Time evolution of the thermodynamic temperature scale

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CCT Meeting Session 5

February 9th, 2021
Outline

Reflection on the historical development of:
• The concept of temperature
• Its measurement scales

➢ Part 1:
• Main milestones in the path to our current understanding of the thermodynamic temperature and its measurement scale
• Basic concepts of measurement theory

➢ Part 2:
• Evolution of the thermodynamic temperature scale over the past 100 years

➢ Conclusions
The definition of thermodynamic temperature

➢ BIPM website:

• SI unit of thermodynamic temperature

  o How SI unit is defined:
    “by taking the fixed numerical value of k to be \(1.380649 \times 10^{-23} \text{ JK}^{-1}\)”

  o How SI unit is realized
    → Mise en pratique
The definition of thermodynamic temperature

How is thermodynamic temperature defined?

- **Phenomenological approach (Kelvin, 1854):**
  - Principles of classical thermodynamics
    
    \[
    \frac{Q_1}{Q_2} = \frac{T_1}{T_2}
    \]

- **Axiomatic approach (Caratheodory, 1909):**
  - Mathematical theorem on differential forms
  - Demonstrates the existence of temperature as an integrating factor \( \tau(x, y, z) \) for \( dQ \)
    
    \[
    \frac{dQ}{\tau} = dS
    \]

- **Microscopic approaches:**
  - Kinetic theory of gases
    
    \[
    E_{\text{Kin}} = \frac{3}{2} kT
    \]
  - **Statistical mechanics**
    
    \[
    P(E)dE = \Omega(E) \exp\left(-\frac{E}{kT}\right)
    \]
  - Quantum mechanics
    
    \[
    P(E)dE = \frac{1}{\exp\left(\frac{E-\mu}{kT}\right)^{\pm1}}
    \]
Part 1

Major milestones that led to the modern definition of thermodynamic temperature
Thermal equilibrium and zeroth principle

- **Thermal equilibrium:**
  
  Two thermodynamic systems A and B are in thermal equilibrium if:
  
  *when they are brought into mutual thermal contact,*
  
  *they continue to be in the states in which they were prior to the establishment of thermal contact.*

- **Zeroth Principle:**
  
  If A is in thermal equilibrium with C and B is in thermal equilibrium with C,
  
  Then A and B are in thermal equilibrium with each other.
Thermal equilibrium and zeroth principle

- Provide a procedure to determine equality of temperatures:
  two systems $A$ and $B$ have the same temperature if they are in thermal equilibrium
  (when they are brought into mutual thermal contact…)
  - Given any two systems $A$ and $B$, you can determine whether $t_A = t_B$ or $t_A \neq t_B$

Measurement theory (Stevens, 1946)

- We can already create a 1st simple type of measurement scale

- Nominal scale: can establish equality
  - Example: numbers on the uniforms of football players
    - Numbers are used as names, the actual number has no meaning
      (number 10 is not two times better than number 5)
2nd principle of thermodynamics

- Provides a procedure to order temperatures
- We can label each temperature with a serial number but we cannot assign a value to it:
- Hotness series: \( \{h\} = \{h_1, h_2, h_3, \ldots h_k, \ldots\} \)

Measurement theory

- We can create a 2nd (more interesting) type of measurement scale
- **Ordinal scale**: can establish equality and order
  - Not only \( h_i = h_j \) or \( h_i \neq h_j \)
  - But also: \( h_i > h_j \) or \( h_i < h_j \)
Empirical temperature scales

- Empirical temperature scale:
  any order-preserving one-to-one mapping of the hotness series:
  \[ t : h \rightarrow \mathbb{Q} \]

- Non-uniqueness of empirical temperature scale:
  if \( t \) is an empirical temperature scale, then
  any monotonic function \( f(t) \) is also an empirical temperature scale

