

Future trends in acoustic gas monitoring and sensing

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Traditionally, acoustic devices for monitoring gaseous environments have involved measuring the sound speed in the medium. However, measurements of sound speed alone do not always allow a quantitative analysis of the gas species present in the sensed volume. What has been habitually omitted is the acoustic attenuation. The non-classical or relaxational attenuation of sound in fluids arises from the inability of internal molecular degrees of freedom (vibration, rotation, isomerism etc.) to follow the acoustic fluctuations. This feature relates it directly to relaxation times, which are characteristic of the molecular species. Together with sound speed, attenuation can be used to obtain the effective specific heat of the fluid, which is the fundamental macroscopic footprint of all internal relaxation processes. It is the purpose of this paper to describe trends and challenges in the development of the next-generation "smart" acoustic gas sensors. We outline, from physical principles, the operational "line of thought" that might be adopted in the processing units of future intelligent sensors to quantitatively detect and identify contaminant gases leaking into a host gaseous environment.

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1. Introduction

Surveillance of gaseous species in the atmosphere is made usually by chemically sensors. It was shown, recently, that excepting the electrical conduction data, the monitoring of the semiconductor work function [1] and electron affinity [2] could improve the selectivity of the sensor. Various chemoresistive materials are tried. For example platinum doped WO_3 , which exhibits a very good sensitivity to SO_2 and H_2S [3].

Gas-coupled acoustic techniques for analyzing gas mixtures are based on measurements of attenuation and phase velocity (speed of sound) in the gas under study. The mechanisms responsible for the frequency-dependent attenuation and dispersion in gases have been studied extensively for almost a century. Non-empirical modeling of the molecular collision-based processes inherent in the non-classical dispersion and attenuation still poses challenges for various molecular families. Experimental techniques have been continuously refined over time, reaching a point where extremely accurate values for the complex-valued wave number have been achieved. Good reviews of theoretical and experimental work on acoustic propagation in molecular fluids can be found in Refs. [4] and [5]. The price one often pays for accuracy is processing time. Sensors designed to monitor critical environments need to operate on much shorter time scales. Surface Acoustic Wave (SAW) devices can sense changes in the wave number on the order of several parts per million (ppm). However, they need regular replacement of the sensitive adsorptive coating and also require periodic

re-calibration using reference gases. Gas-coupled sensors, on the other hand, do not need calibration and are usually more rugged and versatile since they are able to accommodate any gas mixtures. In most practical cases, sensors are "passive" in the sense that they only *record* data streams. The next step will be to "teach" a sensor how to interpret the acquired data based on physics concepts programmed into its processing unit. In other words, "smart" sensors must be capable of inferring (at least) the *nature* of a contaminant molecular species leaking into the base gas. Thus, the Three Tasks of Smart Acoustic Gas Sensing could be the following:

- **First Task:** Determine how the molecular weight of the mixture compares with that of the base gas based on changes in the sound speed. This task is relatively simple: lighter gases are "faster".
- **Second Task:** Detect the *presence* of molecular relaxation effects in the mixture and estimate relaxation times. This can be accomplished by identifying peaks in the normalized attenuation curve and/or, more reliably, measuring the imaginary part of the effective specific heat, indicative of relaxation effects.
- **Third Task:** Interpret dynamic *shifts* in the relaxation times. These are due to different inelastic collision processes whereby energy is exchanged between internal and external (or acoustic) degrees of freedom.

Based on changes in sound speed and attenuation, the sensor will ultimately know how to make initial inferences as to the nature of the contaminant species. This constitutes a complex job for it implies one must know what kind and amount of knowledge should be programmed into the sensor. *Complete* identification of contaminants from acoustic attenuation and dispersion is mathematically difficult if not impossible because of the ill-posedness of the *inverse problem*: given two acoustic propagation parameters, complete tagging of the gases implies obtaining information down to the level of intermolecular collisions (relaxation times, inelastic scattering transition probabilities, intermolecular forces etc.), as well as knowledge of thermodynamic quantities (heat capacity, viscosity, thermal conduction etc.). Nevertheless, if one imposes some restrictions that bestow “attenuating circumstances” to the problem, one can achieve *partial* identification of contaminant gases. For instance, being able to determine the *nature* and concentration of the foreign gas as it leaks in is tremendously important especially in the process of decision leading to the issuance of a critical threat alert. As a first such attenuating circumstance, restricting the number of contaminant “candidates” reduces the difficulty of the problem. Assume a sensor must be developed to monitor gaseous streams in life-support systems aboard manned spacecraft. Typically, the gases involved in a typical system are nitrogen, oxygen, hydrogen, carbon dioxide, water vapor, and methane. A second attenuating circumstance is that the concentration of contaminant species (governing the dynamics of the activation-relaxation paths of the mixture) is usually much smaller than that of the base gas.

