Characterization of Polymer Based Gas Sensors with a Continuous System Model

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Approved by Chairman
Professor H.F. Nied: _______________________________

Date: _______________________________________________
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1 Abstract

An electronic nose (eNose) is a polymer-based gas sensor that uses an array of pixels to determine the chemical composition of an airborne gas or vapor. Each pixel mounted on the eNose uses increasing and decreasing resistance values to recognize gases that come in contact with the sensor. This change of resistance is not instantaneous and when the sensor is removed from a plume of gas, the resistance values do not immediately return to their original values. The sensor can also give accurate readings for the gas concentration levels near the eNose. In this paper, a continuous system model of the sensor’s material behavior is discussed. A group of programs will be developed using the equations that appear throughout this paper. The results of this model are compared to models derived in other research papers to show validity of the model. These results acquired by this model are also compared to the experimental values taken from a fully functional eNose.
2 Introduction

Polymer-based gas sensors are created by doping a polymer film with highly conductive carbon-black clusters (carbon dopants). The carbon dopants create a path for electrons to conduct through the film. When gas molecules make contact with the polymer that makes up the bulk of the pixels, the gas diffuses into the pixel and significant swelling occurs in the polymer (Figure 1). The swelling of the polymer causes the carbon dopants within the pixel to become farther from one another. This increasing distance between dopants creates a change in resistance (Figure 2).
The change of resistance, $\Delta R$, is divided by the baseline resistance, $R_{\text{base}}$, which is the resistance of a pixel when it is held in a temperature controlled environment with no gas. The ratio $\Delta R / R_{\text{base}}$ is a non-dimensional means of indicating the effect of the diffusion of the gas on each pixel within the eNose.

It has been shown that the change of resistance of the pixel and the gas concentration in the air around the pixel have a linear relationship (Figure 3) [Ryan, 2000]. This linear relation allows the eNose to provide accurate readings of a given gas’s concentration. The threshold concentration is approximately five parts per million. Ideally, this means that if there are 999,995 oxygen molecules near the surface of the eNose when $R_{\text{base}}$ is measured, then $\Delta R$ will increase when 5 non-oxygen molecules are introduced to the sensor.
Figure 3: This graph shows the linear behavior between concentration and the resistance levels of three individual pixels made up of three different polymers. This linear behavior tells us that there is an expansion constant that can be given to each polymer based pixel.

Even though the general understanding of the mechanisms responsible for the eNose’s physical behavior are known, a number of structural behaviors and properties remain a mystery. This model will attempt to broaden this understanding of the eNose’s operations by developing a model of the viscoelastic materials that make up polymer-carbon pixels, the main components of the eNose. This model shows how these viscoelastic components change when a constant concentration of gas molecules is near the eNose’s pixels. Once this engineering model is built, it is compared to a number of other models. This output that comes from this continuous system is compared to actual data collected from a fully functional eNose, as well.
Figure 4: The Maxwell element (a) has a spring in series with a spring. The Kelvin-Voigt element (b) has a spring in parallel with a dashpot. To make a generalized Maxwell element (c) of a viscoelastic model, numerous Maxwell elements with different spring constants and dashpot viscosities can be placed in parallel with one another.

3 Viscoelastic Models

Any metallic material can be modeled by a system of springs. Polymers on the other hand, require slightly more complex models. Like many other viscoelastic models, a Maxwell element (Figure 4a) makes a great model for the materials used to make the pixels on an eNose. The constitutive equation for a single Maxwell element is

$$\dot{\varepsilon} = \frac{\sigma}{k} + \frac{\sigma}{\eta}$$  \hspace{1cm} (1)

Where $\varepsilon$ is the spring’s strain, $\sigma$ is the stress on the spring, $k$ represents the stiffness of the spring and $\eta$ is the dashpot’s viscosity.

Each pixel on an eNose consists of a polymer with known viscoelastic properties. To increase the accuracy of the viscoelastic model, multiple Maxwell elements can be placed in parallel with one another (Figure 4c) to mimic the mechanical behavior of a pixel as it goes through an expansion. This multiple Maxwell element model is covered
in Appendix 1. This section of the thesis derives a viscoelastic model of the eNose’s pixels using Maxwell elements and Kelvin-Voigt Elements.

Note that the spring constant that appears in each of these models is interchangeable with Young’s modulus. Various values for viscosity can be found in Table 1 and values for Young’s modulus can be found in Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (E) in GPa</th>
<th>Young’s modulus (E) in psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber (small strain)</td>
<td>0.01 - 0.1</td>
<td>1,500 - 15,000</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>0.2</td>
<td>30,000</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>1.5 - 2.0</td>
<td>217,000 - 290,000</td>
</tr>
<tr>
<td>Bacteriophage capsids (virus)</td>
<td>1.0 - 3.0</td>
<td>150,000 - 435,000</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>2.0 - 2.5</td>
<td>290,000 - 360,000</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>3.0 - 3.5</td>
<td>435,000 - 505,000</td>
</tr>
<tr>
<td>Nylon</td>
<td>2.0 - 4.0</td>
<td>290,000 - 580,000</td>
</tr>
<tr>
<td>Oak wood (along grain)</td>
<td>11</td>
<td>1,600,000</td>
</tr>
<tr>
<td>High-strength concrete</td>
<td>30</td>
<td>4,350,000</td>
</tr>
<tr>
<td>Magnesium metal (Mg)</td>
<td>45</td>
<td>6,500,000</td>
</tr>
<tr>
<td>Aluminium alloy</td>
<td>69</td>
<td>10,000,000</td>
</tr>
<tr>
<td>Glass (all types)</td>
<td>72</td>
<td>10,400,000</td>
</tr>
<tr>
<td>Brass and bronze</td>
<td>103 - 124</td>
<td>17,000,000</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>105 - 120</td>
<td>15,000,000 - 17,500,000</td>
</tr>
<tr>
<td>Carbon fiber reinforced plastic</td>
<td>150</td>
<td>21,800,000</td>
</tr>
<tr>
<td>Wrought iron and steel</td>
<td>190 - 210</td>
<td>30,000,000</td>
</tr>
<tr>
<td>Tungsten (W)</td>
<td>400 - 410</td>
<td>58,000,000 - 59,500,000</td>
</tr>
<tr>
<td>Silicon carbide (SiC)</td>
<td>450</td>
<td>65,000,000</td>
</tr>
<tr>
<td>Tungsten carbide (WC)</td>
<td>450 - 650</td>
<td>65,000,000 - 94,000,000</td>
</tr>
<tr>
<td>Single Carbon nanotube</td>
<td>1,000+</td>
<td>145,000,000</td>
</tr>
<tr>
<td>Diamond (C)</td>
<td>1,050 - 1,200</td>
<td>150,000,000 - 175,000,000</td>
</tr>
</tbody>
</table>

**Table 1:** This list shows various Young’s Modulus coefficients. Each one of these can be converted into spring constants.

<table>
<thead>
<tr>
<th>Material</th>
<th>Viscosity at 20ºC (Pa-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1</td>
</tr>
<tr>
<td>Olive Oil</td>
<td>100</td>
</tr>
<tr>
<td>Glycerin</td>
<td>500</td>
</tr>
<tr>
<td>Motor Oil</td>
<td>1000 - 2000</td>
</tr>
<tr>
<td>Honey</td>
<td>2000 - 10,000</td>
</tr>
<tr>
<td>Molasses</td>
<td>5,000 - 10,000</td>
</tr>
<tr>
<td>Ketchup</td>
<td>50,000 - 70,000</td>
</tr>
<tr>
<td>Peanut Butter</td>
<td>250,000</td>
</tr>
<tr>
<td>Polymers</td>
<td>1x10^10 - 10^12</td>
</tr>
</tbody>
</table>

**Table 2:** This list shows various viscosity coefficients.
Figure 5: In the left is a picture of the sensor array that makes up the eNose. In the right is a close up of a single polymer-carbon pixel on board the eNose’s ceramic surface. The three lines shown in the right most picture are the electric leads that drive electrons through the pixel.

4 Ceramic Substrate

Now, with an expression for the stress within a single pixel, a model that includes the ceramic substrate beneath the polymer pixel must be considered. Each pixel on an eNose is a polymer-carbon composite deposited on a ceramic substrate with Au-Pd electrode sets [Amy Ryan, 1998] (Figure 5). The ceramic substrate is stiffer than the soft polymer used to create the pixels (Figure 6). To determine the significance of the interactions between the ceramic substrate and the swelling behavior of each pixel’s expansions, the polymer/ceramic system is examined as if the polymer were independent of the ceramic substrate. With the same viscoelastic modeling methods as the ones used for the pixel’s stress and strain characteristics, a spring and dashpot model will be created for this case.
Figure 6: The stress and the strain on the soft polymer pixel will be affected by the stiff ceramic substrate that anchors the pixel.

Figure 7: To help the derivation of stress/strain relations in the pixel/substrate model, the diagram shown in Figure 6, can be reduced to this duel beam diagram.

4.1 Horizontal Expansion

Imagine the point where both materials connect to one another as a system of beams in parallel that are connected at both ends by two rigid end plates (Figure 7). To ease this process, the polymer-carbon composite will be treated as a single Maxwell
element rather than the generalized Maxwell element discussed above and due to the stiff behavior of the ceramic; it will be treated as a purely elastic element (Figure 8). In this model the expansion of both the polymer pixel and the ceramic substrate are assumed to be uniform across each of their heights.

Figure 8: The generalized Maxwell model combined with an elastic spring model to simulate the stress/strain behavior of a viscoelastic pixel attached to a stiff substrate.

