ISSN 1726-5479

SENSORS & TRANSDUCERS

5 vol. 140
/12

Sensor Buses and Interfaces

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 140, Issue 5, May 2012 | www.sensorsportal.com | ISSN 1726-5479

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).
Available in electronic and on CD.

Sensors & Transducers Journal

Contents

Volume 140
Issue 5
May 2012

www.sensorsportal.com

ISSN 1726-5479

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International Frequency Sensor Association (IFSA).

Sensors & Transducers Journal, Vol. 140, Issue 5, May 2012, pp. 1-7

www.sensorsportal.com

Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

Research in Nanothermometry. Part 1: Temperature of Micro- and Nano- sized Objects

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Received: 27 March 2012 /Accepted: 21 May 2012 /Published: 31 May 2012

Abstract: The concept of temperature measurement for micro- and nano- sized objects is under consideration in this article. According to decrease in the linear sizes of the controlled patterns, the role and value of fluctuations in the characteristic formation for the objects and metrological set of instruments tend to rise. *Copyright © 2012 IFSA.*

Keywords: Temperature, Measurement, Nanosized objects, Fluctuations, Statistical thermodynamics.

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1. Introduction

Nanotechnology has not arisen at the empty place but is the natural upshot of the scientific cognition directed into the depth of a substance. Micro-, nano-dimensioned and structured materials evince new totalities of properties and functions in comparison with the bulk analogs. Their retrievable research and production are assured by the development of nanometrology, and first of all, the methods and means of temperature measurement, since any physical property is meaningful at some controlled temperature. That is why all sorts of measurement are based on the temperature monitoring, and in general temperature measuring make ~50 % of a total measurement amount [1]. However, there are doubts as to the possibility to adopt the notion “temperature” for nanoobjects in the same way it concerns macroobjects.

2. Task Definition

The aim of the article consists in the provision of the temperature support for production methods; the research and use of micro- and nano-objects at the expense of developing the methodological notions about temperature at the nano-level; and assessment of the measured temperature values due to the determined methodical, instrumental and other errors as well as uncertainties.

3. Work Methodology

The further development of nanotechnologies could not be possible without the improvement of measurement methods and means on the basis of temperature background development (***nanometrolog***y); as well as data transferring and interpretation (***nanometrological supply***); the evaluating standard development (***standardization and certification***) and the study of the properties and structure (***scientific research***) [2].

The notion "Temperature of a certain nanoobject" has not been formed yet, although the particles under study are getting smaller with every year, drawing to atoms. In general, to introduce the notion "temperature", one should consider the function of statistical distribution (a postulate of statistical physics). There are two approaches, according to which the micro-canonical or canonical distribution must be adopted as the basis. The differences are revealed in the treating of fluctuation [3].

3.1. Transformation Function. Temperature, its Modes. Fluctuations and Size Effects

Especially in nanometrology that deals with nanoobjects, a measuring tool would detect the changes caused by fluctuations. In statistical physics, a thermodynamic system with the given temperature corresponds to the two objects. The first object is a non-isolated system that interacts with a thermostat. Its temperature is supposed to be fixed; since there is a state of thermodynamic equilibrium, it is equal to the thermostat temperature. The second object is an isolated system that consists of the row of subsystems and is equable. Its temperature as a thermodynamic parameter is the averaged inner-movement characteristic whose value could be defined with uncertainty as to small fluctuations. We deal with the statistical temperature. The more atoms are present in a system, the lesser fluctuations are observed. Let us highlight a principle statement of nanothermometry as a component of nanometrology: the presence of fluctuations makes a principle accuracy-threshold for any temperature measuring. It is predetermined by the thermal movement of atoms that constitute the measuring instruments, which consequently can not deliver absolutely exact indices [4].

The case of macrothermostat (macroobject). While measuring the macroobject's temperature, practically stable during the interaction with a thermometer (the second system), the uncertainty of the balanced temperature identification decreases with the increment of a macroobject.

The case of microthermostat (microobject). A notion of the fixed temperature is getting vague: the uncertainty of measurement rises at the decrement in a quantity of atoms constituting the studied object.

The case of nanothermostat (a nanoobject). In the system comprising a negligible matter quantity, a notion of the fixed temperature is completely absurd.

A thermodynamical notion of temperature is related to heat exchange between two systems. The quality of supplying or not to the balance among themselves under some predetermined conditions pertains to all macroscopic systems. The necessity to characterize a state of thermodynamic systems by some specific quantity becomes obvious. So, a notion of ***thermodynamic temperature*** has been introduced for this purpose. The objective measurement of temperature is possible due to the transitivity of a thermodynamic equilibrium. Therefore there is a possibility to compare the object temperatures among themselves without the objects' per se contact. To measure temperatures, one should take a system of bodies in certain states and assign them some quantitative temperature values. In this way we chose a *scale of temperatures*. Temperature as a physical value that characterizes the inner energy of bodies is not being measured directly nowadays. All usable means of measurement transform temperature in some other physical value that could be used immediately. Temperature that is defined by indices of a concrete thermometer is named the ***empirical temperature*** [1, 4].

