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Article

A Trandisciplinary Overview about the Electronic Nose

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Abstract: The mechanism by which the human nose perceives an odor is complex and involves various chemical reactions in the transformation of the odorous molecule into an electrical impulse sent to the brain that returns the sensation of smell. The smell is classified and quantified, and its instrumental detection can be carried out through the “electronic nose”, an interactive device that lends itself to various applications. In the agri-food sector, the development of portable devices makes possible to smell foods and measure their level of deterioration and maturation; this is undoubtedly useful for reducing waste, identifying the best moment for food consumption, and improving the level of food safety. With regard to the environmental compatibility of materials and techniques for packing and laying conglomerates (for example bituminous), the problem of olfactory nuisance for the population residing in the neighborhood is still an unresolved problem. The approach based on electronic noses is very effective. The electronic nose also represents an important resource in the screening of respiratory pathologies, where there is the need to identify a rapid and reliable diagnostic test for pathologies such as pneumonia or seasonal flu. Environmental monitoring of pollutants is of particular relevance today and the electronic nose is an important candidate for the use in this field. The gas sensor market leverages physics, chemistry and materials engineering to develop highly sensitive, reliable and stable sensor platforms, capable of detecting very small amounts of gas molecules in the environment. To develop competitive gas sensing platforms, new materials are being considered, including polymers, nanostructured metal oxides and nanostructured carbon-based materials (CNTs). In addition to the experimental aspects, in particular Raman and electron spectroscopy techniques together with atomic force microscopy, theoretical-mathematical modeling plays an extremely important role in this sector, with particular attention to the case of micro and nanometric dimensions. Many efforts are now aimed in improving the sensitivity of these devices and this is related to the diffusion of carriers in them. The paper also offers an overview of the mathematical models relating to mechanical processes and dynamics at the micro-nanometric scale, lastly focusing on the Drude-Lorentz type models, with related more recent generalizations.

Keywords: electronic nose; sensoristics; (Nano-)biotechnology; environment; Pollution; agri-food sector; diagnostics; mathematical modeling

1. Introduction

The effects of human activities on the environment have always been a subject of attention and today even more so; there are indicators of ongoing phenomena that do not fall directly under the common senses of man, such as the levels of micro pollutants in the air in urban areas or the quantity of CO₂ in the atmosphere. However, we also detect direct sensations such as the strong summer heat, the presence of smog, the altered flavor of foods and drinks.

The human being is equipped with five senses, of which smell is one of the most directly stimulated by the presence of human activity; in many cases it is possible to correlate the source of emission with their presence in the environment of emitted substances, but most of the time it is not easy to establish a correspondence between the perceived odor and the causes that generate it.

Odor emissions from industrial or waste treatment and disposal plants cause problems for the population living nearby, also with possible direct effects on people's health. This fact is most acute



with plants for the disposal or treatment of domestic and industrial solid waste, chemical industries, refineries, food industries, livestock farms, tanneries.

The annoying olfactory impact is therefore a problem alongside the environmental impacts linked to polluting emissions; the definition of regulatory limits relating to odor emissions constitutes a delicate problem, considering the subjectivity of olfactory perception and the methods of determining odors in the environment.

The smell can significantly deteriorate the quality of life and negatively affect economic activities, such as the value of properties and the tourism; in recent years, the olfactometry, a sensorial technique for measuring the odor concentration, has been subjected to national and international standardized objective methods, freeing odor from being just a subjective sensation, not related to regulations.

The smell is one of the oldest senses; for a lot of animals, smell is the sense of most vital importance. To date, it has not been possible to find a precise and defined correlation between the odorous sensations and the chemical structure of the molecules causing it. An odor can be accurately described by specifying its main characteristics:

- perceptibility or threshold
- intensity
- diffusivity
- quality
- hedonic tone.

