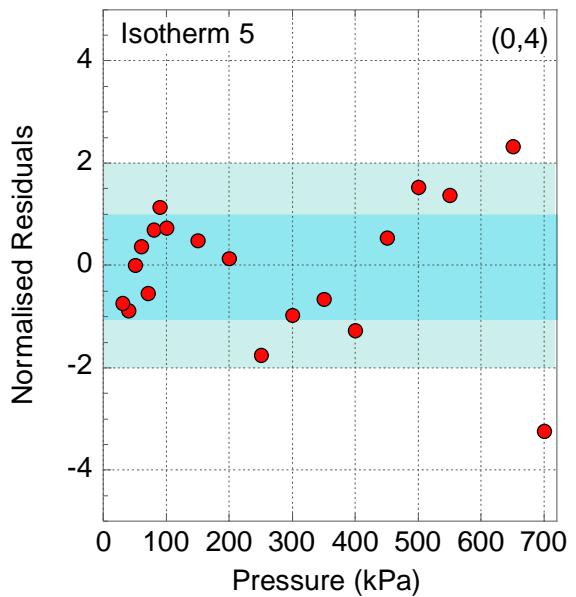
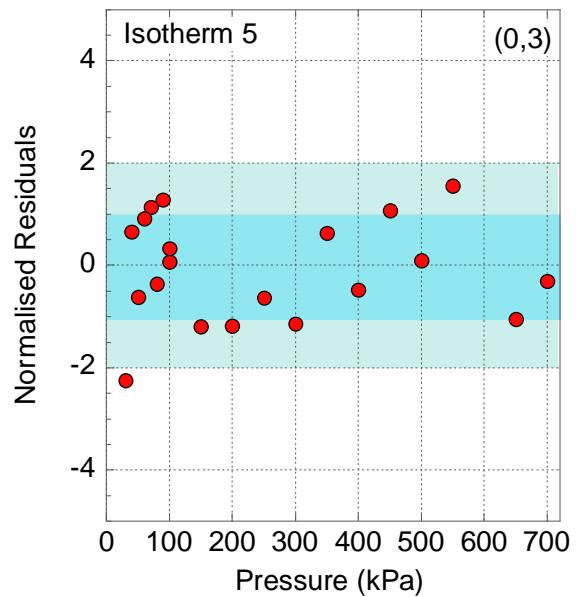
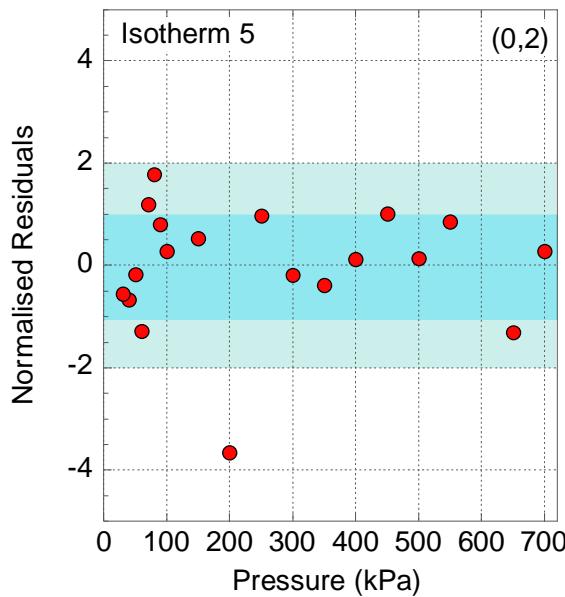
Normalised Residuals of Individual Fits: Isotherm 3



