Adsorption 11: 433–436, 2005

A Simplified Model for Acoustic Measurement of Diffusion in Microporous Solids

MASSIMILIANO NORI AND STEFANO BRANDANI*
Department of Chemical Engineering, University College London, Torrington Place WC1E7JE, London, UK
s.brandani@ucl.ac.uk

Abstract. An analytical model for sound propagation between two layers of a microporous material is presented in order to investigate the application of acoustic techniques for measuring adsorption and diffusion in microporous materials. The attenuation coefficient for the system CO_2—Silicalite crystals is analysed in the range of pressure [2 Torr-3 bar] at $T = 304.55$ K, and indicates the potential feasibility of a novel experimental technique.

Keywords: microporous diffusion, sound propagation, modelling

1. Introduction

The measurement of diffusion in zeolite crystals and other microporous solids has attracted much attention in the past and a large number of different experimental techniques are now available (Kärger and Ruthven, 1992). These techniques can be classified broadly into microscopic methods, which measure the mean square displacement of molecules in the crystals, and macroscopic techniques which measure the mass flux being transferred from the solid to the gas phase or vice versa (Ruthven and Brandani, 1997). For many sorbate-sorbent systems, agreement can be found among the various experimental results. For a few systems there are still large discrepancies of several orders of magnitude in the reported diffusivity values, therefore this area of research represents a scientific open challenge (Kärger, 2003). This limited success can be attributed also to the fact that it is not always possible to carry out experiments using the various techniques. In general terms, microscopic techniques are limited to fast diffusing species, while macroscopic methods are more reliable for slow diffusing systems. It is evident that it would be advantageous if one could devise a new macroscopic technique that significantly increases the range of applicability by several orders of magnitude in measurable diffusional time constants. This would also provide the further advantage of allowing to study and measure the kinetic properties of industrial crystals which tend to be of the order of 1 μm in size, much smaller than the crystal size often required for macroscopic measurements.

Among the various macroscopic techniques, the Frequency Response method is one of the more advanced techniques, since relatively fast diffusing species can be followed and it identifies clearly the controlling mass transfer mechanism (Yasuda and Sugasawa, 1982). Van Den Begin and Rees (1989) significantly improved the original design of Yasuda and reached an upper limit in frequency of 10 Hz. More recently Bourdin et al. (1998) have increased the range up to 30 Hz, and this can be seen as the mechanical upper limit of the technique.

When reviewing the FR response literature, one can immediately see that the current limit of applicability corresponds to the lower range of audible sound. It seems reasonable to suggest considering to study the effect of a microporous adsorbent on the properties of sound in order to determine the feasibility of an acoustic technique used to extend the range of FR diffusion measurements by at least 2 orders of magnitude. With the aim of a qualitative understanding

---

*Holder of the Royal Society/Wolfon Research Merit Award.

and preliminary evaluation of this approach, a simplified analytical model for sound propagation between two layers of a microporous material is presented.

2. Model

We consider the simple geometry of two layers of an adsorbent microporous solid of infinite width separated by a gas that adsorbs on the solid's surface. A planar sound wave propagates in the x direction (Fig. 1).

The assumptions made, allow us to consider the 2-D problem and sound propagation can be described (Landau and Liftshitz, 1997) using the Navier-Stokes equations in vertical and horizontal directions,

$$\begin{aligned}&\bar{\rho}\left[\frac{\partial \bar{u}}{\partial t}+\bar{v}\frac{\partial \bar{u}}{\partial z}+\bar{u}\frac{\partial \bar{u}}{\partial x}\right]\\&\quad=-\frac{\partial \bar{p}}{\partial x}+\mu\left\{\frac{\partial^2 \bar{u}}{\partial x^2}+\frac{\partial^2 \bar{u}}{\partial z^2}+\frac{1}{3}\frac{\partial}{\partial x}\left[\frac{\partial \bar{u}}{\partial x}+\frac{\partial \bar{v}}{\partial z}\right]\right\}\\&\quad=0\end{aligned} \tag{1}$$

$$\begin{aligned}&\bar{\rho}\left[\frac{\partial \bar{v}}{\partial t}+\bar{v}\frac{\partial \bar{v}}{\partial z}+\bar{u}\frac{\partial \bar{v}}{\partial x}\right]\\&\quad=-\frac{\partial \bar{p}}{\partial z}+\mu\left\{\frac{\partial^2 \bar{v}}{\partial x^2}+\frac{\partial^2 \bar{v}}{\partial z^2}+\frac{1}{3}\frac{\partial}{\partial z}\left[\frac{\partial \bar{u}}{\partial x}+\frac{\partial \bar{v}}{\partial z}\right]\right\}\\&\quad=0\end{aligned} \tag{2}$$

the continuity equation,

$$\frac{\partial \bar{\rho}}{\partial t}+\bar{u}\frac{\partial \bar{\rho}}{\partial x}+\bar{v}\frac{\partial \bar{\rho}}{\partial z}+\bar{\rho}\left[\frac{\partial \bar{u}}{\partial x}+\frac{\partial \bar{v}}{\partial z}\right]=0 \tag{3}$$

the equation of state.