Regarding the quantification of the problem, different types of measurements are carried out:

- *analytical measurements*: qualitative and quantitative measurements of the composition of a mixture of analytes through analytical separation and identification techniques;

- *sensory measurements*, such as the dynamic olfactometry;

- *sensor instrumental measurements*, using artificial noses which instrumentally perform the functions of the sense of smell [1,2].

The electronic nose is a device equipped with a multi sensor structure capable of emulating the human olfactory system; an array of chemical sensors provides a unique fingerprint of the odor, allowing its subsequent recognition. The multi sensor matrix of the electronic nose can be created with different types of sensors.

Electronic noses are used in the field of the food industry for the recognition of product freshness, in the detection of fraud (origin control, adulteration), in the detection of contaminants, in the fishing industry, in the control of raw materials, in particular relatively to freshness, rancidity, composition studies, foreign odors, characterization and determination of geographical origin, evaluation of odorous intensity, degree of maturation.

The electronic nose includes a set (array) of partially specific electrochemical sensors and an appropriate olfactory fingerprint recognition system (pattern recognition system), capable of recognizing simple or complex odors [3].

The generic architecture of the electronic nose follows the structure of the mammalian olfactory system and can be divided into three main components:

- a gas detection system, based on a certain number of sensors capable of responding to a wide range of odorants;
- a system for processing signals coming from the sensors, with the function of compressing the information;
- An odor identification/recognition system, i.e., a processing system that identifies odors by comparing them with already stored data.

In the following, the paper deals with the electronic nose in the light of sensoristics, the problem of smell in relation to food system, the question of the odor emissions into the atmosphere, the importance of smell in medical diagnosis and environmental monitoring, an overview on the mathematical modeling related to (nano-)bio-sensoristics, ending with the conclusions. A wide detailed reference list completes the work.

2. The Electronic Nose: Sensoristics

In recent years, interest has grown in the development of electronic devices capable of detecting and recognizing gases and odors thanks to an array of chemical sensors and a PC. The sensors have different characteristics, so that each chemical mixture gives rise to a set of responses that constitutes a type of characteristic fingerprint.

The variation in the physical quantity that characterizes the sensitive element is then transduced into an electrical signal. The most important aspects to consider in the choice of a sensor concern in particular:

- a) *the response time*: the sensor must provide a response in a not too long time;
- b) *the detectability threshold*: the sensor should be able to detect the presence of odorous molecules at the ppm or even ppb level;
- c) *the reproducibility among sensors of the same type*: if a sensor deteriorates, it must be possible to replace it without recalibrating the system, being able to reuse the results of the calibration of a sensor matrix for all matrices made in the same way.

Chemical Sensors are capable of converting a chemical quantity into an electrical signal and are sensitive to the concentration of specific particles such as atoms, molecules, ions present in gases or liquids. A first classification includes Metal Oxide Semiconductor (MOS), MOS Field Effect Transistor (MOSFET), Quartz Crystal Micro balance (QCM), Surface Acoustic Wave (SAW), Surface Plasmon Resonance (SPR) sensors [4].

Chemoresistors: the operating principle of chemoresistors is based on the variation in conductivity occurring in MOS or CPs (Conducting Polymers), due to chemical reactions between the sensitive layer of the sensor and the gaseous molecules; they are among the simplest gas sensors and are widely used in gas and odor recognition.

Organic CPs: this type of sensor exhibits a change in conductance when exposed to reducible or oxidizable gases, showing a reversible change in conductance when chemicals are adsorbed or desorbed by the polymer. They respond to polar compounds, operate at temperatures close to room temperature, take few seconds to interact with a volatile chemical to reach equilibrium, and come in a wide variety of types.

Chemocapacitors (CAPs): this type of sensor has two stable states during operation for the sensitive layer: air sample without gaseous molecules and with the presence of molecules.

Potentiometric Odor Sensors: gas sensors using the electrical characteristics of Schottky diodes and MOSFETs are based on the change in operation due to the presence of chemical species on their surface and on the fact that the gate metal is a catalyst for gas sensing [5,6]. These devices respond to any gas that changes their surface potential or the functioning of the gate metal.

