

Multi-scale modelling on PM2.5 encapsulation inside doubly-layered graphene

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Published in Micro & Nano Letters; Received on 22nd May 2015; Revised on 5th October 2015; Accepted on 23rd October 2015

PM2.5 is classified as particles with radii $<2.5 \mu\text{m}$. It is evident that the continuous inhalation of such particles results in respiratory diseases such as lung cancer. Therefore, more effective adsorption of PM2.5 becomes crucial to comb the problem and the recent development of nanomaterials could provide a means to absorb and store PM2.5. In this reported work, a multi-scale modelling is used to investigate the storage of PM2.5, in particular carbon monoxide (CO), sulphur dioxide (SO₂) and nitrogen monoxide (NO) inside doubly-layered graphene sheets. While the molecular adsorption is modelled by a modified equation of states in the adsorption regime, the interactions between molecules are captured using a mean field theory. The maximum gravimetric uptake for CO, SO₂ and NO between the graphene of separation 20 \AA is shown to be 19.45, 26.64 and 24.32 wt%, respectively, where the validity of the current model is confirmed by the case of hydrogen molecules with other experimental and simulations results. For higher temperatures, stronger pressure is needed to reach the same maximum uptakes as given at $T = 77 \text{ K}$. The current model possesses the merit of rapid computational speed and is ready to be applied for other nanomaterials without conceptual difficulties. This graphene could be incorporated into an air purification system so as to raise the system's capacity in PM2.5 adsorption.

1. Introduction: The majority of developed cities and an increasing number of developing cities are overwhelmed by poor air quality. The inhaled PM2.5 (particles with radii $<2.5 \mu\text{m}$) will be accumulated in human lungs, leading to respiratory decreases and even lung cancer [1]. The World Health Organization (2014) claims that more than two million premature deaths each year are related to outdoor or indoor air pollution. The adsorption of such PM2.5 before human inhalation could tackle such problems. Due to the superior physical and chemical properties, and the huge surface area-to-volume ratio of nanomaterials, nanomaterials by themselves or embedded into a membrane system could provide an effective medium for storing gases [2]. In particular, certain materials such as metal-organic frameworks could alter their topology to accommodate more gases [3].

Numerous experimental and numerical investigations have been performed to determine the storage capacity of gases inside nanomaterials [2]. However, they are either too expensive or possess severe spatial and temporal constraints. In the literature, a multi-scale modelling [4] is proposed where the conventional van der Waals gas equation is used to model gaseous adsorption in the bulk regime. On the other hand, the modified gas equation taking into account molecular interactions between PM2.5s and between the PM2.5 and the doubly-layered graphene is used to model gaseous adsorption in the adsorption regime. A single-layered graphene, referred to as graphene, has also been discovered and proved to possess unique and exceptional mechanical, chemical and optical properties, which could serve as a media for gas storage [5]. To facilitate faster computational speed, a mean field theory [6, 7] is used assuming that carbon atoms are smeared on the surface of graphene so that pairwise interactions are approximated by surface integrals. It is noted that the mean field theory adopted in this Letter has been successfully used for numerous problems including the axial buckling of nanopeapods [8], sea-water desalination [9] and hydrogen yield [10] using functionalised

nanomaterials, gas storage inside nanomaterials and shuffle nanomemory device [11].

For simplicity, the storage of carbon monoxide (CO), sulphur dioxide (SO₂) and nitrogen monoxide (NO), which are the common hazardous components of PM2.5 inside doubly-layered graphene, is investigated, and the hydrogen uptake will be used as a benchmark for the accuracy of the present methodology.

Although the general theory is presented in Section 2, numerical solutions, along with discussion, are given in Section 3. Our conclusions are presented in Section 4.

