# Atomistically-Informed Continuum Model for Hydrogen Storage on Graphene

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ydrogen is considered to be a possible "clean energy" solution and the associated problem of hydrogen storage (and retrieval on demand) has seen intense activity in recent years. Carbon-based storage materials in general and graphene<sup>1-4</sup> in particular have attracted much attention due to their efficient hydrogen sorption capabilities. While some of the early works focused on pristine graphene, decorated graphene (usually with metal atoms) appears to show significant promise in terms of storage capacity albeit at the cost of complications of fabrication and stability.<sup>5</sup> Most of the interesting insights into the mechanisms of hydrogen storage and interpretations of experiments on undecorated and decorated graphene are based on atomistic calculationseither first-principles based or predicated on empirical force fields. For example, some early questions like, why does molecular H<sub>2</sub> chemisorption occur on graphene despite the fact that molecular binding energy is 2.4 eV in contrast to the relatively weaker 0.8 eV binding energy of hydrogen to graphene were addressed through first principles calculations.<sup>6</sup>

Atomistic methods, while providing (if used properly) accurate insights, are limited in both spatial and temporal scales they can access. For example, pressure-temperatureconcentration evolution of the hydrogenation process is inaccessible by any of the atomistic methods. The latter are precisely the parameters required to guide experiments. In this brief note, we propose a phenomenological continuum model that readily connects to parameters (such as binding energies) available from atomistic calculations and provides a first order computation of the dynamics of hydrogen absorption on graphene. While we focus on pristine graphene, the presented framework can be modified to account for decorated graphene as well as incorporate other subtleties such as impurities, significant elastic deformations among others. As example, a prediction of considerable experimental interest, we present results for the maximum concentration that can be achieved for given initial pressure.

#### The Model and Results

We consider an extended (perfect) graphene sheet placed in a fixed amount of  $H_2$  gas. We consider the absorption and desorption of  $H_2$ . We show first that computations of energy reported in Ref. 6 for absorption of small clusters of hydrogen are consistent with a model whose energy depends on two terms: (1) an on-site contribution, and (2) a nearest neighbor contribution. We use a continuum analog of the resulting Ising model to deduce the free energy for the system.

The total free energy *G* of the system is the sum of  $G_{H_2}$ , and  $G_{g_1}$ , which are the free energies of the hydrogen gas and the hydrogenated graphene sheet respectively.

$$G = G_{H_{\gamma}} + G_g \tag{1}$$

The hydrogen gas is regarded as ideal gas, and hence its Gibbs free energy is<sup>7</sup>

$$G_{H_2} = U_{H_2} + PV - TS_{H_2}$$
(2)

where  $U_{H_2}$  is its internal energy, and  $S_{H_2}$  is the entropy of the hydrogen gas.

The internal energy is

$$U_{H_{\star}} = c_{\nu} n k_{B} T \tag{3}$$

where  $c_v$  is the heat capacity at a constant volume, n is the number of the hydrogen molecules,  $k_B$  is the Boltzmann constant.  $S_{H_2}$  is given by<sup>7</sup>

$$S_{H_2} = k_B \ln(Z_{trans} \cdot Z_{rot}) + k_B T \left(\frac{\partial \ln(Z_{trans} \cdot Z_{rot})}{\partial T}\right)$$
(4)

Where  $Z_{trans}$  and  $Z_{rot}$  are the translational the rotation contribution to the partition function. Substituting:

$$Z_{trans} = \frac{1}{n!} \left[ \frac{\left(2\pi m kT\right)^{\frac{3}{2}} V}{h^3} \right]^n, \text{ and } Z_{rot} = \left(\frac{8\pi^2 l kT}{\sigma h^2}\right) \text{ into Eq. 2, we}$$

find that

$$S_{H_{2}} = k_{B}n \left( \frac{\frac{3}{2} \ln \frac{2\pi m k_{B}T}{h^{2}} + \ln \frac{V}{n} + \frac{5}{2}}{\frac{5}{s_{rates}}} + \frac{\ln \frac{8\pi^{2} l k T}{\sigma h^{2}} + 1}{\frac{5}{s_{rate}}} \right)$$

$$= k_{B}n \left( \frac{\ln \frac{8\pi^{2} l k_{B} (2\pi m k_{B})^{\frac{3}{2}}}{\sigma h^{5}} + \frac{7}{2}}{\frac{6}{2}} + \ln \frac{5}{2} + \ln \frac{V}{n} \right)$$
(5)

where  $m = 1.66 \times 10^{-24}$  kg is the mass of a hydrogen molecule,  $I = 4.72 \times 10^{-48}$  kg is the moment of inertia of a hydrogen molecule, h is the Planck constant.

Free energy of the graphene sheet is given by

$$G_g = E_g - TS_g \tag{6}$$

The process of the hydrogenation can be analyzed using

$$E_g + \frac{n_1}{2} \varepsilon_H \rightarrow E_{H@G} + n_1 \varepsilon_b \tag{7}$$

where  $E_g$  is the internal energy of the graphene with no H attached,  $\varepsilon_H$  = 2.3eV is the binding energy of the hydrogen gas, and  $\varepsilon_b$  is the mean binding energy of the hydrogenation.

Rescaling Eq. 7 and setting  $E_s = 0$ 

$$E_{H@G} = n_1(\varepsilon_H - \varepsilon_b) \tag{8}$$

Combining Eq.1, Eq. 6, and Eq. 8, we find that

$$G = G_{H_2}\Big|_{n=n_b-n_b} + n_1(\varepsilon_H - \varepsilon_b) - TS_g \tag{9}$$

where  $n_0$  denotes the original number of hydrogen molecules in the system before the absorption,  $n_1$  is the number of the hydrogen atoms bound to the graphene sheet.