Gravimetric Odor Sensors: gravimetric odor sensors work by sensing the effects on the propagation of acoustic waves by the absorbed molecules; QCMs (or Bulk Acoustic Wave, BAW) and SAWs are mainly used [7–9].

PID Sensors: PID sensors (Photoionization detectors) have a high response speed and can be used in the detection of many dangerous volatile organic substances (VOCs) in ppm quantities. They can detect up to a few thousand ppm, with a lower limit of around 0.1 ppm in the best conditions [10].

Signal processing and recognition: there is a relationship between the response of sensors and the recognition of the odorous fingerprint; a few number of electronic circuits are involved in the analysis and recognition work. The response of sensors is measured and converted into an electrical signal (for example a voltage), an operation carried out by interface circuits. The signal is then conditioned, filtered, cleaned to obtain satisfactory information; the analogic signal is then sampled, digitized and stored; finally, the samples are analyzed [11].

The interface circuits constitute the first stage of an electronic nose; they generate an electrical signal that reflects the changes occurring in the sensors, and are highly dependent on the type of used sensors.

The electrical signals coming from sensors and interface circuits are not suitable to be converted into numerical form and therefore treatable by a computer; they must therefore be processed by the conditioning circuit stage. This occurs in 4 phases: buffering, amplification, filtering and a series of functions (compensation, linearization, etc.). Signal conditioning devices transform the electrical

signal supplied by a generic source into a voltage signal, with the suitable characteristics for being treated within the measurement system.

The basic component of an analogic processing circuit is the operational amplifier (op-amp), at least for frequencies not exceeding a few tens of kHz. The first application of an op-amp is the buffer. An amplification is usually necessary to bring the signal from the interface circuits to a level useful for the dynamic range of a subsequent analogic digital converter.

Analogic filters are used to remove unwanted frequency components by signals coming from sensors. Some circuit structures allow to compensate for the linearity, zero and sensitivity deviations of the calibration curve of a sensor. By using analogic circuits, it is possible to create a mixture of compensation functions.

Signal pre-processing: the purpose of signal pre-processing concerns the extraction of useful information from the sensor responses and prepares the data for the subsequent multivariate pattern analysis phase. After an appropriate conditioning stage, the signals of the sensor array are digitized and then processed in real time or stored for next analysis [12,13]. The signal processing involves the pre-processing of dynamic responses, the feature extraction, the classification and the final decision making [14].

Noise: the noise is an undesirable effect that worsens the analysis of a given signal; it can occur in any part of the measurement process, it can propagate and be amplified in the signal path; noise sources can relate to the sensors and electronic components physics and be not reducible, and even be originated during the process such as the quantization and transmission noise.

The three crucial steps in the design of artificial olfactory systems are:

- the *sensing material*, which must capture the odorant molecules;
- the *transducer*, which transforms the chemical information into physical information;
- the *basic device*, which translates this variation of physical quantity into an electronic signal.

The particular choice of chemical interactive material (CIM) allows the ability to be sensitive to chemical compounds; the array strategy with different CIMs allows different response patterns that represent something similar to smells.

The transducer translates the information into a signal suitable for further processing; transducers are available in a wide range, some examples of which are as follows:

- Change in Work Function: Chemfet, Light Addressable Potentiometric Sensors [15];
- Change in Conductivity: Chemoresistance [16];
- Change in Ionic Current: Amperometric Gas Sensor [17];
- Change in Dielectric Constant: Chemocapacitor [18];
- Change in Temperature: Thermopile, Pellistor Catalytic Sensor [19];
- Change in optical spectrum: Colorimeter and Spectro-photometer [20];
- Change in Fluorescence: Optical Fiber [21];
- Change in Refraction index: Optical Fiber, Surface Plasmon Resonance [22];
- Change in Mass: Cantilevers, Surface Acoustic Wave, Quartz Crystal Microbalance [23].

