

Temperature.nb

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■ 36.1. Question

Are there sensible alternatives to the *thermodynamic temperature*?

■ 36.2. Answer

■ 36.2.1. Preparation

The following replacing rule is helpful:

IntegralCondition = {If[a_, b_, _] := (Print[a]; b)}

{If[a_, b_, _] := (Print[a]; b)}

■ 36.2.2. Formula of Textbook

The following formula (see [HMS2004], formula (3-76), page 174) yields:

CarnotProcess = $\{\eta_{th,C} \rightarrow \frac{T_2 - T_1}{T_2}\}$ // Simplify

$\{\eta_{th,C} \rightarrow 1 - \frac{T_1}{T_2}\}$

■ 36.2.3. Actual Efficiency

The efficiency *always* is defined in technical physics the following:

Efficiency = $\{\eta \rightarrow \frac{\text{ResultingPower}}{\text{InvestingPower}}\}$ /.

$\{\text{ResultingPower} \rightarrow \frac{\text{Abs[WorkingEnergy]}}{\text{SpaceOfTime}}, \text{InvestingPower} \rightarrow \frac{\text{HeatSupply}}{\text{SpaceOfTime}}\}$

$\{\eta \rightarrow \frac{\text{Abs[WorkingEnergy]}}{\text{HeatSupply}}\}$

Thus for a circular process it is possible to consider the involved energies, also if this process would need endless time like the Carnot process.

Since for the efficiency of the Carnot process is divided number zero by number zero, this kind of consideration sometimes is not sufficient for the measuring purpose.

■ 36.2.4. Historical Context

The definition of absolute (thermodynamic) temperature by the efficiency of the Carnot process has already been legal before the end of world war II. (see [BS1945], volume 1, section 103, page 536). In 1954 (see [dtv1969], volume 9, keyword *Temperaturskala* (i.e. *temperature scale*), page 92) the 10th General Conference for Measurement and Weight decided due to recommendation of the Comité Consultatif de Thermométrie, that the thermodynamic temperature scale is defined by use of the triple point of water being a fixed point. This is the actual state of the art (see [HMS2004], table 1-2, page 7).

■ 36.2.5. Hurdle to Insight

The efficiency of the Carnot process is valid also for gases that own an unknown thermal capacity $C_{m,v}[T]$, because both the heat supply $-Q$, and the heat increase Q , occur as an integral of this heat capacity:

$$\text{Integral} = \left\{ Q \rightarrow \nu \int_{T_1}^{T_2} C_{m,v}[T] dT \right\}$$

$$\left\{ Q \rightarrow \nu \int_{T_1}^{T_2} C_{m,v}[T] dT \right\}$$

In the balance both of these integrals add to number zero, thus the efficiency of the Carnot process turns out to be independent of the heat capacity $C_{m,v}[T]$ of the gas being in use.

Not all textbooks (e.g. [BS1945], volume I, section 102, pages 528-529) use the heat integral in the general form, which can cause a hurdle to insight of the universal applicability of the *thermodynamic temperature*.

■ 36.2.6. Boltzmann's Alternative?

■ 36.2.6.1. Idea

Temperature T is an *intensive* quantity, while the internal energy U is an *extensive* quantity. Thus it seems to be sensible to discuss the square velocity momentum of the distribution function to be proportional to temperature. This idea corresponds to the considerations by James Clerk Maxwell and Ludwig Boltzmann (see [HMS2004], formulae (3-26) to (3-28), page 153):

$$U = N \overline{E_{\text{kin}}} = N \frac{1}{2} m \overline{v^2} = N \frac{3}{2} k_B T \quad (36.1)$$

■ 36.2.6.2. Historical Trial

An intensive quantity results by division of the extensive mean energy $\overline{E_{\text{kin}}}$ by the extensive mass m . This second momentum of the velocity v has historically been classified by Boltzmann to be the kinetic temperature.

■ 36.2.6.3. Confusion with Entropy?

Due to an elaboration by Albert Einstein the second momentum of a distribution rather is to be discussed as a measure for disorder. A more detailed consideration also turns out, that the Gaussian variance σ^2 is a very good measure for disorder and thus can loosen the quantity entropy S .

The unit of entropy so far has been $\left[\frac{J}{K}\right]$, this also is the unit of Boltzmann's constant.

Now there results the question, which unit should have a mechanical equivalent for temperature.