The stresses found in the combination of spring constants and dashpot viscosities that make up the generalized Maxwell element are combined to make a single stress and a single strain (Figure 8) acting on the element, and the uniform stress found in this system is given by

$$\sigma_M = k_M \varepsilon_M = \eta_M (\dot{\varepsilon} - \dot{\varepsilon}_M),$$  \hspace{1cm} (2)

where $k_M$ and $\eta_M$ are the spring constant and the dashpot viscosity, respectively. This stress plus the stress in the elastic element, namely

$$\sigma_C = k_C \varepsilon,$$  \hspace{1cm} (3)

sum to give the total stress of the system

$$\sigma = \sigma_M + \sigma_C = k_C \varepsilon + \eta_M (\dot{\varepsilon} - \dot{\varepsilon}_M).$$  \hspace{1cm} (4)

Solving this expression for $\dot{\varepsilon}_M$ yields

$$\dot{\varepsilon}_M = \dot{\varepsilon} + \frac{k_C}{\eta_M} \varepsilon - \frac{\sigma}{\eta_M},$$  \hspace{1cm} (5)

and taking the time derivative of this result gives

$$\ddot{\varepsilon}_M = \ddot{\varepsilon} + \frac{k_C}{\eta_M} \dot{\varepsilon} - \frac{\dot{\sigma}}{\eta_M}. \hspace{1cm} (6)$$

Taking the time derivative of the stress found on the generalized Maxwell element gives
\[ k_M \ddot{\varepsilon}_M = \eta_M (\ddot{\varepsilon} - \ddot{\varepsilon}_M). \]

Substituting the expressions for \( \dot{\varepsilon}_M \) and \( \ddot{\varepsilon}_M \) just found into this derivative expression, followed by a bit of algebra yields

\[ \sigma + \frac{\eta_M}{k_C} \dot{\sigma} = k_M \varepsilon + \eta_M \left( 1 + \frac{k_C}{k_M} \right) \dot{\varepsilon} \tag{7} \]

or equally,

\[ \sigma + \frac{\eta_M}{k_C} \dot{\sigma} = k_M \varepsilon + \eta_M \left( \frac{k_M + k_C}{k_M} \right) \dot{\varepsilon}. \tag{8} \]

This is the defining relation between the stress and the strain of a Maxwell element in parallel with a purely elastic element.

To simplify the stress/strain relationship between the ceramic and a polymer pixel, we will assume that \( k_C >> k_M \). After a bit of algebra, the resulting equation will be

\[ \frac{\sigma}{\eta_M} \left( \frac{k_M}{k_M + k_C} \right) + \frac{\dot{\sigma}}{k_C} \left( \frac{k_M}{k_M + k_C} \right) = \frac{k_M}{\eta_M} \left( \frac{k_M}{k_M + k_C} \right) \varepsilon + \dot{\varepsilon} \tag{9} \]

where

\[ \left( \frac{k_M}{k_M + k_C} \right) \approx 0. \tag{10} \]

This shows us that

\[ \dot{\varepsilon} = \frac{\partial \varepsilon}{\partial t} \approx 0 \tag{11} \]

when \( k_C >> k_M \).
4.2 Vertical Expansion

The previous section shows that the ceramic substrate is much too stiff to allow significant polymer expansion in the horizontal direction. Due to the fact that the pixel is not restrained at the sides or the top, expansion cannot be nullified. The pixel will expand upwards (Figure 9) and the stress/strain relation for a Maxwell element can be used to model this case.

4.3 The Kelvin-Voigt Model

As shown in Figure 4b, there is a second model that can be used to describe the pixel’s behavior. The strain of a pixel changes with every single gas molecule that is absorbed. When these sudden changes occur, the Kelvin-Voigt model predicts creep within the pixels more realistically than the Maxwell model, since for

$$\lim_{t \to \infty} \varepsilon = \frac{\sigma_0}{E}$$

(12)

while a Maxwell model predicts a linear relationship between strain and time, which is most often not the case.

Figure 9: The hard substrate will force the swelling polymer pixel to expand upwards instead of outwards.
The Kelvin-Voigt model, can be represented by a purely viscous damper and purely elastic spring connected in parallel. Since the two components of the model are arranged in parallel, the strains in each component are identical:

\[ \varepsilon = \varepsilon_D = \varepsilon_S. \]  

(13)

Similarly, the total stress of the element is equal to the sum of the stress in the dashpot and the stress in the spring.

\[ \sigma = \sigma_D + \sigma_S. \]  

(14)

From these equations, the Kelvin-Voigt model and the polymer pixel’s stress and strain will be governed by

\[ \sigma = k\dot{\varepsilon} + \eta \dot{\varepsilon} \]  

(15)

where \( k \) is the spring constant of the polymer and \( \eta \) is the viscosity of the polymer.

If some constant stress \( \sigma_0 \) was suddenly applied to a Kelvin-Voigt material, then the deformations would approach the deformation for the pure elastic material \( \sigma_0/E \) with the difference decaying exponentially:

\[ \varepsilon(t) = \frac{\sigma_0}{k}(1 - \exp(-\lambda t)) \]  

(16)

where \( t \) is time and the rate of relaxation is

\[ \lambda = \frac{k}{\eta}. \]  

(17)

\( \lambda \) is also the inverse of the relaxation time.

When this function of strain is plotted in Figure 10, it shows that dependence of dimensionless deformation \( k\varepsilon/\sigma_0 \) upon dimensionless time \( \lambda t \). The material is loaded by the stress at time \( t = 0 \) and this stress is released at a dimensionless time \( t_1' = \lambda t_1 \).
When a pixel has been saturated with a gas, the maximum strain $\varepsilon(t_1)$ will be reached. If the gas is taken away at $t_1$, then the elastic properties of the pixel would relax the polymer back until the deformation becomes zero [Meyers, 1999]. The relaxation process obeys the following equation:

$$\varepsilon(t > t_1) = \varepsilon(t_1) \exp(-\lambda t).$$

But that is unlikely due to the slow desorption process that must occur before relaxation can take place. It is expected to see that the relaxation time will be slower. The next step is to show how the

5 Diffusion

When the eNose is in the presence of any gas, the polymers that make up the individual pixels absorb this gas and the expansion that results in an increase of resistance occurs. Diffusion of gas into the pixel’s polymer must be broken down into smaller, less complicated systems before its behavior can be understood. The basic models can be combined to develop the numerical estimations.
The first simplified model shows the unidirectional diffusion of a steady concentration of gas molecules through a polymer that has an infinite depth in the x-direction (Figure 11). A single dimensional model such as this is governed by Fick’s first law, the fundamental law of diffusion [Comyn, 1985].

\[ F_x = -D \frac{\partial c}{\partial x} \]  \hspace{1cm} (19)

This law says that, \( F_x \), the flux in the x-direction is proportional to, \( (\partial c/\partial x) \), the concentration gradient. The flux is the measure of the gas molecules that are diffusing through a unit area in a unit of time and \( D \) is the diffusion rate. The dimensions for the diffusion constant are length over time (i.e. – \( m^2/t \)). A method of calculating the maximum amount of concentration and mass uptake within a pixel at any given time using this diffusion constant is discussed in Appendix 2.

Diffusion through a multidimensional polymer by a gas whose concentration is varying with time requires a more complex equation. Fick’s second law of diffusion will provide this equation.
To build the needed equations, a polymer with side lengths of 2dx, 2dy, and 2dz that has a point P located at the center of the volume (Figure 12) will be used. The gas flux that crosses the six faces of this polymer will control the build up or decay of diffusant. If the flux gradient is traveling through the polymer in the x-direction and the flux found at a point in the center of the volume, point P, is $F_x$ then the flux at the face ABCD is $(F_x - (\partial F_x / \partial x))dx$ and the face at abcd has a flux of $(F_x + (\partial F_x / \partial x))dx$. The gas entering ABCD in a unit of time is $4 \ dy \ dz \ (F_x - (\partial F_x / \partial x))dx$ and leaving face abcd is $4 \ dy \ dz \ (F_x + (\partial F_x / \partial x))dx$. This means that the gas accumulating in the pixel due to diffusion in the x-direction is

$$R_x = -8 \ dx \ dy \ dz \left(\frac{\partial F_x}{\partial x}\right)$$

(20)

Similarly,

$$R_y = -8 \ dx \ dy \ dz \left(\frac{\partial F_y}{\partial y}\right)$$

(21)

$$R_z = -8 \ dx \ dy \ dz \left(\frac{\partial F_z}{\partial z}\right)$$

(22)
The rate of concentration increase in the polymer

\[ \frac{\partial c}{\partial t} = \frac{R_x + R_y + R_z}{8 \, dx \, dy \, dz} \]  \hspace{1cm} (23)

So,

\[ \frac{\partial c}{\partial t} = -\frac{\partial F_x}{\partial x} - \frac{\partial F_y}{\partial y} - \frac{\partial F_z}{\partial z} \]  \hspace{1cm} (24)

When the flux, \( F_x \), is differentiated, the flux gradients are produced

\[ \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \]  \hspace{1cm} (25)

The general diffusion equation is a nonlinear partial differential equation. This equation describes the fluctuation of density within a material. It is also known as Fick’s second law of diffusion. When the diffusion is limited to the x-direction

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]  \hspace{1cm} (26)

If the diffusion constant depends on concentration through a volume and hence on concentration location in three dimensions, Fick’s second law can be written as

\[ \frac{\partial c}{\partial t} = \frac{\partial c}{\partial x} \left( D \frac{\partial c}{\partial x} \right) + \frac{\partial c}{\partial y} \left( D \frac{\partial c}{\partial y} \right) + \frac{\partial c}{\partial z} \left( D \frac{\partial c}{\partial z} \right) \]  \hspace{1cm} (27)

where \( c \) is the density of the gas being absorbed into the polymer pixel, \( t \) is time and \( D \) is the diffusion coefficient.
Figure 13: This graphical depiction of an eNose’s pixel shows the length and the area used to determine the resistivity of the material. The area, A, is a constant value and the length, L, changes with concentration. This shows that the change of resistance depends solely on the change in length. 

Note: The scale of the graphical representation is altered to show the various dimensions. The actual pixel is much smaller in height.

The polymer pixels of an eNose are disks of radius R and of height, or length, L. Figure 13 is a graphical representation of the pixel. The actual pixels are significantly wider than they are thick (i.e. - $R >> L$) which means that the diffusion rate through the walls of the pixel is significantly smaller than the diffusion rate through the top of the pixel. The diffusion rate through the walls is so much smaller that it can be considered negligible. The unique shape and dimensions of a pixel allows diffusion flow in one direction. In the model being developed, the airborne gas only diffuses through the tops of the pixels.
Figure 14: This figure shows the graphical interpretation of the model being created in this paper. An individual pixel on the eNose (grey block). The number of sites located within the pixel (red dots). The gas surrounding the polymer (blue dots).

Note: The sites are smaller than the molecules to show that effort is required insert a gas molecule into the polymer
Note: In this diagram, none of the sites are filled.