2. Theory: The molecular interactions between PM2.5s and between the PM2.5 and the doubly-layered graphene, are modelled by the Lennard-Jones potential [12], where the latter interaction could be obtained using a mean field theory [6, 7]. Given that, the energy density for the graphene system E_{total} is obtained as

$$E_{\text{total}} = E_1 + E_2 = \eta\pi \left\{ -\frac{A}{2} \left(\frac{1}{h^4} + \frac{1}{(S-h)^4} \right) + \frac{B}{5} \left(\frac{1}{h^{10}} + \frac{1}{(S-h)^{10}} \right) \right\} + \gamma(h)\varepsilon_{\text{max}} \quad (1)$$

where E_1 , E_2 , η , A , h , S , B , $\gamma(h)$ and ε_{max} denote the interactions between PM2.5 and the host material, interactions between PM2.5s, the number density of the graphene, the attractive constant, the perpendicular distance from the lower layer to a PM2.5, the separation between graphene layers, the repulsive constant, the strength constant for PM2.5 interactions and the maximum interaction between PM2.5s, respectively.

The numerical values for all constants used in this Letter are given in Table 1. In addition, the cavity between layers comprises the bulk and adsorption regimes, where the energy density E_{total}

Table 1 Numerical values adopted in this Letter, where A and B are the parameters determined using Lorentz-Berthelot mixing rule [13]

Description	Parameter	Value
number density for graphene	H	0.381 \AA^{-2}
attractive constant for H ₂ -G	A	9.61 eV\AA^6
repulsive constant for H ₂ -G	B	$8695.5 \text{ eV\AA}^{12}$
attractive constant for CO-G	A	36.97 eV\AA^6
repulsive constant for CO-G	B	$73121.19 \text{ eV\AA}^{12}$
attractive constant for SO ₂	A	93.85 eV\AA^6
repulsive constant for SO ₂	B	$305645.2 \text{ eV\AA}^{12}$
attractive constant for NO	A	32.80738 eV\AA^6
repulsive constant for NO	B	$54365.35 \text{ eV\AA}^{12}$
van der Waals radius for H ₂	r_H	2.968 \AA
van der Waals radius for CO	r_H	3.676 \AA
van der Waals radius for SO ₂	r_H	4.29 \AA
van der Waals radius for NO	r_H	3.47 \AA

in the adsorption regime is less than zero so that the bulk and adsorption volumes are determined using Boltzmann's distribution and are given, respectively, by

$$V_{\text{bulk}} = \int \exp\left(-\frac{|E_{\text{total}}|}{K_B T}\right) dV$$

and

$$V_{\text{ad}} = \int \left\{ 1 - \exp\left(-\frac{|E_{\text{total}}|}{K_B T}\right) \right\} dV \quad (2)$$

where E_{total} , k_B , T and dV denote the energy density given in (1), Boltzmann's constant, the temperature and the volume elements, respectively. While the conventional van der Waals equation of states is used to describe the adsorption properties in the bulk regime, the molecular uptake in the adsorption regime is modified by the heat of adsorption $Q = |E_{\text{avg}}| + k_B T/2$, where $|E_{\text{avg}}|$ denotes the average energy density so as to take into account the molecular effects arising from the graphene. The multi-scale model for the bulk [left in (3)] and adsorption [right in (3)] regimes is thus written, respectively, as

$$P\left(\frac{V_{\text{bulk}}}{n_{\text{bulk}}} - \mu\right) = RT; \quad P\left(\frac{V_{\text{ad}}}{n_{\text{ad}}} - \mu\right) = RT \exp\left(-\frac{Q}{RT}\right) \quad (3)$$

where P , n_{bulk} , n_{ad} , μ , R and T denote the external pressure, the number density in the bulk regime, the number density in the adsorption regime, the densely occupied molar volume, the molar gas constant and the temperature, respectively. Equation (3) could be solved for n_{bulk} and n_{ad} , and the total number density of PM2.5 is therefore given by $n = n_{\text{bulk}} + n_{\text{ad}}$. However, due to the point mass assumption of the PM2.5, singularity arises when the external pressure or the temperature approach to infinity or zero, respectively, which is physically infeasible. To combat this problem, a hard-sphere model is adopted to terminate our numerical iteration whenever the work done on PM2.5 in conjunction with their kinetic energy is larger than their maximum binding energy E_{max} or the physical volume occupied by PM2.5 is larger than the total volume for the cavity. Symbolically, our numerical iteration will be terminated whenever

$$\left\{ n > \frac{3V}{4\pi r_H^3 N_A} \cup P > \frac{|E_{\text{max}}| - (K_B T)/2}{4\pi r_H^3/3} \right\} \quad (4)$$

where r_H , N_A and V denote the van der Waals radius of PM2.5, Avogadro's constant and the cavity volume of graphene, respectively.