The use of an array of sensors over single sensors for chemical analysis offers advantages in sensitivity to a wider range of analytes, improves the selectivity and the ability to recognize both single and complex analytes.

The chemical recognition translates information from the chemical domain into a physical output signal with a defined sensitivity. The main purpose of the recognition system is to provide the sensor with a unique selectivity profile for the analyte to be measured [24]. Considering the different interactions occurring in the binding processes between odorant molecules and CIMs, we have two main types of solid-gas interaction: physisorption and chemisorption.

The forces involved in physisorption are inter molecular forces, with insignificant changes in the electronic orbital patterns of the involved species, the others are valence forces involved in the formation of chemical compounds. Tailoring the physical and chemical properties of the coating materials used in sensors can control the selectivity and sensitivity of each sensor [25].

3. Smell and Food System

Food safety is a current issue of great importance. The increasingly pronounced needs of consumers in rich countries and the requests for guaranteed food safety are bringing the problem of nutrition to the utmost attention and highlight the relationships among agriculture, production, transformation, transport, food conservation and nutrition.

Food freshness and food quality are inextricably linked; each food has its own characteristics related to freshness. The natural tool that man possesses for evaluating the qualities of a food is the human sensorial capacity, the sense of smell. An aromatic substance is characterized not only by qualities that allow it to be identified and distinguished from others, but also by a threshold value, an intensity that determines its olfactory impact.

Food safety is understood in a general sense as the possibility of guaranteeing water and food in a constant and generalized way to satisfy the energy needs that the organism needs for survival and life, in adequate hygienic conditions.

From a hygienic-sanitary point of view, food safety is also understood as the hygienic safety of food and feed from the perspective of the integrated environmental supply chain. From an economic-social point of view, food security means first of all the measures that ensure coverage of the needs of the population from one harvest to the next, with a sufficient level of stocks for possible negative events.

The presence of microorganisms inside foods, in addition to cause alterations with consequent changes in organoleptic characteristics, can also cause poisoning, infections and food poisoning.

Industrial food measurement and monitoring are not simple processes, considering the interference caused by environmental parameters such as humidity and temperature, which require particular care in the sampling technique, sensor array and data analysis techniques. Sensors are sensitive to surrounding gases as well as target gases, so their sensitivity needs continuous improvement to detect increasingly lower compound concentrations [26,27].

4. On Odor Emissions into the Atmosphere

The attention to atmospheric emissions, in particular the odorous ones connected to industrial production sites, has increased in recent years, considering the growing sensitivity towards the environment and human health, and also due to the frequent proximity of emission sources to urbanized areas. The inclusion of an industrial plant and its acceptance by the population is conditioned by the environmental impact linked to polluting emissions and also by the possible annoying olfactory impact often associated with such installations [28].

Polycyclic aromatic hydrocarbons (PAHs), due to their known mutagenic and carcinogenic properties, represent the main toxicological problem present in the fumes generated for example by bituminous conglomerate; these emissions must therefore be adequately monitored, together with SO_x (sulphur oxides) and NO_x (nitrogen oxides), despite the existing and newly installed plants are equipped with technologies that use bag filters for the treatment of conveyed emissions [29].

The exposure to these fumes can occur either through inhalation or absorption through the skin, and the intensity of exposure depends on the characteristics of the workplace. The experimental procedure involves a global chemical-morphological identification of the source following complementary methodological approaches: the analytical one and that based on artificial olfactory systems [30].

Several operators in the bitumen industry require simpler and more flexible techniques for an almost real-time instrumental screening of the bituminous binder and the associated emissions, that are generated during all phases of construction of road pavements, often responsible for persistent nuisance olfactory for the population living near the plants [31].