5.1 Site Occupancy and Concentration

In every polymer pixel there are a finite number of sites available to absorb airborne gas molecules (Figure 14). As these sites absorb the gas, they are also releasing, or desorbing the gas at a steady rate as well. The energy used to break through the first layer of monomers at the surface of the pixel is the average thermal energy

\[ KE_{\text{ave}} = \frac{3}{2} kT. \] (28)

At room temperature, this thermal energy is high enough to force the gas molecules into the center of the pixel via diffusion. The amount of force required to break through the polymer pixel’s wall is

\[ dF = \sum_{j=1}^{N} \sigma_{ij} dA_j. \] (29)

where \( \sigma_{ij} \) is the amount of stress built up within the monomer at the surface of the pixel and \( dA_j \) is the bit of area required for the entry of the moving airborne molecule. Figure 15 gives a general visual interpretation of the polymer/gas dynamics at a magnified level.
Imagine hundreds of the gas molecules hitting the pixel’s surface and sinking as deep as their momentum and trajectory will take them until they get stuck in the polymer. Once these gas molecules are stuck in the polymer, they are just as energetic as they were on the outside of the polymer. Each molecule is still violently vibrating while they are entangled in the polymer. Random movement occurring due to the thermal energy in the air causes the entangled molecules to go deeper into the polymer and sometimes the random movement can help the gas molecules escape the polymer. What keeps the absorbed molecules inside of the pixel is the momentum of the molecules on the outside of the polymer. Even though the thermal kinetic energies of the entangled molecules are identical to that of the airborne molecules

\[ KE_{\text{air}} = KE_{\text{polymer}} \quad (30) \]

the average momentum of the airborne gas molecules is greater

\[ m_{\text{gas}} v_{\text{air}} \gg m_{\text{gas}} v_{\text{polymer}} \quad (31) \]
Due to this high concentration of high momentum gas molecules with a downward path there is a net downward movement of the entangled molecules. Hence, the diffusion process is taking place and as mentioned before, this behavior is described by Fick’s second law.

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right). \tag{32}
\]

In this model, the diffusion coefficient depends on the change of \( x \) in the vertical direction. The diffusion coefficient at the top of the pixel is not the coefficient throughout the pixel. It changes with the depth of the pixel.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Gas</th>
<th>( D_0 (\text{m}^2/\text{s}) )</th>
<th>Polymer</th>
<th>Gas</th>
<th>( D_0 (\text{m}^2/\text{s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET (Poly Ethylene Terephthalate)</td>
<td>CO₂</td>
<td>5.4x10⁻¹⁴</td>
<td>PC (Poly Carbonate)</td>
<td>CO₂</td>
<td>9.6x10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>5.6x10⁻¹³</td>
<td></td>
<td>O₂</td>
<td>4.2x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>1.4x10⁻¹³</td>
<td></td>
<td>N₂</td>
<td>2.6x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>8.0x10⁻¹²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP (Poly Propylene)</td>
<td>CO₂</td>
<td>1.4x10⁻¹¹</td>
<td>PS (Poly Styrene)</td>
<td>CO₂</td>
<td>5.8x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>2.5x10⁻¹¹</td>
<td></td>
<td>O₂</td>
<td>1.1x10⁻¹¹</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>1.1x10⁻¹²</td>
<td></td>
<td>N₂</td>
<td>9.6x10⁻¹²</td>
</tr>
<tr>
<td>HDPE (High Density Poly Ethylene)</td>
<td>CO₂</td>
<td>1.2x10⁻¹¹</td>
<td>PVC (Poly Vinyl Chloride)</td>
<td>CO₂</td>
<td>2.5x10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>1.7x10⁻¹¹</td>
<td></td>
<td>O₂</td>
<td>1.2x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>9.3x10⁻¹²</td>
<td></td>
<td>N₂</td>
<td>3.8x10⁻¹³</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>2.6x10⁻¹¹</td>
<td></td>
<td>H₂</td>
<td>5.0x10⁻¹¹</td>
</tr>
<tr>
<td>LDPE (Low Density Poly Ethylene)</td>
<td>CO₂</td>
<td>3.7x10⁻¹¹</td>
<td>Butyl Rubber (Poly Isobutylene)</td>
<td>CO₂</td>
<td>5.8x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>4.6x10⁻¹¹</td>
<td></td>
<td>O₂</td>
<td>8.1x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>3.2x10⁻¹¹</td>
<td></td>
<td>N₂</td>
<td>4.5x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>4.7x10⁻¹¹</td>
<td></td>
<td>H₂</td>
<td>1.5x10⁻¹⁰</td>
</tr>
</tbody>
</table>

| **System Temperature:** | 25° Celsius |
| **System Pressure:**    | 1 Bar       |

**Table 3:** This list shows various diffusion coefficients.

Figure 16 shows a visual interpretation of concentration change with respect to time. At the surface of the pixel there will be an interface of air and a polymer. The molecules going through the surface will encounter macroscopic and microscopic forces that will resist the molecule’s attempts at diffusion. These resisting forces can cause the diffusion coefficient at the polymer to air boundary to be higher than the diffusion coefficient found between polymer layers. The values for this coefficient depend on the
type of polymer being used in the pixel and the type of gas bombarding its surface. Table 3 has several examples of diffusion coefficients for various gasses being absorbed into a number of common polymers.

**Figure 16:** This diagram shows the polymer’s diffusion processes. The empty sites (red dots) are being filled with the energetic gas molecules (blue dots).

**Note:** The net movement of the molecules is in the downward direction due to the high momentum of the airborne gas molecules.

In this interpretation of concentration change, the number of molecules found in the first layer will be a constant value. The density of molecules in the air will not change once the pixel begins absorbing. The second layer in the system is the first layer of the polymer. This second layer has the highest number of filled spots in the pixel at any given time. Every layer beneath the second layer will depend on its concentration. The second layer will have more molecules than the third layer, so the concentration of the
third layer will rely directly on the concentration of the second. The concentration of the fourth layer will depend on the third layer, and so on. The gas molecules will go deeper through the polymer. They will travel downwards until they reach the point where the lowest layer; where the polymer meets the ceramic substrate. Due to the impermeability of the ceramic, no traveling gas molecule will cross this boundary. These molecules can only move upwards or towards the sides. The expression for this behavior is

\[ C_{i,i+1} = D_{i,i+1} (c_{i+1} - c_i) \]  

(33)

where \( c_i \) and \( c_{i+1} \) are the concentrations in layer \( i \) and \( i+1 \) respectively. These concentrations are integer numbers that represent the number of molecules found within in a cube unit of length (i.e. - 1/m^3). When the concentrations are multiplied by the diffusion coefficient, \( D_{i,i+1} \), for that boundary a value for the molecule transfer rate between the \( i \)th layer and the \( (i+1) \)th layer is given. The units for this transfer rate, \( C_{i,i+1} \), will be unit length per unit of time (i.e. – m/s).

With the expression for the gas transfer rate, an equation for the number of molecules in each layer at any given time can be deduced.

\[ \frac{\partial C_{i+1}}{\partial t} = C_{i,i+1} - C_{i+1,i+2} \]  

(34)

when the expressions for \( C_{i,i+1} \) and \( C_{i+1,i+2} \) are plugged into this equation,

\[ \frac{\partial C_{i+1}}{\partial t} = \left( D_{i,i+1} (c_{i+1} - c_i) - D_{i+1,i+2} (c_{i+2} - c_{i+1}) \right). \]  

(35)

This equation tells us how many molecules will be found in each layer. If the model of the pixel is divided into a more layers, the model will become more complicated, but it will be more detailed.

For example, if there are four layers of polymer topped by an infinite layer of molecules at a constant concentration as in Figure 16, the value for \( i \) will range from 0 to 5. This is how the number of molecules in each layer will be tracked. Beginning with the values for \( i = 0 \), the first step is to find the transfer rates at each of the five boundaries

\[ C_{01} = D_{01} (c_1 - c_0) \]  

(36)
where $C_{01}$ is the rate of concentration change between the layer of air and the first layer in the polymer. The gas concentration in air, $c_0$, is a constant value in this case.

$$C_{12} = D_{12} (c_2 - c_1) \quad (37)$$

where $C_{12}$ is the rate of change between the first polymer layer and the second. Similarly,

$$C_{23} = D_{23} (c_3 - c_2) \quad (38)$$

$$C_{34} = D_{34} (c_4 - c_3) \quad (39)$$

and

$$C_{45} = D_{45} (c_5 - c_4) \quad (40)$$

where $C_{45}$ is the rate of concentration change at the boundary of the final polymer layer and the ceramic substrate. The value for the concentration within the ceramic substrate, $c_5$, is always going to be zero.

Now, to find the rate at which the concentrations throughout the polymer changes with time. The first layer’s expression is

$$\frac{\partial c_1}{\partial t} = C_{01} - C_{12} \quad (41)$$

the second, third and fourth layer follow

$$\frac{\partial c_2}{\partial t} = C_{12} - C_{23} \quad (42)$$

$$\frac{\partial c_3}{\partial t} = C_{23} - C_{34} \quad (43)$$

$$\frac{\partial c_4}{\partial t} = C_{34} - C_{45} \quad (44)$$

The results seen in Figure 17 show a working model of diffusion. These graphs are the output of a Simulink program written using the above equations. Each one of the six boxes represents a single layer within a pixel. The first block is the layer of air, the second is the first layer of the polymer, the third is the second layer of the polymer and so on. The last layer is the ceramic substrate. Notice that the second layer has less than the first, the third layer has less than the second. The air layer has a constant level of 1000 units of gas concentration and the ceramic has none. This diffusion model depends only on time and the diffusion constants of each boundary.
Figure 17: This shows the results of a diffusion program written in Simulink. This program uses the mathematics covered in this section. The readings show concentration versus time. At the limit $t \rightarrow \infty$ all three four of the concentration levels will reach 1000. (Simulink)

Note: The fourth layer is on a different scaling.

If one so chooses, the number of layers can be large. The detail will get better due to the higher number of plot points, but that would not be necessary. Splitting the pixel into four creates plots with plenty of plot points.

5.2 Number of Molecules

To find the number of gas molecules in each layer can be done by assigning various constants. The concentration has units of length cubed over time.

$$c = \frac{N_{mol}}{d^3} \quad (45)$$
where \( N_{mol} \) is a constant value that says how many molecules will be found in one unit of concentration. The amount of volume that makes up one unit of concentration is \( d^3 \). Solving for the number of gas molecules found in one unit of concentration is simple as multiplying the concentration by the unit of volume used to describe the layer where the air is found

\[
N_{mol} = d^3 c
\]  
(46)

knowing the number of gas molecules in each unit of concentration will be important in the next few sections of this model.