$$\bar{p}=\bar{\rho}R_oT \tag{4}$$

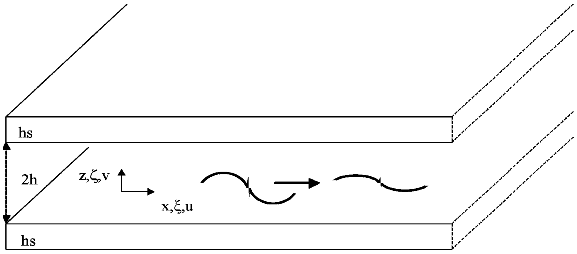

Figure 1. Schematic diagram of the system and sound wave propagation and attenuation.

and the energy balance

$$\begin{aligned}&\bar{\rho}C_p\left[\frac{\partial \bar{T}}{\partial t}+\bar{u}\frac{\partial \bar{T}}{\partial x}+\bar{v}\frac{\partial \bar{T}}{\partial z}\right]\\&\quad=\lambda\left[\frac{\partial^2 \bar{T}}{\partial x^2}+\frac{\partial^2 \bar{T}}{\partial z^2}\right]+\frac{\partial \bar{p}}{\partial t}+\bar{u}\frac{\partial \bar{p}}{\partial x}+\bar{v}\frac{\partial \bar{p}}{\partial z}+\mu\Phi\end{aligned} \tag{5}$$

where

$$\begin{aligned}\Phi_v&=2\left[\left(\frac{\partial \bar{u}}{\partial x}\right)^2+\left(\frac{\partial \bar{v}}{\partial z}\right)^2\right]+\left(\frac{\partial \bar{v}}{\partial x}+\frac{\partial \bar{u}}{\partial z}\right)^2\\&\quad-\frac{2}{3}\left(\frac{\partial \bar{u}}{\partial x}+\frac{\partial \bar{v}}{\partial z}\right)^2\end{aligned} \tag{6}$$

These equations have to be coupled, in the simplest case, to the isothermal solid phase mass balance

$$\frac{\partial \bar{q}}{\partial t}=D\frac{\partial^2 \bar{q}}{\partial z^2} \tag{7}$$

where the solid flux along the sound propagation axis can be neglected.

Equations (1)–(7) can be linearized according to the acoustic approximation (i.e. terms superior to the first order are eliminated) and made dimensionless following Tijdeman's notation (1975). A general procedure is available to solve this set of equations if they are formulated in terms of the gas pressure (Tijdeman, 1975). To achieve this, consider the dimensionless mass balance of the solid which can be rewritten as:

$$\frac{\partial q}{\partial \tau}=\frac{1}{k'_d}\left(\frac{\partial^2 q}{\partial \zeta^2}\right) \tag{8}$$

where q is the relative variation of the sorbate concentration with respect to the average value (i.e. $\bar{q}=q_s(1+q(\xi,\zeta,\tau)))$, $\tau=\omega t$, $k'_d=\frac{\omega h^2}{D}$ and the dimensionless vertical coordinate $\zeta=z/h$, and the corresponding set of boundary conditions:

(a) At the gas-microporous solid interfaces, the continuity of the mass flux:

$$\zeta=1,-1,u=0 \quad \text{and} \quad v=-\frac{Dq_sK_p}{e^{i\omega t}\rho_s a_0}\frac{\partial q}{\partial \zeta} \tag{9}$$

where a_o is the isentropic sound velocity

(b) Solid temperature fluctuations are zero:

$$\zeta=1,-1 \quad T=0 \tag{10}$$

(c) At the gas-microporous solid interfaces, pressure and sorbate concentration are in equilibrium:

$$\zeta = 1, -1, \quad q = K_p p \cdot e^{i\tau} \tag{11}$$

To recast the model equations in a form that allows the application of the solution procedure of Tijdeman (1975) in the case of sound propagation in a tube it is therefore necessary to express the surface concentration gradient $\partial q/\partial \zeta$ as function of the external pressure. In chemical engineering terms this corresponds to finding the transfer function $G_q(\vartheta)$ so that:

$$\left.\frac{\partial \tilde{q}_l}{\partial \zeta}\right|_{\zeta=-1} = G_q(\vartheta)\tilde{p} \tag{12}$$

