THE BOLTZMANN CONSTANT
FROM THE SPEED OF SOUND
IN A NON-QUITE SPHERICAL CAVITY

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Measurement of the Boltzmann Constant

The situation in 2008

Uncertainty is 7 times lower compared to the other results

Colclough, Quinn, and Chandler.

Moldover et al.

Schmidt et al.

Daussy et al.

He et al.

year


(k - k codata)/k codata \times 10^6
Uncertainty on the Boltzmann Constant

For the new definition of the kelvin, the relative uncertainty on the Boltzmann constant has to be < $1 \cdot 10^{-6}$

Codata 2006 Uncertainty on $k_B = 1.8$ ppm

<table>
<thead>
<tr>
<th>Uncertainty on $k_B$, $k=1$, ppm of $k_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>April 2009</td>
</tr>
<tr>
<td>(Volume)$^{2/3}$</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Molecular weight</td>
</tr>
<tr>
<td>Zero-pressure limit of</td>
</tr>
<tr>
<td>$(f_n + \Delta f_n)^2$</td>
</tr>
<tr>
<td>Repetability</td>
</tr>
</tbody>
</table>

April 2008 and April 2009: LNE-CNAM determinations, 0.5 L quasi-spherical copper resonator, hand polished inner surface, filled with helium

In 2009, the LNE-CNAM has set up a new 0.5 L quasi-spherical copper resonator with a diamond turned inner surface

* Pre print L. Pitre, F. Sparasci, D. Truong, A. Guillou, L. Risegari, M. E. Himbert, »Measurement of the Boltzmann Constant $k_B$ using a Quasi-Spherical Acoustic Resonator », the article have been sent to IJOT the 31/12/2010
Acoustic Determination of the Boltzmann Constant

Principle of the experiment

For real gas:

\[ U_A^2 = \gamma \frac{kT}{m} \left(1 + \beta_a(T) p + \ldots\right) \]

Boltzmann constant

specific heats ratio

acoustic virial coefficient

atomic mass

\[ U_{\text{exp}}(\text{ms}^{-1}) = \sqrt{\frac{5kT}{3m}} \]

Gas helium

Pressure (MPa)

Laboratoire Commun de Métrologie LNE-CNAM
Simultaneous acoustic ($u$) and microwave ($c$) resonances in a cavity

**Acoustic resonances measurement**
⇒ Boltzmann constant but linked to a volume

**Microwave resonances measurement**
⇒ Volume measurement

Gas flow minimizes the effects of impurities

Non-quite spherical simplify the microwave measurements
Acoustic Determination of the Boltzmann Constant

Relationship between the Boltzmann constant
and acoustic/microwave measurements

\[ k_B = \left( \frac{3}{5} \frac{m c_0^2}{T_{tp,water}} \left( \frac{Z_{nl}^E M}{Z_{nl}^A} \right)^2 \right) \left\{ \lim_{p \to 0} \left( \frac{< f_{nl}^A + \Delta f_{nl}^A >}{< f_{nl}^E M + \Delta f_{nl}^E M >} \right)^2 \right\} \]

- Gas atomic mass
- Speed of light in vacuum (exact)
- Measured resonance frequency
- Correction (theory)
- Quasi-sphere’s eigenvalues
- Polynomial extrapolation to Zero pressure limit
- Ratio: removes artefact effects at the first order
- Average over measured acoustic and electromagnetic modes
A Non-Quite Spherical Cavity

- The use of a slightly deformed spherical geometry, a triaxial ellipsoid, removes the degeneracy of resonator modes

\[
\frac{x^2}{(49.950)^2} + \frac{y^2}{(49.975)^2} + \frac{z^2}{(50.000)^2} = 1
\]

**Inner shape:** the difference between \(r\), \(R\) and \(H\) is 0.025 mm:

- \(H = 50.000\) mm
- \(R = 49.975\) mm
- \(r = 49.950\) mm

\[k_B = \frac{3}{5} \frac{mc_0^2}{T_{tp,water}} \left( \frac{Z_{nl}^{EM}}{Z_{nl}^A} \right)^2 \lim_{p \to 0} \left( \frac{<f_{nl}^A + \Delta f_{nl}^A>}{<f_{nl}^{EM} + \Delta f_{nl}^{EM}>} \right)^2\]
A Non-Quite Spherical Cavity

- The use of a slightly deformed spherical geometry, a triaxial ellipsoid, removes the degeneracy of resonator modes

Electromagnetic measurements in very good agreement with the theoretical model

Acoustic measurements in a good agreement with the theoretical model

\[ k_B = \left( \frac{3}{5} \frac{mc^2}{T_{tp,water}} \left( \frac{Z_{EM}}{Z_{nl}^A} \right)^2 \lim_{p \to 0} \left( \frac{< f_{nl}^A + \Delta f_{nl}^A >}{< f_{nl}^EM + \Delta f_{nl}^EM >} \right)^2 \right) \]
Measurement of the Volume

\[ \text{Radius} = \frac{\frac{Z_{nl}^{EM}}{c}}{2\pi < f_{nl}^{EM} > + \Delta f_{nl}^{EM}} \]