5.2.1 Relative Concentration

The gas molecules in the air closest to the surface of the pixel will have an average density. This average density is, as mentioned earlier, the concentration. It measures the number of molecules in a volume. As the gas molecules enter the empty sites in the pixel, the average density of gas molecules is going to either increase or decrease depending on the number of available sites and the spacing of the sites in the pixel. To find a set of concentrations that will relate the concentration of one layer to another, the following equation can be used

\[
c_i = \frac{N_{mol}}{A_i t_i}
\]  
(47)

where \( c_i \) is the concentration in the \( i \)th layer of the polymer, \( A_i \) is the area of the \( i \)th layer and \( t_i \) is its thickness. This equation will show the concentration of molecules within the various polymer layers to be relative to one another, instead of being relative to the air. It is not completely unrealistic to find polymers with various numbers of available sites and with the help of this equation, polymers with a smaller number of sites will not give skewed results. This version of the concentration equation also takes expansion of the layers into account. To find the number of gas molecules in each layer

\[
N_{mol} = A_i t_i c_i
\]  
(48)

can be used. This value for the number of molecules may be either higher or lower than the number given by Equation 46.
Figure 18: This diagram shows the polymer pixel after all of the empty sites (red dots) have been filled with the airborne gas molecules (blue dots).

Note: There is no thinning of gas molecules around the pixel after diffusion has occurred. The reservoir of gas molecules is infinite.

5.3 Volume Change

Due to the fact that the absorption rate for each pixel is significantly higher than the desorption rate, at the limit \( t \to \infty \) the polymer will become saturated with gas molecules (Figure 18). With the new addition of gas molecules the pixel will grow, and due to the stiffness of the ceramic substrate, the pixel will grow upwards. The added mass that results from the saturation of gas molecules will change the overall length of the pixel and in doing so, increases the pixel’s volume. The first order differential equation that governs this behavior is

\[
0 = -N_0 \frac{\partial V_{\text{new}}}{\partial N_F} = V_0
\]

where \( V_{\text{new}} \) is the volume change of the pixel, \( N_F \) is the number of filled sites within the pixel \( V_0 \) is the volume of the pixel before any absorption takes place and \( N_0 \) is the number of sites before the diffusion occurred (Figure 14). When that differential equation is solved, the equation of the change of volume with respect to the site availability is shown to be
\[ V_{\text{new}} = V_0 \left( 1 - \exp \left( - \frac{N_i}{N_0} \right) \right) \] (50)

The absorption curve that results from this volume relation is shown in Figure 19. This curve shows that there is a point where the volume change must stop growing. When the number of filled sites is equal to the number of available sites the line plateaus and the maximum value for expansion is reached.

![Figure 19](image)

**Figure 19**: This diagram shows the volume change in a polymer pixel after all of the empty sites (red dots) have been filled with the gas molecules (blue dots). (Mathematica)

The maximum amount of volume change due to gas absorption will roughly be

\[ V_{\text{max}} = V_{\text{mol}} N_0 \] (51)

where \( V_{\text{mol}} \) is the volume of a single gas molecule being absorbed and \( N_0 \) is the number of sites before any absorption takes place.

### 5.3.1 Volume Change in Layers

The equations listed above assume that there is a uniform distribution of gas molecules and a uniform amount of stretching. To show how these volume changes occur over the discrete layers of this model Equation 50 can be rewritten as

\[ V_{i,\text{new}} = V_{i,0} \left( 1 - \exp \left( - \frac{N_{i,F}}{N_{i,0}} \right) \right) \] (52)

And Equation 51 can be rewritten as
where \( i \) represents a particular layer. The sums of these two equations will give a more accurate depiction of gradual volume change and the maximum change in volume.

\[
V_{i,\text{max}} = V_{i,\text{mol}} N_{i,0}
\]  

(53)

Figure 20: These plots show the stress of each layer in a pixel as the diffusion process occurs. (Simulink)

5.4 Stress and Volume Change

With every gas molecule that becomes absorbed into the pixel there will be an increase in stress. This increase in stress is believed to be linear due because change in volume is not large enough to cause plastic deformation. Each new gas molecule will have the same mass. Hence, each new gas molecule will displace the same amount of volume which will cause the same amount of stress. The completely saturated pixel will have a stress of

\[
\sigma = \left( \frac{\sigma_{\text{max}}}{N_0} \right) N_f
\]  

(54)
where $\sigma_{\text{max}}$ is a constant value, it is the stress that is acting on the pixel when it is completely saturated with gas. (Figure 20)

### 5.4.1 Stress in Layers

To find the function of the stress of each layer, Equation 54 can be rewritten as

$$\sigma_i = \left( \frac{\sigma_{i,\text{max}}}{N_{i,0}} \right) N_{i,F}$$

(55)

where $i$ represents various polymer layers. The linear behavior of this reaction is shown in Figure 21.

![Stress vs N_F](image)

**Figure 21:** This plot shows the relation between a pixel’s stress and the number of molecules that diffuse into it. (Mathematica)

### 5.5 Strain of a Single Molecule

Now that the stress in the pixel due to absorption of gas molecules is known, the next step is to calculate the strain on the pixel due to the diffusion process. With the stress/strain relation that comes from the Kelvin-Voigt model, the stress equation can be written as

$$\left( \frac{\sigma_{\text{max}}}{N_0} \right) N_F = k\varepsilon + \eta \dot{\varepsilon}$$

(56)
These two equations combine to provide a relation between the number of filled sites and the strain in each layer of the polymer pixel. After some rearrangement, the stress will be solved for strain,

\[ \varepsilon = \left( \frac{\sigma_{\text{max}}}{N_0k} \right) N_F - \left( \frac{\eta}{k} \right) \dot{\varepsilon} \tag{57} \]

To find the change in strain, the Kelvin-Voigt model was used. Equation 16 shows the response of a single molecule’s addition.

![Figure 22](image)

**Figure 22:** These plots show the strain of each layer in a pixel as the diffusion process occurs. (Simulink)

### 5.6 Strain per Discrete Polymer Layer

Now that a function for the strain of a single molecule’s addition has been derived, an equation for the stress as a function of concentration is developed. With the change in strain,

\[ \dot{\varepsilon}_i = \left( \frac{\sigma_{\text{max}}}{N_0\eta} \right) N_{i,F} - \left( \frac{k}{\eta} \right) \varepsilon_i, \tag{58} \]
the strains can be solved for via integration. In the Simulink model the change of strain is integrated to find the value for the strain, $\varepsilon$. This equation for strain in the $i$th layer of the polymer and the plots from the Simulink model are shown in Figure 22.

6 Electronic Properties

Resistance and resistivity are the key electronic properties in this model. The fact that the resistance of a material changes with respect to the length of that material will link the expansion of each pixel to its own resistance. The resistance of a material is defined by

$$R = \frac{\rho L}{A}$$

(59)

where $\rho$ is the static resistivity, $R$ is the electrical resistance of a uniform specimen of the material, $l$ is the length of the specimen, and $A$ is the cross-sectional area of the specimen (Figure 13).

6.1 Baseline Resistance

The various eNoses produced by NASA’s Jet Propulsion Laboratory can have an array of 8 to 132 pixels on board one sensor (Figure 5). Each pixel consists of a different carbon doped polymer. Every one of these organic polymers has unique chemical properties. Assuming that temperature is kept constant, each pixel has a distinguishable baseline resistance (Figure 23), and each pixel will have a predictable reaction when exposed to particular vapors and gases [Ryan, 2004].
Figure 23: $R_{base}$ is the resistance of pixel (blue disks) before a gas or vapor is introduced to the eNose. As the gas molecules diffuse through the pixel $\Delta R$ begins to increase. When the pixels have absorbed as much gas as they possibly can the $\Delta R$ value begins to level off. The $\Delta R / R_{base}$ pattern (green graph) is the unique fingerprint of this gas.

The production procedure of each eNose pixel is the same. First, 160mg of a base polymer is dissolved in 15mL of organic solvent. The solvents used were tetrahydrofuran (THF), acetone, dichloro methane, toluene or a mixture of those solvents. When the polymer has dissolved, 40mg of carbon black was added to the solution, and dispersed by sonication. Once the carbon dopants have imbedded themselves randomly throughout the polymer, 1-3\(\mu\)L of solution was pipetted onto the sensor area and allowed to dry in a flowing stream of clean dry air while the sensor chip was held at 28$^\circ$C. The resistance of the resulting films was in the 1-50k\(\Omega\) range. Solution was added to the ceramic substrate in increments of 1\(\mu\)L until the desired resistance was reached [Ryan, 1998]. The only difference between the individual pixels is the type of polymer and the number of layers used during construction. A list of the polymers used by the JPL can be found in Table 4. The carbon black used in the films was Black Pearls 2000, a furnace black made by the Cabot Corporation.
<table>
<thead>
<tr>
<th>Sensor Position</th>
<th>JPL ID</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2</td>
<td>C71</td>
<td>Poly(2,4,6 – tribromostyrene)</td>
</tr>
<tr>
<td>3,4</td>
<td>A</td>
<td>Poly(4-vinylphenol)</td>
</tr>
<tr>
<td>5,6</td>
<td>Q</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>7,8</td>
<td>C38</td>
<td>Polyamide resin</td>
</tr>
<tr>
<td>9,10</td>
<td>C7</td>
<td>Cellulos triacetate</td>
</tr>
<tr>
<td>11,12</td>
<td>C58</td>
<td>Poly(2-hydroxyethyl methacrylate)</td>
</tr>
<tr>
<td>13,14</td>
<td>C90</td>
<td>Vinyl alcohol/vinyl butyral copolymer, 80% vinyl butyral</td>
</tr>
<tr>
<td>15,16</td>
<td>E15</td>
<td>Poly(caprolactone)</td>
</tr>
<tr>
<td>17,18</td>
<td>C</td>
<td>Poly(vinylchloride-co-vinyl acetate)</td>
</tr>
<tr>
<td>19,20</td>
<td>D</td>
<td>Poly(vinylchloride-co-vinyl acetate) 10% vinyl acetate</td>
</tr>
<tr>
<td>21,22</td>
<td>E</td>
<td>Poly(vinyl acetate)</td>
</tr>
<tr>
<td>23,24</td>
<td>F</td>
<td>Poly(N-vinylpyrrolidone)</td>
</tr>
<tr>
<td>25,26</td>
<td>C88</td>
<td>Styrene/isoprene, 14/86 ABA Block copolymer</td>
</tr>
<tr>
<td>27,28</td>
<td>C80</td>
<td>Poly(vinyl stearate)</td>
</tr>
<tr>
<td>29,30</td>
<td>C22</td>
<td>Methyl vinyl ether/maleic acid 50/50 copolymer</td>
</tr>
<tr>
<td>31,32</td>
<td>C20</td>
<td>Hydroxypropyl methyl cellulose, 10/30</td>
</tr>
</tbody>
</table>

Table 4: The list of polymers used for the sensor films in the JPL eNose. Polymers C71, C38, C7, C58, C90, C88, C80, C22, and C20 were purchased from Scientific Polymer Products, Inc. Polymers A, D, E, and Q were purchased from Polysciences, Inc. Polymer F was purchased from Fisher Scientific and polymer C was purchased from Aldrich.