2. Proposed sensing philosophy

As an example, consider a base atmosphere of nitrogen, which is “contaminated” successively with 3% water vapor, 5% methane, and 5% carbon dioxide (molar fractions). Let’s assume that a multi-frequency acoustic device is able to measure the phase velocity and normalized attenuation at a number of frequencies, simultaneously, as shown in Fig. 1. The values of these quantities at three frequencies (22, 92, and 215 kHz), are shown for easy reference.

The acoustic quantities at three distinct frequencies, 22, 92 and 215 kHz, are indicated, respectively, by the diamonds, squares and circles. For convenience, the curves for pure molecular nitrogen (the base gas) and its successive mixtures with 3% water, 5% methane, and 5% carbon dioxide are labeled 1, 2, 3, 4, respectively. The attenuation in pure nitrogen is mostly classical (due to viscous and thermal effects), the non-classical contribution being restricted to very small frequencies (<0.1 Hz). The relatively small amounts of either methane or carbon

dioxide contribute sizable molecular relaxation effects to the mixture, as observed in the frequency dependence of both phase velocity and attenuation.

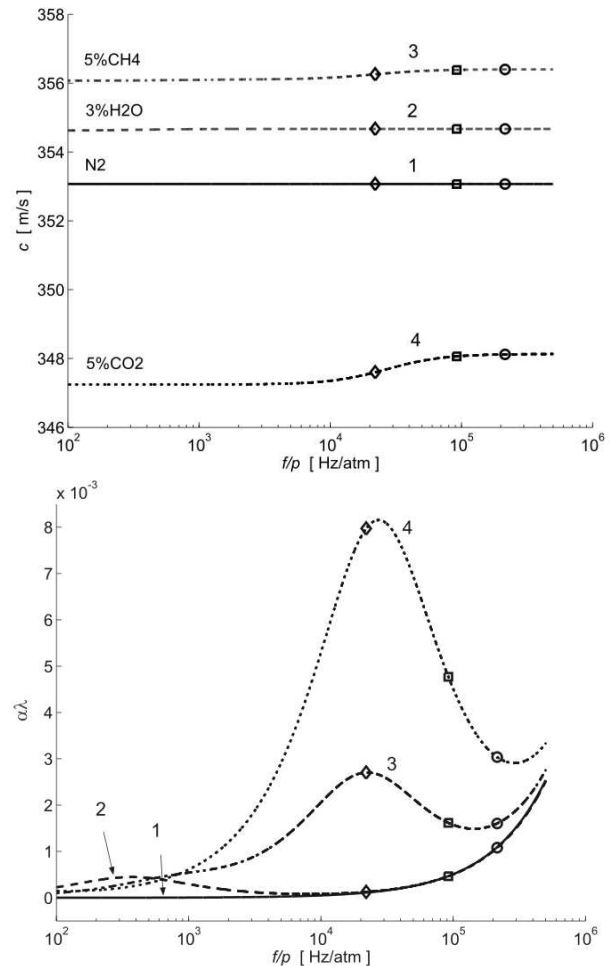


Fig. 1. Frequency dependence of the sound speed (left) and of the non – dimensional absorption (right). Diamonds, 22 kHz; squares, 92 kHz; circles, 215 kHz.

At this point, the knowledge base pre-programmed into the sensor should enable it to differentiate between the four mixtures based on the following five “operational statements”:

1. “I know the properties of the base gas and those of the contaminant candidates.”
2. “As the base gas is contaminated, I can detect inflexion points in the speed of sound and/or peaks in the attenuation. Therefore, there exist thermal relaxation processes.”
3. “From the sound speed data, I infer that, most likely, Gas 2 is lighter than Gas 1, Gas 3 is lighter than Gas 2, and Gas 4 is heavier than Gas 1.”
4. “From the positions of the (main) attenuation peaks, I infer that Gas 4 relaxes faster than Gas 3,

Gas 3 relaxes faster than Gas 2, which in turn relaxes faster than Gas 1.”

