Problem Modeling Chemical Vapour Deposition of Graphene

Graphene can be thought as the mother of the nanostructured allotropes of carbon, as well as of the thermodynamically stable form at ambient conditions, graphite – that is made out of graphene layers weakly bounded by Van der Waals forces. The ease with which layers of graphite peel off with friction is at the basis of usability of a well-known tool such as the pencil, used since about the XVI century. However, only about four hundreds years later graphene was isolated in its free state of a single sheet of carbon atoms (in 2004, the discovery was worth the Nobel prize in physics).

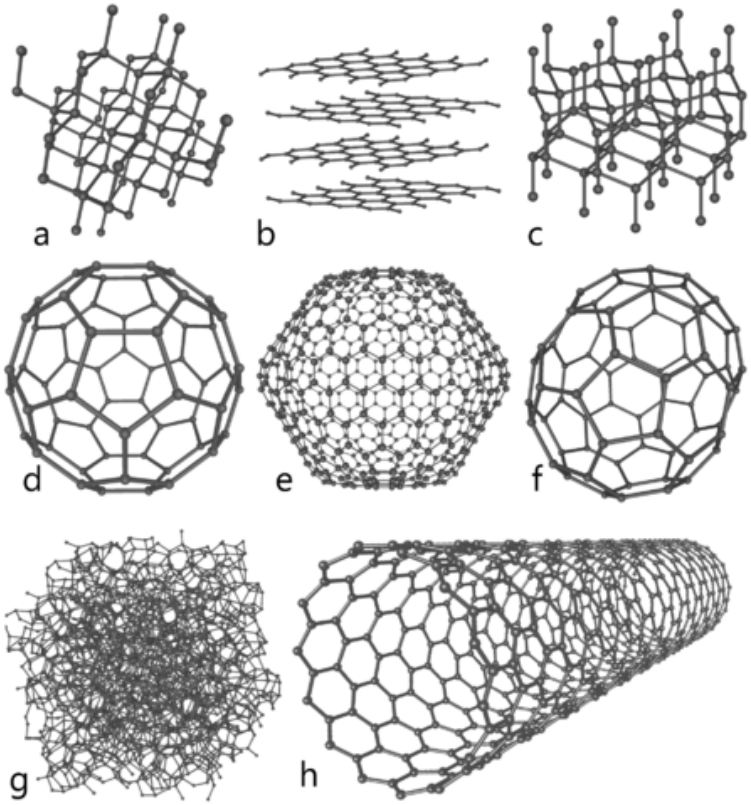


Figure 1: Eight allotropes of carbon. From (a) to (h): diamond, graphite, lonsdaleite, fullerene, fullerite, C70-fullerene, amorphous carbon and a carbon nanotube.

As with many examples in nanotechnology, experimental techniques to obtain a nano-material often anticipates the full comprehension of its properties. In fact, the ability to grow graphene foils epitaxially by catalytic decomposition of alkanes on a metal substrate is known since at least 1974.

The goal of this walk-through problem is to show how one can model the kinetic process of the graphene monolayer synthesis, by heating metallic surfaces that have been put in contact with some hydrocarbon compound. Since the precursor is usually a gas mixture present in the reaction chamber, the technique is named Chemical Vapor Deposition (CVD).
We consider the experimental setup of CVD with copper as the catalytic surface. The following sketch

depicts the overall process of deposition: from the flowing of the gas mixture of CH_4 and H_2 into the reaction chamber, to the coverage of the metallic surface with a carbon monolayer, after gases desorption.

(a) With the help of the review article[1], list the main points that underlie the process of CVD of graphene using a copper catalyst. What precursors are used? What processes must occur to convert these precursors into graphene? Which concepts from surface science can be important to understand this process?

A first process that has to happen involves the adsorption of CH_4 on copper. This process can be seen as the result of the following reaction

$$CH_4(\text{gas}) + \cdot \longleftrightarrow CH_4$$

where $\cdot$ represents a surface site.

