

Development of Noise Measurements. Part 8. Nanometrology and Nanothermodynamics as its Scientific Basis

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Abstract: A number of nanoobjects information parameters have been studied on basis of which new nanometrology development directions have been displayed. It is shown that the further nanotechnology development must be grounded on the works which moreover simultaneously develop nanometrology principles. The basis of these works is thermodynamics as integral systems of thermodynamical coordinates which are marked out by the noncorrelated impact on objects. Under the transition into nanosphere some separate thermodynamic degrees of freedom are gradually changing because of surface tension forces prevails over gravity forces. The thermodynamics is complicated by taking into account nonlinearity and interrelations of its coordinates and new discovered physical effects. *Copyright © 2013 IFSA.*

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1. Introduction

Nanometrology development [1] as an integral part and main tool of nanotechnology is hindered by a number of difficulties. One of the main difficulties lies in that to minimize the method error as demonstrated in [2], sensors dimension-mass characteristics must be commensurable with set characteristics of studied nanoobjects. But then sensors and nanoobjects characteristics expose specific peculiarities determined by the objects low-size and substance discreteness.

The basis of nanotechnology is materials engineering. Its phenomenology is quite efficiently described by nanothermodynamics means [3].

Accordingly nanometrology focuses on the similar concentrating its attention on the specificity of methods, measurement means and sensors in particular. A little different but similar by their character problems concern the non-contact methods and sensors [4], [5]. At the thermometry-processing of small objects, a sensor (for example, a laser bunch) breaks thermodynamic equilibrium of controlled object so that the considerable methodical error (~27 K) appears.

The effort to minimize errors, to increase nanometrology measurement means sensitivity to appropriate level without accuracy lost under this and other similar tasks of elaboration undoubtedly quantitative but not qualitative [6] methods have led

to appearance of this particular series of works. In it authors tried gradually to show [7]-[10] the advantages of the most useful and prevailing substance research method including at the micro-, nanolevel – electrical noise method (the study of electrical noise is known problem which was set and resolved by Nyquist [11] and it concerns exclusively the interrelation between electric power and noise temperature in quasi-equilibrium case) in non-equilibrium, non-stationary or in other specific manifestation for metrology tasks solution. One year ago in work [12] of nanothermometrical series we tried to show abilities of the thermodynamics of sensitive substance of the noise thermometer as thermodynamic system which is partly opened concerning control environment. Fluctuation-dissipation character of the environment effect on the sensor material determines [13] the sensitivity threshold and measurement error of measurement means. Poor understanding of the mentioned factors role in terms of new discipline forming - nanometrology with nanothermometry inclusively [14] – leads to accumulation of a number of inaccuracies. In the case of nanotechnological studies when measurements mainly are carried out once and without repeat, this specifies the significant decrease of received information adequacy.

2. Work Goal

The work goal is the nanometrological study of nanoobjects information parameters on the basis of developing nanothermodynamic basic principles.

3. Basic Methodology and Determining Role of Fluctuations in Nanomeans Metrological Characteristics Creating

3.1. Nanothermodynamics and Its Basic Equation

In a system with independent thermodynamic degrees of freedom, the state equation of thermodynamics takes the form of the classic Gibbs equation with supplementing it the Gibbs-Duhem equation [15]:

$$dU = TdS - pdV - \sum_k \mu_k dm_k - \varphi \sum_k dq_k + HdJ + \sigma_n dM \quad (1)$$

$$SdT - Vdp + \sum_k m_k d\mu_k + JdH + Md\sigma_n = 0, \quad (2)$$

where S is the entropy; T is the temperature; U is the internal energy; p is the pressure; V is the volume; μ is the chemical potential; m is the mass; φ is the electric potential; q is the charge; H is the magnet field intensity; J is the magnetization; σ is the surface

tension; M is the surface area. It enables to formulate the dependence of system internal energy on its thermodynamic qualities.

Parameters linear interrelation is considered to be equitable for processes running quite slowly however the system is not too far from the equilibrium state. This mentioned demand of linear dependence of generalized flows on generalized forces for transfer processes is not quite strict. It concerns the physics, chemistry and biology under macroworld phenomena describing.

