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Towards Determining the Interaction of Fluids with Nanostructured Carbons

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Abstract—Development of efficient approaches for modeling of nanostructures and nanofluidics is a major goal of theoretical and computational scientists. Here we focus on developing a scheme to accurately and efficiently predict the interactions of fluid molecules with nanostructured carbons where the interactions are weak and relatively short-range. As a model of these systems we consider the interaction of neon with simple polyaromatic hydrocarbons, and demonstrate that the use of basis sets of high local quality can provide a very useful approach.

Keywords—*ab initio* calculations, graphene, fluids in nanopores, interaction potentials

I. INTRODUCTION

With the advent of nanotechnology there has been a drive towards understanding the transport behaviour in small systems. Standard fluid dynamics no longer applies due to the strong influence of the wall that cannot be neglected [1-4], and new techniques and relations that allow us to understand and predict the properties of these systems must be developed. From the computational perspective, Monte Carlo, molecular dynamics simulations and nonequilibrium molecular dynamics simulations are playing a lead role in both predicting properties and expanding understanding and testing new relationships such as those derived from density functional theory (DFT), dynamical systems theory and perturbation theory [5-8].

Transport, adsorption isotherms and other properties, as well as the molecular dynamics of these systems are all strongly influenced by the fluid-wall interactions. While model potentials for these systems exist, the performance of these potentials when dilute fluids, polar fluids, very narrow pores and when the system is highly amorphous needs to be carefully examined. Simultaneously, determination of accurate interaction potentials for these systems is a challenge to computational and experimental science. When considering transport in nonporous materials, the interactions between the fluid and the walls are typically weak (i.e. ‘chemical bonds’ are not usually formed), and while the fluid might be a small molecule, the wall is a macrostructure. The issue of the weak

interactions combined with large systems ensure that the computational task is difficult.

In this paper we consider an approach that we intend using to model graphene-fluid and carbon nanotube-fluid interactions. Here we use a series of polyaromatic hydrocarbons (PAHs) to provide simplistic models of graphene. We demonstrate the use of basis sets of high local quality can provide a useful and efficient route to intermolecular potential interactions. In Section II we describe some of the simple models used to describe graphene-wall interactions. In Sections III and IV, we develop and test the approach, and compare it with the combined quantum mechanical-molecular mechanical methods that are currently popular. We anticipate that this approach is widely applicable and provides an efficient route to accurate potentials.

II. MODEL POTENTIALS

The Lennard Jones (LJ) interaction potential is the mostly commonly used model potential and gives reasonable properties for small non-polar molecules. Its great use lies in the simplistic mathematical form, which is a relatively computationally efficient algorithm, which still maintains good accuracy. Furthermore, parameters for effective Lennard-Jones pair potentials are widely available [9]. The Lennard-Jones potential, U , is given by,

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right] \quad (1)$$

where r is the interparticle separation and ϵ and σ are parameters which relate to depth of the potential well and the separation of the particles respectively. To model the interaction of a fluid with a graphene wall, one simple approach is to assume pair-wise additivity and sum the interaction of the fluid with each of the carbon atoms in the wall.

The interaction of molecules with a graphene wall is often modelled by the 10-4 Steele potential. It is obtained by integration of a Lennard-Jones potential over the directions parallel to the graphene sheets, and therefore only varies with distance from the wall [10]. It is given by,

$$U(x) = 2\varepsilon\sigma^2\rho \left[\frac{2}{5} \left(\frac{\sigma}{x} \right)^{10} - \left(\frac{\sigma}{x} \right)^4 \right] \quad (2)$$

where x is the distance of the fluid particle from the wall, ρ is the separation of the graphene planes and ε and σ are the Lennard-Jones parameters that relate to depth of the potential well and the separation of the particles respectively.

Lennard-Jones potentials are usually effective pair potentials. That is, their parameters are determined from empirical measurements usually in bulk systems, and therefore often “effectively” take into account many body interactions. However, if we are in a dilute system, these might not be the best parameters. In this case, it might be more accurate to use computationally determined parameters and computationally, the pair potential is the most easily accessible. We are currently exploring the parameters that can be used and their effects on properties of fluids in pores [11]. Furthermore if the environment does not match that where the empirical parameters are determined, they might not be optimal. If the environment that one wishes to study is complex and not easily accessible by experiment, such as in nanostructures, computation approaches might be the only way of accurately determining interaction potentials. However, determining accurate potentials of parameters from calculations is still a demanding task.