When an eNose pixel is immersed in a bath of gas, it absorbs the gas, the polymer film swells, the carbon dopants shift with respect to one another (Figure 2) and due to the changing distance between the dopants the resistance for that pixel will increase or decrease (Figure 23). The volume of the swollen pixel will increase and the resistance ratio, $\Delta R/\text{R}_{\text{base}}$, will increase with its volume.

### 6.2 Electronic Properties of Polymer

As mentioned in the paragraph above, the carbon dopants within an eNose’s pixel provides a pathway for the electrons to travel through the polymer. Knowing that, one can be sure that electrons are able to flow through the purely polymer sections of the pixels. This means that each polymer used during fabrication of the eNose has nonzero resistances. Although the resistivity of each pixel relies on its thickness and the density of carbon dopants, the transfer of electrons through the polymer is important enough to briefly discuss.
<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity ( r ) (ohm m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>( 1.59 \times 10^{-8} )</td>
</tr>
<tr>
<td>Copper</td>
<td>( 1.68 \times 10^{-8} )</td>
</tr>
<tr>
<td>Aluminum</td>
<td>( 2.65 \times 10^{-8} )</td>
</tr>
<tr>
<td>Tungsten</td>
<td>( 5.6 \times 10^{-8} )</td>
</tr>
<tr>
<td>Iron</td>
<td>( 9.71 \times 10^{-8} )</td>
</tr>
<tr>
<td>Platinum</td>
<td>( 10.6 \times 10^{-8} )</td>
</tr>
<tr>
<td>Manganin</td>
<td>( 48.2 \times 10^{-8} )</td>
</tr>
<tr>
<td>Lead</td>
<td>( 22 \times 10^{-8} )</td>
</tr>
<tr>
<td>Mercury</td>
<td>( 98 \times 10^{8} )</td>
</tr>
<tr>
<td>Nichrome</td>
<td>( 100 \times 10^{8} )</td>
</tr>
<tr>
<td>Constantan</td>
<td>( 49 \times 10^{8} )</td>
</tr>
<tr>
<td>Carbon* (graphite)</td>
<td>3 to ( 60 \times 10^{3} )</td>
</tr>
<tr>
<td>Germanium*</td>
<td>( 1-500 \times 10^{3} )</td>
</tr>
<tr>
<td>Silicon*</td>
<td>0.1-60</td>
</tr>
<tr>
<td>Glass</td>
<td>( 1-10000 \times 10^{9} )</td>
</tr>
<tr>
<td>Quartz</td>
<td>( 7.5 \times 10^{17} )</td>
</tr>
<tr>
<td>Hard rubber</td>
<td>( 1-100 \times 10^{13} )</td>
</tr>
</tbody>
</table>

**Table 5:** A table of various materials and their resistivities.

Due to the uncommon use of polymers as conductors, there is not an easy way of figuring out the resistances for the various polymers used to make pixels in an eNose. Just like any other material, a model of the electronic properties can be developed by deriving an expression for the band structure, and in doing so, an expression for the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) emerges.

A method based on the density function theory (DFT) can be applied to this problem. This method does not rely on any experimental parameters. This allows quick and accurate approximations of the band structure. Hohenberg and Kohn proved that the electron density of a system is the only property required to calculate the ground state properties [Hohenberg, 1964]. The year after, Kohn and Sham show that a great model can be formed by capturing all of the many-body effects into a function which depends on the electron density of the system [Kohn, 1965]. The problem with this method is that, although a function like this exists in principle, no exact expression has been developed to date [Cote, 2003].
With the available functions, the electronic properties of the polymers used in the eNose can still be studied and the property that controls the band structure can be partially understood. The basic Kohn-Sham equation to be solved is

\[
\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{ion}}(r) + V_{\text{H}}(r) + V_{\text{xc}}(r) \psi_i(r) = \varepsilon_i \psi_i(r)
\] (60)

where \( V_{\text{ion}} \) is the ionic potential created by the atoms of the system, \( V_{\text{H}} \) is the Hartree potential which can be found if the electron density is known, and \( V_{\text{xc}} \) is the exchange and correlation potential.

For a given electron density, the Hamiltonian can be written and once that is solved, the density can be determined by occupying the lowest eigenstates

\[
n(r) = \sum_{i=\text{occupied states}} \psi_i^*(r) \psi_i(r).
\] (61)

The density obtained here must be the same as the one used to formulate the Hamiltonian, so the procedure must be iterated until the values for the initial and the final electron densities converge to a single value. For known materials, the eigenvalues that are found using this method have been found to be a good approximation of the band structure of the targeted material. Even though the values of the polymer’s band gaps obtained with this method are going to be estimates, the results can still be used to predict trends within a single family of compounds [Cote, 2003].

### 6.3 Linear Resistance due to Expansion

When a polymer, like most materials, is exposed to a varying temperature, it will shrink or swell in size with respect to the temperature shift. The equation for linear expansion due to temperature is

\[
\delta_T = \alpha(\Delta T)L
\] (62)

where \( \delta_T \) is the change of length, \( \alpha \) is the thermal expansion constant, \( \Delta T \) is the change of temperature and, \( L \) is the total length of the specimen. This temperature dependent swelling is linear just like the linear swelling induced by changing concentration found in the polymer pixels (Figure 3). With the same form as the temperature relation, the length change due to concentration change can be rewritten as

\[
\delta_C = \beta(\Delta C)L
\] (63)
for a pixel submerged in a bath of gas. The change of concentration is $\Delta C$ and $\beta$ is the concentration expansion constant.

Just as the length changes in a material, the randomness of the collisions becomes greater. There will be a higher number of collisions. Mobility within the sample will decrease. The change in length correlates to the change in resistance.

$$R = R_o\left[1 + \alpha(T - T_o)\right] \quad (64)$$

which can be converted to concentration

$$R = R_o\left[1 + \beta(C - C_o)\right]. \quad (65)$$

This means that there is a linear relation between the resistivity and the concentration. Discussion of this interesting behavior is limited due to the miniscule changes in resistance that occur because of this effect. These changes in resistance do not compare to the resistance changes that occur due to the separation of the carbon dopants between the electrodes.

### 6.4 Dopants between Electrodes

As shown, deriving the polymer’s electronic properties is rather difficult. The values of resistances found in the pure polymers are orders of magnitude higher than those found in the carbon doped eNose pixels. During the explanation of the fabrication, it was mentioned that the resistance value of these pixels is controlled directly by the number of polymer-carbon layers placed onto the ceramic substrate. Since the electronic properties of the pixels are completely controllable, a specific electronic model can be created with the help of the fabrication process.

When the polymer-carbon pixels mounted onto the eNose are exposed to a gas they absorb the airborne molecules. The molecules that diffuse into the polymer’s matrix will cause the pixels to increase in volume and this increase of volume can be gauged by observing the amount of resistance change takes place. If the average distance between carbon dopants can be found, then the relation between distance and resistance can be created.

It is assumed that exactly 160mg of a base polymer is dissolved in 15mL of organic solvent and when the polymer has dissolved, 40mg of carbon black is added to the solution, and dispersed by sonication then the average distance between carbon black
dopants can be calculated. The densities of the polymers used can be found in Table 6, but for the sake of argument, the density of the polymer modeled will be 1.25 g/cm$^3$. The density of the carbon black used in the JPL sensors is 1.7 - 1.9 g/cm$^3$ at 20°C. For this part of the paper, the density of the each carbon dopant will be 1.8 g/cm$^3$. This information says that of the solution’s volume, 0.128 mL is the polymer and 0.022 mL is made up of conductive carbon dopants. Each carbon black dopant has a radius in between 20 nm and 100 nm, but for the purposes of this model, they are assumed to have radii of ~50 nm or 50 x 10$^{-7}$ cm each. With this information and a little bit of arithmetic, it is known that there are ~4 x 10$^{13}$ carbon dopants in the solvent.