Measurement theory:
- Empirical temperature scales are ordinal scales:
  - Historic Fahrenheit mercury-based scale
  - Historic Celsius mercury-based scale
  - Callendar scale
  - ITS-27, ITS-48, IPTS-68 and ITS-90
Celsius mercury-based centigrade scale

- Celsius mercury-based centigrade scale (1741):
  - Put a mark $P_1$ corresponding to ice point
  - Put a mark $P_2$ corresponding to steam point
  - Divide the interval $P_1P_2 = D$ into 100 equal intervals

- It is a perfectly defined ordinal scale:
  - It preserves equality and order
  - It does not preserve equal intervals (equal intervals do not correspond to equal differences in hotness)

- Assumes $t = 100 \cdot \frac{d}{D}$ (mercury does not expand linearly on temperature)
Carnot theorem (1824)

- Carnot theorem (1824): all Carnot engines (reversible cyclic heat engines) that operate between two thermostats at temperatures $t_1$ and $t_2$ have the same efficiency

$$\eta_R \equiv \frac{W}{Q_1} = 1 + \frac{Q_2}{Q_1}$$

$$\frac{Q_1}{Q_2} = f(t_1, t_2)$$

$$\frac{Q_1}{Q_2} = \frac{F(t_1)}{F(t_2)}$$

- The ratio of the heats exchanged by the two thermostats is equal to the ratio of the same universal function of $t$, at $t_1$ and $t_2$
Thomson’s proposal (1848)

- A cascade of Carnot engines, each producing the same mechanical work \( W \), would operate between thermostats separated by the same temperature interval \( \Delta T \):

\[
T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \ldots = \Delta T
\]

- Each degree of temperature produces the same amount of mechanical work at any \( T \) → Preserves equal intervals of hotness
- Absolute (independent from the physical properties of the working fluid)

Measurement theory:
- Thomson 1\textsuperscript{st} proposal belongs to a 3\textsuperscript{rd} type of measurement scale:

- \textbf{Interval scale} can establish:
  - Equality
  - Order
  - Equal intervals
  - Arbitrary zero
Thomson’s proposal (1854):

- make the simplest possible choice for $F$ in
  \[ \frac{Q_1}{Q_2} = \frac{F(t_1)}{F(t_2)} \]
- $F(t) \equiv t \quad t \to T \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

Measurement theory:
- Thermodynamic temperature scale is a 4\textsuperscript{th} type of measurement scale
- Rational scale:
  - Equality
  - Order
  - Equal Intervals
  - Equal ratios
  - Natural zero
Evolutionary path of temperature scales

**Nominal scale:** Distinguished only between cold and warm

- Snow is cold, fire is hot

**Ordinal scale:** Different degrees of warmer and colder introduced

- 1724: Fahrenheit scale
- 1741: Celsius scale

**Rational scale:** Development of thermodynamics

\[
\frac{Q_1}{Q_2} = \frac{T_1}{T_2}
\]

- 1854: Kelvin thermodynamic scale \( T_{TP} = 273.16 \) K

**Interval scale:** Development of thermodynamics

- 1848: Thomson scale
- Modern Fahrenheit scale
- Modern Celsius scale

Evolution: the more we learnt about temperature and its true nature, the more the scale was able to encode the structure of temperature in the numbers we used to measure it.
A measurement scale is a correspondence between:
- the space of the quantity/magnitude/entity (hotness $h_i$)
- the space of the numbers attributed to the quantity ($t_i$)

**Measurement scale: assigns numbers to a quantity**
- Relations exhibited by numbers (equality, difference, ratio, …) do not always correspond to meaningful relations among the quantities measured by those numbers
- Numbers are adequate for expressing quantities only when the correspondence is one-to-one (homomorphism)
### Types of measurement scale (Stevens, 1946)