With decreasing of linear sizes of control objects and measurement probes substantially increases the proportion of atoms D that directly reach the surface. If for nanoparticle that consists of 3^3 atoms - $D=0.963$ then for particle of 6^3 atoms size - $D=0.704$. It leads to creating a unique characteristics totality of nanosized patterns. For example, the ratio of surface to volume for nanowires is much bigger than for ordinary patterns. The surface “absorbs” dislocations which come out. Therefore nanowires wires cannot be deformed plastically, have not almost microcracks and their strength limit is in ten times higher than ordinary patterns limit. By these characteristics nanowire comes nearer to monocrystal. Moreover the wire surface which has extremely small radius of curvature (~ 10 nm) is greatly compressed. By immediate action of superficial tension forces this leads to a decrease in melting temperature of nanoparticles [16]. Using the calorimeter of sensitivity 0.1 nJ, it was determined [17] that the melting point of aluminum powder (4 nm diameter) falls at 140 °C with decreasing their sizes into a nanoarea.

Another example was considered in detail [18] earlier. The thermometers with liquid sensitive elements are characterized in thermometry by a practically linear graduating characteristic consequently of thermal expanding of liquid. In micro-(nano-) world, while decreasing the dimensions of thermometers with liquid-phase sensitive elements, the forces of superficial tension causing the formation of graduating characteristics are getting more and more considerable on contrary to analogical thermometers of macroworld where the same forces lead to the appearance of a readout error. Development of these nanothermometers is due to the predominance of gravitational forces over the forces of superficial tension (or vice versa), which are characterized by size-free criterion, called Bond number $Bo = \rho g d^2 / \sigma$, where g - gravitational acceleration; ρ ; d - respectively liquid density and diameter of the thermometer tube. At $Bo < 1$ – the capillary forces dominate; at $Bo > 1$ – gravitation forces.

As follows from the foregoing materials the state equation of thermodynamics smoothly passes in the similar equation of nanothermodynamics [3] that acquires the additional submembers relating to certain components - degrees of freedom. Their significance increases with size decreasing to

nanoscale. These components are pV , which is linked with the appearance of a new phase nucleations, and σM , which is caused by the growing role of surface in nanoparticles. Another component can be considered as φq -submember, which causes the appearance of charge-orientation quantization phenomena. Its content consists in consideration the "valley" degree of freedom of electrons", except the well-known electron charge or spin consideration [19]. This novel concept is based on utilizing the wave quantum number of an electron in a crystalline material.

3.2. Development of Thermodynamic Approaches in Nanometrology

Due to advances of nanotechnology it becomes necessary to extend macroscopic thermodynamics and statistical mechanics at the nanoworld with their poorly predictable behavior samples composed of a limited number of nanoscale elements that do not fit within the limits of thermodynamics [12].

Up to date, there are two kinds of fundamental approaches to open out in thermodynamics on nanoscale, based on the microscopic and macroscopic viewpoints respectively. One would go back to the fundamental theorem of macroscopic thermodynamics and establish the new nanothermodynamics formalism by introducing the new function(s) presenting the fluctuations or surface effects of nanosystems. Unfortunately, there subconsciously avoid the issue of the scope of thermodynamics application.

Developing the apparatus of statistical physics, work [20] tries 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 substance size where the notion "local temperature" could be adopted; i. e. the energetic distribution of electrons corresponds to the exponentially falling one-parametric function. Another one approach could directly modify the equations of the macroscopic thermodynamics and establish the new model of the thermodynamics on nanoscale by incorporating the Laplace–Young equation $\Delta P = \sigma \left(\frac{1}{R_x} + \frac{1}{R_y} \right)$, where $R_x; R_y$ — two

local radius of the surface curvature, or Gibbs–Thomson relation, representing the density fluctuation of nanosystems in the corresponding thermodynamic expressions [3, p. 89].

Let us apply both of mentioned approaches to the description of sensors behavior and metrological characteristics including the sensitive elements made from nanoscaled and nanostructured materials.

For example, it is interesting to consider the study of polycrystalline structures produced from barium-strontium ferrite. Main physical and chemical phenomena which are responsible for final patterns

qualities take place at the stage of final sintering of compressed powder during the grains interaction through the liquid phase layer [16].

