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Effect of structural anisotropy and pore-network accessibility on fluid transport in nanoporous Ti$_3$SiC$_2$ carbide-derived carbon

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ABSTRACT

We develop an atomistic model of disordered Ti$_3$SiC$_2$ carbide-derived carbon (Ti$_3$SiC$_2$-DC) through hybrid reverse Monte Carlo simulation, and validate it against experimental adsorption data of Ar and CO$_2$ using grand canonical Monte Carlo (GCMC) simulation. While supporting the atomistic model, the GCMC simulations reveal inadequate accessibility of narrow micropores, leading to small deviation between experimental and simulated isotherms at low pressure. It is found that the Ti$_3$SiC$_2$-DC structure is lamellar and highly anisotropic, with a percolating path in only one direction, which is parallel to the lamellae, leading to anisotropic diffusion. The energy barriers for diffusion in this anisotropic structure are found to be smaller, and the diffusion coefficient larger, than in the more disordered but isotropic SiC-derived carbon, despite the larger pore volume of the latter. These findings, based on molecular dynamics simulations are confirmed by analysis of the free energy landscape, showing larger free energy barriers for SiC-derived carbon. Our findings suggest that diffusion in isotropic carbon structures is hindered by higher energy barriers, arising from greater short-range disorder, in comparison to highly anisotropic structures, consistent with recent literature observations of larger pore wall-mediated scattering in isotropic structures.

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1. Introduction

Nanofluidics, which concerns “the study and application of fluid flow in and around nanosized objects” [1], has recently emerged as a new branch of nanotechnology. Nanofluidic phenomena are studied for macromolecular separation, biomolecules detection, fluid infiltration and in general for lab-on-a-chip fluidic technology [2, 3]. Other applications include adsorptive separation, heterogeneous catalysis, gas-solid reactions and electrochemical processes [4]. In nanoscale dimensions where the level of confinement approaches molecular length scales, the conventional continuum model breaks down and fluidic behaviour displays intriguing features not seen in larger scales [3]. Consequently, serious questions have been raised regarding the application of classical theories of transport to nanoscale confinements [4, 5]. For instance, it is demonstrated that the Knudsen model neglects the effect of fluid–solid interactions on the adsorbed phase; this effect is particularly important, and indeed dominant, when the level of confinement approaches molecular dimensions [4, 6]. However, for bulk and wall-mediated diffusion in macro and mesoporous solids the fluid density generally falls outside the Knudsen limit (i.e. $Kn \ll 1$, where $Kn = \frac{\lambda}{d}$; $\lambda$: mean free path, $d$: pore diameter), and the dusty gas model (DGM) and others based on the Maxwell–Stefan (MS) description of mass transfer provide a tenable approach [4,7-10], albeit with some drawbacks [4]. Among these theories the Oscillator model [11-13] and the generalized MS approach [9,10] account for the effect of the fluid-solid potential field on diffusion more successfully. Nevertheless, Maxwell-Stefan type models disregard the effect of fluid inhomogeneities in mixture adsorption [4], and may not in general be sufficiently accurate for fluid transport in heterogeneous nanoporous materials, where fluid inhomogeneities can be significant.
Although application of classical treatments for fluid transport in nanoscale confinements is limited by several factors, some of which are discussed above, molecular simulation techniques are able to accurately predict nanofluidic behavior, as long as reliable representations of interatomic potentials and of the pore network are available. Atomistic and molecular simulations techniques are in particular very promising when fluid transport is to be modeled in a disordered network of nanopores. Good examples of such pore networks are porous structures of amorphous materials such as activated carbons and carbide-derived carbons (CDC) whose structures lack the long-range atomic ordering seen in crystalline solids. Despite the complexity of modelling disordered materials, several techniques have emerged, albeit having different levels of accuracy, such as density field modelling [14-17], reverse Monte Carlo (RMC) modelling [18-20], hybrid reverse Monte Carlo (HRMC) simulation [21-25] and quench molecular dynamics (QMD) methods [26-29].

In our recent studies, we have demonstrated that the HRMC modelling technique can be successfully employed to reconstruct realistic models of highly disordered nanoporous materials [25, 30]. These studies dealt with highly amorphous SiC-derived carbon, lacking the turbostratic structure of conventional activated carbons, due to the diamond-like morphology of the SiC precursor. Here we use the HRMC method to construct a realistic model for Ti$_3$SiC$_2$-derived carbon (Ti$_3$SiC$_2$-DC), which satisfactorily predicts experimental adsorption isotherms of Ar, CO$_2$ and CH$_4$ at different temperatures and pressures. Ti$_3$SiC$_2$-DC is anticipated to have a more graphitic and anisotropic structure, due to the lamellar morphology of Ti$_3$SiC$_2$, and comparison with the more disordered and isotropic SiC-DC will permit improved understanding of the effect of such structural differences on transport properties of gases, a topic of much current importance. Indeed, characterisation of our HRMC constructed model reveals a more graphitic
structure for Ti$_3$SiC$_2$-DC which is dominated by sp$^2$ carbon bonding, consistent with experimental evidence obtained from characterization of Ti$_3$SiC$_2$-DC synthesized in this laboratory [31, 32]. We demonstrate that there exists a significant inaccessibility problem, in the form of dead-ends and bottle-necks between some of the lamellae comprising the Ti$_3$SiC$_2$-DC. In association with the lamellar structure of this carbon, this leads to unidimensional diffusion of argon molecules, which is in contrast with transport properties of disordered SiC-DC carbon recently modeled in this laboratory [25]. Our simulations reveal that while inaccessibility is the major cause of unidimensional fluid transport in the Ti$_3$SiC$_2$-DC model, the same phenomenon gives rise to lower diffusion of argon in the SiC-DC model, despite its larger pore volume, higher porosity and better structural isotropy. The results provide new insight into the relation between pore accessibility and transport properties of nanoporous materials, suggesting need for further investigation of this issue through targeted simulations.