<table>
<thead>
<tr>
<th>Scale</th>
<th>Mathematical operations among numbers</th>
<th>Allowed scale transformations $f: x \rightarrow f(x)$</th>
<th>Examples</th>
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<tbody>
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<td>Nominal</td>
<td>equality</td>
<td>$f$ any 1:1 function</td>
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<td>$f: x \rightarrow ax + b$</td>
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### Operations

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- **Scale operations with modern Celsius scale (interval scale)**
  - If we have 18 °C in Paris and 9 °C in Moscow, does it make sense to say that temperature in Paris is twice that in Moscow?
  - If we have 18 °C in Paris, 9 °C in Moscow, 32 °C in Bangkok and 23 °C in Los Angeles, does it make sense to say that $T_{Paris} - T_{Moscow} = T_{Bangkok} - T_{LosAngeles}$
# Transformations

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- **Scale transformations**
  - Interval scale: from modern Celsius to Fahrenheit by applying $a = 9/5$ and $b = 32$
  
  - Rational scale: in Kelvin thermodynamic scale change the triple point of water from 273.16 K to 7 K* by applying $a = 7/273.16$
Part 2

Evolution of the thermodynamic temperature scale
Before 1927:
- The unit of thermodynamic temperature was defined by fixing a temperature difference of 100 degrees Celsius between the ice point and the steam point.
1927:
- The “Thermodynamic Celsius Scale” attributed 0 °C and 100 °C to the ice point and the steam point, respectively.
- The Thermodynamic Kelvin Scale was established based on a temperature difference of 100 K between the ice point and the steam point.
1927:
- The International Temperature Scale of 1927 (ITS-27) attributed 0 °C and 100 °C to the ice point and the steam point, respectively.
- The units of \( t \), \( T \) and \( t_{27} \) were identical
1948:
- The CGPM, on the advice of the CCT, accepted the principle of a thermodynamic temperature scale having a single fixed point provided by the TPW
- Problem: which numerical value should be attributed to the TPW?
1948:

- The interval between the ice point and the triple point was accurately known already at that time: 0.00993 °C
1948:
- It was already clear that, in the thermodynamic Celsius Scale, the TPW had to take the value of 0.01 °C
1948:

- Which value should be attributed to the absolute zero in the Thermodynamic Celsius Scale? (and, equivalently, what should the ice point value be in the Thermodynamic Kelvin Scale?)
- CCT not ready yet: the value was not known with sufficient accuracy
Evolution of the thermodynamic scale (8/12)

<table>
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<tr>
<th>Laboratory</th>
<th>Year</th>
<th>Measured</th>
<th>Recalculated</th>
<th>Proposed</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB</td>
<td>1929-1930</td>
<td>273.158</td>
<td>273.149</td>
<td>273.15</td>
</tr>
<tr>
<td>KOL</td>
<td>1934</td>
<td>273.147</td>
<td>273.149</td>
<td>273.15</td>
</tr>
<tr>
<td>TIT</td>
<td>1937-1942</td>
<td>273.144</td>
<td>273.148</td>
<td>273.15</td>
</tr>
<tr>
<td>MIT</td>
<td>1939-1952</td>
<td>273.174</td>
<td>273.174</td>
<td>273.17</td>
</tr>
</tbody>
</table>

Thermodynamic temperature of the ice point
*CCT, Session de 1954, Rapport et Annexes*

\[ u(\theta) = 0.01 \, ^{\circ}C \]
1954:

- $T_{TPW} = 273.16 \text{ K}$
- To preserve continuity with the past scale, the ice point and the steam point were kept at 0 °C and 100 °C, this time by convention not by definition.
Evolution of the thermodynamic scale (10/12)

- 1976: \( t_s = 99.974 \, ^\circ C \) \( (L.A. \text{ Guildner}, \ R.E. \text{ Edsinger}, \textit{J. Res. Natl. Bur. Stand.} \ 1976, \ 80A, \ 703-738)\)
  - The size of the kelvin in the new thermodynamic scale is different (larger) from the size of the kelvin in the old thermodynamic scale
  - To maintain \( T_i = 0 \, ^\circ C \) and \( T_S = 100 \, ^\circ C \) in the thermodynamic Celsius scale, the absolute zero should have been \(-273.22 \, ^\circ C\)
Evolution of the thermodynamic scale (11/12)