The thermodynamical reason of mass transfer appearance in such systems is difference in surfaces curvature of contacting phases boundary (Gibbs–Thomson effect). The informative characteristic of the oversaturated state of multicomponent liquid phase is contact overcooling. In current case it is reasonable to determine overcooling as temperature balance difference of liquid phase of given composition and of solid phase (planar boundary) with regard to the same temperature balance in the case of a certain boundary curvature.

Contact temperatures difference is determined in a few degrees under the gradient in scores degrees on one centimeter. It decreases very quickly if the crystal size grows. For grains surface radii that are bigger than $3 \mu\text{m}$ (grain size is $6 \mu\text{m}$) the contact difference of temperatures practically disappears.

3.3. Improvement of Experimental Methods of Electrical Noise Research

A classic noise method [21] is one of 5 direct methods of thermometry: gas, acoustic, optical, magnetic and noise. Those methods are based on the fundamental physical laws whose mathematical descriptions comprise the thermodynamic temperature; within the range of frequencies 10^3 – 10^7 Hz commonly used in noise thermometry the mean square of the noise voltage is proportional to the thermodynamic temperature.

The attracting of the noise method to the description of a substance at the macro-, micro- or nano-level becomes more effective and exact if a sensitive element of a noise thermometer is made from the mentioned substance. Then the whole metrological experience of manufacturing and exploiting the sensitive elements of noise thermometers as well as developing their metrological supply and assistance [22] could be used for the nanometrological support of nanotechnology efforts.

Noise thermometer is the only metrological device in which thermal noise voltage represents a main metrological characteristic. It lets to determine the thermodynamic temperature T due to the power of the fixed electric thermal noise, making the electric, heat and other transfer processes that take place in a thermodynamic substance available for studying by means of deviations from $U \sim T$. Quite thorough research of electric noise, particularly of $1/f^\gamma$ noise, their theoretical analysis has been conducted [23]. Noise method is becoming intensively applied in nanotechnology and nanobiotechnology [2], to study processes taking place inside the social objects and determine their characteristics.

The follows should be noted as a positive consequence of our studies [22]. The method of measuring the frequency at which the transition from thermal noise to $1/f^\gamma$ noise, can be used [12] to define the minimal pattern size which the “local temperature” would be adopted, i. e. the temperature of a part of thermodynamic system that remains in a canonical state.

Based on the experience of noise thermometry with its determined gauging signals, it was discussed [7] a number of issues of various substances noise, especially in nanotechnology, where the nature of the measured noise is random. It is inherent fluctuation origin. Noise nature of studied signals complicates his distinguishing on the noise interference background; it leads to additional complications because signals and interferences can be proportional by their level.

This fact understanding is another positive conclusion of realized studies within this cycle «Development of noise measurements» [7-10]. In general the noise signal characteristics study that appears in sensitive elements of micro- and nanosensors provide the opportunity to observe not only noise processes of nanometrology but also non-noise parameters and characteristics of nanopatterns substance. That very approach to the noise study demonstrates most completely their actuality for modern electronics elements which are transferred into nanosphere by their sizes.

In most spheres of science and technology, the measurements of determined signals are conducted [23], whilst in the case of noise values the random signals are of interest. The interference could be both determined and random. Besides, taking into consideration the fact that measurements are performed within the wide bandwidth, the determined interference could reveal itself at the various frequencies. Therefore we should use the filters of complicated configuration that combine a band filter for forming the work-bandwidth of a measuring device, and notch filters for some frequencies which could be numerous. Taking into account the specific conditions of measurement as well as difficult construction and working principles of such filters, the synthesis of digital intelligent filters with the usage of rapid Fourier transformation [18] which meets the enumerated requirements is optimal.

Each of the considered problems leads to the appearance of the whole chain of error components of measuring the integral characteristics of noise signals. These components depend on the method of measurement, metrological characteristics of measuring means and their proper noise characteristics (noise- voltage and current). The analysis of possible error sources, minimization of their influence on the result of measurement, consideration of the specificity of the measurand, satisfaction of appropriate ratio “noise-signal being measured – uninformative noise-signal” and etc.

enable gaining the reliable results of measuring the integral characteristics of noise signals.