From the solution of the diffusion equation in the Laplace domain, one can easily find the transfer function to be

$$G_q(\vartheta) = \sqrt{k'_d \vartheta}\,\tanh\left(\sqrt{k'_d \vartheta}\,\frac{hs}{h}\right) \tag{13}$$

Finally Eq. (13) is inverted to the time domain following the inversion theorem for periodic input (Stephanopoulos, 1984). Following the procedure of Tijdeman (1975) the solution for the pressure is given by:

$$p = Ae^{\Gamma\xi} + Be^{-\Gamma\xi} \tag{14}$$

where A and B can be determined by the boundary conditions on the ξ coordinate.

Γ is the propagation constant given by

$$\Gamma = i\sqrt{\frac{\gamma}{n}}\sqrt{\frac{1}{\left(1 - \frac{\tanh(i^{1/2}s)}{i^{1/2}s}\right)}} \tag{15}$$

where s is Stokes number and n is the polytropic equivalent coefficient given by

$$n = \left[1 - \frac{\gamma - 1}{\gamma}\left(1 - \frac{\tanh(i^{1/2}\sigma\, s)}{i^{1/2}\sigma\, s}\right) + \frac{1}{(ik)}\frac{DK_p q_s}{h\rho_s a_o} \cdot |G_q(\vartheta)|e^{i\arg(G_q(\vartheta))}\right]^{-1} \tag{16}$$

where σ is the square root of the Prandtl number and the reduced frequency $k = \omega h/a_o$.

As underlined by Raspet et al. (1999), the Low Reduced Frequency Approximation used to determine this solution yields a simple form for the propagation constant and for our purposes results in a straightforward way to recognize the contributions due to adsorption:

$$\Gamma_{\text{Ads}} = i\sqrt{\frac{\gamma}{n_{\text{Ads}}}} \tag{17}$$

where n_{Ads} is given by

$$n_{\text{Ads}} = \left[1 + \frac{1}{(ik)}\frac{DK_p q_s}{h\rho_s a_o} \cdot |G_q(\partial)|e^{i\arg(G_q(\partial))}\right]^{-1} \tag{18}$$

The real parts of the propagation constants Eqs. (16) and (18) correspond to the Attenuation Coefficients (AC) and (AdsAC) respectively, while the imaginary parts correspond to the Phase Shifts (PS) and (AdsPS).

3. Results and Discussion

To evaluate the applicability of acoustic measurements a simple apparatus is being assembled that will be tested on the system CO_2—Silicalite, for which reliable diffusion data (Shen and Rees, 1994) are available, as well as the adsorption isotherm over wide pressure range (2 Torr–3 atm) (Golden and Sircar, 1994).

The adsorption contribution to the AC is reported in Fig. 2 as function of the natural frequency. This shows a maximum that, similarly to the FR in a slab geometry, corresponds to $f = \frac{0.42D}{hs^2}$.

Figure 3 shows the AC for classical absorption, due to dissipative viscous and thermal effects, and the effect of isothermal adsorption.

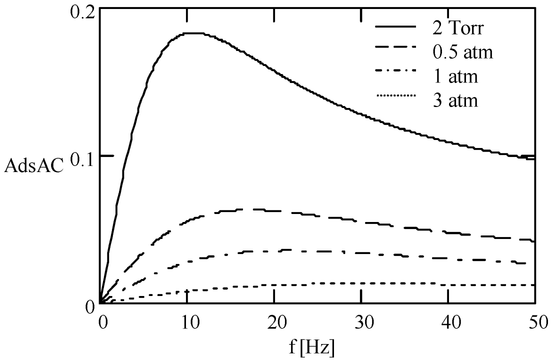

Figure 2. AdsAC as function of the natural frequency (h = 1 mm, hs = 10 μm).