2. Computational details

2.1 Hybrid reverse Monte Carlo method

The hybrid reverse Monte Carlo method is employed to construct the nanoporous structure of Ti$_3$SiC$_2$-DC. The technique provides a detailed atomistic structure of the carbon, based on matching of the experimental radial distribution function of the carbon, while minimizing configurational energy, and is superior to conventional characterisations that estimate a pore size distribution while idealising the pore shapes. The HRMC method has been detailed in the literature [21, 24, 33-40] and thoroughly discussed in recent studies from this laboratory [22, 23, 25, 30], hence we provide only a brief discussion here. The main focus of this is the explanation of different types of HRMC constraints used in this study.
The sample of Ti$_3$SiC$_2$-DC was recently prepared in our laboratory using chlorination of commercial Ti$_3$SiC$_2$ powder (3-ONE-2, LLC, Voorhees, NJ) at 800 °C during which titanium and silicon contents of the carbide lattice were eliminated [31]. Subsequently, the sample was characterized [31, 32], using a wide range of experimental methods including Helium Pycnometer, X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, measurements of adsorption isotherms of argon, CO$_2$ and CH$_4$ and density functional theory (DFT). The structure factor (SF) of the sample was separately measured for this study by neutron scattering over a wave vector range of 0.2 < q < 50 Å$^{-1}$ (where $q = 4\pi \sin(\theta/2)/\lambda$), using the SANDALS small-angle neutron diffractometer at ISIS Rutherford-Appleton Laboratory, U.K. The SF data was used to determine the radial distribution function (RDF) of the carbon sample, needed as input data in the HRMC method, following the inverse Fourier transformation [34]

$$S(q) = 1 + \frac{4\pi \rho}{q} \int r[g(r) - 1] \sin(qr) \, dr \quad (1)$$

To construct a 3D model of Ti$_3$SiC$_2$-DC which can reasonably reproduce structural properties of the actual sample, the following modelling constraints were used in our HRMC procedure.

a) Radial distribution function (RDF) constraint:

The simulated radial distribution function of the atomistic model was matched with the experimental RDF during the HRMC modelling, using the Metropolis Monte Carlo (MMC) algorithm. The matching procedure was performed based stochastic generation of atomic configurations, while simultaneously minimising the discrepancy between the experimental RDF and that from simulation in every MC trial move, with associated error.
\[ \chi^2 = \sum_{i=1}^{n_{\text{exp}}} \left( \frac{g_{\text{sim}}(r_i) - g_{\text{exp}}(r_i)}{\sigma_{\text{exp}}^2(r_i)} \right)^2 \]  

Here \( n_{\text{exp}} \) is the number of experimental data points, \( \sigma_{\text{exp}} \) is the experimental error and \( g(r) \) is the RDF. It is known that the structure factor data obtained from scattering cannot uniquely resolve all local structural features [18]; therefore, additional structural constraints were employed to more closely reproduce structural characteristics of the Ti\(_3\)SiC\(_2\)-DC sample.

\[ H \text{ere} \exp \text{is the number of experimental data points,} \sigma_{\exp} \text{is the experimental error and} \ g \text{(r) is the} \]

**a) Atomic coordination constraint:**

The atomic coordination constraint was initially introduced by O’Malley et al. [41] for modeling of the structure of glassy carbon to ensure that the required atomic coordination is achieved, through the relation

\[ X^2_{\text{coord.}} = \left( \frac{f_{\text{RMC}} - f_{\text{req.}}}{w_{\text{coord.}}} \right)^2 \]  

where \( f_{\text{RMC}} \) is the fraction of atoms properly coordinated in the model, \( f_{\text{req.}} \) is the desired fraction of properly coordinated atoms and \( w_c \) is the weighting factor.

**b) Three-member ring constraint:**

The reconstruction procedure implemented in the RMC algorithm [18, 42] generates by-products which are seen as unphysical carbon structures in the final constructed models [21, 43]. The most common undesired structural features produced during the RMC modelling are the highly strained 3-member and 4-member carbon rings, as well as carbon atoms connected to more than
four neighbouring atoms. Although the use of a suitable three-body potential (e.g. the EDIP force field) in the HRMC method eliminates this problem to a large extent [34], implementation of a 3-member ring constraint which rejects the trial moves leading to formation of 3-member carbon rings will accelerate and improve the modelling procedure. Originally, Rigden and Newport [43] developed structural constraints which prohibit formation of such unphysical features, however in this study we follow the recipe provided by Opletal et al. [36, 37].

c) Total porosity constraint:

Critical to accurately predicting adsorption properties is to achieve the correct total pore volume and pore size distribution (PSD) in the HRMC model. To facilitate this, a porosity (pore volume) constraint recently developed by Opletal et al. [36] was employed, which controls the grid occupancy of the simulation cell defined based on the experimental porosity of the real sample following [25, 36]

$$\chi_v^2 = [(f_0 - \alpha)^2] / W_v^2$$

(4)

Here, $f_0$ is the fraction of cells occupied by at least one atom at the current simulation state, $\chi_v$ is the error representing discrepancy between the experimental and simulation skeletal volume fractions, and the parameter $\alpha$ defines the target occupancy of the grid cells, defined by $\alpha = (1 – \text{porosity})$, where $W_v$ is a weighting factor.

d) Energy constraint:

The use of reactive potential force fields allows the carbon model to evolve more naturally during the HRMC modelling based on formation and disassociation of atomic bonds between carbon atoms [40], while at the same time structural features of the sample are being reproduced...
by imposing several structural constraints on the model. As discussed by Palmer and Gubbins [40], the final product of the HRMC modelling is quite sensitive to the choice of the reactive force field employed. Due to successful use of the EDIP force field [44, 45] in capturing interatomic interactions in different carbonaceous materials, this force field has been employed for modelling of Ti₃SiC₂-DC carbon in this laboratory [22, 23, 25]. For the simulation to evolve through consecutive MC moves, a total error term comprising the energy constraint as well as the individual errors associated with each structural constraint is defined. The total error is then minimized using simulated annealing [46]

$$\chi_{total}^{old} = \sum_i \sum_j \left( A_{ij}^{exp} - A_{ij}^{old} \right)^2 + \frac{E^{old}}{kT} \tag{5}$$