We have researched [9] the possibility and develop the method of estimating the defectiveness of an electronic elements internal structure through the parameters of proper electric noise, following the alteration in spectral density of noise power.

Nowadays, defect revilement in an electronic element structure comes down to endeavors to activate the hidden defects of an element (integral schemes of modules) before its deliverance to a consumer. Those stimuli could be different variants of electro-, thermo- or combined trials, energy-scrappings and so on. Such deeds make apparent the hidden element defects, but consequently the latter might become superficial. In this case potentially unreliable elements either fracture or their characteristics unallowably change. Time consumed by such a quality control and potential unreliability diagnostics makes tens and hundreds of hours.

Following from the aforesaid, the highest topicality should be referred to the methods of nondestructive diagnostics of an element inner structure. One of them is the electronic element diagnostics by dint of elements proper noise that is singled out by rather small time consumption and absence of damage risk for the researched element. In comparison with other nondestructive methods of electronic elements inner structure defectiveness diagnostics, the method of research by dint of electric noise power is multipurpose, and enables detecting the potentially low-reliable elements. With involving the dependence of flicker-noise parameters on the controlled object structure, we could diagnose the electronic element state and its evolution, especially at the primary stages of defects formation.

Owing to the measurement of current fluctuation parameters, the method of electronic element noise spectroscopy could be applied to reliability diagnostics of both analog and digital elements to the same extent. It is based on calculating the frequency above which the flicker-component of noise is equal to zero.

Random errors of measurement results, the averaging of which is treated as a routine way of their reduction at the repeatable measurements, could be minimized only if the energetic spectrum of the measured value is stable within the frequency bandwidth from 0 to over-high values, i.e. could be represented in the form of “white” noise. If the colouring caused by a flicker-noise effect pertains to the energetic spectrum then the random error could not be minimized by averaging the results of repeatable gauges.

Since the energetic spectrum, inherent in real systems, contains a flicker-component, the results of repeatable measurements remain quite undetermined, and their random error could not be considerably diminished by averaging.

In the case of the single measurements of unique properties, especially in nanotechnology, the theory of uncertainty could become expedient [24]. Here the evaluation of a result is supposed to be made with some uncertainty determined by the effect of the same influence-factors. Within the framework of an uncertainty approach the expounded above results could be reduced to the extended standard uncertainty of the A type by introducing the coefficient - $1/\sqrt{3}$.

4. Nanometrology: Means, Tools and Sensors

Noise appearance in studied systems regardless of their kind is specified by the fluctuation of characteristic processes inside them and also by the discrete character of registration and transfer of received information. Concerning measurement instruments we can state the following. Phenomena fluctuation character taking place into the control environment – sensor sensitive substance (with their quite high sensitivity) – can be undoubtedly recorded by the instrument. But the measurement mean due to peculiarities of its production demonstrates fluctuation qualities that inevitably affect the metrological characteristics.

For thermoelectric thermotransducer example we have confirmed in [13] just such nature of fluctuations impact on the metrological characteristics.

Consequently, we have developed a hybrid thermodynamic approach to the estimation of measurement accuracy of micro- and nanoobjects temperature. It roots in the threshold value determination of 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 sensor thermodynamic substance properties, and another – by those of the parameters of the applied outer fields caused by the thermometry-processed environment, meets the sense of the fluctuation-dissipation thermodynamic theorem [15]. Temperature, density, strain and other gradients created by the external effect in thermoelectric substance are subordinated to the same statistical regularities as the gradients that appear consequently of fluctuations impact in this substance.

This approach is quite precious since it enables us to consider a thermosensitive substance thermodynamic system in terms of external environment and to penetrate into the essentiality of fluctuation processes which take place in this substance. As result, thermotransducers with the foreseen and managed value of an instrumental error component are developed on the basis of statistical thermodynamic approach.

As far as the study environment volumes and thermosensitive substance decreasing the fluctuation

deviations of studied parameters (physical, chemical, electrical and other noises) are demonstrated more significantly that is successfully described by nanothermodynamics [3]. Fluctuation parameters and qualities presence in sensors establishes accuracy principle threshold that is shown on the row of examples for different technology branches. Nanometrological means designed without taking into account this fact can be considered ineffective and not enough accurate.