The disquietness about the validity measure of describing objects by the statistical thermodynamic notion "temperature" at the diminishing of their linear sizes to a nanoarea is a natural issue. Developing the apparatus of statistical physics, P. Hohenberg and B. Shraiman [5] try to link the term "temperature" with basic constants of microphysics, on the one hand, and threshold sizes of nanoparticles where this notion is still applicable, on the other hand. The special significance is bestowed to the definition of the minimal particle size where the notion "***local temperature***" could be adopted, i. e. the temperature at which a part of thermodynamic system remains in a canonical state, and the energetic distribution of electrons corresponds to the exponentially falling one-parametric function. Nanoobjects as unequable thermodynamic systems with a slow dynamics could be described by "fluctuation dissipation temperatures", meanwhile, the [6] represents in this respect the related notion of "effective temperatures" involving the values of response and thermodynamic temperature.

3.2. Problems in the Measurement of Nanoobjects Temperature

Measurement is a process of interaction between the studied object and the thermo-sensitive thermometer substance that during energy exchanging with the former alters in its own state, to which some temperature value is assigned then (this situation is perfectly described by the measurement with a regular medical thermometer: temperature mercury widening leads to the increment of its column to some mark which acquires a temperature index). This method is indirect as the majority of known methods are. The amount of direct methods includes five methods of thermometric thermometry: *gas, acoustic, optical, magnetic and noise*. Those methods are based on the fundamental physical laws whose mathematical descriptions comprise the thermodynamic temperature (Fig. 1).

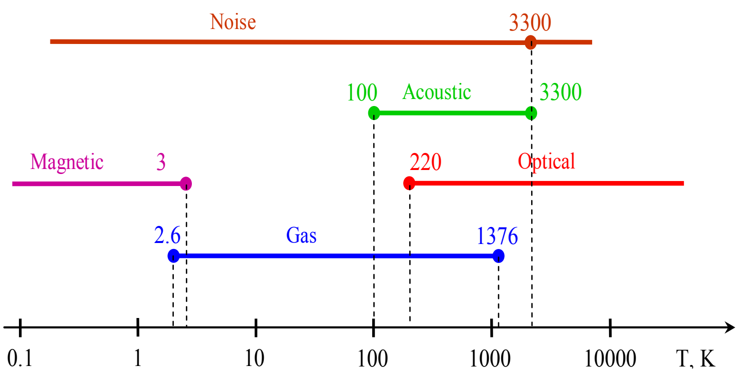

Fig. 1. Temperature scales of the direct methods of thermometry [2].

Among them, gas and optical thermometry have gained the widest application in the reproducibility of thermodynamic temperature. For instance, a casual error component rises in case the thermo capacitances or sizes of the thermometry-processed body and a thermometer become equal as compared to the case when the thermo-capacitance of a thermometer is considerably less than that of a body. To determine the thermodynamic temperature of the objects within the size range 100 nM ... 100 μM, the method of combination dispersion of laser light [7] is used. Moreover, the considered there metrological characteristics are not elaborated enough [8]. The methods of experimental research have been improved to such an extent that it seems possible to measure temperature with the resolution below 100 nm. On the other hand, the principles of reproducing a temperature scale with the usage of melting points are altering. Since the decreasing of the linear sizes of the studied objects to nanosizes, the melting temperature is not generally considered as a stable substance characteristic [9]. It could rise or fall correspondently to the surface energy of the melting points matter.

The questions that demand an immediate solution arise: "What should we do with a thermometer at the decrease in the sizes of the thermometry-processed body to nanosizes? How efficient is the transfer to nanothermometers? What is the size of micro- and nanoobjects we could study with the predetermined error by means of a nanothermometer?"

4. Theoretical and Experimental Research

4.1. Problem of Measurement Accuracy in Thermometry

Peculiarities of thermometric materials manufacturing lead to the emergence of a transfer function dispersion even within the same party of thermometers (Fig. 2, curve P_0). In turn, the manufacturer takes into account that irrespective of operating conditions in thermometric materials occurring the internal processes. They lead to a significant enlargement of transfer function coverage interval (Fig. 2, curve P_2) [3]. The mentioned function changes under the influence of impacts during operation. The correct technology of thermometers stipulates that these changes should not extend beyond the guaranteed by producer instrumental error for the scheduled operating conditions. This extended error modifies as a result of studies [4] that allowed to select a systematic component $\Delta U_{syst} = \Delta U_{known}$ with its own sign and to narrow a coverage interval of casual component (Fig. 2, curve P_1). The specified consideration of error is effective if it has been identified a trend of transfer function drift during the operation. Most often it occurs in the initial 10 hours of operation when changes are directed and intensive [5].