The approach based on artificial olfactory systems can be adequately used, alongside traditional analytical techniques, for the study of bitumen in the phases of the production chain of bituminous conglomerates. The various analytical-sensory analysis conducted with electronic noses, both with bench-top instrumentation and with a commercial portable device [32,33], highlights a compatibility between the sensors operating principle and the emissions type of the bituminous binders; this has

allowed the identification of specific odor fingerprints both of the bitumen solid matrix at room temperature and of the emissions generated at the various process temperatures. Through the development of a specific statistical data treatment and post-processing procedure, it is possible to obtain a quantitative response to the information collected by the electronic nose [34,35].

The electronic nose demonstrates its validity in recognizing the odor generated during the different production and laying phases of bituminous conglomerates, to which limits of olfactory annoyance or nuisance can be associated. These devices are able to give an objective judgment quickly and without the need for sample pre-treatment procedures [36–39].

5. Smell and Medical Diagnosis

Prevention in medicine has a strategic importance, in relation to a rapid qualitative diagnosis of diseases, facilitating the early discrimination between different infections for a rapid treatment [40]. It is well known that microbial species produce a series of volatile compounds; these are components of an odor that could be recognized as characteristic of a particular disease and used to monitor people's health.

The importance of odors for the human health was well understood in ancient medicine, such as the Chinese medicine, which diagnosed diseases by analyzing the body odor [41]. Conventional Western medicine has recognized that some pathologies produce characteristic unpleasant odors.

Studies based on analytical tools, such as Gas Chromatography (GC) or GC linked to Mass Spectrometry (GC-MS), have shown that microorganisms produce many volatile organic compounds, including alcohols, aliphatic acids and terpenes, some of which have characteristic odors, monitoring the production of volatile compounds as an aid to the clinical diagnosis of aerobic and anaerobic bacterial infections and cardiopulmonary diseases [42–44].

The human odor results from the combined action of cutaneous glands and sequestering organic compounds, whose regulation is subjected to the human hormonal control, and to bacterial populations located on the skin surface, which live by metabolizing and transforming the organic compounds that are capable of absorbing by their external environment.

However, the potential of GC/GC-MS in medical diagnosis is undermined by a series of limitations, such as the cost of analytical equipment, the expertise needed to operate these instruments and the time needed to obtain results. By managing to amplify the reactions between volatile markers and the various sensors, an increase in sensitivity would be obtained, allowing the measurement of qualitative differences among markers at relatively low concentrations, with odor as a significant synthesis of the properties of a disease revealed by a particular interaction of components present in a very low concentration, using non-invasive investigation methods.

It has been also demonstrated the possibility of discriminating between different aerobic bacteria, such as *Helicobacter pylori*, *Escherichia coli* and *Enterococcus* species that are present in the samples, both alone and as a mixture of the three species, based on the difference produced in the quantities of terpenes, trimethylamine and ketones [45,46].

Various bacterial species responsible for eye infections (*Escherichia coli*, *Haemophilus influenzae*, *Moraxella catarrhalis*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Streptococcus pneumoniae*) have also been studied using data obtained with portable electronic noses [47]. Patients with kidney disorders have been shown to produce characteristic volatile compounds, which may be a useful tool in the diagnosis and control of renal dialysis [48], and thus the lung cancer detectable by breath analysis using non-selective gas sensors [49,50].

6. On Environmental Monitoring

The problem of environmental monitoring is complex for multiple reasons, mainly in relation to the different sources of pollution (industrial plants, landfills, purification plants) and in relation to the different monitoring targets.

Regarding pollution monitoring, there are many instrumental controls available to reduce the emission of polluting compounds such as CH_4 , CO_2 , H_2S , but the problem of pollution monitoring

remains of primary importance to keep emissions below the safety thresholds, hopefully through reproducible and non-invasive devices.

Biosensors are very sensitive and selective, but have a short lifespan, from a few days to a few months, and this limits their application to continuous online monitoring. Optical sensors are fast, versatile, with low operating costs, limited or no sample manipulation, but also have problems such as biofouling of probe tips, calibration stability and selectivity [51]. The electronic nose, being in principle non-invasive and versatile, has a great potential for real-time and online monitoring of air quality, as well as wastewater [52,53].