4.1. Sensitive Elements of Fire Sensors and their Random Error

Size decreasing of gas sensitive elements of fire sensors results into increasing the volume fluctuations impact on measurement result. It was shown in [25] that the random error of temperature measurement by gas sensor is determined only by volume of its gas thermosensitive substance but not the volume of controlled environment. It decreases to null if quantity of molecules of thermosensitive substance increase, and vice versa it increases if volume decreases.

It was expressed the heat quantity dispersion depending on the value n of gas moles in volume, the specific heat of gas C_w , Avogadro number N_A ; the mass of thermosensitive substance m :

$$D[Q] = C_w m \frac{T^2}{nN_A} = C_w m \frac{T^2}{N_A} \frac{22,4}{V}, \quad (3)$$

Taking into account that 1 mole of gas occupies the volume of 22.4 l under normal conditions the root-mean-square deviation and relative root-mean-square deviation of heat quantity Q as function of chamber volume of sensor sensitive element are respectively equal to:

$$\begin{aligned} \sigma[Q] &= T_1 \sqrt{\frac{22,4 C_w m}{V N_A}}, \\ \delta\sigma[Q] &= \frac{\sigma[Q]}{Q} = \frac{6.1 \cdot 10^{-12} T_1}{T_2 - T_1} \sqrt{\frac{1}{C_w m V}}, \end{aligned} \quad (4)$$

where T_1 ; T_2 are the temperature of sensitive substance and environment accordingly.

Offered formulas enable to calculate the value of random error depending on volume of sensitive element chamber and sensor mass or to calculate the parameters of chamber by means of random error value which is given beforehand. Under significant decrease of fire sensor sensitive element volume (to 4 ml) – relative root-mean-square deviation increases to $\pm 0,007$ %. Such value of random error is absolutely admissible for fire technology. Then thermal inertia constant doesn't exceed 1 s.

4.2. Accuracy Threshold of the High Sensitivity Spring Balance and Ballistic Galvanometer

The study of fluctuation deviations of readouts in measurement instruments and tools is one of the main problems studied by the statistic thermodynamics in its early period [26, 27]. Under accurate measurement of very small values of mass and electrical current the movable parts of instruments must be small; so they consist of small amounts of atoms. Therefore the fluctuations inside them are significant.

The example is torsion balance where the main constructive part is a thin thread on which a light mirror hangs. It should be noticed the same part is the basis for a ballistic galvanometer construction. Molecules thermal motion of the environment leads to irregular in time molecules bombarding of the mirror that limits instruments sensitivity and not let to better the measurement accuracy. Thread torsion module is $a = \frac{\pi^2 d^2 G}{8l}$, where G is the shear modulus; d and l are the thread diameter and length. Then moment of force that affects on the thread is linked with rotation angle φ by the next ratio: $M = a\varphi$, and potential energy of curled thread - $U = a\varphi^2/2$. In accordance with Boltzmann formula the rotation angle dispersion around which value the mirror vibrations are going on is equal to:

$$D[\overline{\varphi^2}] = D \left[\frac{\int_{-\infty}^{\infty} \varphi^2 e^{-a\varphi^2/2T} d\varphi}{\int_{-\infty}^{\infty} e^{-a\varphi^2/2T} d\varphi} \right] = \frac{T}{a} \overline{\varphi^2} = \frac{T}{a}, \quad (5)$$

Obviously the mirror rotation angle root-mean-square deviation is [26]:

$$\sigma[\varphi] = \left(\frac{T}{a} \right)^{1/2}, \quad (6)$$

Under the room temperature when $a \sim 10^{-13}$ J the mirror rotation angle root-mean-square deviations are determined as $\sim 10^{-4}$ radian. This is a real limit of single measurement sensitivity for practically all instruments in nanometrology.