Our aim in this work is to develop a procedure that can accurately model interactions of fluid with walls where the interaction is anticipated to be short ranged, but wish to allow for the possibility that the interactions are quite weak. In order to develop a robust approach to studying the interaction of fluids with carbon walls, the test system initially considered is a model for neon with a graphene slit pore wall. The system is partly selected due to the difficulty of accurately modeling this relatively weak interaction. Indeed for the neon dimer it is well known that second order Møller-Plesset perturbation theory (MP2) and most DFT approaches are insufficient [12,13]. To examine if MP2 is sufficient, for our systems we compare with MP4 results. We also compare the results obtained using our approach with those predicted using standard parameters in the Steele 10-4 potential and using a pairwise-additive Lennard Jones potential.

III. METHOD FOR ACCURATE GRAPHENE ADSORPTION POTENTIALS

From the work of Heine et al. [14] on the physisorption of H_2 on graphene, it seems feasible to obtain good estimates of binding energy and pair interaction energy of neon with graphene by extrapolating from the interaction energy of benzene to larger PAHs. For this reason, the set of PAHs shown schematically in Figure 1 are chosen as simplistic models of bulk graphene, and convergence of these properties

with the size of the PAH is monitored. This provided a starting point of investigation for accurately measuring graphene adsorption potentials. Unlike Heine et al. however, we expect that basis set superposition error (BSSE) is required in every case to provide accurate results. It is known that even with large basis sets and theory (aug-cc-pV5Z+bf/CCSD(T)) correction for BSSE is necessary in the case of the neon dimer [12,15]. To account for this error, we use the counterpoise correction [16].

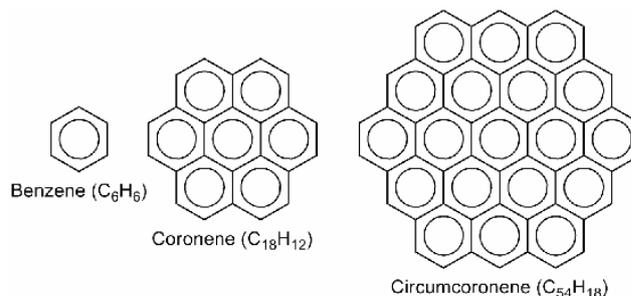


Figure 1. Schematic diagrams of the polyaromatic hydrocarbons considered in this study.

In each case, the geometry of the PAH was optimised using the DFT method of B3LYP/6-31G* as implemented in the Gaussian03 package[17]. The Ne atom was located directly above the centre of the PAH, and the distance of the Ne from the PAH centre was selected to be 0.35nm which not far from, but greater than the minimum energy of the Steele 10-4 potential. The calculation of the interaction energy is performed using MP2 theory in most cases. Initial calculations were carried out using large using aug-cc-pVTZ basis sets on the carbons, hydrogens and neon.

Results for benzene were carried out using the full basis set. However, even for coronene, this calculation was unfeasible on readily available resources. The difficulty of studying large systems with high level theories and large basis sets initially led us to examine the utility of employing localised basis sets. It provides high local accuracy at the central point of interaction, and moderate accuracy outside this region [19]. Unlike QM/MM methods, however, the delocalisation of the electrons is not restricted. Several localised basis sets were considered for coronene, to determine the effect that treating more carbons with a high level basis set would have on the on binding energy. Figure 2 shows a schematic diagram of the basis sets used in each case. For circumcoronene, only a single choice of localised basis set was considered. The use of carefully selected localised basis set provide adequate results for the binding energy, but at a fraction of the computational cost to that obtained using the full basis set. This approach also allowed investigation of circumcoronene, and could be employed for even larger structures if necessary because the site of interaction is small relative to the whole molecule. The coronene-neon dimer using aug-cc-pVTZ basis set on all atoms contained 1426 basis functions, 2149 primitive Gaussians and 1675 Cartesian basis functions whilst the coronene neon dimer with 6-31G* basis set on atoms outside the inner ring contains

only 508 basis functions, 955 primitive Gaussians and 571 Cartesian basis functions.