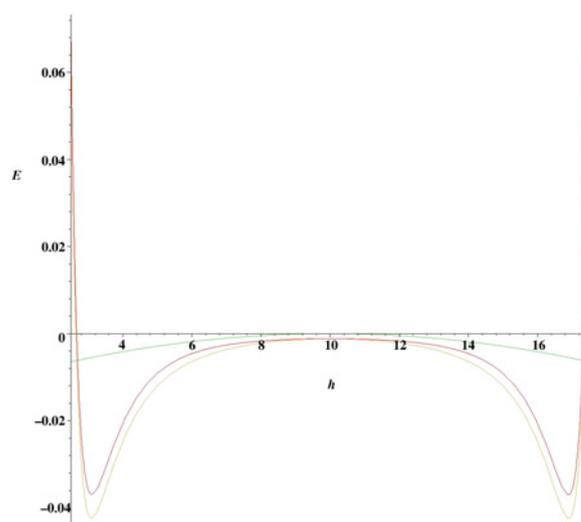


Fig. 1 Red and green lines denote the interactions between a hydrogen and the graphene, and the interactions between hydrogen, respectively. Yellow line denotes the total interaction for the hydrogen inside the graphene. It is noted that h denotes the perpendicular distance from the bottom of the graphene to the hydrogen with the unit of \AA and E has the unit of eV

It is commended that unlike prior works [4], all numerical results given in this Letter are not fitted by any experimental results.

3. Numerical solutions and discussion: Using (1), the molecular interactions between a hydrogen inside the doubly-layered graphene sheets of the separation of 20 \AA are given in Fig. 1. It is noted that from Fig. 1, the hydrogen is densely occupied around 3.2 and 16.8 \AA due to the molecular interactions arising from the graphene. This induces more hydrogen-hydrogen interactions and the strength of such hydrogen-hydrogen fades towards the cavity centre.

To illustrate the effect of hydrogen-hydrogen and hydrogen-graphene interactions, the gravimetric uptake for hydrogen inside graphene at $T = 77 \text{ K}$ is determined using (3) and (3) without the molecular effect, i.e. set $Q = 0$, and a comparison between the gravimetric uptake for hydrogen inside single-layered graphene and doubly-layered graphene at $T = 77 \text{ K}$ is also determined. The numerical solutions are shown in Fig. 2. It is commended that the gravimetric uptake is calculated using $\{m/(m+M)\} * 100$, where m and M denote the total mass of gas and the graphene sheets, respectively.

The numerical results shown in Figs. 1 and 2 indicate that the intrinsic interactions between a hydrogen and the graphene and between hydrogen dramatically enhance the gravimetric uptake for hydrogen from 0.6 to 2.4 wt\% at 1 bar , and the numerical

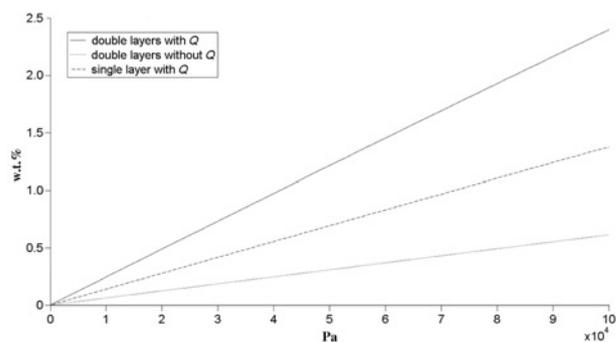


Fig. 2 Gravimetric uptake for hydrogen inside doubly-layered graphene sheets with and without Q , and single-layered graphene at $T = 77 \text{ K}$