By the same way it is considered the fluctuations impact on metrological parameters of a spring balance [27] with coefficient of elasticity k and equilibrium stretching X_0 . The mass center oscillations occur in it as result of the temperature fluctuations presence. That's why counting of equilibrium position of the pointer X_0 cannot be made more accurate than with the root-mean-square deviation of absolute value of the instrumental error random component:

$$\sigma[X_0] = \sqrt{(\Delta X_0)^2} = \pm \sqrt{\frac{T}{c}}, \quad (7)$$

where c is the constant that links mechanical qualities and sizes. On this basis let determine the root-mean-square deviations of absolute and relative value of the instrumental error random component of mass determination:

$$\begin{aligned} \sigma[m] &= \pm \frac{c}{g} \Delta X_0 = \pm \frac{k}{g} \sqrt{\frac{T}{c}}; \\ \delta\sigma[m] &= \pm \frac{\sigma[m]}{m} = \pm \frac{1}{mg} \sqrt{\frac{T}{c}} \end{aligned}, \quad (8)$$

Hence the instrumental error random component is smaller as the spring is weaker. However in this case the equilibrium stretching increases: $X_0 = mg/k$. It specifies practical inconvenience of the balance construction. Hereby fluctuations essentially limit the metrological characteristics of the spring balance.

In electrical measurement means fluctuations specify the absolute error that is independent from the instrument perfection state. So far as the ballistic galvanometer is used as supersensitive mean of very small values of impulse current measurement therefore it will be considered firstly. The galvanometer current I is measured by the mirror deviation angle φ . In equilibrium state when spring forces moment $c\varphi$ is equal to electromagnetic forces effect moment γI the mirror rotation angle is $\varphi_0 = \frac{\gamma I}{c}$.

The root-mean-square deviation estimation of the mirror rotation angle is in line by its content with the absolute value estimation of the instrumental error random component of the thread with the mirror (6) or the spring balance (7). If it is substituted in (8) we shall get root-mean-square deviations of absolute and relative values of the instrumental error random component of the current determination:

$$\sigma[I] = \pm \frac{c}{\gamma} \sqrt{\frac{T}{c}}; \quad \delta\sigma[I] = \frac{\sigma[I]}{I} = \pm \frac{\sqrt{cT}}{\gamma I}, \quad (9)$$

Hence for the galvanometer accuracy improvement it needs to take smaller value of the constant c and higher value of the constant γ (in other words to increase an amount of winds in the galvanometer current coil). This leads to the equilibrium angles deviation φ_0 that contradicts with springiness demands of the hanging thread deformation $\varphi_0 \ll \pi/2$. Therefore here fluctuations also limit the instrument accuracy: $T = 1/|\delta|$. Then the accuracy limit which can be gained within measurements is determined by assigned in advance sensitivity.

4.3. Other Measurement Means and their Fluctuation Limits

Coriolis mass flowmeter belongs to many-parameters measuring devices and is inherent in the ability to measure several parameters. It simultaneously determines the mass flow, density, temperature that can be used to derive such values as volume flow, solid particles content, the concentration and function of complex density.

Temperature measurement is carried out in 4 device points of flowmeter trying to minimize the instrumental error. It is specified by the impact factors due to temperature dependence of controlled medium viscosity and temperature dependence of vibration and mechanical properties of measuring and reference flowmeter tubes.

In this case, most producers ignore to unavoidable dispersion of calibration characteristics of temperature sensors: platinum resistance thermometers or thermocouples. Therefore, the improvement of the flow measurement accuracy can be achieved [28] by increasing the precision of temperature sensors.

Scientific and technological solutions are based on the technology knowledge of thermocouple wires production of platinum and platinum group alloys. Taking into account that in the bobbin of thermocouple wire there are equal by their impact local and extensive inhomogeneities, the action of the last inhomogeneities can be practically eliminated by the significant decreasing of thermoelectrodes length. Especially it concerns the usage of short thermoelectrodes ($l \leq 0.05$ m) in small flowmeters. Then for Pt-10 % Rd wire the thermoelectric inhomogeneity can be decreased in some times: from $\leq \pm 8 \mu\text{V}$ to $\leq \pm 2 \mu\text{V}$.

Thus the differential thermocouple is produced for the flowmeter in Π -shape where 2 vertical thermoelectrodes are made from Pt wire with thermoelectric inhomogeneity $\leq \pm 2 \mu\text{V}$; between them is fixed a short horizontal stick of Pt – 10 % Rd wire with inhomogeneity $\leq \pm 2 \mu\text{V}$. As result the S-type thermocouple inhomogeneity that is determined as root-mean-square deviation of non-correlated values of 2 different wires inhomogeneity; it is estimated as $\pm 2\sqrt{2} \mu\text{V}$ or ± 0.52 °C. This is the reproducibility of temperatures difference measurement in 2 flowmeter neighboring points by the means of replaceable differential S-type thermocouples.