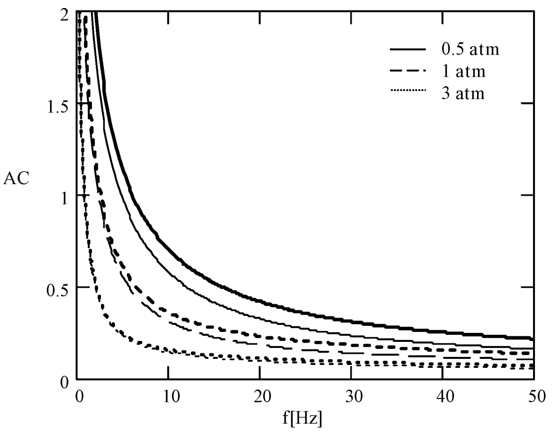

Figure 3. AC (heavy line) and classic AC (thin line) as function of the natural frequency ($h = 1$ mm, $hs = 10$ μm).

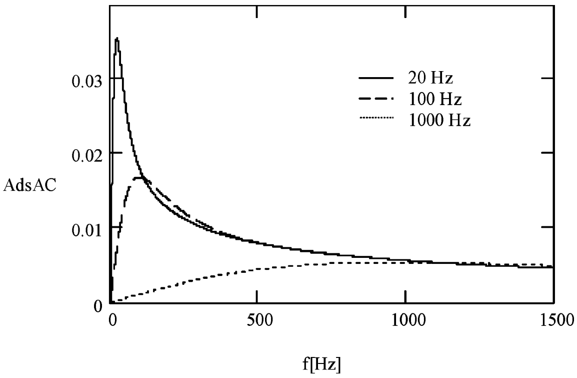

Figure 4. AdsAC as function of the natural frequency at $P = 1$ atm.

From this figure it is possible to see the effect of the adsorption isotherm. As the pressure increases, the slope of the isotherm decreases and the effect on sound propagation is reduced. Below atmospheric conditions, even for this relatively weakly adsorbed system, the effect of adsorption on sound propagation can be distinguished clearly.

Figure 4 shows the AC for 3 different characteristic times corresponding to a solid fraction (hs/h) per unit of length given by: 0.01, $4.5 \cdot 10^{-3}$, $1.5 \cdot 10^{-3}$. The reduction of the crystal size determines a reduction in spectrum amplitude due to the reduction of adsorbent mass for the same half slab distance (i.e. same classic absorption). The determination of the most appropriate operative conditions will be object of a detailed parametric analysis.

4. Conclusions

This simplified model suggests that adsorption affects the sound propagation and this effect can be interpreted in a straightforward analogy with the FR technique, which corresponds to the limiting case of wavelength $\gg$ dimensions of the FR batch volume. The technique should be applicable to fast diffusing strongly adsorbed systems, which are difficult to measure using current macroscopic techniques. Further studies will be focussed on extending the analysis to non-isothermal adsorption and obtaining an experimental proof of concept.

Acknowledgments

Financial support from the Leverhulme Trust (Philip Leverhulme Prize), Royal Society-Wolfson Research Merit Award and the EPSRC is gratefully acknowledged.

References

Bourdin, V., P.G. Gray, Ph. Grenier, and M.F. Terrier, *Rev. Sci. Instrum.*, **69**, 2130–2136 (1998).

Brandani, S., and D.M. Ruthven, *Adsorption*, **2**, 133–143 (1996).

Golden, T.C. and S. Sircar, *J. Colloid Interface Sci.*, **162**, 182–188 (1994).

Kärger, J. and D.M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids*, John Wiley & Sons, New York, 1992.

Kärger, J., *Adsorption*, **9**, 29–35 (2003).

Landau, L.D. and E.M. Liftshitz, *Fluid Mechanics Butterworth-Heinemann*, Oxford, 1997.

Raspet, R., C.J. Hickey, and J.M. Sabatier, *J. Acoust. Soc. Am.*, **105**, 65–73 (1999).

Ruthven, D.M. and S. Brandani, “Measurement of Diffusion in Microporous Solids by Macroscopic methods,” in *Physical Adsorption: Experiment, Theory and Applications*, J. Fraissard (Ed.), Kluwer Academic Publishers, Amsterdam, 1997, pp. 261–296.

Shen, D. and L.V.C. Rees, *J. Chem. Soc. Faraday Trans.* **90**, 3011–3015 (1994).

Stephanopoulos, G., *Chemical Process Control*, Prentice-Hall International, London, 1984.

Tijdeman, H., *J. Sound Vib.*, **39**, 1–33 (1975).

Van-Den-Begin, N.G. and L.V.C. Rees, “Diffusion of Hydrocarbons in Silicalite Using a Frequency-Response Method,” *Zeolites: Facts, Figures, Future*, P.A. Jacobs and R.A. Van Santen (Eds.), Amsterdam, 1989, pp. 915–925.

Yasuda, Y. and G. Sugasawa, *J. Phys. Chem.* **86**, 1913–1917 (1982).