About the Olfactive Impact Monitoring (OIM), this is a serious problem, which has stimulated interest in odor measurements and in defining objective methods of certifying odor emissions, trying to avoid expensive and labor-intensive methods.

Regarding the use of the electronic nose in environmental monitoring, efforts are aimed at monitoring volatile organic compounds present in the air that are released when waste products are discharged into water, soil and air.

- *Water monitoring*: the electronic nose has been used to measure the contaminating residues of insecticides and products from purification plants, often discharged into torrents and rivers [54,55].

- *Monitoring of the territory and air*: the quality of the territory and the air (even inside buildings) is very important; even if the annoying odor does not put public health at risk, it compromises the quality of life [56–58].

7. Mathematical Modeling for (Nano-)Bio-Sensoristics

The study of the mechanical behavior of nano-bio-materials uses solid (or materials) mechanics, searching the determination of materials responses to the action of external forces, as elongations, deformations, fracture behavior [59]. The “Finite Element Method” (FEM) is often used, allowing the decomposition of a complex problem into a set of many small problems via the process of discretization [60]. Experimental results at mesoscopic scale get a valid explanation with nanomechanics, atomic level study and multiscale modeling [61].

The charge transport is one of the most important aspects at the micro-nanoscale, influenced by particles dimensions and with other characteristics with respect to those of bulk. Several techniques have been used for the knowledge of transport phenomena, in particular analytical descriptions based on transport equations and numerical approaches.

An important set of models is the Drude-Lorentz type models, variations of the Drude-Lorentz and Smith models, hopefully allowing the exact calculation of the analytical expressions for the three most important dynamical functions, i.e., the velocities correlation function $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle_T$ at the temperature T , the mean square deviation of position $R^2(t) = \langle [\vec{R}(t) - \vec{R}(0)]^2 \rangle$, the diffusion coefficient $D(t) = \frac{1}{2} \left(\frac{d R^2(t)}{d t} \right)$.

Among the most used semi-empirical formulations, we remember:

a) The “Tight-Binding” Method (T-BM), a semi-empirical method generally preferred when the computational calculation is considerable [62];

b) The “ab-initio” formulations, which produce accurate results, although dependent by the made choices;

b1) The Density Functional Theory (DFT), which gives the total energy of the system by means of the functional of the electrons total density [63];

b2) Local Density Functional Theory (LDFT).

Other approaches are:

c) Non-Local Functional Approach (N-LFA);

d) Car-Parrinello Molecular Dynamic Method (C-PMDM) [64];

e) Conjugate-Gradient Method (C-GM) [65];

f) Augmented Plane Wave Method (APWM) [66];

g) Korringa-Kohn-Rostoker Method (K-K-RM) [67];

- h) Linearized-Muffin-Thin-Orbital Method (L-M-T-OM) [68];
- i) Full Potential Linearized Augmented Plane Wave Method (FPLAPWM) [69].

About the Drude-Lorentz type models, they are mainly improvements of Drude model [70]. In the Smith model appears a parameter c_n accounting for the anisotropy of scattering upon the first scattering event [71]. The “Effective Medium Theories” (EMTs) are variations in which the electromagnetic interactions between pure materials and host matrixes are approximately taken into account. Among EMTs, particular attention is given to the Maxwell-Garnett model (MG) and the Bruggeman model (BR) [72,73].

About recent generalizations of Drude-Lorentz type, Smith models and Effective Medium Theories (EMTs) for transport processes in solid state physics and soft condensed matter, a recent extension showed to fit very well with experimental scientific data and gives also interesting new predictions of various peculiarities at nanolevel. It gives the analytical form of $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle_T$, $R^2(t)$, $D(t)$, the last two writable as a function of $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle_T$. A classical, quantum and relativistic version of the model has been performed [74–76], the quantum-relativistic version is in its final step [77,78].