Trial MC moves were only accepted, if they decreased the total error, $\chi_{total}$, unless complying with the acceptance probability criterion

$$P = e^{(\chi_{total}^{old} - \chi_{total}^{new})} \tag{6}$$

In the simulated annealing procedure, an exponential multi-stage quenching strategy was adopted to cool down the system after it was initially melted at a high temperature, similar to our previous studies [25, 30]. The HRMC procedure was repeated iteratively and the modelling parameters adjusted accordingly until $\Delta \chi_{total}$ was converged.

### 2.2 Preparation of the initial configuration

Ti₃SiC₂ belongs to the Hägg-phases which are ternary layered compounds with crystalline formula $M_{n+1}AX_n$, where $n$ can be 1, 2 or 3, $M$ is an early transition metal, $A$ is an $A$-group element mainly from groups IIIA and IVA, and $X$ is always carbon or nitrogen [47]. In the
unit cell, the $M_3X_2$ layers are separated by $A$-layers, with the carbon atoms distributed non-uniformly within different atomic layers of the crystalline structure of Ti$_3$SiC$_2$ [48-50].

In practice, synthesis of Ti$_3$SiC$_2$-derived carbon (Ti$_3$SiC$_2$-DC) is achieved through chlorination of titanium silicon carbide (Ti$_3$SiC$_2$). In this process, the macroscopic shape and volume of the carbide precursor is retained [48, 51], in such a way that the precursor-inherited structure of Ti$_3$SiC$_2$-DC holds its lamellar structure and remains predominantly graphitic [31]. This is in sharp contrast to collapse of the SiC structure after chlorination, leading to formation of a significant fraction of sp$^3$ and sp carbon bonds and generation of a highly disordered microporous SiC-DC structure [25, 31, 52]. The bulk density of Ti$_3$SiC$_2$-DC (1.027 g/cc) was estimated based on the helium skeletal density of the sample (2.186 g/cc), obtained using helium pycnometry [31, 32], as well as the total pore volume (0.516 cc/g), determined using DFT interpretation of argon adsorption at 87 K [32]. Accordingly, a simulation cell was set up in an orthorhombic unit cell with lattice constants $a = 29.5$ Å, $b = 29.8$ Å and $c = 38.0$ Å. To facilitate successful convergence of the total error term described by eq. (5), an atomistic model of activated carbon fibre (ACF-15) recently developed in this laboratory [23] was adopted to generate the initial configuration for the first modelling stage of Ti$_3$SiC$_2$-DC. The choice of this initial configuration was justified given our knowledge of the lamellar structure of Ti$_3$SiC$_2$-DC carbon, obtained from the recent characterization experiments discussed earlier. Since the structure of the ACF-15 comprises stacked graphene-like carbon sheets [23], it provides a convenient guess for the initial configuration for our HRMC modelling. To match the true bulk density of Ti$_3$SiC$_2$-DC, the atomistic model of ACF-15 was moderately altered by random addition of graphene sheets in between the carbon layers of ACF-15 structure. This was followed
by random removal of individual carbon atoms from this initial configuration until the actual
bulk density of the Ti$_3$SiC$_2$-DC sample was accurately matched.

3. Results and discussion

3.1 Atomistic modelling and structural characterization

The atomistic modelling of Ti$_3$SiC$_2$-DC was performed over three consecutive HRMC modelling
stages for which details of each modelling stage are summarized in Table 1. As indicated above,
the ultimate goal of the HRMC modelling is to minimize the total error described by eq. (5) in
such a way that an energetically stable structure mimicking morphological and topological
characteristics of the target sample can be constructed. Topological characteristics of porous
materials dictate their hydraulic and transport properties both at the pore scale and macroscopic
scales [53]. To successfully predict effective macroscopic properties of porous media, a
satisfactory topological description of the porous system at the microscale is essential [53].

Figure 1 depicts the energy evolution of the system, showing a monotonically descending trend
of potential energy, with increase of temperature at the beginning of each stage (i.e. initial
melting temperatures). As discussed elsewhere [30], this is due to the formation of metastable
configurations, which are equilibrated in the vicinity of deep local minima of the potential
energy surface. The same argument is also true for minimization of the total error, depicted for
each stage of the simulation in Figure 2; thus, although the weighting factor for each structural
constraint is increased at the beginning of every stage (resulting from the quenching protocol),
the overall trend of total error remains monotonically decreasing. This is consistent with the
ultimate goal of the HRMC modelling during which the total energy of the system (Figure 1) is
simultaneously and gradually minimized, along with total error of the structural constraints
(Figure 2) through the quenching procedure. In principle, minimization of the total error should guarantee successful matching of the experimental RDF, which is necessary, but not adequate, to mimic structural features of the actual sample. Figure 3 depicts excellent agreement between the experimental RDF of the Ti$_3$SiC$_2$-DC sample and that obtained from simulation. From this figure it is evident that experimental RDF of the sample decays to near zero within about 10 Å, suggesting that that any long-range structural ordering beyond this distance, albeit likely to be small, is not captured in the data. Through a series of studies, work in this laboratory has shown the importance of access to long-range and high-resolution diffraction data for realistic modelling of disordered materials such as activated carbons and carbide-derived carbons [54, 55]. This is critical for the accurate prediction of macroscopic fluid transport properties, which are significantly affected by the long-range internal barriers inherent to these materials.