5. “The relative magnitudes of the attenuation peaks indicate that Gas 4 has a larger relaxation contribution to the specific heat than Gas 3, which in turn has a larger contribution than Gas 2. Possibly, the contaminant molecules in Gas 4 have more vibrational modes excited than those in Gas 3 and Gas 2.”

Venturing deeper, the next-generation sensor will attempt to “reverse engineer” the acoustic propagation data (attenuation and sound speed) in order to further “understand” the mixture. Thus, the device should be able to “synthesize” an effective wave number from the frequency-dependent sound speed $c(\omega)$ and attenuation $\alpha(\omega)$,

$$\tilde{k}(\omega) = \frac{\omega}{c(\omega)} - i\alpha(\omega). \quad (1)$$

The effective wave number is related to molecular relaxation through the frequency-dependent isochoric and isobaric *effective specific heats*, C_V^{eff} and C_P^{eff} , defined, respectively, as the numerator and denominator of the second factor in Equation (2) [6,7]:

$$\tilde{k}(\omega)^2 = k_0^2 \frac{C_V^{eff}(\omega)}{C_P^{eff}(\omega)} = k_0^2 \frac{C_V^0 + \sum_{i=1}^N x_i C_i^{vib} (\Gamma_i - 1)}{C_P^0 + \sum_{i=1}^N x_i C_i^{vib} (\Gamma_i - 1)}. \quad (2)$$

Here x_i is the molar fraction of the i 'th vibrational mode and N is the total number of modes, distributed among the molecular species that form the mixture. $k_0 \equiv \omega(\rho_0 / p_0)^{1/2}$ and the quantity $\Gamma_i \equiv \Delta T_i^{vib} / \Delta T_i$ represents the ratio of the temperature fluctuations of the vibrational and translational (acoustic) degrees of freedom (complex-valued since the former lag behind the latter). The value of the effective heats at zero frequency, $C_V^0 \equiv C_V^{eff} \big|_{\omega \rightarrow 0}$ and $C_P^0 \equiv C_P^{eff} \big|_{\omega \rightarrow 0}$ are the *static* or *equilibrium* specific heats at constant volume and constant pressure, respectively. In terms of the mixture composition, they are given by

$$C_V^0 = \sum_{i=1}^N x_i C_{V,i}^0 \quad \text{and} \quad C_P^0 = \sum_{i=1}^N x_i C_{P,i}^0. \quad (3)$$

Correspondingly, at very high frequencies, $C_V^\infty \equiv C_V^{eff} \big|_{\omega \rightarrow \infty}$ and $C_P^\infty \equiv C_P^{eff} \big|_{\omega \rightarrow \infty}$ are the *instantaneous* values of the effective heats. The difference between the static and instantaneous specific heat values gives the overall contribution of the internal (here, vibrational) degrees of freedom of the mixture, namely

$$C_V^0 - C_V^\infty = C^{vib} = \sum_{i=1}^N x_i C_i^{vib}. \quad (4)$$

C_i^{vib} is the vibrational specific heat of the i 'th individual mode, given by the Planck-Einstein equation, [8]

$$C_i^{vib} = g_i R \left(\frac{\theta_i^{vib}}{T_0} \right)^2 \frac{e^{-\theta_i^{vib}/T_0}}{\left(e^{-\theta_i^{vib}/T_0} - 1 \right)^2}, \quad (5)$$

where T_0 is the equilibrium temperature, $\theta_i^{vib} = h\nu_i/k_B$ is the vibrational characteristic temperature of the i 'th mode (of frequency ν_i), g_i is its vibrational degeneracy, $h = 6.626 \times 10^{-34}$ Js is Planck's constant, $k_B = 1.380 \times 10^{-23}$ J/K is Boltzmann's constant.

For the mixtures considered, C^{vib} is 0.0145, 0.0209, 0.1354, and 0.1497 J/molK for N_2 and its mixtures with 3% H_2O vapor, 5% CH_4 , and 5% CO_2 , respectively. At each frequency, the effective specific heats are related by

$C_P^{eff} - C_V^{eff} = R$, where $R = 8.314$ J / molK is the universal constant of gases. The complex-valued effective specific heat is the fundamental macroscopic “footprint” of the inability of the vibrational degrees of freedom to follow the acoustic temperature fluctuations. Yet, what makes the effective heat useful in the analysis is the fact that, for each main relaxation process, it traces a *semicircular* path in the complex plane as a function of frequency. The complex plots of the effective specific heats for the four mixtures considered are shown in Fig. 2. The semicircular loci appear distorted due to the format ratio of the plots.

