NEW SEMI-EMPIRICAL MODEL FOR SOUND PROPAGATION IN ADSORBING MICROPOROUS SOLIDS (ACTIVATED CARBON)

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ABSTRACT
The characterisation of sound propagation in microporous heterogeneous material, such as activated carbon, is needed for a better understanding of the unusual effects such a material causes to an acoustic wave. A new semi-empirical model is presented here, based on the model of dynamic tortuosity and dynamic compressibility for the study of rigid-frame porous materials at low frequencies. The new model treats the case where a significant number of air molecules are adsorbed onto the surface of a porous solid, so that the wave propagation through the material is altered. This occurs in materials that have a very large internal surface area and a wide range of pore size distributions. The model incorporates a number of the adsorbed molecules as an extra degree of freedom that depends on the acoustic pressure. Results from the model were compared to measurements of normal incidence absorption coefficient for a thin layer of activated carbon with a grain size distribution between 0.30 and 0.42mm. The results obtained show fair correlation with the model over the particular frequency range of interest.

LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \omega )</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>( (n_s^F)_b )</td>
<td>Equilibrium concentration of adsorbed molecules at atmospheric pressure</td>
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<tr>
<td>( \rho_0 )</td>
<td>Density of air</td>
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<tr>
<td>( p )</td>
<td>Acoustic pressure</td>
</tr>
<tr>
<td>( P_0 )</td>
<td>Atmospheric pressure</td>
</tr>
<tr>
<td>( n_0 )</td>
<td>Maximum number of adsorbable molecules</td>
</tr>
<tr>
<td>( n_s^F )</td>
<td>Concentration of adsorbed molecules</td>
</tr>
<tr>
<td>( k_a )</td>
<td>Adsorption rate constant</td>
</tr>
<tr>
<td>( k_d )</td>
<td>Desorption rate constant</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Flow resistivity</td>
</tr>
<tr>
<td>( \alpha(\omega) )</td>
<td>Dynamic tortuosity</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Relaxation time</td>
</tr>
<tr>
<td>( V )</td>
<td>Volume</td>
</tr>
<tr>
<td>( R_g )</td>
<td>Gas constant</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature</td>
</tr>
<tr>
<td>( c )</td>
<td>Speed of sound in air</td>
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INTRODUCTION
The study of wave propagation in complex porous materials is essential because of the growing use of these materials in the acoustic industry. This paper presents a comparison between two porous materials, sand and activated carbon, in relation to low frequency measurements of normal incidence surface impedance and absorption coefficient. The two samples have the same grain size distribution, hence a similar macroscopic porous region. The difference between the two samples is an extra 'microporous' dimension present in the activated carbon sample, where the grains themselves are porous [1]. It is assumed that this presents an extra effect on the penetrating acoustic wave in the form of adsorption and desorption of air molecules, proportional to the variations in acoustic pressure in compression and rarefaction cycles. The results for the sample of activated carbon are then compared to simulations from a new semi-empirical model for dynamic tortuosity. The model is based on a three parameter model [2] and includes an extra relaxation time parameter, \( \tau \) which relates the adsorption and desorption rate constants to the total number of molecules in the system at equilibrium, as well as the maximum possible number of adsorbable molecules. Results from the modelling show
good correlation with the absorption measurement for the sand sample. Initial results from the ‘relaxation time model’ show fair correlation with the measured data for absorption coefficient, although work needs to be done to improve the simulation at low frequencies, as well as accounting for the peak in absorption at around 300 Hz.

SAMPLE DESCRIPTION AND MEASUREMENT PROCEDURE

Description of the test samples
The sand and activated carbon samples were chosen and prepared in such a way as to highlight the effects of an extra microscopic porous region on surface impedance and absorption coefficient. The two samples have the same grain size distribution, between 0.30mm and 0.42mm. The same grain size distribution will ensure a similar macroscopic porous region between the two samples, provided that the two samples compact in a similar manner. The extra ‘microporous’ region is inherent to activated carbon, specifically to the carbon grains themselves as each of which is highly porous, with pore widths ranging from a few nanometres to thousands of nanometres. In this part of the work, the microscopic porous region caused by the porous activated carbon granules is considered as one extra porous dimension, even though it is usually described as having three distinct regions, the macro-, meso- and microporous region. Both samples were dried in an oven at 110 °C for four hours to ensure any excess water in the sand sample to evaporate. The samples were then placed in a controlled environment at a constant temperature of 21 °C and relative humidity of 32% for ten hours. This will ensure that the adsorption and desorption of water vapour molecules in the activated carbon sample will have reached an equilibrium. It is assumed that the vapour molecules will be mostly adsorbed into the microporous region hence will have little effect on the macroscopic air flow in the carbon sample.

Description of the measurement procedure
For the impedance tube measurement, the two samples were compacted into a measuring tube to obtain a compressed volume of 4 litres for each sample, and then compacted into the sample holder in order to obtain the characteristics of a rigid-frame sample. The sample holder has a diameter of 34.6cm, which means that the sample thickness, \( h \approx 3.76cm \). The measurements were performed over the frequency range 16 - 500Hz for a linear-swept sinusoidal input signal. The pressure inside the tube is measured at four microphone positions, and the transfer function between the various positions is calculated and used to derive the normal incidence absorption coefficient and surface impedance for the two samples.