As shown in Figure 4, the final constructed model of Ti$_3$SiC$_2$-DC appears to be largely graphitic, consistent with the experimental evidence reported earlier [31, 32]. This figure compares the atomistic structure of Ti$_3$SiC$_2$-DC with that of SiC-DC [25], highlighting the distinctly different levels of structural disorder and anisotropy between the two materials. The graphite-like structure of the Ti$_3$SiC$_2$-DC model is supported by the formation of a significant fraction of sp$^2$ carbon bonding throughout the modelling process, illustrated in Figure 5, which depicts the evolution of carbon hybridization during the HRMC simulation. It is clear from this figure that formation of sp$^2$ carbon-hybridization remains essentially unchanged over the entire simulation time. The inset depicts the fraction of atomic coordination numbers in the final constructed Ti$_3$SiC$_2$-DC model, and demonstrates that the final structure is almost completely made of sp$^2$ carbons with no sp$^3$ bonding being detected in the model.
To further characterize structural properties of the constructed model, we have determined the pore size distribution (PSD) of the Ti$_3$SiC$_2$-DC using the spherical probe geometric approximation technique [56, 57]. As illustrated in Figure 6a, Ti$_3$SiC$_2$-DC has a noticeable fraction of large pores around 15 Å in size, which do not appear in the HRMC constructed models of SiC-DC [25] and ACF-15 [23]. Despite the similarity of PSDs of the Ti$_3$SiC$_2$-DC and SiC-DC models in the ultra-microporos region (pores < 5 Å), Ti$_3$SiC$_2$ contains a smaller fraction of micropores between 3 Å and 10 Å. Figure 6b compares the geometrically-probed He-PSD of Ti$_3$SiC$_2$-DC with that determined by DFT interpretation of Ar and CO$_2$ adsorption data [32], with CO$_2$ confirming the presence of ultra-microporosity (<3.6 Å) evident in the He-PSD. The absence of this in the Ar-based PSD confirms the inaccessibility of such ultra-microporosity to Ar.

We have also computed other structural characteristics of the Ti$_3$SiC$_2$-DC model including pore limiting diameter, pore volume and surface area following the computational methodology developed by Sarkisov and Harrison [58]. The results of these calculations are reported in Table 2. In this table, Connolly and accessible surface area are compared with the experimental BET and DFT-based surface area reported by Bae et al. [32]. In our calculations, the accessible surface area is the surface formed of the locus of the points of the centre of a rolling spherical probe at the probe–solid collision distance of $2^{1/6}\sigma$ [56, 58]. Following Coasne et al. [59], we showed in our recent studies on SiC-DC carbon [25] that the geometric (Connolly) surface area can provide a reasonable approximation of BET surface area, if the pore-wall surfaces of the target carbon comprise both negative and positive curvatures. Likewise for the Ti$_3$SiC$_2$-DC model, the Connolly surface area is equal to the BET value, as seen in Table 2, while the accessible surface area is closer to that obtained from DFT based on interpretation of argon
adsorption isotherm at 87 K. Table 2 also reports on the value of pore volume obtained from the spherical probe geometric approximation technique with the probe diameter taken to be equal to the value of $\sigma$ of the helium atom. As reported in this table, the pore volume of the HRMC model of Ti$_3$SiC$_2$-DC is reasonably close to that estimated from DFT based on interpretation of argon adsorption isotherm at 87 K (0.516 cc/g) [32], however it is considerably smaller than the theoretical pore volume (1.35 cc/g). This is due to collapse of the pore architecture during Ti$_3$SiC$_2$ synthesis, which results in low pore volumes of Ti$_3$SiC$_2$-DC, as explained by Hoffman et al. [51].

We note here that while the structure reported here has been obtained starting from an initial configuration prompted by lamellar structure of the Ti$_3$SiC$_2$, we also attempted simulations with random and FCC initial configurations. However, these were unsuccessful and could not converge even after long simulation runs.

### 3.2 Modelling equilibrium gas adsorption

In order to examine performance of the constructed Ti$_3$SiC$_2$-DC model, equilibrium adsorption isotherms of argon, CO$_2$ and CH$_4$ were predicted using grand canonical Monte Carlo simulation. For each simulation run, the phase space was sampled over 20 million MC steps, of which the first 10 million steps were used to equilibrate the system. The 6-12 Lennard Jones potential was used to model van der Waals interactions with potential cut-off equal to 14.0 Å. Force-field parameters used for the molecular simulations are similar to those used in our previous studies [25, 55]. Our calculations show that the value of $\epsilon^{c-c}/k_B$ for Ti$_3$SiC$_2$-DC is equal to 35.0 K, which is higher than the graphite potential well depth ($\epsilon^{c-c}/k_B = 28$ K). Several authors have shown [23-25, 60] that this increase is due to the effect of carbon sheet curvature and structural
tortuosity. The value of 35.0 K in this study is the optimum value for $\varepsilon^{c-c}/k_B$, for which the best fit to the adsorption isotherms of target gases could be achieved. We note that the value of $\varepsilon^{c-c}/k_B$ of 35.0 K for Ti$_3$SiC$_2$-DC is somewhat smaller than that calculated for SiC-DC in our recent study ($\varepsilon^{c-c}/k_B = 36.5$ K), which is consistent with the more graphitic and less disordered structure of Ti$_3$SiC$_2$-DC [25].

