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Slow and Fast (Fickian) Diffusion Modes for Argon Confined in BPL Activated Carbon

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1. Introduction

Activated carbons are amorphous materials that have found widespread use in industry due to their low production cost, high adsorption capacity and predominately microporous (pores < 2 nm) features [1]. Calgon Co.'s bituminous coal-based carbon (BPL) is among the most widely studied activated carbons and has been used extensively in environmental applications as an adsorbent for the removal of toxic and odorous industrial chemicals [2]. Using the Hybrid Reverse Monte Carlo method, Palmer et al. [3] have recently developed a morphologically realistic model of BPL, that successfully predicts the adsorptive properties of the real material [4]. We examine the self-diffusion behavior of argon in BPL using the generated model and show that the heterogeneous features of the material lead to a multi-modal diffusion mechanism, with both slow (quasi-single-file) and fast (Fickian) diffusion modes.

2. Simulation Details

The model for BPL was previously constructed [3] using the Hybrid Reverse Monte Carlo (HRMC) method. The cubic unit cell length was 3.0 nm. Using Grand Canonical Monte Carlo (GCMC) simulations, adsorption isotherms were calculated at 77 K and 120 K for argon, in the reduced pressure range of $P/P\text{o} = 1.0 \times 10^{-7}$ to 1. At each state point, the unit cells containing the final GCMC configurations were replicated to produce supercells that contained a minimum of 1000 argon atoms. Molecular Dynamics (MD) simulations were initiated from the supercell configurations using the LAMMPS simulation package [5]. The MD simulations were equilibrated for 1 ns in N,V,T using a Nosé-Hoover thermostat with a 1 fs timestep, followed by production runs of 10 ns with a 1 fs timestep in the microcanonical ensemble (N,V,E). The resulting microcanonical MD trajectories were used to measure the mean squared displacement (MSD) of the argon atoms.

3. Results and Discussion

The isotherms of argon at 77 K and 120 K are shown in Fig 1. As is evident in Fig. 2, showing simulation snapshots, at low pressures argon first fills the smallest pores, which are the most attractive adsorption sites due to their highly confined geometries. At higher pressure, larger pores begin to fill until the argon reaches a liquid-like density, indicated by the approach to the plateau in the adsorption isotherms near P_o. The diffusion results are indicated in Fig. 3 with plots of the MSDs at various pressures. At 77 K, all of the MSDs appear to first approach a plateau and then slope upward. This initial plateau effect appears to result from the slower diffusion in the most attractive (smaller pore) sites. At the lowest pressure at 77 K (P/P_o = 1.0 x 10^{-5}), taking nearly 1 ns (1000 ps) to begin its eventual upward slope, the slope of the MSD on the log-log scale below 1 ns is nearly ½, the slope found for single-file diffusion in carbon nanotubes and zeolites [6]. The slopes for the higher pressures are less than 1 (Fickian diffusion) but greater than ½. At the longest times, all of the slopes for the MSDs approach 1, indicating eventual Fickian diffusion of the overall system. At 120 K, similar effects are seen, except that the slower initial mode of diffusion due to the small pores is not as evident except for reduced pressures (P/P_o) less than 10^{-3}. At both 77 K and 120 K, there is a maximum diffusion in the pressure ranges which are in the region of the pore filling in the isotherms (seen as P/P_o = 7.5 x 10^{-3} for 77 K and P/Po = 0.12 for 120 K in Fig. 3). This maximum in diffusion has been observed previously in simulation of fluids diffusing in activated carbon [7], and in experimental studies of water diffusing in activated carbon [8]. It is also well known for molecular fluids diffusing in zeolites [9]. From movies of the MD simulations, it is apparent that the cause of the initial slower diffusion in the MSDs is the trapping of the argon atoms in the lower energy (and smaller pore) adsorption sites.

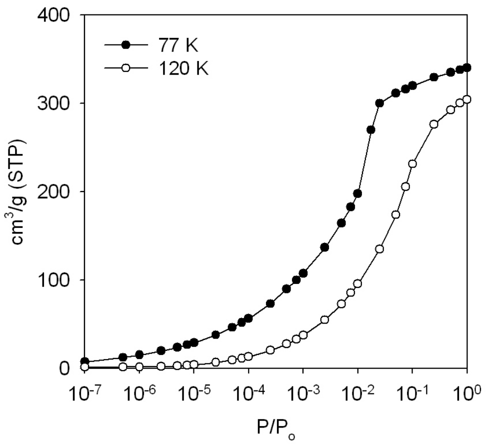
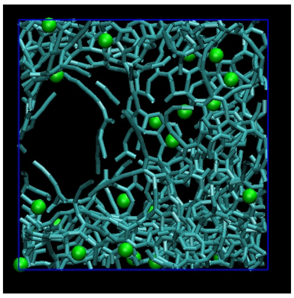
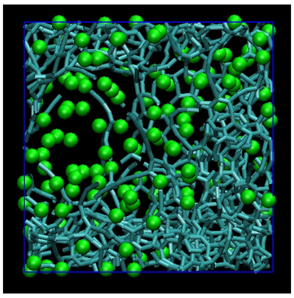


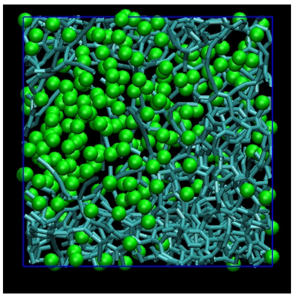
Figure 1: Isotherms for Ar in BPL at 77 and 120 K. Points are from GCMC simulation and lines are a guide to the eye.