RESULTS

Surface Impedance Results

![Figure 1. Real part of surface impedance for two different boundary conditions.](image)
The results for normal incidence surface impedance, as shown in Figures 1 and 2, show a peak in the real part at a resonance for the sand sample at around 70Hz and for the activated carbon at 55Hz. The resonant peak for the activated carbon sample is evidence of larger damping due to the presence of the extra microporous region in the carbon sample. It can also be deduced from the above plots that the activated carbon sample will produce a higher absorption as compared with the sand sample across the measured frequency range. This added absorption is thought to be due to the relaxation time of the system. This relaxation time is related to the adsorption and desorption rate constants, which will be shown in the next section. Adsorption is considered as a dynamic process in which the rates of adsorption and desorption are equal at equilibrium. The concentration of adsorbed molecules on the activated carbon surface is a function of the ambient pressure and temperature. This means that the periodic oscillations in an acoustic wave can violate the local adsorption equilibrium when penetrating the material. This causes a transition of a certain number of molecules into what is called an “adsorbed” state during the compression part of an acoustic cycle. In the desorption state, the transition of the adsorbed molecules back into the surrounding medium are accompanied by internal processes tending towards the equilibrium state. Processes of establishing equilibrium are irreversible and therefore involve energy dissipation [3].

**SEMI-EMPIRICAL MODEL**

In order to explain the added absorption at low frequencies in the activated carbon sample, a new semi-empirical model was designed, based on the three-parameter model for dynamic tortuosity and dynamic compressibility. In the new model, an equation for the adsorption dynamics is added and the equation of state is modified to include a number of the adsorbed molecules.

To begin, consider the Langmuir adsorption isotherm,

\[ n_s^* = \frac{k_a PN}{k_d + k_a P} \]  

(Eq. 1)

where \( P \) is pressure in the pores.

The adsorption dynamics equation is

\[
\frac{dn_s}{dt} = k_a P(N - n_s) - k_d n_s = k_a P N - n_s (k_a P + k_d) = -(k_a P + k_d) \left( n_s - \frac{k_a P N}{k_a P + k_d} \right) = (k_a P + k_d) \left( n_s - n_s^* \right) 
\]

(Eq. 2)
Let $P = P_0 + p$. Assuming $p << P_0$, the above equation can be modified as

$$\frac{dn_s}{dt} = -(k_a P_0 + k_d) \left( n_s - \frac{k_a P_0 N}{k_a P_0 + k_d} \right) + k_d P - \frac{k_a P_0 N}{k_a P_0 + k_d} \tag{Eq.3}$$

Equation 3 in turn can be simplified by introducing a new variable $\Delta n = n_s - (n_s^0)_{P_0}$ to become

$$\frac{d(\Delta n)}{dt} = -\frac{1}{\tau} \Delta n + k_a (n_s^0)_{P_0} \tag{Eq.4}$$

where $\tau = \frac{1}{k_a P_0 + k_d}$. This equation describes relaxation time of the number of adsorbed molecules to its equilibrium value.

Now consider the acoustic equations, i.e. Continuity equation:

$$\partial \rho \frac{\partial v}{\partial t} + \rho_0 \frac{\partial v}{\partial x} = 0 \tag{Eq.5}$$

and momentum conservation equation:

$$\rho_0 \frac{\partial v}{\partial t} = -\frac{\partial p}{\partial x} + F(v) \tag{Eq.6}$$

At low frequencies, wave propagation is considered isothermal, and the operator $\hat{F}(v)$ for the viscous friction forces inside the adsorbent will tend towards $-\sigma_0 \phi v$, where $\phi$ is porosity.

Equation of state has to be derived now to relate acoustic pressure variations $p$ with gas density and the number of the adsorbed molecules.

Equation of state for an ideal gas states

$$PV = mR_s T \tag{Eq.7}$$

where $m$ is mass of the gas molecules in volume $V$, i.e.

$$m = \mu (N_0 - n_s) = \mu (N_0 - (n_s^0)_{P_0} - \Delta n) \tag{Eq.8}$$

and $\mu$ is molecular mass. Let $N_0 - (n_s^0)_{P_0} = N_0^0$ and $\mu N_0^0 = m$, then

$$PV = \mu N_0^0 \left(1 - \frac{\Delta n}{N_0^0}\right) R_s T ; \mu N_0^0 = m \tag{Eq.9}$$

which can be modified to give the following equation by division of both its parts by volume $V$

$$P = \rho \left(1 - \frac{\Delta n}{N_0^0}\right) R_s T \tag{Eq.10}$$

For small increments in pressure ($p$), density ($\rho$) and the number of the adsorbed molecules ($\Delta n$) this gives:

$$\rho = \frac{1}{c^2} p + \mu \Delta n \tag{Eq.11}$$

where $c = \sqrt{R_s T}$, $\mu = \frac{\rho_0 c^2}{N_0^0}$ and $\mu = \frac{\rho_0}{N_0}$.