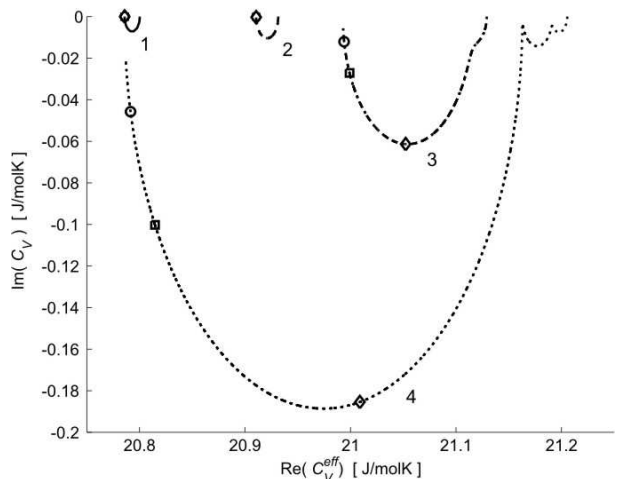


Fig. 2. Complex plot of the effective isochoric specific heat per mole. Solid, N_2 ; dashed, $N_2+3\%H_2O$; dot-dashed, $N_2+5\%CH_4$; dotted, $N_2+5\%CO_2$. Along each curve, the frequency increases clockwise from right to left. For each curve, the quantity $C_V^{eff} \big|_{\omega \rightarrow 0} - C_V^{eff} \big|_{\omega \rightarrow \infty} = C^{vib}$ is the vibrational contribution to the effective specific heat. Diamonds, 22 kHz; squares, 92 kHz; circles, 215 kHz.

For each mixture, with increasing frequency, the effective specific heat moves clockwise in the complex plane from the right ($\omega \rightarrow 0$) to the left ($\omega \rightarrow \infty$), along single or multiple semicircular paths, depending on composition as well as the number and magnitudes of thermal relaxation processes. In the absence of internal relaxation, the specific heat would be real-valued at all frequencies. The effects of vibrational relaxation on the specific heat are obvious in all four cases. Pure molecular nitrogen (Curve 1) is the least affected, while the successive mixtures of nitrogen with 3% water vapor, 5% methane, and 5% carbon dioxide (Curves 2, 3, and 4, respectively) are progressively richer in the relaxational contributions to the effective specific heat. The model predicts weak secondary relaxation processes for mixtures of N_2 with CH_4 and CO_2 (Curves 3 and 4, respectively), possibly due to the deactivation of the N_2 vibrational mode (2331 cm^{-1}) and of the CO_2 symmetrical stretch mode (1337 cm^{-1}). For methane as an additive, the secondary effective frequency is approximately 850 Hz. For carbon dioxide as the additive, the additional relaxation frequencies are very small: 7.4 Hz/atm and 0.09 Hz/atm. The discussion of these secondary relaxation processes is outside the scope of this paper. For N_2 - CO_2 mixtures in particular, it may be necessary to step outside the SSH-Tanczos framework and account for supplemental processes such as three-quantum transitions [9], vibrational deactivation by Fermi resonances [10], and induced multipole fields [11]. Nonetheless, the smallness of these secondary relaxation frequencies makes them impractical in fast-response acoustic gas sensors. That is why these effective frequencies for the N_2 - CO_2 mixture are not shown in Fig. 1. On the other hand, the effective specific heat extrapolated at $\omega \rightarrow 0$ is important since it represents the composition-dependent equilibrium specific heat of the mixture, C_V^0 , determined by Equation 3.

Looking at Fig. 3, one notes that Curves 1 and 4 both extrapolate to $C_V^\infty \approx \frac{5}{2}R$. This means that, at high frequencies, both mixtures have three fully activated translational and two fully activated rotational degrees of freedom. This is correct for pure N_2 (Curve 1) and it is a valid approximation for the mixture of N_2 and CO_2 (Curve 4), the latter being a quasi-linear molecule. Curves 2 and 3, on the other hand, extrapolate to larger values of C_V^∞ . This indicates that the non-linear H_2O and CH_4 molecules have three rotational degrees of freedom. At this point, the sensor would be able to formulate two extra-operational statements, namely:

6. “Gas 1 and Gas 4 have $C_V^\infty \approx \frac{5}{2}R$. Therefore, the contaminant species in Gas 4 is likely to be either a diatomic or a linear polyatomic molecule.”