■ 36.2.6.4. General Variance

Variance σ^2 is defined to be the centered second momentum of a normalized distribution function and can be presented by the momenta of the same (see [BrS1987], section 5.1.3., page 665-668):

$$\text{Variance[General]} = \left\{ \sigma^2 \rightarrow \frac{\text{Momentum}[f[v], 2]}{\text{Momentum}[f[v], 0]} - \left(\frac{\text{Momentum}[f[v], 1]}{\text{Momentum}[f[v], 0]} \right)^2 \right\}$$

$$\left\{ \sigma^2 \rightarrow - \frac{\text{Momentum}[f[v], 1]^2}{\text{Momentum}[f[v], 0]^2} + \frac{\text{Momentum}[f[v], 2]}{\text{Momentum}[f[v], 0]} \right\}$$

Since the velocity distribution function also for Maxwell is valid in three dimensions, the following result is yielded by a threefold integral being the second momentum presented in sphere coordinates:

$$\text{Momentum}[f, m \text{ ? OddQ}] := 0$$

$$\text{Momentum}[f, m \text{ ? EvenQ}] := 4 \pi \int_0^\infty f v^{2+m} dv$$

Here, this yields the following variance σ^2 :

$$\text{Variance[General]}$$

$$\left\{ \sigma^2 \rightarrow \frac{\int_0^\infty v^4 f[v] dv}{\int_0^\infty v^2 f[v] dv} \right\}$$

In this case, variance σ^2 is identical to the normalized *second momentum*, since kinetic gas theory deals with a non-moving substance by $\bar{v} = 0$.

■ 36.2.6.5. Concrete Variances

The distribution function $f[v]$ in the easiest case is *Boltzmann's factor*, or respectively *Maxwell's velocity distribution* (see [HMS2004], Formulae (3-31) and (3-34), page 154 and 155):

$$\text{BoltzmannsFactor} = \{f[v] \rightarrow \text{Exp}\left[-\frac{m v^2}{2 k_B T}\right]\}$$

$$\{f[v] \rightarrow E^{-\frac{m v^2}{2 T k_B}}\}$$

$$\text{MaxwellsDistribution} = \left\{f[v] \rightarrow \frac{\text{Exp}\left[-\frac{m v^2}{2 k_B T}\right]}{\text{Momentum}\left[\text{Exp}\left[-\frac{m v^2}{2 k_B T}\right], 0\right]}\right\} /. \text{IntegralCondition} // \text{PowerExpand}$$

$$\text{Re}\left[\frac{m}{T k_B}\right] > 0$$

$$\left\{f[v] \rightarrow \frac{E^{-\frac{m v^2}{2 T k_B}} m^{3/2}}{2 \sqrt{2} \pi^{3/2} T^{3/2} k_B^{3/2}}\right\}$$

In both cases variance yields to be:

$$\text{Variance[Boltzmann]} = \text{Variance[General]} /. \text{BoltzmannsFactor} /. \text{IntegralCondition}$$

$$\text{Re}\left[\frac{m}{T k_B}\right] > 0$$

$$\text{Re}\left[\frac{m}{T k_B}\right] > 0$$

$$\{\sigma^2 \rightarrow \frac{3 T k_B}{m}\}$$

$$\text{Variance[Maxwell]} = \text{Variance[General]} /. \text{MaxwellsDistribution} /. \text{IntegralCondition}$$

$$\text{Re}\left[\frac{m}{T k_B}\right] > 0$$

$$\text{Re}\left[\frac{m}{T k_B}\right] > 0$$

$$\{\sigma^2 \rightarrow \frac{3 T k_B}{m}\}$$

$$\text{Comparison} = \text{Variance[Boltzmann]} == \text{Variance[Maxwell]}$$

True

This confirms that $\overline{v^2}$ in equation (36.1) is variance σ^2 being discussed here, and thus it's *not* the absolute temperature T .

■ 36.2.6.6. Mechanical Temperature Equivalent?

There should result a *mechanical temperature equivalent*—here discussed by the example of the idealized helium, or respectively hydrogen, thermometer (see [HMS2004], formulae (3-27) and (3-28), page 153):

$$\text{Variance[GasKinetics]} = \text{Solve}\left[\frac{M}{2} \overline{v^2} == \frac{f}{2} R_m T, \overline{v^2}\right] // \text{Flatten}$$

$$\text{Variance[Helium]} = \% /. \left\{M \rightarrow 4.0026 \frac{\text{"g"}}{\text{"mol"}}, f \rightarrow 3, R_m \rightarrow 8.3145 \frac{\text{"J"}}{\text{"mol"} \text{"K"}}, T \rightarrow 1 \text{"K"}\right\} /.$$

$$\left\{\text{"g"} \rightarrow \frac{\text{"kg"}}{1000}, \text{"J"} \rightarrow \frac{\text{"kg"} \text{"m"}^2}{\text{"s"}^2}\right\}$$

$$\text{Variance[Hydrogen]} = \% \% /. \left\{M \rightarrow 2 * 1.008 \frac{\text{"g"}}{\text{"mol"}}, f \rightarrow 3, R_m \rightarrow 8.3145 \frac{\text{"J"}}{\text{"mol"} \text{"K"}}, T \rightarrow 1 \text{"K"}\right\} /.$$

$$\left\{\text{"g"} \rightarrow \frac{\text{"kg"}}{1000}, \text{"J"} \rightarrow \frac{\text{"kg"} \text{"m"}^2}{\text{"s"}^2}\right\}$$

$$\left\{\overline{v^2} \rightarrow \frac{f T R_m}{M}\right\}$$

$$\left\{\overline{v^2} \rightarrow \frac{6231.82 \text{ m}^2}{\text{s}^2}\right\}$$

$$\left\{\overline{v^2} \rightarrow \frac{12372.8 \text{ m}^2}{\text{s}^2}\right\}$$

This calculation trial clearly shows that variance σ^2 is dependent from the mass of the gas particles being in use and thus *cannot* be interpreted to be a generalized *temperature* T .