<table>
<thead>
<tr>
<th>JPL Polymer List</th>
<th>Density (g/cm$^3$) at ~20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(2,4,6-tribromostyrene)</td>
<td>2.1</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>1.21</td>
</tr>
<tr>
<td>Polyamide resin</td>
<td>0.99</td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td>1.31</td>
</tr>
<tr>
<td>Poly(2-hydroxyethyl methacrylate)</td>
<td>1.15</td>
</tr>
<tr>
<td>Poly(vinyl butyral)</td>
<td>1.1</td>
</tr>
<tr>
<td>Poly(caprolactone)diol</td>
<td>1.08</td>
</tr>
<tr>
<td>Poly(vinyl stearate)</td>
<td>1</td>
</tr>
<tr>
<td>Hydroxypropyl methyl cellulose</td>
<td>1.39</td>
</tr>
<tr>
<td><strong>Average Value</strong></td>
<td><strong>1.26</strong></td>
</tr>
</tbody>
</table>

**Table 6:** A table of various densities of polymers that make up the pixels in the JPL eNose sensors.

Once the carbon dopants have imbedded themselves randomly through the polymer, 1-3 μL of solution is pipetted onto the sensor area. There will be ~8 x 10$^9$ carbon dopants uniformly spread throughout each individual pixel. If it is assumed that the pixel’s radius, R is two orders of magnitude larger than the length, L (i.e. – $R = 100$ and $L = 1$) then it can be calculated that there are ~1 x 10$^4$ carbon dopants between the middle electrode and the two on the edges of the pixel. This means that the electrons traveling through the polymer pixel must travel across ~1 x 10$^4$ dopants to get from one electrode to the other.
7 Pixel Resistance-Length Relation

The main goal of this paper is to model the relation between a change in concentration and the change in resistance. With the model for the resistance, this goal has been reached. Knowing that the resistivity of the pixel has a linear relationship with length, it is shown that

$$\Delta R = \frac{\Delta L}{A} \rho. \quad (66)$$

It is clear that a division of the initial level of resistance will give us the expression that is output by every pixel on an eNose. This expression is as follows:

$$\frac{\Delta R}{R_{\text{base}}} = \frac{\Delta L}{R_{\text{base}} A} \rho. \quad (67)$$

By replacing the pixel’s base resistance on the right hand side with the definition of resistance in terms of the original length, the following equation can be written as

$$\frac{\Delta R}{R_{\text{base}}} = \frac{\Delta L A \rho}{R_{\text{base}} L_0}. \quad (68)$$

The final expression for ratio of $\Delta R/R_{\text{base}}$ is

$$\frac{\Delta R}{R_{\text{base}}} = \frac{\Delta L}{L_0}. \quad (69)$$

By applying the general equation for the strain,

$$\varepsilon = \frac{\Delta L}{L_0}, \quad (70)$$

this tells us that the resistance change of each pixel will rely directly upon the total strain of the pixels. The resistance relation for each layer is

$$\frac{\Delta R_i}{R_{\text{base}}} = \varepsilon_i. \quad (71)$$
7.1 Electronic Model

The amount of distance between a pixel’s carbon dopants is what controls the resistance of the pixel. Due to the stiffness of the ceramic substrate, the polymer pixel cannot expand in the x,y-plane during the absorption process. This means that the distance between carbon dopants in the x,y-plane will stay constant, hence the resistance in the x,y-plane will stay constant. Because of the same ceramic substrate that eliminates the x,y-planar movement, there is significant expansion in the z-plane. This expansion causes the dopants in the pixel’s z-plane grow farther apart. The more the pixels grow, the higher the electrical resistance goes.
Figure 25: The gray spheres are highly conductive carbon dopants. These carbon dopants make a path for the electrons to flow. The electrons will travel the paths of least resistance.

The resistance change occurs because the electrons must travel farther distances once the pixel has expanded. Electrons leave the positive lead and they choose the path of least resistance (Figure 25). Depending on how much expansion has occurred in the z-plane, these paths of least resistance will change and these changes are seen as higher resistances (Figure 2).

Figure 26: The two gold rectangles are the leads. The groups of resistors in the vertical direction (z-plane) are affected by changing length. These resistances increase as the pixel grows. The resistances facing horizontally (x,y-plane) do not change in resistance.
The diagram shown in Figure 26 shows this paper’s proposed circuit model. This model was created in attempt to achieve simplicity. To model a more intricate resistance model would be too time consuming. This resistance model says that the maximum resistance will be

\[ R_{\text{max}} = 2 \sum_{i=1}^{5} R_i + R_{\text{Const tan} t} \]  

(72)

And the minimum resistance will be

\[ R_{\text{min}} = 2R_1 + R_{\text{Const tan} t} \]  

(73)

For simplicity, the simulation program uses the average of these two resistance equations to find the total resistance of the pixel

\[ R_{\text{total}} = \frac{R_{\text{max}} + R_{\text{min}}}{2} \]  

(74)

This resistance equation at any given time can be written as

\[ R_{\text{total}} = \sum_{i=1}^{5} R_i + R_1 + R_{\text{Const tan} t} \]  

(75)

Changes in this total resistance are found by taking the difference between the total resistances of an increment of time. The plot that shows the final output of this simulation’s absorption curve in terms of the resistance ratio is shown in Figure 27.

Figure 27: This is the simulated response from the diffusion process for a single pixel. This graph is in terms of \( \Delta R / R_{\text{base}} \) versus time. (Simulink)
A more complicated model of this behavior was derived by J.W. Gardner. That model was altered to fit the eNose pixels specifically and the discussion of that model can be found in Appendix 5.

7.2 Compare Models to Actual Data

Each one of the models shown was programmed by the author of this paper. The main model’s code was written in Simulink 6.1. The plots that show the general shape of an equation were programmed in Mathematica 5.2. The portions in the Appendix that require large summations and iterative loops are programmed in Matlab 7.0.1. The actual eNose data presented in the next two sections was plotted in MS Excel 2003. Screenshots of the main Simulink program can be found in Appendix 6.

Values for the constants that appear in this model were chosen to output values near unity. The models that will be compared to the one derived in this paper have done the same. The significance of the actual values found in these plots was taken lightly, the shapes of the curves with respect to time are more important to the success of these theories. The values used as constants in the Simulink program can be found in Table 7. If the actual values for these constants are needed, they can be found throughout this paper.

<table>
<thead>
<tr>
<th>Constant Used in Simulink</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion Coefficient (Air-Polymer Boundary)</td>
<td>1x10⁻⁴</td>
</tr>
<tr>
<td>Diffusion Coefficient (Polymer-Polymer Boundary)</td>
<td>2x10⁻⁴</td>
</tr>
<tr>
<td>Value for Concentration Volume</td>
<td>1</td>
</tr>
<tr>
<td>Maximum Stress in each Layer</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity of the Polymer</td>
<td>1</td>
</tr>
<tr>
<td>Spring Constant of the Polymer</td>
<td>10</td>
</tr>
<tr>
<td>Resistivity of the Pixel</td>
<td>1.5</td>
</tr>
<tr>
<td>Area in Between Leads</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 7: A table of each constant used in the model that was developed in Simulink

The data plots created with this paper’s model will be compared to the plots found using equations that are developed in the Appendix. Just as the model derived in this paper, the constants in the Appendix models were chosen to give plots with values near or around unity. The dimensionless parameters used in those equations are set to $\kappa = 1$, $\lambda = 0.01$, $\eta = 0.01$. All of the sites in the polymer pixel will be assumed to be empty (i.e.
\( \theta = 0 \) and \( \tau = 0 \) to mimic the ideal absorption process and the external gas concentration is a step function (i.e. \( \gamma = 0 \) for \( \tau < 0 \) and \( \gamma = 1 \) for \( \tau \geq 0 \)). For the ideal desorption process, the gas concentration and the site occupancy will start off at equilibrium (i.e. \( \gamma = 1 \) and \( \theta = \theta_\infty \) at \( \tau = 0 \)). Even though a testing environment can never be this ideal in an actual lab, these simple parameters will help achieve general understanding.

![Graph](image.png)

**Figure 28:** The absorption profile versus the distance parameter, \( \chi \). Each line represents a different time parameter, \( \tau \). (Mathematica)

### 7.2.1 Absorption Plots

Figure 28 shows the distance parameter plots from the appendix models. Figure 29 shows the results of the resistance response plots created by the equations found in the Appendix 5 model. Verification of the accuracy of these approximate analytical expressions will be difficult due to the dimensionless values used as constants. The only option is to compare these plots to the continuous system model plots developed in this paper (Figure 27).
Another option for verification is to compare the shape of Figures 27 the actual data shown in Figure 30. The data displayed in Figure 30 comes from an operational eNose.

Figure 30: The output of fourteen sensors obtained for the first sample of Chateau Haut la Pierriere during the 6s data acquisition phase using the Bloodhound Mass-Flow System. (Excel)

The resemblance of this group of plots is undeniably accurate; especially the peach and pink lines in Figure 30.
7.2.2 Desorption Plots

Figure 31 shows the distance parameter plots from the appendix models. Figure 32 shows the results of the resistance response plots created by the equations found in the Appendix 5 model. Verification of the accuracy of these approximate analytical expressions will be difficult due to the dimensionless values used as constants.

The Simulink program used to create the pixel’s absorption profiles have not been modified to show the resistance change during the desorption process. As of now, the concentration level of the model is a constant value. To run a simulation that plots a pixel’s resistance change during the desorption process, the value for concentration of airborne gas must become a controllable variable. The programs that are developed during the next step of this research will have feature.
Figure 33: The output of fourteen sensors obtained for the first sample of Chateau Haut la Pierriere during the 12s data acquisition phase using the Bloodhound Mass-Flow System. (Excel)

7.3 Entering Sinusoids

Once the computer model is verified and the Simulink codes have been modified to show continuous system desorption profiles, a series of experiments will be developed. These experiments will be designed to help develop a better understanding of the carbon doped polymers. The computer model is necessary for these tests because actual experiments are unrealistic to perform with an actual eNose set up. Difficult and expensive lab set-ups can be avoided by using this computer simulation.

An example of one of these tests would involve time varying sinusoidal concentration levels. It is believed that continuously changing concentration levels will provide more meaningful and interesting results. The polymers used to make these eNose pixels should have frequency response times that cannot be seen, let alone understood without such a simulation.

In search for means of quantifying some of the various parameters utilized in the models presented, parameter identification methods will be used. This identification procedure will be based on actual eNose data. An adaptive Kalman filter is suggested for such future work.
8 Conclusions

The resistance ratio plots created during the production of this thesis show promising results. The shapes of the curves provide the only obvious method of verification. This method of verification shows that the simulation is working as it should. Once variable concentration is added to the model and once the sinusoidal experiments are carried out, a better method of validity can be developed.