Normalised Residuals of Individual Fits: Isotherm 4

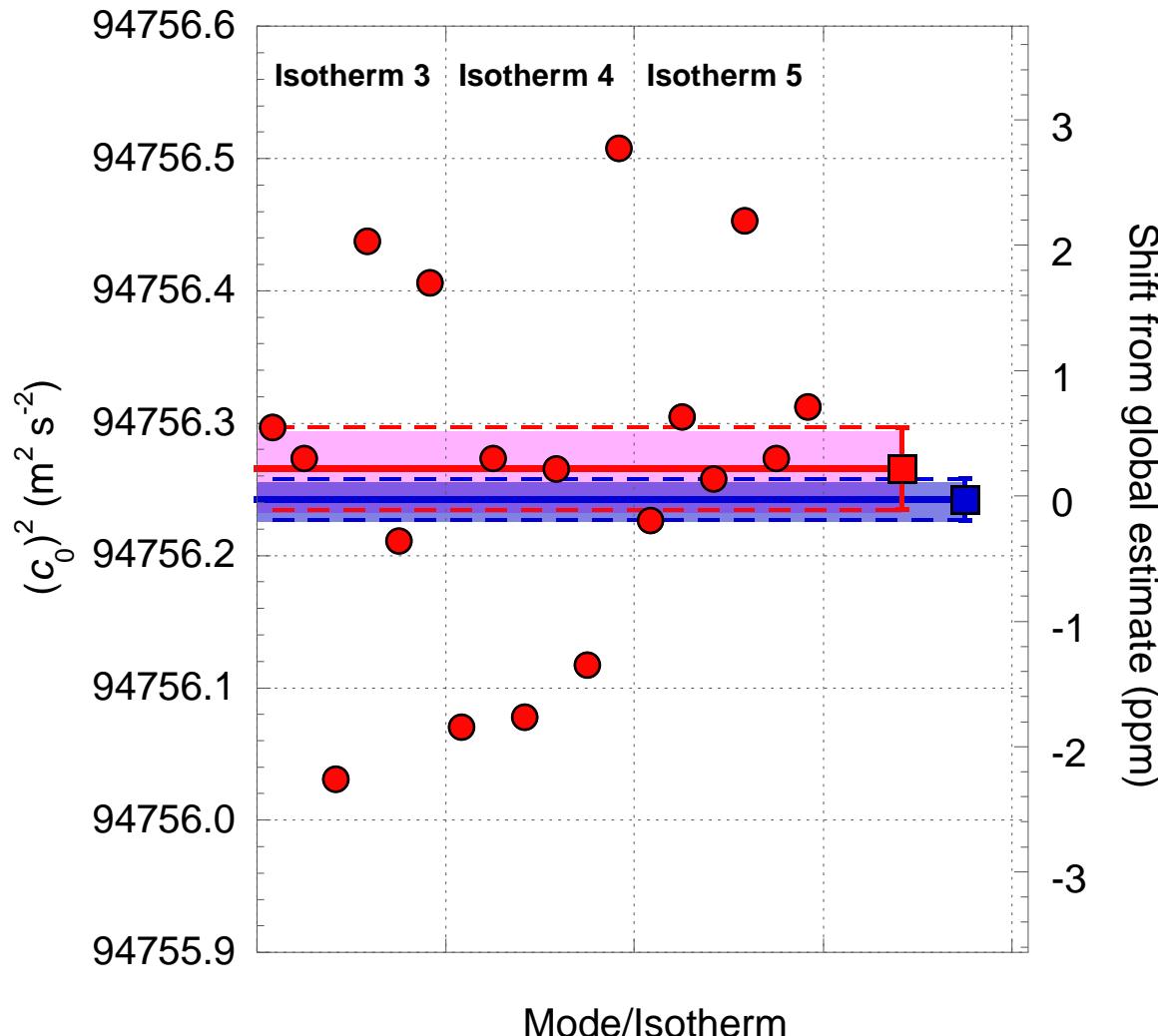


Normalised Residuals of Individual Fits: Isotherm 5



NPL Strengths#3: Alternative Analysis

- Fit each isotherm individually and produce 18 estimates for c_0^2 .
- Average value is $\sim 0.25 \text{ ppm}$ higher than 'global' estimate ($+1.4u$)



Reflections on the NPL-2013 Estimate of the Boltzmann Constant

- 1. Background**
- 2. History**
- 3. The NPL uncertainty estimate**
- 4. NPL Update February 2015**
- 5. The NPL Analysis**
- 6. Summary**

Summary

1. NPL-2013 estimate of k_B has $u_R = 0.71 \times 10^{-6}$
2. Differs significantly from LNE-CNAM-2011
3. Significant differences in analytical assumptions and estimated sensitivity to errors
4. Possible reconciliation is through a molar mass error by either NPL or LNE-CNAM.
5. Time will tell.

BOLTZMANN DN

BOLTZMANN AS