- 1927: Absolute zero
- 1948: Ice point
- 1954: Steam point
- 1976: Triple point

2019:
- $T_{TPW} = 273.16 \text{ K}$ not by definition (standard relative uncertainty $3.7 \cdot 10^{-7}$)
Evolution of the thermodynamic scale (12/12)

<table>
<thead>
<tr>
<th>Absolute zero</th>
<th>Ice point</th>
<th>Triple point</th>
<th>Steam point</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 °C</td>
<td>0 °C</td>
<td>0.01 °C</td>
<td>100 °C</td>
</tr>
<tr>
<td>(X) K</td>
<td>(X+0.01) K</td>
<td>(X+100) K</td>
<td></td>
</tr>
</tbody>
</table>

-273.15 °C -273.22 °C

<table>
<thead>
<tr>
<th>0 °C</th>
<th>0 °C</th>
<th>0.01 °C</th>
<th>100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15 K</td>
<td>273.16 K</td>
<td>373.15 K</td>
<td></td>
</tr>
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</table>

-273.15 K

<table>
<thead>
<tr>
<th>0 °C</th>
<th>0 °C</th>
<th>0.01 °C</th>
<th>100 °C</th>
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<tbody>
<tr>
<td>273.15 K</td>
<td>273.16 K</td>
<td>373.15 K</td>
<td>373.124 K</td>
</tr>
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</table>

-273.16 K (U = 202 µK)

273.160XX K (U < 202 µK)

1927

1948

1954

1976

2019

20XX

NATIONAL RESEARCH COUNCIL CANADA
Evolutionary path of temperature scales

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Conclusions

- What has changed since 2019:
  - in the thermodynamic temperature scale
  - in the definition of thermodynamic temperature that the scale assumes

- Type of scale: unchanged, still a rational scale
  - TPW value can change, without affecting the size of the kelvin (because the size of the kelvin is not linked anymore to the TPW value)

- Size of the unit: change not perceptible
  - 2 μK at TPW and 9 μK at Ag fixed point

- Definition (meaning) of temperature: basically unchanged
  - Temperature is the average thermal energy per degree of freedom in the system
  - Not only a thermodynamic temperature but also a statistical thermodynamic temperature
Acknowledgement

- Rod White (zoom discussions and correspondence)
- Richard Rusby (correspondence)
THANK YOU

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Consistency between the old and the new unit

- Old kelvin (before 20 May 2019):
  - TPW is the exactly known defining constant

- New kelvin (after 20 May 2019):
  - TPW is inexactly known

- $T_{TPW}$ does not depend on the SI unit adopted:

- Consistency factor $f$:

<table>
<thead>
<tr>
<th>CODATA 2017</th>
<th>$k_{old}$</th>
<th>$k_{new}$</th>
<th>$f$</th>
<th>µK at TPW</th>
<th>µK at Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>CODATA 2017</td>
<td>$1.38064901 \times 10^{-23}$</td>
<td>$1.380649 \times 10^{-23}$</td>
<td>1.000000007</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>CODATA 2014</td>
<td>$1.38064852 \times 10^{-23}$</td>
<td>$1.380649 \times 10^{-23}$</td>
<td>0.999999652</td>
<td>95</td>
<td></td>
</tr>
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</table>
Definition of the kelvin

The kelvin is:
the change of thermodynamic temperature that results in a change of mean thermal energy of $1.380649 \times 10^{-23}$ J for the molecules of the system

If $\langle E_2 \rangle - \langle E_1 \rangle = 1.380649 \times 10^{-23}$ J

$\rightarrow T_2 - T_1 = 1 \text{ K}$