P/P_o = 1.0 x 10^{-5}



P/P_o = 7.5 x 10^{-3}



P/P_o = 1.0

Figure 2: Simulation snapshots at 77 K. Snapshots at 120 K are similar in the comparable regions of the isotherm. Argon atoms first adsorb in the lowest energy (smallest) pores followed by complete filling in the larger pores.

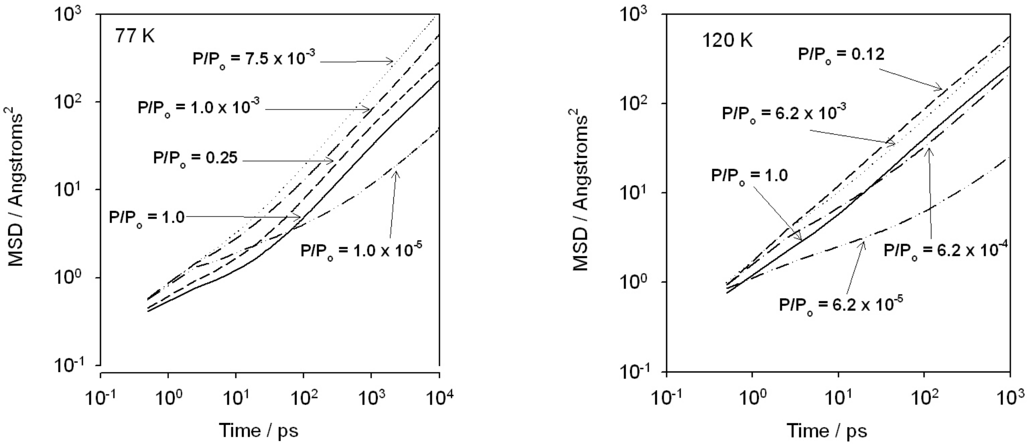


Figure 3: Mean squared displacement for Ar diffusing in BPL at 77 K (left) and 120 K (right) from microcanonical (NVE) MD simulation.

As time increases, these atoms are sometimes able to escape and move out of these sites; other atoms are sometimes able to move back into these sites. For the higher temperature (120 K), these entrances and exits of the smaller pores happen more frequently than at the lower temperature (77 K). Thus, the Fickian diffusing particles dominate the MSDs at 120 K, even at short times, except for the lowest pressures. At 77 K, the initial mode of diffusion seems to always be dominated by the lower energy (smaller pore) adsorption sites.

4. Conclusion

Two diffusion mechanisms seem to occur in BPL. A slower diffusion mechanism which may be quasi-single-file occurs in the smallest (lowest energy) adsorption sites. A faster Fickian diffusion mechanism occurs in the larger pores. At small times and low pressures (before the onset of pore filling) the total diffusion seems to be dominated by the slower diffusion. However, for all pressures, the eventual overall diffusion mechanism is Fickian, owing to the much faster diffusion in the larger pores. Atoms in the small pores also seem to be able to escape into the larger pores, which aids in the overall diffusion mechanism becoming Fickian. This occurs more frequently at higher temperatures.

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References

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[1] B. Kastening, M. Heins, Electrochim Acta. 50 (2005) 2487-2498.; Y. Zhou, Y. Wang, H. Chen, L Zhou, Carbon 43 (2005) 2007-2012.; J. Zhu, F. Figueiredo, J. Faria, Catal. Commun. 9 (2008) 2395-2397.

[2] Y. El-Sayed T. Bandosz, Colloid Interface Sci. 242 (2001) 44-51.

[3] J.C. Palmer, J.K. Brennan, M.M. Hurley, A. Balboa, K.E. Gubbins, Carbon, in press (2009).

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[4] G. Opletal, T. Petersen, B. Malley, I. Snook, D. McCulloch, N. Marks, I. Yarovsky, Mol. Sim. 28 (2002) 928-938.; S.K. Jain, R. Pellenq, J. Pikunic, K.E. Gubbins, Langmuir, 22 (2006) 9942-9948.

[5] S. J. Plimpton, J. Comput. Phys. 117 (1995) 1-19.

[6] K. Hahn and J. Kärger, J. Chem. Phys., 100 (1996) 316-326.

[7] B. Coasne, S.K. Jain, K.E. Gubbins, Eur. Phys. J. Special Topics, 141 (2007) 121-125; B. Coasne, S.K. Jain, K.E. Gubbins, Mol. Phys., 104 (2006) 3491-3499.; J. Pikunic, K.E. Gubbins, Eur. Phys. J. E., 12 (2003) 35-40.

[8] J. Kärger, H. Pfeifer, R.S. Vartapetian, A.M. Voloschuk, Pure Appl. Chem. 61 (1989) 1875 – 1880.

[9] S. Brandani, D.M. Ruthven, J. Kärger, Zeolites, 15 (1995) 494-495.