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Contributions of adsorption and growth of droplets in a mirage experiment

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Abstract: A concentration wave model and mirage effect experiments are used to demonstrate that the mirage effect in presence of condensable gases is sensitive to the growth of droplets on a solid surface.

1. INTRODUCTION

A few experiments [1] have demonstrated that photothermal methods are sensitive to adsorption of liquids on solid surfaces. The basic idea is to monitor a periodic desorption by absorption of a periodic light flux at the surface [2]. The detection proposed in this paper is achieved by measuring the deflection of a light beam skimming the surface with a quadrant cell (Mirage Effect) [3].

In section 2, we give the hypotheses and the result of a one dimensional calculation of the mirage deflection in presence of adsorbable molecules. This result contains two terms corresponding to the periodic variation of the probed medium refractive index due to the periodic variation of the temperature and to the periodic variation of the concentrations in the gas mixture. In section 3, we discuss the influence of thermal and concentration contributions on the mirage amplitude and phase as functions of the pressure and the surface temperature. After a brief description of the experimental set-up built to check the validity of the model, the experiments presented will be analysed to determine the sensitivity of the mirage effect to the adsorption of organic molecules on unprepared surfaces in conditions close to Normal Temperature Pressure (N.T.P.).

2. THEORETICAL MODEL

Let us consider a closed cell containing a solid sample (s) at temperature T and a mixture of two gases (g); A is non-condensable and B is condensable, with C_A and C_B the respective numbers of moles per unit volume. We assume that a thin film (f) of adsorbed molecules B is formed at the surface of (s) which receives a modulated flux of light (pump beam), that the film is transparent and that all the pump beam energy is absorbed at the sample surface. This film is partially vaporized during the half period of illumination of the sample. A probe beam, parallel to the sample surface at a distance z , is deflected by the gradient of the gas refractive index n produced by both the temperature and the molecular gradients.

Fig1 : Definitions and schematic representation of the mirage detection

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In order to obtain an analytical result, three classical hypotheses are assumed: the diffusion processes are one dimensional, the mirage deflection is produced only by the index of refraction gradients and not by the sample thermoelastic deformations, the absorption of the pump beam takes place at the solid surface. Concerning the diffusion of the gas molecules, we also assume that the cell length is much smaller than the sound wavelength at modulation frequencies used. The adsorbed and gaseous molecules B are supposed in equilibrium so that the thermodynamic laws of adsorption can be used [4]. Finally the perturbations produced by the pump absorption are considered in a first order of approximation. Within these major approximations, a rather simple calculation leads to the following result [5]:

$$\Phi_n = -(1+i) \frac{1}{n} T_{go} \frac{RT_o}{P_o T} \left\{ [C_A(n_A^o - 1) + C_B(n_B^o - 1)] \frac{e^{-\frac{(1+i)z-l_f}{\mu_g}}}{\mu_g} - C_B(n_B^o - n_A^o) \frac{(1-X) \left(\frac{L}{RT} - 1 \right)}{1-X+(1-i)X \frac{\mu_D}{2l_g} \left[1 + \frac{l_g}{Y_p R T X} \right]} \frac{e^{-\frac{(1+i)z-l_f}{\mu_D}}}{\mu_D} \right\} \quad (1)$$

where, $\mu_g = (\alpha/\pi f)^{1/2}$ and $\mu_D = (D/\pi f)^{1/2}$ are the thermal and the concentration wavelengths respectively, T_{go} is the periodic solid surface temperature, R perfect gas constant, P_o and T_o the N.T.P., n , n_A^o and n_B^o the refractive indexes of the gas mixture, A and B at N.T.P., respectively, $X = C_B / C_A + C_B$, L heat of adsorption, $Y_p = Y_1 g_{ad}(P_B/P_{saturation})$, Y_1 is the number of moles of B adsorbed in the first layer per unit surface of the solid sample, the function g_{ad} is deduced from the physical model of adsorption, the most famous being the BET model [6]. The models differ only for the description of the mode of generation of the first adsorbed layer and are very similar for what concern the other layers.

The first term in equation (1) is the thermal contribution and the second one the concentration contribution. The minus sign between the two terms (which are positive) means that a phase shift of 180° occurs when passing from a situation where the thermal term dominates to another one where the concentration term dominates.

From this expression, it is clear that the two diffusion coefficients (α and D) can be deduced from separated measurements of the phase of the deflection versus the probe-beam distance z and corresponding to situations in which one of the two effects dominates. Such experiments (not reported here) are very useful since the diffusion coefficients of a binary mixture are often difficult to find in the literature.

Figure 2 : Amplitude and phase of mirage signal vs total pressure for Ar+CH₂Cl₂ on steel. Calculated values for $f=121\text{Hz}$; $z=200\mu\text{m}$; $T=294\text{K}$; $l_f=0.1\mu\text{m}$.