**Argon adsorption**

The adsorption isotherm of argon is commonly used for structural characterization of porous materials. Figure 7 compares the simulated adsorption isotherm of argon with that from experiment, showing the simulation-based result to reasonably mimic the trend of the experimental isotherm. In Figure 7, a type I isotherm is seen (an indication of nanoporous structure of Ti$_3$SiC$_2$-DC), which overestimates the experimental adsorption isotherm at pressures below 1.45 kPa due to poor accessibility of argon to narrow micropores existing in the Ti$_3$SiC$_2$-DC sample. The existence of ultra-microporosity in nanoporous carbon materials has been experimentally demonstrated by Bhatia and co-workers [31, 32, 61-63]. In one of their studies on Ti$_3$SiC$_2$-DC-800, Bae et. al [31] demonstrated under-prediction of experimental CO$_2$ adsorption at 273 K by a model isotherm calculated based on the PSD obtained from interpretation of argon adsorption at 87 K using DFT. This is a clear indication of pore network inaccessibility for argon diffusion. They provided additional evidence for pore network inaccessibility of argon by comparing the PSDs and total pore volumes of virgin and heat treated samples of Ti$_3$SiC$_2$-DC 800 [31], showing that new pores appeared in the heat treated samples that were not detectable in the virgin Ti$_3$SiC$_2$-DC. They also reported an increase of the helium skeletal density with increase in heat treatment temperature. In a more recent study, Bae et. al [32] calculated the PSD
of Ti$_3$SiC$_2$-DC 800 obtained from DFT based on interpretation of CO$_2$ adsorption isotherm at 273 K, and compared the results with a DFT-based PSD obtained from interpretation of argon adsorption isotherm at 87 K. Their results provide unequivocal evidence for the existence of 3 to 4 Å ultra-micropores which are accessible to CO$_2$ but not to argon.

As mentioned above, our simulations show over-prediction of experimental argon adsorption at low pressures, suggesting inadequate pore network accessibility of argon. In principle, low pressure adsorption corresponds to adsorption of molecules in narrow micropores which provide very attractive adsorption sites. It is known that adsorption of Ar at 87 K in highly narrow pores is kinetically very slow compared to CO$_2$ at 273 K, partly due the larger kinetic diameter of Ar, as a result of which it faces larger pore mouth energy barriers, and partly due to its lower kinetic energy at 87 K, which retards its ability to surmount these barriers [64-66]. As a result, the measurement of Ar adsorption at low pressures is unreliable due to practical limitations in measuring very slow diffusion rates. Nevertheless, the effect of large diffusional barriers is conveniently bypassed in GCMC simulation, so that low-pressure over-prediction of experimental adsorption can be associated with inaccessibility of Ar molecules. Several other simulation studies of gas adsorption also report low-pressure overestimation of experimental argon and nitrogen adsorption isotherms in the microporous structure of activated carbon [23, 24] and carbide-derived carbon [25].

Figure 7 also reveals under-prediction of the experimental argon isotherm at pressures larger than 31.55 kPa. Here, the steep increase close to the saturation pressure of argon is mainly due to adsorption of liquid-like argon inside the large inter- and intra-particle void spaces; the later are formed as a result of anisotropic structural shrinkage of the ternary carbide during the
chlorination process [48, 51]. Such large pore spaces are not captured in the nano-size unit cell of the HRMC model, and thus are not relevant to the calculation of total pore volume for the reconstructive modelling techniques. Nevertheless, they reveal their fingerprint through under-prediction of experimental adsorption close to the saturation pressure of the adsorbate.

To summarize, it seems despite unaltered macroscopic shape and volume of the Ti$_3$SiC$_2$ during chlorination [48, 51], the crystalline structure of the carbide precursor undergoes internal micro- and meso-scale changes leading to generation of pore restrictions and network inaccessibilities which are the source of the overestimation of experimental argon isotherms by GCMC simulation at low pressures.

On the other hand, as explained by Barsoum and co-workers [47, 48, 51], the anisotropic structure of M$_{n+1}$AX$_n$ phases gives rise to shrinkage of the CDC structure “in the direction of the lowest linear density of carbon” [48] after removal of metal (e.g. Titanium) and metalloid (e.g. silicon) components from the original carbide structure. Therefore, the crystalline structure of the resulting CDC (e.g. Ti$_3$SiC$_2$-DC) becomes unstable so that the remaining carbon atoms cannot sustain their original configuration in the CDC lattice. This results in contraction of the CDC structure leading to the formation of carbon “microcracks” [47] in which large amount of bulk fluids can be adsorbed at high pressures. As indicated before, these spaces cannot be easily accommodated in nano-size simulation unit cells, thus giving rise to under-prediction of experimental adsorption isotherms at high relative pressures.

**Carbon dioxide adsorption**

Figure 8 compares the experimental adsorption isotherm of carbon dioxide at 273 K with that from simulation, showing good agreement. Low pressure over-prediction by simulation is not
seen here because carbon dioxide molecules are able to penetrate through narrow entries of ultra-
micropores. Also, due to the high saturation pressure of CO\textsubscript{2} at 273 K (∼34.7 bar), no
condensation occurs in the large space inter-granular pores and the carbon microcracks discussed
earlier, thus no high-pressure under-prediction is observed. To shed more light on the issue of
pore network accessibility, we examine the isosteric heat of adsorption of CO\textsubscript{2} at 273 K and Ar
at 87 K, obtained using the established fluctuation formula, whose pressure variation is depicted
in Figure 9. As seen here, the isosteric heat of adsorption of CO\textsubscript{2} is always larger than that of Ar
in the Ti\textsubscript{3}SiC\textsubscript{2}-DC model, and is ∼44% larger compared to that of Ar at zero-loading. A steep
drop in the isosteric heat of Ar at low pressure is evident; this is indicative of large heterogeneity,
and consistent with poor accessibility, whereby large pores with narrow necks are abruptly filled
by small increase in pressure.