(b) Write the equations for the chemical equilibria that underlie the adsorption and desorption of methane, indicating the fraction of occupied sites with θ, the desorption rate constant with $k^{DES}_{CH_4}$ and the adsorption rate constant with $p_{CH_4} \times k^{ADS}_{CH_4}$

(c) Solve the differential equation for $\theta'(t)$ and find the time evolution of $\theta(t)$, assuming $\theta(0) = 0$.

(d) Take the $t \to \infty$ limit and show that you recover Langmuir adsorption isotherm.

The flow gas that is used in CVD is typically a mixture of methane and H_2. This determines a competitive adsorption process.

(e) Write the kinetic equations that correspond to the two adsorption processes, assuming they are independent from each other but the total coverage is the sum of that of the two gases, $\theta = \theta_{CH_4} + \theta_{H_2}$. Introduce a separate adsorption and desorption rate for hydrogen, controlled by $k^{DES}_{H_2}$ and the adsorption rate with $p_{H_2} \times k^{ADS}_{H_2}$.

(f) The stationary state is governed by a competitive adsorption Langmuir isotherm. What is the expression for the equilibrium θ_{CH_4} and θ_{H_2}? Why would it be a problem if there was too much hydrogen in the flow gas or if the hydrogen bound too strongly to the surface?

In practice the process of CVD involves a series of reactions in which adsorbed methane loses H atoms. Assuming these stick to the Cu surface and occupy the same sites to which physisorbed molecules and CH_x groups adsorb, the process can be understood in terms of the schematic representation below.

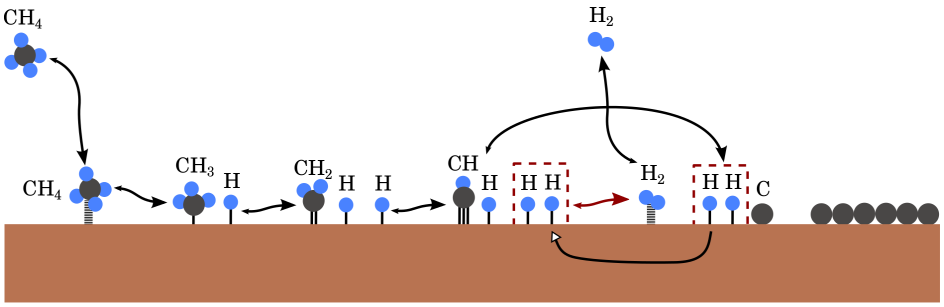


Figure 2: Schematic drawing of the chemical reactions within the chamber.

[1] Y. Zhang, L. Zhang, C. Zhou,"Review of Chemical Vapor Deposition of Graphene and Related Applications", Acc. Chem. Res. 46, 2329 (2013)

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(g) Ignore for a moment the role of H_2, i.e. consider a pure methane flow gas and that H atoms cannot leave the surface once they are adsorbed. Write the full set of chemical reactions that are involved in the decomposition process: $CH_4 \longrightarrow CH_3 \longrightarrow CH_2 \longrightarrow CH \longrightarrow C$.

(h) Write the kinetic equations that correspond to this model, including also that for the gas-phase equilibrium of methane. For the decomposition reactions, consider that the forward and backward rate constants k_{FW} and k_{BW} are the same for all decomposition processes. Consider that the coverage θ now corresponds to the sum of all the coverages of individual species. Why cannot we use the competitive adsorption Langmuir equation to determine the stationary distribution?

(i) This kinetic model is way too complex to be solved analytically. Use the Mathematica notebook to explore how the different parameters change the behavior. Try to optimize the $t \to \infty$ coverage of C atoms (the amount of graphene produced) and the speed at which you get there (the time you have to wait to process one batch).

The kinetic equations obtained this far contain several rate constants that are considered as adjustable parameters. It is much more insightful to write the rate constants in physical terms.