The other way to test the accuracy of this model is to find each one of the constants that appear in the simulation through experimental means. Once these constants are found, they can be plugged into the Simulink program. This method of verification would be rather time extensive and unrealistically pricy.
9 Appendix 1

9.1 The Development of a Multiple Maxwell element

The original formulation used to develop this Appendix were covered in research papers by Hughes. When two Maxwell elements that are governed by

\[ \dot{\sigma}_1 = \frac{\sigma_1}{k_1} \eta_1 \]  

and

\[ \dot{\sigma}_2 = \frac{\sigma_2}{k_2} \eta_2 \]  

are placed in parallel, a simple combination model is created. The relation between these two elements will be

\[ \sigma = \sigma_1 + \sigma_2 = \eta_1 \dot{\sigma}_1 + \eta_2 \dot{\sigma}_2 - \frac{\dot{\sigma}_1}{k_1} \eta_1 - \frac{\dot{\sigma}_2}{k_2} \eta_2 \]  

To make a more involved spring and dashpot model, n parallel Maxwell elements are used and a definition similar to that given above would apply. The differential equation of a generalized Maxwell model, or any combination of Kelvin and Maxwell elements with n elements, will have this form

\[ a_0 \sigma + a_1 \frac{d\sigma}{dt} + a_2 \frac{d^2 \sigma}{dt^2} + \cdots + a_n \frac{d^n \sigma}{dt^n} = \]  

\[ b_0 \varepsilon + b_1 \frac{d\varepsilon}{dt} + b_2 \frac{d^2 \varepsilon}{dt^2} + \cdots + a_n \frac{d^n \varepsilon}{dt^n} \]  

With each element added to the model, the complexity of the differential equation will become more complicated. The more elements in the model, the better the theoretical results will be. The problem with including a large number of elements is that the solution to the differential equation will become difficult, if not impossible, to solve. So, to simplify the model’s mathematics, a larger number of simpler differential equations will be used to gain a higher level of resolution. But to help simplify this model

\[ \varepsilon_1 = \varepsilon_2 = \cdots = \varepsilon_n = \varepsilon \]  

and

\[ \sigma_1 = \sigma_2 = \cdots = \sigma_n = \sigma \]
This assumption is valid because of the fact that a uniform polymer will have the same mechanical behavior at any layer under observation. This simplification allows us to rewrite the Maxwell element’s stress, strain relation as

\[ \dot{\varepsilon}_i = \frac{\dot{\sigma}_i}{k_i} + \frac{\sigma_i}{\eta_i}, \]

which can be written as

\[ \dot{\sigma} = k_i \cdot \dot{\varepsilon} - \frac{\sigma_i}{\tau_i}, \]

where

\[ \tau_i = \frac{\eta_i}{k_i}, \]

where \( \tau_i \) is the material’s relaxation time. The multiple Maxwell elements allows

\[ \dot{\sigma} = \sum_{i=1}^{n} \dot{\sigma}_i. \]

And the differential equation becomes

\[ \dot{\sigma} = k^u \cdot \dot{\varepsilon} - \sum_{i=1}^{n} \frac{\sigma_i}{\tau_i}, \]

where \( k^u \) is the unrelaxed modulus of a pixel’s polymer.

To implement the differential form, a solution to the differential equations that can calculate the stresses for given strains needs to be developed. This solution will be for a model where the moduli are constant. The 2nd order accurate Crank-Nicholson (or central difference scheme) is used [Hughes, 1987]. The solution of the polymer’s governing differential equations is

\[ \sigma_i^{p+1} = \frac{k_i \cdot \Delta \varepsilon + \frac{1}{2} \sigma_i^p \cdot \frac{\Delta \varepsilon}{\tau_i}}{1 + \frac{1}{2} \frac{\Delta \varepsilon}{\tau_i}}. \]

Which shows that relaxation time, elapsed time, the strain on the material, and the previous amount of stress control the behavior of the polymer. Equation 87 will yield a plot that has a steadily increasing slope that ends with a plateau (Figure 34).
Figure 34: This graph shows the stress plateau that governs the saturation level. The values of kai is unity, the change in time is 30. (Matlab)
Appendix 2

10.1 Maximum Concentration and Mass Uptake

To find the concentration of a gas found within a single pixel is governed by the following equation

$$\frac{C}{C_1} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\frac{D(2n+1)^2 \pi^2 t}{4\ell^2}\right) \cos\left(\frac{(2n+1)\pi t}{2\ell}\right)$$

(88)

where $D$ is the diffusion coefficient and $\ell$ is the length of the pixel. If the concentration equation is integrated, the equation yields measures the amount of mass the polymer uptakes.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{D(2n+1)^2 \pi^2 t}{\ell^2}\right)$$

(89)

Where $M_\infty$ is the maximum amount of gas mass that can be absorbed into a pixel, and again $\ell$ is the thickness of the pixel under observation. At small increments of time, the equation can be written as

$$\frac{M_t}{M_\infty} = \frac{4}{\ell} \left(\frac{-D}{\pi}\right)^{\frac{1}{2}}$$

(90)

which allows us to measure the diffusion constant, $D$, from the maximum amount of gas mass that can diffuse into a pixel’s polymer.
11 Appendix 3

Figure 35: This is the final model. The gas is on the outside, the polymer pixel only expands in upwards in the direction L and the ceramic substrate is completely inert and inelastic when compared to the soft polymer.

11.1 Diffusion Reaction

In this section of the paper an in-depth polymer absorption and desorption model is covered and discussed. In this model, there is a gas, A, diffusing into a homogeneous polymer film of thickness, L, that is deposited onto an impermeable ceramic substrate (Figure 35). Although there are carbon dopants distributed equally throughout the pixel, they are inert and due to this fact, they do not need to be considered in this part of the model. The polymer contains a uniform distribution, N, of immobile absorption sites, <site>. Assuming that the absorption process is described by the Langmuir absorption isotherm

\[ A + \langle \text{site} \rangle \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \langle A \rangle \]  \hspace{1cm} (91)

where \( k_f \) represent the forward rate (absorption) and \( k_b \) the backward reaction rate (desorption). By exploiting the geometry of a planar film (i.e. - height \( \ll \) width) an expression that allows sorbate concentration, \( a \), and site occupancy, \( \theta \), to be dependant on the distance \( x \) and time \( t \). Taking advantage of this geometry, Fick’s second law can be reduced to a unidirectional absorption process and by adding a function that describes the site occupancy to Fick’s second law, this modified diffusion equation
can be developed. Where $\chi$ is the dimensionless distance parameter ($x/L$), $\tau$ is the time parameter ($Dt/L^2$), $\gamma$ is the normalized gas concentration ($a/a_\infty$) and $a_\infty$ is the concentration of the gas surrounding the pixel. The $\eta$ and the $\lambda$ are both dimensionless parameters given by $KN$ and $Ka_\infty$, respectively. Therefore, $\eta$ and $\lambda$ depends on the material properties like the density of sites $N$, and the ratio of $\left( k_f / k_b \right)$, which is known as the equilibrium constant, $K$. The gas that is bound during absorption or released during the desorption process by sites can be related to the sorption kinetics by,

$$\eta \frac{\partial \theta}{\partial \tau} = \kappa \lambda \gamma (1 - \theta) - \kappa \theta$$

where $\kappa$ is a dimensionless parameter that equals the ratio of forward reaction rate to diffusion rate, $k_f NL^2 / D$. With this, Equations 92 and 93 can be solved and by applying suitable boundary conditions the absorption and desorption concentration $\gamma(\chi, \tau)$ can be obtained along with the site occupancy $\theta(\chi, \tau)$ profiles. [Gardner, 1995]

### 11.2 Applying Boundaries

There has been no exact analytical solution found for the nonlinear partial differential equations 95 and 96, but there are approximate analytical solutions derived by the Garner, Pratt and Bartlett. The six limiting cases they used to solve the equation are as follows [Gardner, 1995]:

- **Case 1** ($\lambda < 1, \kappa < 1, \kappa > \eta$) - Pure diffusion process because the diffusion rate is much lower than the reaction rate and there are few absorption sites to modify the diffusion process. Most of the following discussion will be based off of this case because the polymers used to create the eNose pixels.

- **Case 2** ($\lambda < 1, \kappa > 1, \eta > 1$) - There are a significant number of reaction sites available to absorb the diffusing gas and slow the diffusion process down by a factor of $\sim 1/\eta$. 
• Case 3 ($\lambda < 1, \kappa < 1, \kappa < \eta$) - Diffusion rate is much faster than the reaction rate. Reaction kinetics are in the linear (unsaturated) region of the isotherm (i.e. $\theta << 1$).

• Case 4 ($\lambda > 1, \kappa < 1, \kappa < \eta$) - Diffusion rate is much faster than the reaction rate. Describes the saturated region of the isotherm (i.e. $\theta \approx 1$)

• Case 5 ($\lambda > 1, \lambda^2 > \eta, \kappa > 1, \kappa > \eta$) - Describes the saturated region of the isotherm when the kinetics are fast so that the equilibrium is maintained between the free and bound species.

• Case 6 ($\lambda > 1, \lambda^2 < \eta, \kappa > 1, \eta > 1$) - The situation in between cases 1 and 5 in which neither the reaction process nor the diffusion process dominates. This case is referred to as the “moving boundary problem”.

As mentioned in the case definitions, Case 1, the pure diffusion case is the only case that applies to the polymers usual to create eNose pixels and it will be the only case discussed in this paper. The other cases are listed in Appendix 4 and they are discussed in the Gardner group’s paper. The depth in the absorption profile for Case 1 ($\lambda < 1, \kappa < 1, \kappa > \eta$) is

$$\gamma(\chi, \tau) = 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right]}{(-1)^n (n + \frac{1}{2})}$$

and the site occupancy that goes with this absorption profile is

$$\theta(\chi, \tau) = \lambda \gamma .$$

The desorption profile for Case 1 is

$$\gamma(\chi, \tau) = \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right]}{(-1)^n (n + \frac{1}{2})}$$

and the site occupancy that goes with this absorption profile is

$$\theta(\chi, \tau) = \lambda \gamma .$$
12 Appendix 4

12.1 Complete List of Absorption and Desorption profiles

Absorption Profile:

Case 1: \((\lambda < 1, \kappa < 1, \kappa > \eta)\)

\[
\gamma(\chi, \tau) = 1 - 2 \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right]}{(-1)^n(n + \frac{1}{2})}
\]

\[
\theta(\chi, \tau) = \lambda \gamma
\]

Case 2: \((\lambda < 1, \kappa > 1, \eta > 1)\)

\[
\gamma(\chi, \tau) = 1 - 2 \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau/\eta\right]}{(-1)^n(n + \frac{1}{2})}
\]

\[
\theta(\chi, \tau) = \lambda \gamma
\]

Case 3: \((\lambda < 1, \kappa < 1, \kappa < \eta)\)

\[
\gamma(\chi, \tau) = 1 - 2 \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right]}{(-1)^n(n + \frac{1}{2})}
\]

\[
\theta(\chi, \tau) = \lambda \left[1 - \exp\left(-\frac{\kappa \tau}{\eta}\right)\right]
\]