One of the main objectives of an electronic nose is the potential of its sensitivity; this last is one of the most important feature of a nano-bio-sensor and generally nano-bio-device, resulting in its ability to detect in very deep way. The sensitivity is highly connected with the diffusion of charges in carrier transport.

For completeness, we report the analytical form of the diffusion coefficient D in the classical (C), quantum (Q) and relativistic (R) case of this recent analytical model [74–76]:

C₁) Case $\Delta_{Cl} > 0$

$$D(t) = 2 \left(\frac{k_B T}{m^*} \right) \left(\frac{\tau}{\alpha_R} \right) \left[\sin \left(\frac{\alpha_R}{2} \frac{t}{\tau} \right) \exp \left(-\frac{t}{2\tau} \right) \right] \quad (1)$$

with:

$$\alpha_R^2 = 4\tau^2 \omega_0^2 - 1 \quad (2)$$

C₂) Case $\Delta_{Cl} < 0$

$$D(t) = \left(\frac{k_B T}{m^*} \right) (\tau) \left(\frac{1}{\alpha_I} \right) \left(-\exp \left(-\frac{1+\alpha_I}{2} \frac{t}{\tau} \right) + \exp \left(-\frac{1-\alpha_I}{2} \frac{t}{\tau} \right) \right) \quad (3)$$

with:

$$\alpha_I^2 = 1 - 4\tau^2 \omega_0^2 \quad (4)$$

Q₁) Case $\Delta_{Quant} > 0$

$$D(t) = 2 \left(\frac{k_B T}{m^*} \right) \sum_i \left(\frac{f_i \tau_i}{\alpha_{iR}} \sin \left(\frac{\alpha_{iR}}{2} \frac{t}{\tau_i} \right) \exp \left(-\frac{t}{2\tau_i} \right) \right) \quad (5)$$

with:

$$\alpha_{iR}^2 = 4\tau_i^2 \omega_i^2 - 1 \quad (6)$$

Q₂) Case $\Delta_{Quant} < 0$

$$D(t) = \left(\frac{k_B T}{m^*} \right) \sum_i \left(\left(\frac{f_i \tau_i}{\alpha_{iI}} \right) \left(-\exp \left(-\frac{1+\alpha_{iI}}{2} \frac{t}{\tau_i} \right) + \exp \left(-\frac{1-\alpha_{iI}}{2} \frac{t}{\tau_i} \right) \right) \right) \quad (7)$$

with:

$$\alpha_{iI}^2 = 1 - 4\tau_i^2 \omega_i^2 \quad (8)$$

R₁) Case $\Delta_{R_{rel}} > 0$

$$D(t) = 2 \left(\frac{k_B T}{m_0} \right) \left(\frac{1}{\gamma} \right) \left(\frac{\tau}{\alpha_{R_{rel}}} \right) \left[\sin \left(\frac{\alpha_{R_{rel}}}{2\rho} \frac{t}{\tau} \right) \exp \left(-\frac{t}{2\rho\tau} \right) \right] \quad (9)$$

with:

$$\alpha_{R_{rel}}^2 = 4\gamma\tau^2\omega_0^2 - 1 \quad (10)$$

R₂) Case $\Delta_{R_{rel}} < 0$

$$D(t) = \left(\frac{k_B T}{m_0} \right) \left(\frac{\tau}{\gamma} \right) \left(\frac{1}{\alpha_{I_{rel}}} \right) \left(-\exp \left(-\frac{1+\alpha_{I_{rel}}}{2\rho} \frac{t}{\tau} \right) + \exp \left(-\frac{1-\alpha_{I_{rel}}}{2\rho} \frac{t}{\tau} \right) \right) \quad (11)$$

with:

$$\alpha_{I_{rel}}^2 = 1 - 4\gamma\tau^2\omega_0^2 \quad (12)$$

The coefficients $\alpha_R \in \mathbb{R}^+$ (positive real numbers); the α_I ones $\in (0,1) \subset \mathbb{R}$.

