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Understanding the diffusional tortuosity of porous materials: An effective medium theory perspective

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HIGHLIGHTS

- Analysis of diffusion of several gases in mesoporous Shell silica spheres.
- Tortuosities based on a single arbitrary pore size vary with temperature and gas.
- Tortuosities based on different representative pore size display different trends.
- Effective medium theory is successful, while using only transferable parameters.
- Knudsen and viscous flow regimes display different limiting tortuosities.

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ABSTRACT

The interpretation of experimental data on transport in porous materials is often based on the use of a single representative pore size, overlooking effects of the pore size distribution (PSD) and pore network connectivity, and fitting a tortuosity into which all such uncertainties are consigned. Using literature data on the diffusion of N_2, Xe and i-C_4H_{10} in mesoporous Shell silica spheres, we demonstrate that the tortuosity depends on the choice of the representative pore radius as well as gas species. Both the Knudsen model and the Oscillator model considering dispersive fluid–solid interactions, developed in this laboratory, are found to adequately interpret the data in conjunction with effective medium theory (EMT) by fitting a network coordination number instead of tortuosity. This insensitivity to model is due to the large mean mesopore radius of 7.4 nm for this silica; however, the Oscillator model is found to yield a value of the coordination number closer to the range of values expected for this material. Using the EMT we demonstrate that the tortuosity is dependent on temperature and diffusing species, because of differences in temperature dependence between the conductance at the representative pore radius and the true conductance which depends on the network connectivity and PSD. In the slip flow regime, which is obtained at large pore size, we show that the superposition of Knudsen and viscous mechanisms leads to temperature and species dependence of tortuosity, because of the different pore size dependence of the two contributions. This leads to different limiting tortuosities and PSD dependence in the Knudsen and viscous flow regimes. These critical aspects are largely unappreciated in the literature, and even systematic variations of tortuosity with temperature or diffusing species usually overlooked, often leading to misrepresentation of the underlying mechanism.

1. Introduction

Advances in templating methods and techniques of nanomaterials synthesis have led to the rapid growth of a vast array of novel nanoporous materials, which hold potential for applications in areas such as adsorption and gas storage, membrane separation, heterogeneous catalysis and drug delivery (Zhao et al., 1998; Diniz da Costa et al., 2002; Grosso et al., 2004; Yoshimune et al., 2008; Dai et al., 2012). These developments have stimulated considerable interest in the modeling of adsorption and fluid transport in the confined spaces of such materials, which is central to their applications (Bhatia and Sonwane, 1998; Sonwane and Bhatia, 1999; Yoshioka et al., 2004; Higgins et al., 2009; Krishna and van Baten, 2009). The most common approach in the modeling of transport in nanoporous materials relates the flux (J) to an effective diffusion coefficient (D_e) and the bulk pressure gradient (∇P) through the phenomenological relation (Xiao and Wei, 1992a; Bhatia, 1996; Hwang, 2011):

$$J = \frac{D_e}{R_g T}(-\nabla P) \tag{1}$$

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where R_g is the gas constant and T is the temperature. Since nanoporous materials often comprise a network of pores that is disordered and has a pore size distribution, the interpretation of the effective diffusivity therefore generally involves pore network parameters, such as porosity (ε), and an apparent tortuosity (τ_{app}). In general, the various theories developed to estimate the effective diffusivity based on the properties of the fluids and the porous medium, have the form (Mason et al., 1967; Bhatia, 1986; Burganos and Sotirchos, 1987; Deepak and Bhatia, 1994; Bhatia et al., 2011)

$$D_e = \frac{\varepsilon \overline{D}_a}{\tau_{app}} \tag{2}$$

where $\overline{D}_a$ is the apparent pore diffusivity, commonly evaluated using an appropriate diffusion models while choosing an appropriate representative pore size. Although the porosity can be extracted from gas adsorption or mercury porosimetry analysis (Gao et al., 2013a), the apparent tortuosity is often empirically estimated by fitting experimental flux data to a correlation suggested by an assumed transport model. Apparent success of the correlation (e.g. effective diffusivity versus $\sqrt{T/M}$, where M is molecular weight, as per the established the Knudsen model), and proximity of the fitted tortuosity to the theoretical value of 3 for a random walk, is often used as a criterion to validate assumptions regarding transport mechanisms in disordered nanoporous materials; however, this approach has been criticized on fundamental grounds (Bhatia and Nicholson, 2010a, 2010b). Nevertheless, due to its simplicity, the above approach has become routine in investigations of diffusion in the newly-synthesized nanoporous materials (De Bruijn et al., 2003; Yoshioka et al., 2004; Yoshimune et al., 2008). In this spirit, the most commonly used model is the Dusty Gas model (DGM) of Mason et al. (1967), which arbitrarily superposes pore wall-affected diffusion and hydrodynamic fluxes. When adsorption is negligible, the pore wall-affected diffusion is often represented by the Knudsen model, which is supplemented by a surface diffusion contribution when adsorption is significant (Krishna and Wesselingh, 1997).