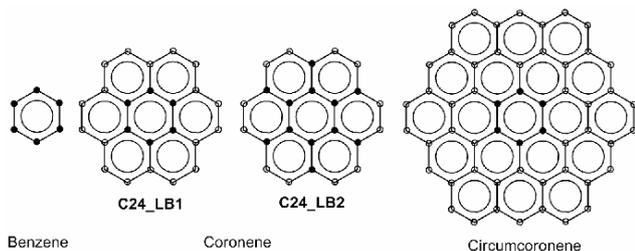


Figure 2. Schematic diagrams illustrating the localised basis sets used. The carbon atoms highlighted with black dots are treated with a high level basis set (HLBS), whilst the carbons marked with unfilled circles are treated with a lower level basis set (LLBS). The neon atom is also treated with the HLBS and the hydrogen atoms with LLBS in cases where localised basis sets are used.

To check that the level of theory was sufficient, an MP4 level calculation was carried out for C24. Contrary to the neon-neon system which required CCSD(T) to obtain good results, our results show neon-PAH systems do not require such a high level of theory as although the interaction is weak, redistribution of electron density in the PAH is now possible, and the overall interaction is stronger.

For completeness, the interaction energies were compared to the 10-4 Steele potential with the sum of pairwise-LJ interactions. Two sets of LJ parameters were selected: those of bulk Ne [9], and the Ne dimer [11].

IV. RESULTS AND DISCUSSION

Initially, the benzene – neon dimer was considered and preliminarily results and earlier works on similar systems indicated that it was necessary to use an aug-cc-pVTZ basis set to obtain accurate interaction energies at the MP2 level [14, 18]. A binding energy of $-588.4 \mu\text{E}_\text{H}$ at a separation of 0.35 nm was obtained, and this is in good agreement with the results of Kloppe et al. of $\sim -600 \mu\text{E}_\text{H}$ (extracted from graph in [18]). We note that the BSSE in this calculation is large, and similar to the interaction energy itself ($692.4 \mu\text{E}_\text{H}$). The simple system also provides data on computational times, computer memory and data for estimating a converged Ne-graphene interaction potential. Using a pair-additive Lennard-Jones approximation, and bulk Ne parameters [9], an interaction energy of benzene of $-620.78 \mu\text{E}_\text{H}$ is obtained at 0.35 nm, and using the Ne dimer parameters, a value of $-584.1 \mu\text{E}_\text{H}$ is obtained [11]. We note that although these are calculated using a simple Lennard-Jones potential function, the parameters used require extensive computational or experimental data for their accurate determination. The consistency of these values with our calculations indicate that the method we are using is reasonable.

To improve our graphene model, we increased the size of our PAH to coronene. MP2 calculations were still performed, however we made use of localised basis sets to improve the efficiency of the calculation. In the basis set C24_LB1 the inner ring of the coronene as well as the neon atom had the

aug-cc-pVTZ basis set attached to them, and the other carbon atoms had smaller basis sets, either 6-31G or 6-31G**. In basis set C24_LB2 the inner 2 rings of the coronene as well as the neon atom had the aug-cc-pVTZ basis set attached to them, whilst the rest of the atoms in coronene had a 6-31G basis set. The differences in energies are about $20 \mu\text{E}_\text{H}$ in both cases, which is much less than the increase in binding energy obtained with an increase in the size of the PAH. Finally, circumcoronene was examined, with C54_LB1 localisation where the HLBS was aug-cc-pVTZ, and the LLBS was 6-31G. Figure 2 demonstrates that the interaction energy converges with the increase in the size of the PAH. The value of r in this figure is an approximation to the distance of the outer carbons of the PAH from its centre. Although the data is too few to be confident in its functional form that will be valid at larger r , it is clearly converging, and this data is consistent with a $1/\sqrt{r}$ behaviour. Should this behaviour continue, it would result in extrapolation to an infinite system interaction energy of $-1500 \mu\text{E}_\text{H}$. However we anticipate that this behaviour may very well change for larger PAH, and anticipate that the convergence would go more quickly. A study of the next PAH in this series would allow a more confident extrapolation to the large system PAH value.