It holds also: $\gamma = 1/\sqrt{1-\beta^2}$, $\beta = v/c$, $\rho = 1 + \beta^2$, $\gamma^2 = \gamma^2$, $m_0 = \text{rest mass}$.

Equations, governed by parameter of type α_I , are a superposition of exponentials; the behavior of curves is similar to a typical Drude-Lorentz behavior. Equations, governed by parameter of type α_R , are a product of an exponential with a sinusoidal type function; the behavior of curves is a typical damped oscillation in time.

The model includes also a gauge factor, which allows its use from sub-pico-level to macro-level. Interesting applications have been performed also for economics, neuroscience and brain processes, nano-medicine. Acting on all chemical, physical, structural and model-intrinsic parameters, i.e.:

- the temperature T of the system,
- the parameters α_I and α_R ,
- the values of τ_i (relaxation times) and ω_i (frequencies),
- the effective mass m^* ,
- variations of the chiral vector,
- the quantum weights of each mode (in the quantum case),
- the carrier density N ,
- the velocity of carriers (in the relativistic case),

it is possible to perform a fine and accurate tuning of $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle_T$, $R^2(t)$ and $D(t)$ and therefore to calibrate the performance of nano-bio-devices, with both an "a-priori" (predictive) and "a-posteriori" (confirmatory) use of the model.

8. Conclusions

In many application fields it is possible to exploit the great potential of artificial olfactory systems through the design of dedicated sampling systems depending by the different field. The operating principle and the sensitive material form the basis of development of these devices; the sampling, within the measurement chain, serves to optimize the performance of the entire system. It is thus possible to design "ad hoc" experimental sets through specific sampling procedures for each application.

A chemical sensor is a device that transforms chemical information into an analytically useful signal. The meaning of the reality "smell" contains many chemical concepts and it is a complex sensory process, consisting of a series of steps that lead the interaction with the external world to become a sensation in the nucleus of the human brain. The artificial smell consists of the translation

of each of these individual steps into chemical, electronic and mathematical processes for the measurement of this perception.

The electronic nose is an instrument that includes an array of chemical electronic sensors with partial specificity and an appropriate pattern-recognition system, capable of recognizing simple or complex odors.

Regarding the diagnostic potential of smell, the importance of this technology is underlined, due to its less invasive peculiarity, often cheaper and probably more suitable for early diagnosis than classic diagnostic tools. The challenge is to exploit these techniques in medical fields where an early, cheaper and non-invasive diagnosis is desirable, such as lung cancer and various other types of disease.

In daily life it is possible to find various applications that an electronic nose could satisfy, and it can replace man in all situations in which the environment can be harmful or lethal for him. The research is directed towards the use and optimization of modular sensory systems; this can offer the necessary flexibility in adapting the system to a greater number of applications and in allowing new technologies and new concepts to extend the chemical-sensory analysis.

On the market we find tools for the military field, the food safety, the medical and pharmaceutical field (to diagnose infections, intoxications and other metabolic problems), to recognize and distinguish different types of fungi and bacteria, for the automotive field and the environmental monitoring. The electronic nose can be used in the detection of toxicity or harmful components, surpassing the normal olfactometry techniques that use panels [79,80].

About modeling related to nano-bio-sensoristics, Drude-Lorentz type models are very interesting tools for the theoretical and predictive study of sensors behavior, considering also quantum and relativistic effects. Recent extensions are mathematically very elegant, because totally analytical, therefore non time consuming, and are giving confirmations with respect to the previous models, so as new information about the dynamics of systems at nanoscale, which can be conveniently tested through experimental time-resolved techniques, like TRTS, Photon-Induced Near-Field Electron Microscopy and Graphene based Plasmonics [81–96].

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