Consequently

$$\frac{\partial \rho}{\partial t} = \frac{1}{c^2} \frac{\partial p}{\partial t} + \mu \frac{\partial \Delta n}{\partial t} \tag{Eq.12}$$

which allows exclusion of density variations from continuity equation (5) to give
\[ \rho_0 \frac{\partial v}{\partial t} + \frac{1}{c^2} \frac{\partial p}{\partial t} + \mu \frac{\partial \Delta n}{\partial t} = 0 \]  

(Eq.13)

Next step is to find a dispersion relationship for the system described by equations (4), (6) and (13) assuming \( e^{-j(\omega-t-kx)} \) dependence on time \( t \) and distance \( x \):

Equation 13 gives: 
\[ -\frac{j \omega p}{c^2} - j \mu \omega \Delta n + j \rho_0 k v = 0 \]  

(Eq.14)

Equation 6 gives: 
\[ -j \omega \alpha_\omega \rho_0 v + j k p + \sigma_0 \phi v = 0 \]  

(Eq.15)

Equation 4 gives: 
\[ -j \omega \Delta n + \frac{1}{\tau} \Delta n - \kappa p = 0 \]  

(Eq.16)

For this system to have non-trivial solution the following determinant has to be zero:

\[ \text{Det} = \mu \kappa (\omega^2 \alpha_\omega \rho_0 + j \omega \sigma_0) - \rho_0 k^2 \left( \frac{1}{\tau} - j \omega \right) \]

+ \( \frac{1}{c^2} \left( \frac{1}{\tau} - j \omega \right) (\omega^2 \alpha_\omega \rho_0 + j \omega \sigma_0) = 0 \)  

(Eq.17)

By rearranging the following dispersion relation can be easily derived:

\[ k = \pm \frac{\omega}{c} \sqrt{\alpha_\omega \left( 1 + \frac{j \phi \sigma_0}{\omega \alpha_\omega \rho_0} \right) \left( 1 + \frac{\tau \mu \kappa c^2}{(1 - j \omega)} \right)} \]  

(Eq.18)

This in turn leads to the following expression for dynamic tortuosity function that includes contribution from adsorption process:

\[ \alpha(\omega) = \alpha_\omega \left( 1 + \frac{j \phi \sigma_0}{\omega \alpha_\omega \rho_0} \right) \left( 1 + \frac{\tau \mu \kappa c^2}{(1 - j \omega)} \right) \]  

(Eq.19)

\[ \lim_{\omega \to 0} \alpha(\omega) = \frac{j \sigma_0}{\omega \rho_0} (1 + \tau \mu \kappa c^2) \]  

(Eq.20)

Initial results for the sand and activated carbon samples are shown below.

Figure 3. Comparison between theory and experiment for the absorption coefficient of sand sample.
To get reasonable agreement with the data in the whole range of frequencies, the full version of equivalent fluid model [4] has been used in simulations.

<table>
<thead>
<tr>
<th></th>
<th>γ</th>
<th>N_Di</th>
<th>Λ (m)</th>
<th>η (Pa.s)</th>
<th>φ</th>
<th>σ  (kg.m⁻³.s⁻¹)</th>
<th>α∞</th>
<th>N₀ (mol)</th>
<th>N₀* (mol)</th>
<th>k₁=k₂ (mmol/g)</th>
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</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>1.41</td>
<td>0.7</td>
<td>2.7e-4</td>
<td>1.73e-5</td>
<td>0.65</td>
<td>19000</td>
<td>2.4</td>
<td>2.5e6</td>
<td>1.6e6</td>
<td>0.12</td>
</tr>
<tr>
<td>Sand</td>
<td>1.41</td>
<td>0.7</td>
<td>3.8e-5</td>
<td>1.73e-5</td>
<td>0.38</td>
<td>28000</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1. Parameter values used in the two semi-empirical models.

The results for the sand sample show good correlation with the simulation except at low frequencies. For the activated carbon sample, initial results from the model show an average correlation with the measured data for absorption coefficient, but improvement to the model need to be made in order to account for the increased low frequency absorption and the absorption peak at around 300Hz.

CONCLUSIONS

The results for surface impedance and absorption coefficient presented in this paper illustrate the similarities and differences between two porous materials, sand and activated carbon. The main physical difference between the two materials is the existence of an extra microscopic porous region in the activated carbon granules. This region encourages the processes of adsorption and desorption inside the activated carbon sample as a function of change of pressure and temperature. It is this process of a change in entropy which leads to energy loss in the system as it is driven back to equilibrium. A new semi-empirical model for dynamic tortuosity was presented. The model relates the changes in acoustic pressures to the deviation of the concentration of adsorbed molecules from the equilibrium value, as well as the time it takes for the system to reach equilibrium, which is called the relaxation time. Results from a conventional semi-empirical model and the new 'relaxation-time' model are compared to measurements of sand and activated carbon respectively, and the results for absorption coefficient show a good agreement for the sand sample, and a fair agreement for the activated carbon sample. Further work will include testing various samples of activated carbon, of varying pore and grain size distributions, as well as improving the new model, especially in the low frequency range.

References