It is insightful to compare these values with the isosteric heat obtained using GCMC simulation
and the 10-4-3 potential using single carbon slit-pore models. The widths of the slit-pores were
chosen to be equivalent to the size at the first peak of the PSD of Ti\textsubscript{3}SiC\textsubscript{2}-DC based on DFT
interpretation of experimental Ar and CO\textsubscript{2} isotherms, shown in Figure 6(b), having values of 3.44
Å and 4.87 Å respectively. These calculations lead to an isosteric heat of adsorption of 32.0
kJ/mol for CO\textsubscript{2}, and 13.3 kJ/mol for Ar. These values are comparable to those calculated for the
isosteric heat of CO\textsubscript{2} and Ar in the Ti\textsubscript{3}SiC\textsubscript{2}-DC model, which are equal to 28.22 and 19.63
kJ/mol respectively. The somewhat higher heat for Ar, based on the HRMC model, compared to
that from the slit pore corresponding to the first peak of the DFT-PSD, is most likely related to
adsorption in the narrowest pore spaces (ultra-micropores) of the HRMC-based structure at low
pressure, which are smaller than the pore size of the first peak detected by DFT. Nevertheless,
with very small increase in pressure the heat for the HRMC structure drops steeply to about 11
kJ/mole, close to that from slit pore calculation, adding support to the argument of inadequate accessibility of micropores to Ar.

**High-pressure methane adsorption**

Figure 10 compares the experimental high-pressure adsorption isotherms of methane at 313 K and 333 K with the simulated isotherms obtained from GCMC. As depicted here, the simulation-based isotherm closely predicts the experimental data. Here, the predicted excess adsorbed amounts are calculated following [25, 52]

\[
m^f_{\text{fluid}} = m^f_{\text{absolute}} - \frac{m^H_{\text{He}}}{\rho_{\text{He}}} \cdot \rho_{\text{fluid}}^\text{bulk} - \Delta V_{\text{max}} \cdot \rho_{\text{fluid}}^\text{bulk}
\]

(7)

where, \(m^f_{\text{fluid}}\) is the calculated excess adsorbed amount and \(m^f_{\text{absolute}}\), \(\rho^{\text{fluid}}_{\text{bulk}}\) and \(\Delta V_{\text{max}}\) denote the absolute adsorbed quantity obtained directly from GCMC, bulk fluid density, and maximum excess adsorbent volume respectively. As discussed in prior work from this laboratory [23, 31, 25, 52], the total pore volume is an obscure parameter in high-pressure GCMC simulations, because the constructed adsorbent model employed in GCMC is taken to be rigid; however, in reality porous materials have flexible structures that can undergo structural shrinkage or swelling at very high pressures [31, 52]. In equation (7), the maximum excess adsorbent volume \(\Delta V_{\text{max}}\) is used to account for the amount of volume change due to shrinkage or swelling of the pore structure, and is calculated by fitting the simulated maximum adsorbed amount to its corresponding experimental value. In Figure 10, the maximum excess adsorbent volumes at 313 and 333 K are -0.195 and -0.20 cc/g respectively, indicating an average of 43% reduction in total pore volume of Ti\(_3\)SiC\(_2\)-DC under 20 MPa pressure. For SiC-DC, this value is 35%, under the same pressure and temperature conditions [25], despite having pore volume and porosity that are
respectively ~18% and ~12% higher than those of Ti$_3$SiC$_2$-DC. This suggests that SiC-DC
carbon has better mechanical resistance against structural shrinkage under high-pressure
adsorption. Although, this appears contrary to the understanding that in general porosity
decreases strength and hardness of the porous materials [67], sintering and mechanical properties
of the sample are also influenced by other factors such as synthesis and preparation conditions
[67]. The larger mechanical strength of SiC-DC might be due to its disordered and more
isotropic structure, as compared to the more easily shrinkable lamellar structure of Ti$_3$SiC$_2$-DC.
Finally, we note that pore accessibility can affect high-pressure adsorption of gases in such a way
that accessible pores can be filled by tightly packed adsorbate molecules, increasing shrinkage
resistance of the accessible pore structure; however in contrast, inaccessible spaces remain empty
and vulnerable to shrinkage at elevated pressures due to high solvation pressures in neighbouring
filled pores [25, 31, 52].

3.3 Fluid transport and the issue of pore network accessibility
As shown above, pore network accessibility plays an important role in the adsorption of argon,
CO$_2$ and CH$_4$ in the microporous structure of Ti$_3$SiC$_2$-DC, despite its lamellar morphology. To
further probe this issue, we have investigated the transport properties of Ti$_3$SiC$_2$-DC and
analysed the internal energy barriers for Ar self-diffusion. We have also examined the correlation
between fluid transport and intrinsic structural properties of the Ti$_3$SiC$_2$-DC model such as its
percolation path, pore network topology and internal resistances.

To this end, internal energy barriers of the model were determined through two different
methods: 1) using a combination of percolation path and pore space accessibility analyses [58],
and analysis of the Helmholtz free energy landscape of the system based on the methods
developed by Sarkisov [68, 69], in the infinite dilution limit, and 2) estimation of the activation energy barriers based on self-diffusion coefficients obtained from molecular dynamics (MD) simulation.

For self-diffusivities, equilibrium molecular dynamics (EMD) simulations were performed for argon in the atomistic models of Ti$_3$SiC$_2$-DC and SiC-DC at 87, 200, 310 and 400 K. We utilized the LAMMPS simulation package [70] to run MD simulations in the canonical (NVT) ensemble using the Nose–Hoover thermostat [71-73]. The Verlet time integrator with time step equal to 1 fs was used in the simulations. Short-range intermolecular interactions were modelled using the 12–6 Lennard Jones potential description, with cut-off distances for Ti$_3$SiC$_2$-DC and SiC-DC models chosen as 14.5 and 18 Å respectively, which were less than half the corresponding box size. Electrostatic interactions were calculated using the standard Ewald formalism with cut-off distances similar to those of LJ interactions. Self-diffusivity of argon was calculated using the well-known Einstein equation with mean-squared displacements (MSD) of the centre of mass of the molecules being collected in the Fickian regime [55].