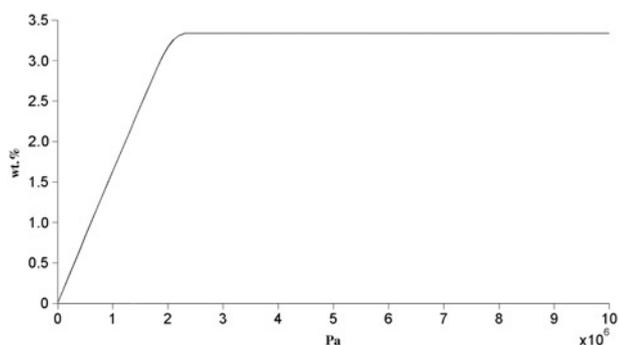


Fig. 3 Gravimetric uptake for hydrogen inside doubly-layered graphene sheets at $T = 300\text{ K}$

results for the present model are in a good agreement with both experimental and theoretical results [14, 15], which predict the storage capacity of around 2 wt% at $T = 77\text{ K}$ and 1 bar. Also, the doubly-layered graphene possesses higher hydrogen uptake than that of single-layered graphene, i.e. 2.4 wt% in comparison with 1.38 wt% at $T = 77\text{ K}$ and 1 bar due to the extra binding forces arising from the other graphene sheet. This effect could be generalised into other gases including PM2.5. It is worth noting that the present numerical results are obtained in a few minutes mincing rapid computational time. However, in practice, most gas filling processes are performed under room temperature. To investigate the temperature effect, the temperature is raised from 77 to 300 K, which could be done easily under the current mathematical frameworks and the numerical result is given in Fig. 3.

Due to the high temperature effect, high pressure is needed to squeeze hydrogen into the system in comparison to that at low temperatures. In addition, a plateau is formed for P greater than 2.3 MPa due to the constraints enforced in (4). Now, the same technique is used, and CO, SO_2 and NO adsorption inside doubly-layered graphene is investigated. Corresponding attractive and repulsive constants for PM2.5 are used (see Table 1), and the numerical results for the proposed PM2.5 inside graphene are given in Fig. 4.

It is noted that SO_2 possesses the highest gravimetric uptake, followed by NO and CO at 77 K. Due to the keener interactions between the PM2.5 and the graphene, the saturation (or plateaus) is formed in much lower pressure in comparison to that of hydrogen at $T = 77\text{ K}$. This could be partially explained by scrutinising the heat of adsorption, which is the modification constant for the equation of states in the adsorption regime. At 77 K, the heat of adsorption for H_2 , CO, NO and SO_2 is given by 0.37571×10^{-20} , 0.63734×10^{-20} , 0.62385×10^{-20} and 0.10687×10^{-19} eV, respectively. It is commended that the heat of adsorption for the proposed PM2.5 is either twofold or threefold higher than that of hydrogen,

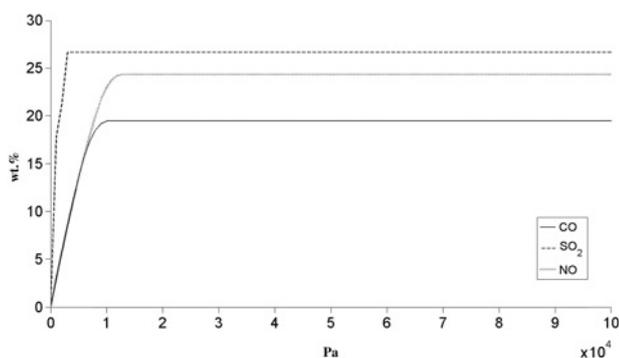


Fig. 4 Gravimetric uptake for CO, SO_2 and NO inside doubly-layered graphene at $T = 77\text{ K}$