■ 36.2.7. Universal Gas Constant

■ 36.2.7.1. Molar Consideration

Equation (36.1) can further be written differently, i.e. for the *molar* energy:

$$U = N \overline{E_{\text{kin}}} = \frac{1}{2} \nu M \overline{v^2} = \frac{3}{2} \nu R_m T \quad (36.2)$$

Here R_m is the *universal* gas constant, which is valid for *all* gases:

$$\text{GasConstant} = \left\{R_m \rightarrow 8.3145 \frac{\text{"J"}}{\text{"mol"} \text{"K"}}\right\}$$

$$\left\{R_m \rightarrow \frac{8.3145 \text{ J}}{\text{K mol}}\right\}$$

Variance $\overline{v^2}$ does not change by this consideration at all, but there results an amazing simple *mechanical temperature equivalent*:

If the internal energy U is divided by the *extensive* matter quantum ν , the result is an *intensive* quantity, which is proportional to absolute temperature T :

TemperatureEquivalent = Solve[U == $\frac{3}{2} \nu R_m T$ /. {U → u ν}, u] // Flatten

$$\left\{ u \rightarrow \frac{3 T R_m}{2} \right\}$$

The unit of this reduced internal energy u is $\left[K \frac{J}{\text{mol} K} \right] = \left[\frac{J}{\text{mol}} \right] = \left[\frac{\text{kg} m^2}{\text{mol} s^2} \right] := [K]$.

■ 36.2.7.2. Mechanical Temperature Equivalent

By this a reduced energy quantum is found that corresponds to the temperature difference of **1 K**:

TemperatureEquivalent /. GasConstant /. {T → 1 "K"}

$$\left\{ u \rightarrow \frac{12.4717 \text{ J}}{\text{mol}} \right\}$$

This is the reduced internal energy that is changed by an *ideal* gas per each Kelvin.

Since *real* gases often own more freedom degrees $f \geq 3$, it is to be expected and also to be measured, that the molar heat capacity $C_{m,\nu}[T]$ especially for low temperatures corresponds to the phenomenon $0 \leq f \leq 3$. The same is valid for solid bodies, which often enough own $f = 6$ —even for solid iodine I_2 can be determined thereby, that the iodine crystal consists of I_2 molecules.

Heat capacity of an idealized gas for all temperatures is constant and yields to be:

$$C_{m,\nu}[\text{Ideal}] = \partial_T \frac{\left(\frac{3}{2} \nu R_m T \right)}{\nu}$$

% /. GasConstant

$$\frac{3 R_m}{2}$$

$$\frac{12.4717 \text{ J}}{\text{K mol}}$$

Even this is the *mechanical temperature equivalent*.

■ 36.2.7.3. Result

By this is shown, that there is an *absolute* temperature scale, which corresponding to theory can be set over all real thermometers. Thus there is a theoretical alternative to the temperature definition via the Carnot process.

The unit of entropy S therefore is $\left[\frac{J}{K} \right] = \left[\frac{J}{\text{mol} K} \right] = [\text{mol}]$ and becomes even less clearly than before: The permanent increase of entropy S cannot be determined by the phenomenon, that the experimental construction would increase by matter quantum ν or mass m . Thus entropy S is a quantity with a density (near?) of number zero. This forces the supposition, that the quantity *entropy* according to Rudolf Clausius might have been a reprint of the heat substance *phlogiston* (see [HMS2004], section 3.3.2., page 159).

The alternative to the entropy S according to Ludwig Boltzmann is the older variance σ^2 according to Carl Friedrich Gauss:

Variance[Maxwell]

$$\left\{ \sigma^2 \rightarrow \frac{3 T k_B}{m} \right\}$$

Its unit is $\left[\frac{KJ}{kgK} \right] = \left[\frac{m^2}{s^2} \right]$, i.e. a square of velocity—being obvious.

■ 36.3. Protocol

The *Mathematica* version has been:

{ \$Version, \$ReleaseNumber, \$LicenseID }

{Microsoft Windows 3.0 (October 6, 1996), 0, L4526–3546}

The calculation time needed:

TimeUsed[] "s"

4.76 s

References

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