It has been shown that self-diffusion of simple gases such as argon, nitrogen, CO$_2$ and CH$_4$ has an anomalous loading-dependence in heterogeneous microporous carbons [22, 55, 74]. Moore et al. [74] have investigated adsorption and diffusion of argon in ordered Faujasite zeolite-templated nanostructured carbon (C-FAU) [75] and disordered bituminous coal-based microporous BPL carbon [24]. They have demonstrated that self-diffusivity of argon is affected by the narrow pore size distribution of these carbons and their internal structural constrictions [74]. More recently, Farmahini et al. have explored the influence of structural heterogeneity and pore morphology on transport of CO$_2$ and CH$_4$ in the microporous structure of SiC-DC [55], also
finding strong dependence of nanoscale fluid transport on structural heterogeneity of the microporous carbon. They demonstrated that internal energy barriers of microporous carbon originate from the highly heterogeneous energy landscape of the solid network, governed by the pore size distribution, disordered pore morphology, existence of bottle-necks at pore interconnections and other internal constrictions in the carbon structure.

Prompted by these results, and to further probe the effects of pore network inaccessibility and structural heterogeneity on fluid transport, we have calculated self-diffusivity of argon at two distinctly different loadings in the Ti$_3$SiC$_2$-DC and SiC-DC models; these were chosen so that the argon loading in the former structure is almost twice as large as that for the latter model (1.55 mmol/g v.s 0.87 mmol/g). As illustrated in Figure 11, the argon diffusivity in the SiC-DC structure is always smaller than that in Ti$_3$SiC$_2$-DC for the temperature range of Figure 11, despite the lower loading of argon in this model. The slopes of the Arrhenius plots in Figure 11 show that activation energy barrier of argon in Ti$_3$SiC$_2$-DC is 30% smaller than that in SiC-DC.

To confirm that the observed difference in the self-diffusion of argon in these two structures is due to their difference in pore network accessibility, and not the different level of loading, we have calculated internal free energy barriers of the system for argon at consistent temperatures and loadings. As depicted in Figure 12, the internal free energy barrier for argon in Ti$_3$SiC$_2$-DC at 87 K, and at the limit of infinite dilution, is 52% smaller than that in SiC-DC. We repeated this calculation for a 3-site carbon dioxide model at 273 K and zero-loading, for which the outcome is also illustrated in Figure 12. As shown in this figure, the results for CO$_2$ and argon are similar. Thus, despite having larger total pore volume and porosity, SiC-DC is less accessible to argon and CO$_2$ compared to Ti$_3$SiC$_2$-DC. This is due to significantly greater topological disorder of
SiC-DC, which is the underlying reason for stronger internal resistances and larger energy barriers of its model.

To provide deeper insight into the effect of physical pore accessibility on transport properties of fluid molecules in nanoporous carbon, percolation path analysis was performed for both Ti$_3$SiC$_2$-DC and SiC-DC [25] models; this determined how many percolation paths physically accessible to argon exist in these models which can span across the simulation unit cells from one side to the opposite side. A detailed description of the percolation path analysis method is provided elsewhere by Sarkisov and Harrison [58]. Illustrations of the percolation paths for argon in both Ti$_3$SiC$_2$-DC and SiC-DC carbon models are provided in Figure 13, in which the red volumes represent areas that are physically accessible to argon, while the green structures depict the pore network of the HRMC carbon models. Here, void space and solid structures are occasionally shown or hidden for better visibility. The analysis shows that for argon there is only one percolation path spanning the Ti$_3$SiC$_2$-DC model. This accessible area is extended in both $X$ and $Y$ directions, occupying 0.94% of total pore volume of the model. This path is seen in Figure 13(a) as a thick slab of red volume filling a channel-like space between two upper and lower layers of carbon sheets in the model. As given in Table 2, the limiting pore diameter in Ti$_3$SiC$_2$-DC is 11.36 Å, which roughly corresponds to the geometric width of this channel. Interestingly, despite two-dimensional proliferation of the physical percolation path in the Ti$_3$SiC$_2$-DC model, it appears that the actual diffusion path is only unidimensional when the free energy landscape and internal energy barriers of the system are taken into account. Our MD simulations show that diffusion of argon in Ti$_3$SiC$_2$-DC is essentially unidimensional with negligible diffusion in $Y$ and $Z$ directions and the argon molecule cannot escape the sub-diffusion regime even after 40 ns. Thus, the real diffusion path that is energetically accessible to argon is only extended in the $X$
direction corresponding to the channel-like pore space illustrated in Figure 13(a). Unidimensional diffusion of argon is evident in Figure 14(a) where the log-log dependence of MSD with time in $Y$ and $Z$ directions has nearly zero slope even at 400 K and after 40 ns. Thus, Ar molecules cannot enter the Fickian regime in these two directions where they face large energy barriers, and the mean squared displacement appears to reach a limiting value of about 100 Å$^2$ by about 100 ps. However, the slope of the MSD in the $X$ direction approaches unity only after a few pico-seconds, signifying entry into the Fickian (diffusive) regime.