7. “Gas 2 and Gas 3 have $C_V^\infty > \frac{5}{2}R$. Therefore, the contaminants in those mixtures are likely to contain nonlinear polyatomic molecules”.

For each complex path in Fig. 2,

$$C_V^\infty \leq \text{Re}(C_V^{eff}) \leq C_V^0 \quad (6a)$$

and

$$0 \leq \left| \text{Im}(C_V^{eff}) \right| \leq \frac{1}{2} C^{vib}. \quad (6b)$$

The inequality (6b) is easily obtained considering a simple relaxation process characterized by a single relaxation time τ , the temperature fluctuation ratio is $\Gamma = (1 + i\omega\tau)^{-1}$. Hence,

$$C_V^{eff}(\omega) = C_V^\infty + \frac{C^{vib}}{1 + i\omega\tau} = C_V^\infty + C^{vib} \frac{1 - i\omega\tau}{1 + (\omega\tau)^2}. \quad (7)$$

The effect of relaxation on acoustic propagation is the strongest when $\omega\tau = 1$ (i.e. the acoustic period is commensurate with the relaxation time). Hence,

$$\text{Im}(C_V^{eff})_{relax} = -\frac{1}{2} C^{vib}. \quad (8)$$

In the simple relaxation case described above, Fig. 3 shows the locus of $C_V^{eff}(\omega) \equiv x(\omega) + iy(\omega)$, which is a semicircle of radius $r \equiv C^{vib}/2$ centered on the point $x_0 = C_V^\infty + C^{vib}/2$ [12]. The frequency at which $x = x_0$ and $y = -r$ is the effective relaxation frequency, satisfying $\omega_{relax}\tau = 1$.

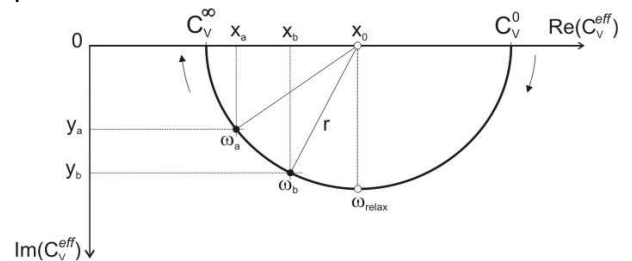


Fig. 3. Complex plot of the effective specific heat ($C_V^{eff} \equiv x + iy$) for a simple relaxation process. If the sensor operates at (at least) two frequencies, ω_a and ω_b , it is possible to “synthesize” the locus of the effective specific heat from its real (x_a, x_b) and imaginary parts (y_a, y_b), determined from attenuation and phase velocity data.

The minimum number of probing frequencies necessary for the sensor to be able to “synthesize” this locus from the raw data (attenuation and phase velocity) is two. From Fig. 3, it is easy to show [2] that, if the effective specific heats are known at frequencies ω_a and ω_b , then

$$x_0 \equiv C_V^\infty + \frac{C^{vib}}{2} = \frac{x_b^2 - x_a^2 + y_b^2 - y_a^2}{2(x_b - x_a)} \quad (9a)$$

and

$$r \equiv \frac{C^{vib}}{2} = \sqrt{x_a^2 + y_a^2 + x_0(x_0 - 2x_a)}, \quad (9b)$$

where (x_a, x_b) and (y_a, y_b) are the real and imaginary parts, respectively, of the effective specific heats at the two frequencies, are also known.

The ability to determine the effective specific heat is a large bonus since it gives access to a more fundamental level of information than either the speed of sound or the attenuation, individually, namely to the molecular geometry, through the high-frequency limit C_V^∞ , and to the number of internal modes which lag behind the acoustic temperature fluctuations, through the internal (here, vibrational) contribution, C^{vib} , for instance via Equations (9). The shape of the complex locus of the frequency dependence of C_V^{eff} is indicative of the number of activation/relaxation processes. For example, any deviation from a semicircular path points to the existence of multiple relaxation pathways [5].

3. Conclusions

Gas-coupled acoustics offers a unique approach to the quantitative analysis of gas mixtures. If sound speed and attenuation can be measured with a high degree of

accuracy, the effective or dynamic specific heat of the mixture can be obtained. The three frequency-dependent quantities can effectively quantify the gas mixture under study. This characteristic makes acoustic relaxational spectroscopy extremely attractive to use in fast and accurate devices for in-line sensing and monitoring of gaseous environments.

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