Accuracy and stability problems of 3-D positioning in precise means of nanomachines, shift mechanism in atomic-force microscopes are considered to be principal in the nanotechnology.

To create Z-shift realization means the step standard method usage is not enough as well as the thickness special measure usage: monomolecular layer coating, multilayer film etc. The main shortcomings of the mentioned means are gradation positioning, some measure quantity necessity,

calibration process complication and its significant duration and cost.

During the creation of hydraulic positioning unit along the axis Z of the nanomachine with providing stepless shift and position control possibility along this axis it is suggested [29] to use hydraulic potential. To this purpose U-shaped hydraulic construction is proposed with ends of larger and smaller diameters. In case of level liquid movement control in a narrow arm with error $\pm 2.5 (\pm 1.0) \mu\text{m}$ it appears possible to ensure the smooth and accurate shifting level in the wider arm at $1.12 \pm 0.56 \text{ nm}$ ($0.45 \pm 0.22 \text{ nm}$). If the average atom size of liquid is approximately equal to $\approx 0.3 \text{ nm}$ then current device enables to set the liquid level and nanoobject mounted on the floating platform with absolute error which is slightly more than atom size.

Under accurate settings of very small Z-axis values the movable means elements (hydraulic liquid molecules) determine the noise device features. The latter are determined by the viscosity fluctuating deviations. They may be specified, for instance, by the temperature deviations from optimal regime, the diversions from the horizontality, the non-discrete character of the every layer filling and some other factors.

5. Insufficiency of Linear thermodynamics Approach for consideration the Processes in Nanoworld

Nanothermodynamics is enhancing by the way of thermodynamic formalism improvement that shows more significant role of surface tension forces under the size decreasing of systems to nanosystems [3] and by the way of taking into account multiphonon processes in real atomic-crystal structures, for example, on tensile quasi-defects of thermofluctuation origin [12]; the statistical mechanics is responsible for this aspect as integral part of nanothermodynamics that fills up it by the physical content.

Hereby, the issues of influence of the change in a phonon spectrum, so-called effect of phonon confinement, are of primary significance in forming the calibration characteristics of Raman, ultrasonic and noise thermotransducers. Particularly, this effect explains the appearance of $1/f$ noise and its transformation into the thermal noise that has a special sense in nanothermometry and eventually in nanometrology. Thermodynamically stipulated phase equilibrium is replaced due to the contribution of surface boundaries or superficially predetermined mechanical tensions to free energy of thermosensitive substance system which enables us to produce new quasi-nonequilibrium materials with a high stability of calibrating characteristics for thermoelectric thermotransducers, and also to create functionally gradient thermocouples that are a bright example of structures, quasi-distributed in space [14].

Thermodynamic flows J and forces X are connected by Onsager reciprocity proportion (1) in linear thermodynamics valid for the systems that are not too remote from its equilibrium. The reason to consider transform processes in linear approximation under the condition $J_i(0) \rightarrow 0$ [30]:

$$J_i(X_1, \dots, X_6) = J_i(0) + \sum_j \left. \frac{\partial J_i}{\partial X_j} \right|_{(0)} (X_j - 0) = \sum_j \beta_{ij} X_j \quad (10)$$

is thermoelectric materials research results [31], where $grad T = 10^4 K/mm$ is determined experimentally and above this value the relationship of thermodynamic forces and flows becomes nonlinear. Mainly such a considerable gradient is not achievable even for nanoparticles.

Remarkably that in the case of thermometer application in the area of temperature gradient influence, the effect of thermocapillary flow arises. It lies in the appearance of superficial tension difference and thus, in the difference of capillary pressure in the liquid, which leads to the transposition of the liquid itself in the unevenly heated medium. This factor could become determinative in forming the additional source of a thermometer error in nanoworld. Anyway, it is already applied in nanotechnology while manufacturing nanoengines [10] which driving force is the effect of a thermocapillary flow.