Eigenvector \quad Speed of light

Resonance frequency \quad Skin depth

Holes and Antennas effect

Cooperation between LNE-CNAM, NPL and Jim Mehl


\[ k_B = \sqrt{\frac{3}{5} \frac{m c_0^2}{T_{ip,water}} \left( \frac{Z_{nl}^{EM}}{Z_{nl}^A} \right)^2 \lim_{p \to 0} \left( \frac{< f_{nl}^A + \Delta f_{nl}^A >}{< f_{nl}^{EM} + \Delta f_{nl}^{EM} >} \right)^2} \]
Measurement of the Volume

- Comparison of the microwave technique to CMM measurements
- Use of a CMM as a comparator
- Cooperation between LNE-CNAM, NPL, INRiM, UWA, Jim Mehl

\[ k_B = \left( \frac{3}{5} \frac{mc_0^2}{T_{tp,\text{water}}} \left( \frac{Z_{nl}^{EM}}{Z_{nl}^{A}} \right)^2 \right)^2 \lim_{p \to 0} \left( \frac{\langle f_{nl}^A + \Delta f_{nl}^A \rangle}{\langle f_{nl}^{EM} + \Delta f_{nl}^{EM} \rangle} \right)^2 \]

Acoustic Field Modeling

A new model for the acoustic field was developed with coupling effect.

Cooperation between LNE-CNAM and the Acoustics Laboratory LAUM

New model gives the same results as the acoustic model used by NIST for the determination of $k_B$

Pressure field


$$k_B = \left\langle \frac{3}{5} \frac{mc^2}{T_{tp,water}} \left( \frac{Z_{EM}^{nl}}{Z_{nl}^A} \right)^2 \lim_{p \to 0} \left( \frac{f_{nl}^A \pm f_{nl}^A}{f_{EM} \pm f_{EM}} \right) \right\rangle$$
Characterization of the microphones

- Acoustic measurements are performed with ¼” condenser microphones
- Microphones are extensively modeled and characterized in air at ambient temperature and static pressure, ≠ from experimental conditions of the Boltzmann project
- Microphone calibrations have been performed in pure helium and argon gas at ~ 273 K, between 10 kPa and 600 kPa
- A good agreement between microphone literature model and experimental data has been found
- Cooperation between LNE-CNAM and INRiM

Acoustic Field Modeling

Comparison between measured half-width and calculated from thermal physical propriety of helium gas and acoustic model

$2 \times 10^6 (g_{\text{meas}} - g_{\text{cal}})/f$

Mode 03

Mode 04

Mode 05

Mode 06

Density (mol/m$^3$)

No fitted parameter at 273.16K helium gas

$k_B = \left\langle \frac{3}{5} \frac{mc^2}{T_{\text{lp, water}}} \left( \frac{Z_{n}^{EM}}{Z_{n}^{A}} \right)^2 \lim_{p \to 0} \left( \frac{<f_{nl}^{A} + \Delta f_{nl}^{A}>}{<f_{nl}^{EM} + \Delta f_{nl}^{EM}>} \right)^2 \right\rangle$
Thermal Cartography of the Resonator

Four capsule thermometers

- \( C_1, Ar, \Delta T = 7.21 \text{ mK} \)
- \( C_1, Ar, \Delta T = 6.59 \text{ mK} \)
- \( C_1, Ar, \Delta T = 8.66 \text{ mK} \)
- \( C_1, Ar, \Delta T = -15.68 \text{ mK} \)
- \( C_2, Ar, \Delta T = 65.21 \text{ mK} \)
- \( C_2, Ar, \Delta T = 69.86 \text{ mK} \)
- \( C_2, \text{He}, \Delta T = 8.00 \text{ mK} \)
- \( C_2, \text{He}, \Delta T = -223.07 \text{ mK} \)

\[
k_B = \left\langle \frac{3}{5} mc_0^2 \left( \frac{Z_{EM}^{nl}}{Z_{nl}^A} \right)^2 \lim_{p \to 0} \left( \frac{f_{nl}^A + \Delta f_{nl}^A}{f_{nl}^{EM} + \Delta f_{nl}^{EM}} \right) \right\rangle
\]
We need to remove impurities from Ar ➔ use of a getter and a cold trap

### Impurities in a Ar sample (IRMM)

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>&lt; (2 ± 2) ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>&lt; (150 ± 100) ppb</td>
</tr>
<tr>
<td>H₂O</td>
<td>&lt; (600 ± 500) ppb</td>
</tr>
<tr>
<td>CO₂</td>
<td>&lt; (0.5 ± 0.5) ppm</td>
</tr>
<tr>
<td>H₂</td>
<td>not measured</td>
</tr>
<tr>
<td>THC</td>
<td>&lt; (0.5 ± 0.5) ppm</td>
</tr>
<tr>
<td>He</td>
<td>&lt; (1± 1) ppm</td>
</tr>
<tr>
<td>Ne</td>
<td>&lt; (1± 1) ppm</td>
</tr>
<tr>
<td>Kr</td>
<td>not measured</td>
</tr>
<tr>
<td>Xe</td>
<td>not measured</td>
</tr>
</tbody>
</table>