In contrast to the Ti$_3$SiC$_2$-DC structure, Figure 14(b) depicts 3-dimensional diffusion of Ar in SiC-DC even at a low temperature of 200 K and after a much shorter simulation time (< 15 ns). Percolation path analysis of the SiC-DC model also shows that there exists a large and three-dimensionally percolated diffusion path for argon which takes up 0.98% of the total pore volume of the unit cell. This is clearly illustrated in Figure 13(b). Significant structural disorder and large tortuosity of the SiC-DC carbon are evident in these snapshots. Our calculations show that the limiting pore diameter of the SiC-DC model is only 6.8 Å which is much smaller than that of Ti$_3$SiC$_2$-DC (11.36 Å). For more comprehensive discussion of surface heterogeneity and structural disorder of SiC-DC carbon, we refer to our previous publications [25, 30, 55, 76]. In one of these studies [30], we have investigated directional diffusion of CH$_4$ in several HRMC constructed models of SiC-DC showing there are slightly different activation energy barriers for CH$_4$ in $X$, $Y$ and $Z$ directions, which suggests some structural anisotropy in SiC-DC. An analysis of diffusional barriers for Ar in SiC-DC is illustrated in Figure 15 which demonstrates only small or insignificant short-range anisotropy for Ar diffusion in this carbon, with activation energy barriers for argon being very close in different directions. Nevertheless, given the small degree of
anisotropy reported in this work and in our previous study [30] for the SiC-DC model, and the fact that the nano-size unit cells used in the HRMC modelling are probably not large enough to capture isotropy of disordered materials, one expects that the long-range structure of SiC-DC may actually appear to be fully isotropic at macroscale dimensions. On the other hand, unidimensional diffusion of argon in the Ti$_3$SiC$_2$-DC, along with the evidence derived from percolation path analysis of this model, demonstrates a highly anisotropic short-range carbon structure comprising stacks of defective lamellar sheets of graphene that can form strong bottle-necks in the atomistic structure of this carbon. Unidimensional transport in ACF-15, having similar lamellar structure, and displaying single file diffusion, has also recently been reported for water [77], suggesting that this behaviour may be a common feature of such anisotropic structures. Nevertheless, in practice the random aggregation of anisotropic nanoscale crystallites may lead to macroscopic isotropy.

Overall, comparison of argon transport in the two carbon models with completely different structural isotropy suggests that highly anisotropic microporous carbon materials with unidimensional pores, such as channel- or tunnel-like pores, results in faster diffusion of fluid molecules; however in contrast, carbon structures with large degree of isotropy give rise to slower fluid diffusion due to multi-dimensional internal barriers distributed nearly uniformly in the system. This conclusion is consistent with a recent simulation study by Ranganathan et. al [79] on high temperature diffusion of simple gases in micro- and mesoporous carbons, in which they find that homogeneous carbon structures lead to slower diffusion than anisotropic structures, due to significant molecule-wall scattering. Such scattering may be expected to be enhanced in the presence of larger energy barriers as in SiC-DC.
4. Conclusions

We have constructed a realistic model of Ti$_3$SiC$_2$ carbide-derived carbon using the hybrid reverse Monte Carlo modelling technique, and validated it against experimental adsorption isotherms of carbon dioxide, methane and argon. We have also investigated the adsorption and transport properties of this model, and compared the results with performance of the HRMC model of silicon carbide-derived carbon recently constructed in this laboratory.

In agreement with experimental evidence, we observe ultra-microporous regions in Ti$_3$SiC$_2$-DC using PSD characterization of the HRMC model. Our studies of low-pressure adsorption isotherms of Ar at 87 K and CO$_2$ at 273 K reveal limited accessibility of Ar to these regions, due to its larger kinetic diameter and lower kinetic energy at 87 K compared to CO$_2$ 273 K. Under-prediction of experimental argon adsorption by GCMC simulation at pressures close to the saturation pressure of Ar suggests that internal shrinkage of the lamellar structure of Ti$_3$SiC$_2$-DC gives rise to formation of inter-granular carbon microcracks, not captured by the nanosized HRMC unit cell and the short-range RDF based on which our atomistic model is constructed using the HRMC technique.

The results from comparison of the isosteric heats of adsorption of Ar and CO$_2$ in our Ti$_3$SiC$_2$-DC model demonstrate a steep drop in the heat for Ar at low pressures, indicative of large heterogeneity and consistent with poor accessibility of this molecule to very narrow pores. Our studies suggest that structural disorder originated from shrinkage of carbide precursors during the chlorination process is the main reasons for pore-network inaccessibility and slow diffusion of
adsorbate molecules in the microporous carbon structures, as is the case for SiC and Ti$_3$SiC$_2$-derived carbons.

Our MD simulations along with percolation path analysis and determination of internal free energy barriers of SiC-DC and Ti$_3$SiC$_2$-DC models demonstrate that pore network accessibility and structural isotropy play important roles in dictating the different transport behaviour in these materials. The results suggest that the more isotropic structure of SiC-DC enhances adsorbate scattering by the pore wall, as observed in recent literature, which in turn leads to larger and more homogeneous distribution of internal energy barriers for fluid transport. In contrast, the lamellar structure of Ti$_3$SiC$_2$-DC promotes unidimensional transport of adsorbates through its pore network, with smaller overall energy barriers. Carbon materials with nano-channel pore architecture providing such unidimensional transport may have important applications in nanofluidics and medical devices.
Acknowledgment

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REFERENCES


Table 1 - Simulation parameters of the three consecutive HRMC stages

<table>
<thead>
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<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial Configuration</strong></td>
<td>Modified ACF-15 model 1</td>
<td>Final configuration from stage 1</td>
<td>Final configuration from stage 2</td>
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<td>7000</td>
<td>500</td>
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<tr>
<td><strong>Simulation length</strong></td>
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<td>0.0001</td>
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<td><strong>σ_{exp}</strong></td>
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<td>0.0324</td>
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1 The HRMC constructed model of ACD15 recently developed in this laboratory [23]
Table 2 – Structural characteristics of the HRMC constructed model of Ti$_3$SiC$_2$-DC compared with those of the SiC-DC carbon model [25]

<table>
<thead>
<tr>
<th>Carbon model</th>
<th>Argon surface area (m$^2$/g)</th>
<th>Argon BET surface area (m$^2$/g)</th>
<th>Argon DFT surface area (m$^2$/g)</th>
<th>Pore limiting diameter (Å)</th>
<th>Maximum pore diameter (Å)</th>
<th>He pore volume (cc/g)</th>
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<td>Ti$_3$SiC$_2$-DC</td>
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<td>968</td>
<td>11.36</td>
<td>15.10</td>
<td>0.46</td>
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<tr>
<td>SiC-DC</td>
<td>1581</td>
<td>1556</td>
<td>1912</td>
<td>6.81</td>
<td>13.0</td>
<td>0.56</td>
</tr>
</tbody>
</table>
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