Not to go deeper in nonlinear thermodynamics [32] it should be noticed that even in macroworld under quite sufficient gradients of thermodynamical potentials the so-called coherence effects appear [33]. With their help interrelations between certain independent (in the linear thermodynamics) thermodynamic forces or / and flows are realized. In nanoworld the transition to non-linear thermodynamics can regard other thermodynamic values (forces and flows). For example, the monatomic thickness solid film has been got already [34]; it is planned to use it in the wide nanotechnology sphere. Under this film usage some deviations from linearity in nanothermodynamic treatment can appear by virtue of surface effects.

Another prominent example can be the anharmonicity of atomic interaction that is especially exposed in nanoworld. It is known [35]-[36] the anharmonicity specifies a fractal structure appearance in solids (polymers, carbon nanomaterials and others), peculiarities in bulk thermal expansion qualities, phonon interactions, the temperature dependence of elastic constants, the thermal capacity increase under high temperatures. On the other side the phonon interaction features are experimentally studied by Raman method on carbon nanotubes [37] that can be used as universal calibration artifacts in nanotechnology research.

Hope the gained results can be used for further improvement nanothermodynamics statements and hence through the nanometrology for providing advancement in nanotechnology. Besides that in the

case of nanopatterns the surface Rayleigh phonon role significantly increases [38] so far as more atoms part is becoming surface with size decreasing. Electron dispersion on the mentioned phonons leads to some specific effects creation the meaning of which has been not realized by nanotechnology yet. The important object of study in theory of non-markovian thermodynamic systems (systems with after-effect) becomes the fluctuations in shape of admittances or impedances which efficiently describe the system [32].

6. Conclusions

1. Different kinds of noise are the manifestation of fluctuation-dissipation processes taking place inside the researched substances. Their role is strengthening rapidly in nanotechnology where studied substances are often unstable. It becomes important to study noise special qualities, their types, characteristic points of change of certain noise type with others to establish the thermodynamic substance state, its stability and so on.

2. The proper noise studying as method of non-destructive testing could lie into the basis of passive noise spectroscopy. It could be realized the most precisely owing to the usage of noise thermometers - calibrated measuring devices.

3. Under objects and sensors downsizing to nanoarea the methodology control role strengthens as well as providing of informative signals exposing on the background of increasing noise specified by the fluctuations qualities increasing. Understanding the sense of gauged changes enables to influence purposefully a thermodynamic state of the researched substance providing the further cognition of deep inner processes.

4. Methodology correctness acquires of particular importance in nanometrology that is shown in the following examples:

- *gas fire sensor*, where with volume decreasing the fluctuations qualities strengthen and performance dispersions enhance;

- *precise balance and ballistic galvanometer* where air pressure fluctuations on the plane mirror superimpose on the hanger spring elastic qualities fluctuations which limit their sensitivity and accuracy;

- *coriolis mass flowmeter*, which metrological characteristics dispersion decreasing demands to take into account deviation peculiarities of temperature sensors substance production;

- *nanomachines*, where Z-coordinate establishing accuracy increasing by the means of the hydraulic drive meets some limitations specified by the fluctuations of temperature, viscosity and positioning.

5. From the other side as result of quantum discreteness qualities extend in nanosphere, for example, charge effects, an ability appears to realize not only measurement means but to create also the measurand standards [39]. So thanks to "quantum

metrological triangle” study [40] which consists of quantum pump, Hall quantum effect and Jefferson effect basing only on two constants (e and h) it becomes possible to realize electrical standards – current, voltage and power.

6. Further progress in nanometrology is inseparably related to the nanothermodynamic investigations. To generalize thermodynamics on nanoscale, we should understand well the unique properties of nanosystems. First one is the predominance of surface tension forces on gravitational forces described by dimensionless criterion - the number of Bond.

7. As the accumulation of experimental data, we can predict expediency of consideration of nonlinear nanothermodynamics mechanisms and thermodynamic coordinates coherence effects.

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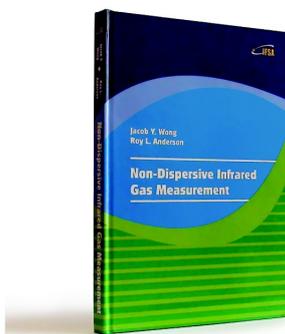
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