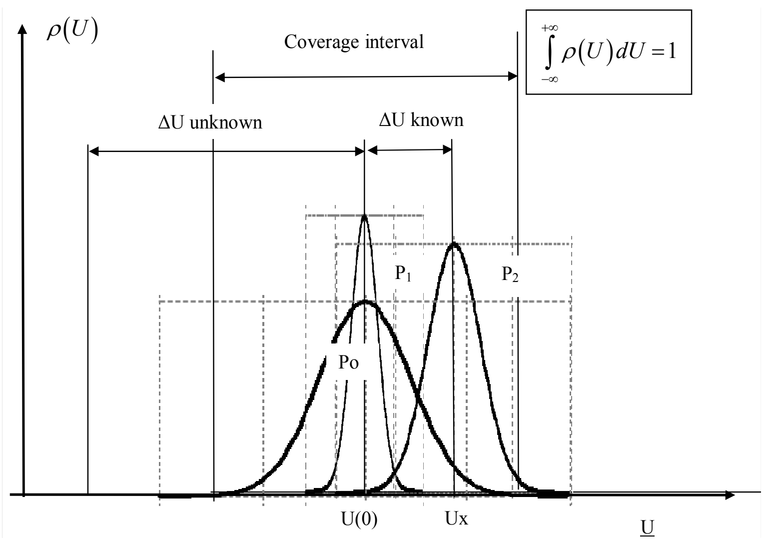

Fig. 2. Instrumental error and transfer function dispersion.

4.2. Significance of Metrological Approach to the Solution of Nanotechnology Problems

Identification of the standard characteristics at the nanolevel is related to the predetermined temperature. To measure it, the high-accuracy thermometers have to be improved in terms of sensitivity. In the world of nanotechnology *the combination of measuring technologies and theoretical research* is getting more and more significant, since:

a) It concerns a single, non repeated measurement where a classical approach of the error theory could not be applicable [10];

b) A measuring tool is getting more important; its intrusion during the energetic exchange disturbs the dimension of the studied value.

Moreover, *the accuracy of measurement results and that of experimental investigations are two different notions*, and the experimental accuracy evaluation itself implies not just the study of experimental results' accuracy; but an estimation of nanosamples as well as the selection of possible and correlated research methods.

On contrary to macroobjects where the improvement of research accuracy could be reached by the increment in the experiment extent, the improvement of measurement conditions, and the minimization of outer factor influence, in the case of nanoobject. The problem of correlation between expediency and significance of instrument energetic intrusion with the purpose to determine the quantitative object characteristics as well as the problem of reproducibility of the gained research results with the help of various sets of instruments of the same direction as well as the research results obtained at different scientific centers are frequent. At the thermometry-processing of small objects, a sensor (for example, a laser bunch) breaks thermodynamic equilibrium of object so that the considerable methodical error (~27 K) appears [8].

5. Discussion

The task of measurement result evaluation is of high importance today. It is quite good elaborated for macroobjects, having not been even established in the case of nanosamples. The general approaches are known. The extraction of a systematic error component with its own sign enables us to narrow the interval of covering a casual error component and serves as the basis for the formation of a cognizable component of a summary measurement error. In the most practicable case of correlation among the different components of a summary error, one should apply the IMC approach to the summing of correlated values' uncertainties. Following it, the summary result uncertainty is determined by an average quadratic uncertainty value of certain quantities. It reveals the possibility of simultaneous application of errors and uncertainties' approaches, which corresponds to a hybrid approach of measurement result assessment. To wit, an error is being calculated and evaluated as a physical value whose particular coefficients are defined with some uncertainty (Fig. 3) [11].

The mentioned approach has been modified by the way of cognizing the certain components of an instrumental error through the extraction, study and evaluation of the factors influencing a measuring tool, on the basis of statistical thermodynamic nature of their formation [12]. The results of thermometric substance fluctuation concerning the summary influence function $\delta T_{Met\_max} = K_{\Sigma}$ of thermoelectric thermotransducers at the presence of external thermodynamic fields are determined as:

$$K_{\Sigma} = \left(K_X + K_M\right) K_T \,, \tag{1}$$

where $K_X ; K_M ; K_T$ are the chemical, mechanical and thermal influence functions respectively caused by specific transport processes created by the external effect in thermometric substance. Temperature, density, strain and etc. gradients are the typical examples of external fields effect in thermometric substance being subordinated to the same statistical regularities as the gradients that appear consequently of fluctuations in thermometric substance are (according to the sense of a fluctuation-dissipation thermodynamic theorem). At the availability of fluctuations, additional influence functions ($K_P;K_\Pi;K_E$) applicating multiplicatively on influence functions related by the fluctuation affect of external environment are formed:

$$K_\Sigma\left[F\left(T,p,V,...,t\right)\right]=\left(K_X K_P+K_M K_\Pi\right)K_T K_E, \tag{2}$$

where $K_P;K_\Pi;K_E$ are the recrystallization, porous and entropy influence functions respectively [11].