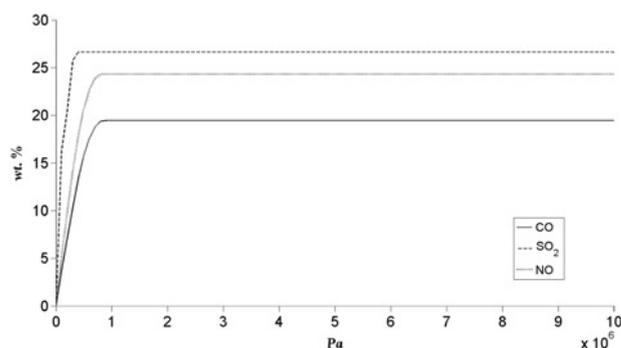


Fig. 5 Gravimetric uptake for CO, SO_2 and NO inside doubly-layered graphene at $T = 300\text{ K}$

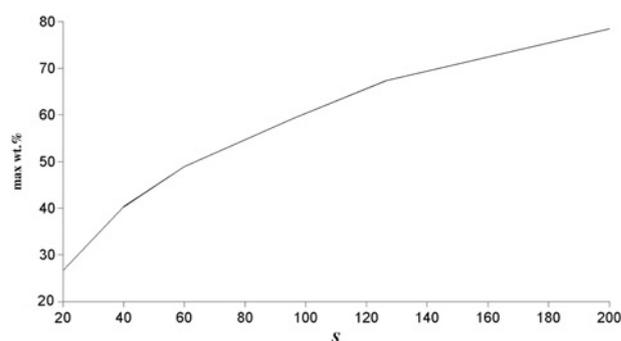


Fig. 6 Maximum gravimetric uptake of SO_2 for different separations S at $T = 77\text{ K}$

and the higher heat of adsorption results in a more distinct adsorption landscape for PM2.5 in comparison to that of H_2 . Likewise, taking into account the usual operation temperature, the gravimetric uptake for CO, NO and SO_2 at 300 K is shown in Fig. 5.

Owing to the high temperature, much higher pressure has to be adopted to squeeze more PM2.5 into the system so that the range of pressure for the occurrence of maximum uptake extends from kilopascal at 77 K to megapascal at 300 K. It is worth noting that the first inequality of (4) takes into effect for lower temperatures including the room temperature. Not until a much higher temperature is reached, the second inequality of (4) comes into effect and the maximum uptake will drop significantly from the present value.

Last but not least, the maximum gravimetric uptake against the separation S is investigated. SO_2 is taken as an example and the numerical solution is given in Fig. 6.

It is noted that as the separation between graphene sheets increases, the maximum gravimetric uptake also increases. However, during the simulations, we have also noticed that the pressure required to reach the maximum uptake increases with S . This increase in the maximum gravimetric uptake could partially be explained by the fact that as S increases, more hydrogen could be accommodated between the graphene (could be achieved by higher pressure), however the mass of graphene remains unchanged (refer to the definition of the gravimetric uptake).

4. Conclusion: In this Letter, a multi-scale model has been adopted to investigate the adsorption of PM2.5 inside doubly-layered graphene sheets separated by 20 Å. Three hazardous molecules, namely SO_2 , NO and CO, are investigated, and SO_2 turns out to possess the highest gravimetric uptake in comparison to others at $T = 77\text{ K}$. Graphene could then be incorporated into an air purifier system to absorb and store more PM2.5. The induced nature of the present model has also been shown by investigating the

PM2.5's storage capacity under room temperature and various separations between graphene layers. The present model could be applied to other nanomaterials without conceptual difficulties.

5. Acknowledgments: This work was supported by the Natural Science Foundation of the PRC-Young Scientist Program (NSFC51506103/E0605), the Qianjiang Talent Scheme (QJD1402009), the Zhejiang Natural Science Foundation-Young Scientist Programme (Q15E090001), and the Ningbo Natural Science Foundation (2014A610025, 2014A610172, 2015A610281).

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