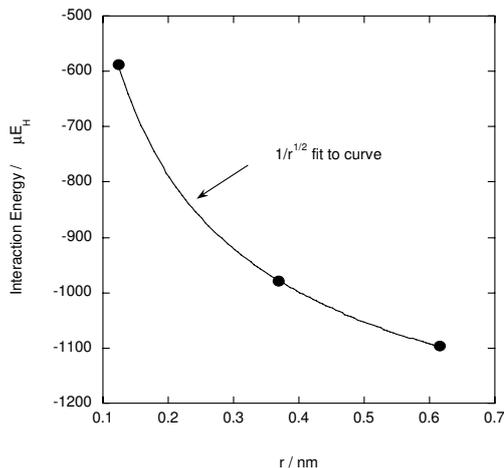


Figure 3. Change in interaction energy with size of PAH.

TABLE I. INTERACTION ENERGIES OF PAHS WITH Ne AT A SEPARATION OF 0.35nm.

Model ^a	Interaction Energy ^b / μE_H
Benzene C6	-588.4
Coronene C24_LB1 (LLBS:6-31G)	-978.7
Coronene C24_LB1 (LLBS:6-31G**)	-1008
Coronene C24_LB2 (LLBS:6-31G)	-1020
Circumcoronene C54_LB2 (LLBS:6-31G)	-1096

^a All systems used the MP2 method. If not otherwise specified, the basis set was aug-cc-pvtz. If a local basis set was used the LLBS is specified, and a aug-cc-pvtz HLBS was employed.

^b We note that all interaction energies were corrected for BSSE.

A comparison of MP2 and MP4 results for coronene with C24_LB1 (LLBS:6-31G) shows a difference of only $7.2 \mu\text{E}_\text{H}$,

with the MP4 interaction energy being $-985.92 \mu E_H$. Clearly this improvement is small compared to the other changes.

We also consider the interaction energy of Ne with graphene using a Steele 10-4 potential incorporating the standard Lennard-Jones parameters [9], and find an interaction energy of $-1238 \mu E_H$ at 0.35nm. If the Ne dimer parameters are used [11], then an interaction energy of $-1179 \mu E_H$ is obtained at this geometry. The fact that the results we obtain are similar is encouraging. However we note that we would not expect convergence to these values since they are parameterised with different systems to those considered here.

The change in the BSSE with the localisation of the basis set was examined. We also examined the possibility of using MM/MD methods. In particular, the interaction energies were determined where carbon atoms on the coronene were classified using the C24_LB1 scheme, however a UFF force field replaced the LLBS and the ONIOM approach was used. A difficulty with this approach from a physical perspective is that it does not allow for delocalisation of the electrons. The incorporation of BSSE in these systems is also an issue that has not been studied in detail, so we have assumed that it is similar to that obtained with the benzene system (the only additional atoms included being the hydrogens on the benzene). This method gave an interaction energy of $-1593 \mu E_H$, which seems an significant overestimation. Even though this calculation performed very quickly, it does not seem to be a good approach for this system.

Using the basis sets selected in this work, the size limit of PAHs in which we could feasibly compute interaction energies at the MP2 level was circumcoronene ($C_{54}H_{18}$). Whilst this calculation was by far the longest and most resource intensive MP2 calculation it provided the most accurate representation of graphene – neon interaction potential. This calculation was similar to coronene in that the inner ring and neon atom was calculated using the aug-cc-pVTZ basis set, while the rest of the circumcoronene molecule was calculated using 6-31G basis set. It is likely that even smaller basis sets can be used on the carbons and hydrogens far from the interaction site without large loss in accuracy, and this would increase the size of the system that could be examined. However, since reasonable convergence to the large system size was already obtained with circumcoronene, this might not be necessary for some applications. In particular, in the transport studies we are most interested in the forces for which the shape of the surface rather than the absolute values of the energies are most important. In this case we need the full potential energy surface. Work in this direction is underway [11].

V. CONCLUSIONS

Calculations on the interaction between Ne and PAHs demonstrate that the use of localised basis sets provide an accurate and useful approach to the modelling of their binding.

The MM/MD methods, although performed very quickly, do not model the wall very well, however a different parameter set may improve the result. In consideration of properties such as vibrational frequencies, which are sensitive to the mass and geometry of the wall molecule, a combination of localised basis sets and MM/MD methods might be the most accurate.

We selected neon for use in this work as it was a challenging interaction to model well, as well as our interest in modeling flow of Ne through nanoporous systems. We should note, however that this approach is expected to work equally well with a range of other adsorbates. In fact for many small molecules even better results will be obtained, and larger PAHs will be able to be considered since the HLBS will not need to be as large as was required here.

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