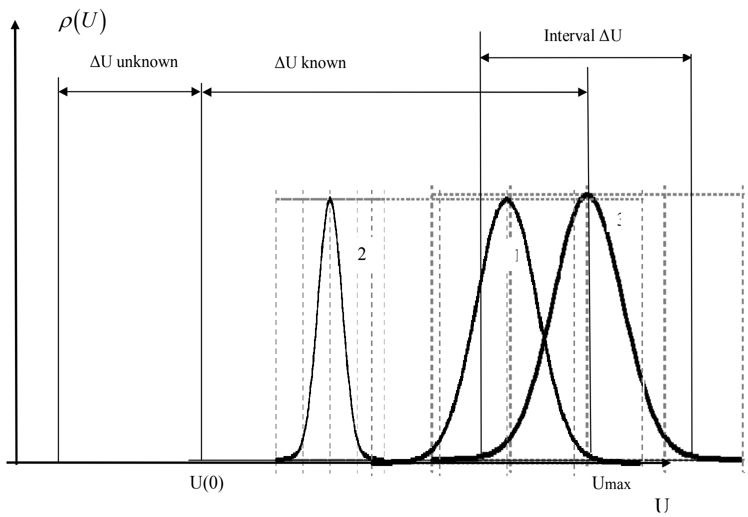

Fig. 3. Threshold weight of summary error and its uncertainty of result (3): its systematic component due to the influence of the measurement instrument and fluctuation of its properties (2); similar factor due to the influence of thermometry-processed object (1).

The summary influence function of temperature measurement is defined in the received by summation coverage interval: changing from $\pm\left(\frac{K_P+K_\Pi}{K_X+K_M}+\frac{K_E}{K_T}\right)$ in the presence of two independent systematic constituents; by $\pm\left(\frac{\sqrt{K_P^2+K_\Pi^2}}{K_X+K_M}+\frac{K_E}{K_T}\right)$ for the correlated constituents; to $\pm\left(\frac{\sqrt{K_P^2-K_\Pi^2}}{K_X+K_M}+\frac{K_E}{K_T}\right)$ for uncorrelated values ($C_{cor}=-1$). This shows the possibility of applying the error approach and uncertainty approach that corresponds a hybrid approach evaluation of measurement results [13].

Consequently, we have developed a hybrid thermodynamic approach to the estimation of measurement accuracy of micro-, nano- object temperature. It roots in the threshold value determination of an instrumental error systematic component as an additional totality of influence-functions' multiplicative pairs. Joining in the pairs, where one of the multipliers is defined by the fluctuations of thermodynamic substance properties, and another – by those of the parameters of the applied outer fields caused by the thermometry-processed object, meets the content of the fluctuation dissipation thermodynamic theorem.

This approach is quite precious since it enables us to consider a thermometric substance thermodynamic system in terms of external environment and to penetrate into the essentiality of fluctuation processes which take place in the mentioned substance. As result, thermotransducers with the foreseen and managed value of an instrumental error component are developed on the basis of statistical thermodynamics approach. Thus firstly, the decrement of an unrecognizable error component of nanoobject temperature measurement (absolute values, covering intervals and so on) has been reached, and secondly, the fluctuation restrictions of statistical physics for the improvement of metrological characteristics have been employed [14, 15].

7. Conclusions

The development of nanotechnology is impossible without the temperature evaluation of micro- and nano- objects which demands the further progress in nanothermometry and nanothermodynamics.

To decrease the issues of metrological instrument intrusion, the hybrid thermodynamic approach to the estimation of measurement accuracy of micro- and nanoobjects' temperature should be developed comparing the intrusion and measurement accuracy factors on the basis of developing the fundamental notions of statistical thermodynamics concerning micro- and nano-sized objects as well as the approaches to the error and uncertainty in measurements. It allows to determine the recognizable component of systematic error component of the measuring tool and significantly reduce the instrumental error guaranteed by manufacturers.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because of it is a peer reviewed international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per year by International Frequency Sensor Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc. Since 2011 the journal is covered and indexed (including a Scopus, Embase, Engineering Village and Reaxys) in Elsevier products.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
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- Signal processing;
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- Nanosensors;
- Microsystems;
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