Although the DGM based approach utilizing the Knudsen diffusion model has been successfully used to correlate experimental data, its validity for multicomponent systems has been criticized by Kerkhof and Geboers (2005) and Bhatia et al. (2011), who demonstrate internal inconsistencies in its development. Nevertheless, while not inconsistent in pure component systems, it yields unphysical parameter values when adsorption effects are not negligible, and the fluid molecular size is not insignificant in comparison to the pore size. Under these conditions, very high tortuosities are often obtained for mesoporous materials if the Knudsen diffusivity is utilized in the DGM approach (Uchytil et al., 2000; Kärger et al., 2003; Preising and Enke, 2007; Markovic et al., 2009); this is attributed to the overprediction of the diffusivity by the Knudsen model, due to its neglect of the dispersive force exerted by the wall (Bhatia, 2010; Bhatia and Nicholson, 2010a, 2010b; Bhatia et al., 2011; Gao et al., 2013a, 2013b). As a result there is much interest in the development of new diffusion models that consider the potential field of the walls (Xiao and Wei, 1992b; Jepps et al., 2003; Bhatia and Nicholson, 2010a; Ruthven, 2010). Significant success has been achieved in this laboratory through the development of the 'Oscillator model' which considers the effect of the solid–fluid dispersive interaction on the diffusion as well as on the adsorption (Jepps et al., 2003; Bhatia et al., 2004; Bonilla and Bhatia, 2011).

Another key deficiency of the DGM approach is that the apparent tortuosity is incorporated as an effective parameter, which is assumed to be exclusively determined by the properties of the porous medium, and is considered constant. However, it has been experimentally confirmed that the apparent tortuosity can be influenced by the operating conditions such as temperature and gas species (Bhatia, 1986; Gao et al., 2012; Gao et al., 2013a). For instance, in the slip flow regime in macroporous materials, to which the DGM is frequently applied, the apparent tortuosity of the macroporous network varies (albeit weakly) with temperature and gas species due to the combined effects of viscous flow and Knudsen diffusion (Gao et al., 2012). At the mesopore scale, where viscous flow is negligible at low pressures, the experimentally observed variation of tortuosity with temperature and gas species can be reconciled by the effect of the fluid–wall interaction, and the resulting differences in temperature dependence of the diffusivity in pores of different size as predicted by the Oscillator model (Gao et al., 2012, 2013a). This leads to short circuiting effects by pores of higher conductance in the network, and to the dependence of the apparent tortuosity on temperature and gas species, as well as pressure (Bhatia, 2010). This shortcoming of the DGM, which considers the tortuosity to be dependent only on the porous medium, has been demonstrated through experiments with a multi-layered supported mesoporous membrane (Gao et al., 2012, 2013a, 2013b), whereby the transport properties of the composite were sequentially investigated as each layer was added. Rigorous layer-by-layer analysis showed the combination of the Oscillator model with an effective medium theory treatment of network effects to be the most successful approach in modeling the transport in each layer (Gao et al., 2013b).

Effective medium theory (EMT) offers a convenient route to model transport in disordered nanoporous materials, while considering the entire pore size distribution, by replacing the actual random network with an effective one having a uniform conductance in each pore. One advantage of this method is that it enables rigorous analysis of the relationship between apparent tortuosity and the pore structure as well as properties of the diffusing fluid. Thus, its application in conjunction with an appropriate diffusion model, such as the Knudsen or Oscillator models (Jepps et al., 2003), has been key to the interpretation of membrane data and the resolution of the temperature and species dependence of the tortuosity of disordered nanomaterials and membranes (Bhatia, 2010; Bhatia and Nicholson, 2010b; Gao et al., 2012, 2013a, 2013b).

In our recent studies (Gao et al., 2012, 2013a), we have demonstrated this technique along with the Knudsen or Oscillator model, to satisfactorily represent the transport in a macroporous support and in a mesoporous γ-alumina membrane having mean pore radius of 5 nm, as well as a mesoporous silica membrane having a mean pore radius of 1.85 nm (Gao et al., 2013b). In addition, our results showed significant differences in predicted dependence of tortuosity on temperature for a given macroporous network in the slip flow regime, when the representative pore radius was based on either the number averaged pore size or on the volume to surface area ratio (Gao et al., 2012, 2013a). Further, in mesoporous silica materials, the trend of the predicted dependence of tortuosity on temperature varies with the gas for the Oscillator model when the representative pore radius is defined based on the volume to the surface area ratio (Gao et al., 2013b), differing from our previous finding that the tortuosity increases with temperature for all the investigated gases when the representative pore radius is represented by the peak of the number distribution (Bhatia, 2010; Bhatia and Nicholson, 2010b). This raises the important question of how the tortuosity trends depend on choice of representative pore radius, when the details of the pore size distribution are overlooked, as is common in interpreting experimental data. Therefore, in the current work, we use this powerful technique (EMT) to investigate how the tortuosity and its variation with temperature is affected by the pore network structure and the choice of representative pore radius in different flow regimes. As an example to illustrate these effects, we examine published data on the diffusion of various gases in mesoporous