Case 4: \((\lambda > 1, \kappa < 1, \kappa < \eta)\)

\[
\gamma(\chi, \tau) = 1 - 2 \sum_{n=0}^{\infty} \frac{\cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right]}{(-1)^n(n + \frac{1}{2})}
\]

\[
\theta(\chi, \tau) = 1 - \exp\left(-\frac{\lambda \gamma \tau}{\eta}\right)
\]

Desorption Profile:

\[
\gamma(\chi, \tau) = \frac{2}{\pi} \sum_{n=0}^{\infty} \cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right]
\]

\[
\theta(\chi, \tau) = \lambda \gamma
\]

\[
\gamma(\chi, \tau) = \frac{2}{\pi} \sum_{n=0}^{\infty} \cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau/\eta\right]
\]

\[
\theta(\chi, \tau) = \lambda \gamma
\]

\[
\gamma(\chi, \tau) = \frac{2}{\pi} \sum_{n=0}^{\infty} \cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right]
\]

\[
\theta(\chi, \tau) = \lambda \left[1 - \exp\left(-\frac{\kappa \tau}{\eta}\right)\right]
\]

\[
\gamma(\chi, \tau) = \frac{2}{\pi} \sum_{n=0}^{\infty} \cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right]
\]

\[
\theta(\chi, \tau) = \left\{\frac{\exp\left(-\frac{\kappa \tau}{\eta}\right)}{1 + \exp\left(-\frac{\kappa \tau}{\eta}\right)}\right\}^{\frac{4 \ln\left(\frac{4 \lambda}{\pi}\right)}{\pi^2}}
\]

\[
\tau_d = \left[\frac{4 \ln\left(\frac{4 \lambda}{\pi}\right)}{\pi^2}\right]
\]
Case 5: \((\lambda > 1, \lambda^2 > \eta, \kappa > 1, \kappa > \eta)\)

\[
\gamma(\chi, \tau) = 1 - \frac{2}{\pi} \sum_{n=0}^{\infty} \cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right] \frac{(-1)^n}{(n + \frac{1}{2})} \\
\theta(\chi, \tau) = \frac{\lambda \gamma}{(1 + \lambda \gamma)}
\]

Case 6: \((\lambda > 1, \lambda^2 < \eta, \kappa > 1, \eta > 1)\)

For \(\tau < \tau_*,\) where \(\tau_* = \frac{0.59 \eta}{\lambda}\)

\[
\gamma_1(\chi < \chi_*, \tau) = \frac{\gamma_*}{\text{erfc}\left(\frac{\eta^{1/2}(1 - \chi)}{2\tau^{1/2}}\right)} + e(\chi, \tau) \\
\gamma_2(\chi > \chi_*, \tau) = 1 - \frac{1 - \gamma_*}{\text{erfc}\left(\frac{(1 - \chi)}{2\tau^{1/2}}\right)} + e(\chi, \tau) \\
\theta(\chi, \tau) = \frac{\lambda \gamma}{(1 + \lambda \gamma)}
\]

\[
\gamma(\chi, \tau) \approx 2 \sum_{n=0}^{\infty} \cos[(n + \frac{1}{2})\pi \chi] \exp\left[-(n + \frac{1}{2})^2 \pi^2 \tau\right] \frac{(-1)^n}{(n + \frac{1}{2})} \\
\theta(\chi, \tau) = \frac{\lambda \gamma}{(1 + \lambda \gamma)}
\]
13 Appendix 5

13.1 Finite Coplanar Thin Electrode Conductance Model

The properties of the surface boundaries differ from the bulk of a polymer. Unlike simple volumes of molecules (i.e. – a puddle of water), a polymer’s surface properties aren’t one atom deep. Due to the polymer’s chain structure, a single monomer can go as deep as a few nanometers. So, to simplify the math and to decrease the number of potential complications, the circular puddle of polymer-carbon (Figure 5) of radius R and a height of h, will be treated as a two dimensional circular plane (i.e. - where the diameter >> length L) (Figure 13).

The flat geometry of the pixel allows for unidirectional diffusion just as the properties used to develop the diffusion reaction rates. Once again, using the planar shape of the pixel will help to further simplify the involved mathematics. The simplest possible way to model the polymer expansion is to use a linear relation between the conductivity \( \sigma(\chi, \tau) \) versus the site occupancy \( \theta(\chi, \tau) \)

\[
\sigma(\chi, \tau) = \sigma_0 [1 - S \theta(\chi, \tau)].
\]  
(98)

Where \( S \) is the gas-sensitivity constant for the polymer-pixel and \( \sigma_0 \) is the base line conductivity of the polymer (i.e. – in a gasless environment). Where this local conductivity is related to the resistivity by

\[
\sigma_0 = \frac{1}{\rho_0}.
\]  
(99)

Luckily, this linear relation describes actual experimental data taken on conducting polymers. The steady-state response of the expanding polymer pixels will follow the form of the Langmuir isotherm [Bartlett, 1989]. The steady-state resistivity response begins to change by 1 to 10% at high concentrations (i.e. – when the polymer is saturated).

This case the separation between electrodes is \( w \) and the electrode’s length is \( b \) and the height of the polymer is \( L \). For a pair of finite coplanar thin electrodes of width \( d \) for which the conformal transformation is a Jacobean elliptical integral of the first kind giving the electric field as
\[ E(\chi,0) = \frac{V}{2A^*L^2} \sqrt{\frac{1}{\chi^2 + w^2/4L^2} + \frac{1}{M^2\chi^2 + w^2/4L^2}} \]  

(100)

where \( V \) is the voltage applied across the electrodes, \( M \) is a geometrical modulus \((w/(w+2d))\) and the constant \( A^* \) is determined from the complete elliptical integral.

\[ A^* = \frac{2}{w} \int_0^1 \frac{1}{\sqrt{1-t^2} \left( 1 - M^2t^2 \right)} \, dt^* \]  

(101)

This equation for the electric field assumes that the medium through which electrons travel from one electrode to the other, \( A \) in Figure 13, will have constant electronic properties. Any differences between the dielectric permitivities of the substrate, polymer and the air or gas will influence the electric fields. The parametric form of Equation 98 has been verified when a similar model was used. In this earlier model, it was found that there was a good fit of steady-state conductance in air against film thickness [Bartlett, 1989]. The same model shows that the Equation 100 is a reasonable functional form for the electric field. A more exact solution would require a numerical solution (e.g. – by using finite element analysis of the device layout) [Gardner, 1995].

By integrating the product of the local conductivity and the electric field over a closed surface the current \( i \) passing between the electrodes can be calculated [Gardner, 1989; Cussack, 1987]. Thus the conductance in air \( G_0 \) can be calculated from the given geometry as

\[ G_0 = \frac{\sigma_0 b}{2A^*L} \int_0^1 \left( \sqrt{\chi^2 + w^2/4L^2} \left( M^2\chi^2 + w^2/4L^2 \right) \right) d\chi \]  

(102)

and with this relation,

\[ G_0 = \frac{1}{R_0} \]  

(103)

the resistance in air can be calculated in terms of the resistivity

\[ R_0 = \frac{\rho_0 2A^*L}{b} \frac{1}{\int_0^1 \left( \sqrt{\chi^2 + w^2/4L^2} \left( M^2\chi^2 + w^2/4L^2 \right) \right) d\chi} \]  

(104)

for coplanar electrodes.
Again the effect of any dielectric behavior of the film could be taken into account by the effective lowering of the electric field by a simple factor. By rearranging Equation 107 and putting the terms in the service integral give the response of the device (i.e. Fractional change in conductance) as

$$\frac{G(\tau) - G_0}{G_0} = -S \frac{\int_0^1 \left( \theta(\chi, \tau) / \sqrt{\chi^2 + w^2/4L^2} \left( M^2 \chi^2 + w^2/4L^2 \right) \right) d\chi}{\int_0^1 \left( 1 / \sqrt{\chi^2 + w^2/4L^2} \left( M^2 \chi^2 + w^2/4L^2 \right) \right) d\chi}$$

Note that in this equation changing our assumptions for the functional form of the conductivity can be accommodated by replacing $\theta(\chi, \tau)$ within the numerator of the integral in the numerator by another functional form. Similarly, we can define the sensor response as the fractional change in resistance when desirable for other sensor materials.

$$\frac{R(\tau) - R_0}{R_0} = -\frac{1}{S} \frac{\int_0^1 \left( \theta(\chi, \tau) / \sqrt{\chi^2 + w^2/4L^2} \left( M^2 \chi^2 + w^2/4L^2 \right) \right) d\chi}{\int_0^1 \left( 1 / \sqrt{\chi^2 + w^2/4L^2} \left( M^2 \chi^2 + w^2/4L^2 \right) \right) d\chi}$$

The steady-state response of the device can now be related to the external gas concentration $a_\infty$ by,

$$\frac{G(\infty) - G_0}{G_0} \approx -S \theta_\infty = -S \frac{K a_\infty}{1 + Ka_\infty}$$

The magnitude and size of the steady-state response depends upon the sensitivity coefficient $S$ and hence the gas detected but not on the device geometry. Typical responses lie in the range of 1 to 10% for organic solvents. Poly(pyrrole) devices generally show a conductance which falls (i.e. $-S > 0$) on the introduction of a gas [10], however the sign seems to depend upon the hydrophobicity of the polymer.

So, Equation 105 give the theoretical dynamic response and Equation 107 gives the steady state response, of two planar polymer gas devices in terms of the site occupancy profiles for each of the six limiting cases discussed above.

In calculating the conductance is of these devices we have assumed that the electrode thickens is much less than the film thickness that the electrodes are long (i.e. $b \gg w$ and $b \gg d$) so that the edge effects become insignificant. In principle the model could be extended to include both of these effects, but in practice this is not necessary.
14 Appendix 6

14.1 Screenshots of the Simulink Program

Figure 36: The top level of the program.

Figure 37: The strain development

Figure 38: The development of the change in resistance
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17 Vita

Adolphe H. Alexander was born in Ventura, California, on April 24th 1983, the son of Lt. Com. Oran T. Alexander and Gloria H. Alexander. After completing his work at Roxborough Highschool in Philadelphia, he went to the prestigious Haverford College where he graduated with a Bachelor of Science in Physics. Immediately after graduating from Haverford, Adolphe began studying for his Master of Science degree in Mechanical Engineering at Lehigh University.

This thesis was typed by the author. Each diagram and every plot but the ones found in Figures 1, 3 and 5 were created by the author as well.