- The adsorption constants can be written as $k_{ADS} = \sigma/\sqrt{2\pi m k_B T}$ (σ is the area of a surface site, m the mass of the adsorbate molecule and T the temperature).
- The desorption constants as $k_{DES} = \frac{1}{\tau}\exp\left\{\frac{\epsilon_{DES}}{k_B T}\right\}$, where ϵ_{DES} is the desorption energy and τ the residence time ($\simeq 1\,ps$).
- Reaction rate constants can be written as $k = \frac{1}{\tau}\exp\left\{-\frac{\epsilon^\ddagger - \epsilon_0}{k_B T}\right\}$, where ϵ_0 is the energy of the starting state and $\epsilon^\ddagger$ the transition-state energy.

The forward and backward rate has to satisfy a detailed-balance condition, which means that one has to assign an energy to each state in the reaction, satisfying internal consistency. A scheme of possible reactions is given in the figure below.

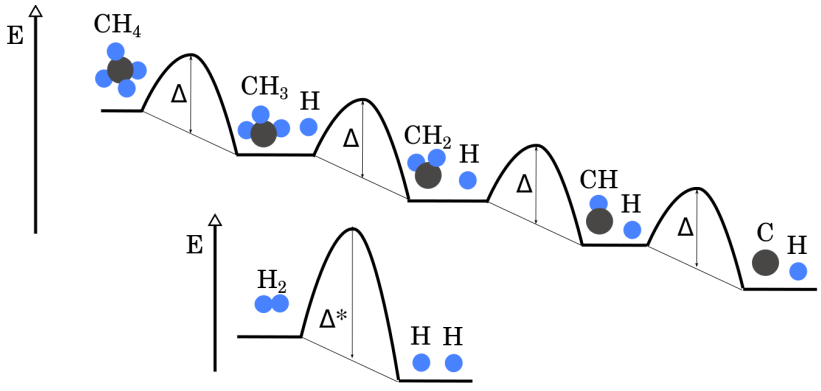


Figure 3: Modeling of the various activation barriers. You can see Δ and Δ^* as the energy-shifts of methane dissociation and of hydrogen dissociation related to the energy average of the initial and final state.

Consider that the energy of an adsorbed molecule can be written in terms of a bond-counting argument, counting also the bonds with the surface. For instance, the energy of an adsorbed CH_2 would be $2\epsilon_{CH} +$

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$2\epsilon_{CS}$ – as we consider that a methylene group forms two "bonds" with the surface even if it occupies a single surface site.

(j) Write down the energy of reactants and products of each decomposition reaction. Consider that at each step a surface site is consumed, and a new HS and CS bond is formed.

(k) We use here a simple model that guarantees detailed balance, in which $\epsilon^{\ddagger} = \Delta + (\epsilon_{\text{REACT}} + \epsilon_{\text{PROD}})/2$. Write the reaction barrier for the forward and backward reaction for each decomposition step. Was it reasonable to assume that the forward and backward rates were the same for every step?

Leaving out H recombination means that the surface will saturate in H atoms, at which point all the reactions will halt. Similar arguments to those we made for the decomposition of methane apply to the decomposition/recombination of molecular hydrogen, for which we can consider ϵ_{HH} and $\Delta^{\star}$ as the bond energy and the activation barrier respectively.

(l) Write the expression for the decomposition/recombination rates for the whole set of reactions, including also $H_2\uparrow + \cdot \longleftrightarrow 2\,H$.

(m) Use the Mathematica notebook to play around with the overall reactor model. What are the "process" parameters you could adjust if you were running a reactor? What are the parameters that are intrinsic materials properties? *Hints: you can play around with those for fun, but there are "true" values that you cannot modify in reality.*

(n) Discuss among yourselves. As a materials scientist, how could you go further manipulating the materials properties that enter the model? What are the most obvious limitations of the model and how could you address them while keeping a relatively simple description of the process?

The End.