### Ar isotopic composition (IRMM)

- \( r \left( ^{36}\text{Ar} / ^{40}\text{Ar} \right) = 0.003 \, 346 \, 0 \) (15)
- \( r \left( ^{38}\text{Ar} / ^{40}\text{Ar} \right) = 0.000 \, 634 \, 77 \) (26)

- 0.1 ppm uncertainty on \( k_B \)

\[
k_B = \left( \frac{3}{5} \right) \left( \frac{m_0}{T_{p,\text{water}}} \right) \left( \frac{Z^A}{Z^{EM}_{nl}} \right)^2 \lim_{p \to 0} \left( \frac{f^A_{nl} + \Delta f^A_{nl}}{f^{EM}_{nl} + \Delta f^{EM}_{nl}} \right)
\]
We need to remove impurities from Ar – use of a getter and a cold trap

Impurities in a Ar sample (IRMM)

<table>
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<tr>
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<td>not measured</td>
</tr>
<tr>
<td>Xe</td>
<td>not measured</td>
</tr>
</tbody>
</table>

\[
k_B = \left\langle \frac{3 m e^2}{5 T_{p,\text{water}}} \left( \frac{Z_{nl}^{EM}}{Z_{nl}^A} \right)^2 \lim_{p \to 0} \left( \frac{\langle f_{nl}^A + \Delta f_{nl}^A \rangle}{\langle f_{nl}^{EM} + \Delta f_{nl}^{EM} \rangle} \right)^2 \right\rangle
\]
We need to remove impurities from Ar ➔ use of a getter and a cold trap

Impurities in a Ar sample (IRMM)

- N₂: < (2 ± 2) ppm
- O₂: < (150 ± 100) ppb
- H₂O: < (500 ± 500) ppb
- CO₂: < (0.5 ± 0.5) ppm
- H₂: not measured
- THC: < (0.5 ± 0.5) ppm
- He: < (1± 1) ppm
- Ne: < (1± 1) ppm
- Kr: not measured
- Xe: not measured

\[
k_B = \left\langle \frac{3}{5} \frac{m c^2_0}{T_{tp, water}} \left( \frac{Z_{nl}^{EM}}{Z_{nl}^A} \right)^2 \lim_{p \to 0} \left( \frac{< f_{nl}^{A} + \Delta f_{nl}^{A} >}{< f_{nl}^{EM} + \Delta f_{nl}^{EM} >} \right)^2 \right\rangle
\]
Ar Molar Mass Evaluation

Ultra clean gas handling system and quasi sphere

The out gassing is less than 4.5 ppb of water
Or 700 picomol/mol
# Uncertainty Budget

## Uncertainty budget on the Boltzmann constant with 0.5 liter cavity in argon

### Uncertainty on \( k_B, k=1, \text{ppm of } k_B \)

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume</strong></td>
<td>0.57</td>
<td>Holes and antenna effect, Dispersion over mode-shape, Conductivity, Uncertainty on frequency measurements</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>0.3</td>
<td>Calibration, Dispersion over thermometers, Uncertainty on resistance measurements</td>
</tr>
<tr>
<td><strong>Molecular weight</strong></td>
<td>0.6</td>
<td>Isotopic ratio, Cold trap experiment, Getter experiment, Impurity, Uncertainty on measurements</td>
</tr>
<tr>
<td><strong>Zero-pressure limit of</strong> ((f_n + \Delta f_n)^2)</td>
<td>0.8</td>
<td>Thermophysical properties of argon, Scatter among modes, Accommodation coefficient dispersion, Flow, Tubing acoustic impedance, Shell</td>
</tr>
<tr>
<td><strong>Repeatability</strong></td>
<td>0.12</td>
<td>Two isotherms</td>
</tr>
<tr>
<td><strong>Root of Sum of Squares</strong></td>
<td>1.19</td>
<td></td>
</tr>
</tbody>
</table>
Boltzmann Constant Determinations at LNE-CNAM

\[ k_B = (1.3806495 \pm 0.0000037) \times 10^{-23} \text{J/K} \]

**Helium** gas, 0.5 liter resonator, surface polished by hand

**Argon** gas, 0.5 liter resonator, surface diamond turned

uncertainty of \( k_B \), \( k = 1 \), ppm of \( k_B \)

\[ k_B = (1.3806476 + 0.0000016) \times 10^{-23} \text{J/K} \]
A 3.1 L Non-Quite Spherical Cavity

3.1 L diamond turned copper triaxial ellipsoid

- The resonator should give even better acoustic, electromagnetic and CMM measurements
- The thermostat is improved
- Experiment planned for this year
The Quasi Spherical Resonator, a New Jackknife for the Metrology?

- Primary Thermometer (LNE-CNAM and NPL)
- Atomic Standard of Pressure (NIST)
- Humidity measurement (INRiM and LNE-CNAM)