In a more general situation, there will be a competition between the two contributions. Figure 2 shows the variation of calculated mirage amplitude and phase vs total pressure. When the amplitude is small and the phase large, at low pressure, the thermal effect dominates. On the contrary, at high pressure, the concentration effect produces the main part of the deflection. The transition is easy to observe since the two contributions are of opposite signs; the amplitude passes a minimum and a phase shift close to 180° occurs. Figure 2 also reveals the major role played by Y_1 , the number per unit surface of adsorbed moles in the first layer. Very similar results are obtained for the temperature dependance: when the sample temperature is larger than the one of the gas, thermal effects dominate and with a sample cooler than the gas, the concentration effects dominate.

3. EXPERIMENTAL SET-UP

The set-up is made of three parts: the cell containing the gas mixture and the solid on which the adsorption takes place, the system for the preparation and the transfer of the gas mixture to the cell, the pump and the probe systems which provide, on the one hand, the modulated beam inducing the periodic gradients close to the sample surface and, on the other hand, the detection of these gradients through the mirage effect.

The gas is prepared by mixing a non condensable gas and a liquid vaporized in a heated balloon, separated from the cell. The temperature and pressure in the balloon, in the cell and at surface of the specimen, are measured by thermocouples and piezo gauges.

The pump beam comes from a chopped filament lamp and the mirage detection is achieved with a compact bench using a diode laser. Measurements of the mirage amplitude and phase are recorded as functions of time simultaneously with all adjustable parameters (temperatures, pressures, frequency) allowing a large variety of presentations.

4. EXPERIMENTAL RESULTS

4.1. Measurements vs the filling pressure.

It can be shown experimentally [5] that the thermal contribution is always dominant at low pressures i.e. during the first layer deposition. As a consequence, the mirage effect is only sensitive to the parameters which govern the growth of the other layers. Once the mixture and the experimental conditions are well determined, these parameters are [6], the number of moles adsorbed in the first layer, Y_1 , which controls the evolution of the layers which are not in contact with the surface, and l_f (film thickness). The experiments confirm the high sensitivity of both amplitude and phase (fig.2) to Y_1 , especially at pressures large enough to let the concentration contribution dominates.

A more surprising result is presented in figure 3. It shows that only the theoretical hypothesis of an infinitely thin film is able to fit the experiment, even at pressures where the number of molecules deposited is certainly very important. This result is the proof that the adsorbed molecules are not deposited as a uniform film. Actually the adsorption produces very small droplets and the periodic adsorption-desorption induced by the pump only occurs along the meniscus where the three phases (solid-liquid-gas) are coexisting. It is the reason while the fit with the theory leads to the conclusion that the adsorption-desorption process occurs in an infinitely thin area.

Figure 3: Fit of experimental points with the theory calculated for different thicknesses l_f of the adsorbed film. Air+CH₂Cl₂ on TiO₂ at $f=40\text{Hz}$, $z=210\mu\text{m}$, $T=297\text{K}$. (o) represents n averaged measurements.

The last and important observation is that the theory cannot interpret the fact that experimental points are obtained above the saturation pressure (the theoretical curves stop in figure 3 at 22 kPa). This experimental result is the evidence for the emergence of the phenomenon called supersaturation.

4.2. Supersaturation.

Thermodynamic studies can explain the dynamic of a droplet growth on a solid surface [4]. The main physical result of interest for this study is that:

- if the pressure is smaller than the saturation pressure, only very small droplets are highly probable.
- if the pressure becomes larger than the saturation pressure, the droplet radius can increase indefinitely as soon as it exceeds a few Å: i.e. very large droplets appear.

This effect strongly influences the mirage experiment. If, after reaching a pressure larger than the saturation pressure, the cell is closed, both amplitude (decrease) and phase (increase) drift as function of observation time (see figure 4). The radii of the droplets increase and thus decrease the number of triple points (solid-liquid-gas) where the adsorption-desorption induced by the pump takes place. As a consequence the influence of the concentration wave decreases with respect to the one of the thermal wave.

Figure 4: Recordings of the mirage phase and total pressure in the cell vs time t .

At $t > 900\text{s}$, $P > 25 \text{ kPa} > P_{\text{sat}}$, the cell is closed and the experimental phase drift (phase increase) starts.

5. CONCLUSION

To investigate the potential value of the mirage effect for the detection of adsorption-desorption of organic molecules on unprepared surfaces at temperatures and pressures close to N.T.P., an analytical 1D model has been established. It demonstrates the good sensitivity of the method to the number of molecules adsorbed in the first layer, i.e. mainly to the surface roughness, and to the ambient conditions of this adsorption, especially surface temperature.

At pressures below the saturation pressure, the experiments confirm the model, proving that the hypothesis of a local thermodynamic equilibrium is valid in the small area probed by the mirage detection.

Due to the dominant thermal effect at low pressures, the mirage effect is proved to be insensitive to the formation of the first layer and thus to the models of adsorption.

At pressures of the order of magnitude of the saturation pressure, the method is sensitive to the growing mode of the adsorption phenomenon, for instance when the liquid does not wet the solid surface, at the meniscus of droplets. In this latter case it seems that the method could be useful for the study of the dynamics of droplet growth under supersaturation conditions.

Water detection on insulating materials and desorption of organic molecules from painted walls in white rooms seem to be potential interesting applications.

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