According to the ideal gas law,

$$n_0 - n_1 = \frac{PV}{k_B T} \tag{10}$$

where *P*, *V*, *T* are the hydrogen gas state variables at the current state. In moving to a continuum,  $n_1$  can be related to the concentration C(x) that is the ratio of hydrogen attached graphene atoms to the unattached ones.

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$$n_{\rm l} = \int \Lambda C dx^2 \tag{11}$$

where  $\Lambda$  is the density of atomic sites.

Next, we derive a continuum model of the binding energy  $\varepsilon_{\rm b}$  based on the results of atomistic computation, given in Ref. 6. It was shown that the total binding energy depends on the number of C-H bonds  $N_1$  (each requiring an energy  $\varepsilon_0$ ), the number of unpaired  $\pi$  electrons  $N_2$  (energy  $\varepsilon_m$ ) and the number of C-C bonds between hydrogenated graphene atoms and non-hydrogenated graphene atoms,  $N_3$  (energy  $\varepsilon_d$ ). The total binding energy is

$$n_1 \varepsilon_b = N_1 \varepsilon_0 + N_2 \varepsilon_\pi + N_3 \varepsilon_d \tag{12}$$

For example, with one absorbed hydrogen atom (shown in blue in Fig. 1), Eq. 12 (using the value 0.8eV from Ref. 6) becomes

$$\varepsilon_b = \varepsilon_0 + \varepsilon_\pi + 3\varepsilon_d = 0.8 \text{ev} \tag{13}$$

With two neighboring sites occupied by H-atoms placed in opposite sides of the graphene layer (Fig. 2), Eq. 12 (using the energy computed in Ref. 6) gives

$$2\varepsilon_b = 2\varepsilon_0 + 4\varepsilon_d = 3.4 \text{ev} \tag{14}$$

When three hydrogen atoms absorbed as shown in Fig. 3,

$$3\varepsilon_b = 3\varepsilon_0 + \varepsilon_\pi + 5\varepsilon_d = 5.2\text{ev} \tag{15}$$

solving Eq. 13, Eq. 14, and Eq. 15.

$$\varepsilon_0 = 2.7 \text{ev} \quad \varepsilon_\pi = -0.4 \text{ev} \quad \varepsilon_d = -0.5 \text{ev}$$
(16)

Note that the energies of all other small clusters computed in Ref. 6 can be evaluated using Eq. 16, and decoupling the interactions into on-site,  $\pi$  bonds and nearest neighbor components. We only consider patches of H-absorption, where there is at most one unpaired  $\pi$  electron. When the number of absorbed H-atoms is large, the contribution of  $\varepsilon_{\pi}$  from the unpaired H-atom can be neglected, and Eq. 12 reduces to

$$n_1 \varepsilon_b = n_1 \varepsilon_0 + N_3 \varepsilon_d \tag{17}$$

This equation can be interpreted as follows: the total energy is a sum of an on-site component ( $\varepsilon_0$ ) and nearest neighbor energy ( $\varepsilon_d$ ). This is our Ising model. Note that using C = 1 at occupied sites and C = 0 at unoccupied sites,  $N_3$  can be expressed as

$$N_{3} = \frac{1}{2} \sum_{i}^{i,j} \left( C_{i} - C_{j} \right)$$
(18)

where i and j are neighboring sites. Now we consider large-scale H-absorbed regions and introduce a continuum formulation of the problem, in terms of a concentration field  $C(\mathbf{x})$  for absorbed H. For example,

$$n_1 = \int \Lambda C dx^2 \tag{19}$$

In the continuum case, Eq. 18 can be written (assuming isotropy)

$$N_3 = \frac{1}{2}a^2\Lambda \int (\nabla C)^2 dx^2 \tag{20}$$

It is worth noting that Eq. 20, in a phenomenological sense, incorporates part of the cost of the elastic energy (caused by the deformation due to binding of hydrogen). It can be rationalized that mechanical strain occurs due to the gradient of the concentration field (in other words for a uniform concentration there is no cost in elastic energy). Substituting Eq. 19, Eq. 20 into Eq. 17, gives



**Fig. 1.** Schematic diagram of a graphene sheet, one of whose C-atoms has absorbed a H-atom.



**Fig. 2.** Schematic diagram of a graphene sheet, where two neighboring *C*-atoms have absorbed H-atoms. The two H-atoms are on opposite sides of the graphene sheet.

$$\eta_1 \varepsilon_b = \Lambda \varepsilon_0 \int C dx^2 + \frac{1}{2} a^2 \Lambda \varepsilon_d \int (\nabla C)^2 dx^2$$
(21)

We only need an expression for the entropy of the graphene sheet in order to compute Eq. 6. The entropy is

$$S_{\sigma} = k_B \ln \Omega \tag{22}$$

where  $\Omega$  is the number of all the possible microscopic states of the system.

Since neighboring H-atoms are assumed to lie on either side of graphene, all we need to do is to identify (n/2) locations for the H-atoms on one side of the graphene. This is approximately



**FIG. 3.** Schematic diagram of a graphene sheet, with H-absorption in 3 neighboring C-atoms. The solid spheres indicate absorption above the graphene sheet while the open circle indicates absorption below the sheet.

$$\Omega = \begin{pmatrix} \frac{1}{2}n_1 \\ \frac{1}{2}n_g \end{pmatrix} = \frac{\left(\frac{1}{2}n_g\right)!}{\left(\frac{1}{2}n_1\right)!\left(\frac{1}{2}(n_g - n_1)\right)!}$$
(23)

where  $n_g$  is the total number of the graphene atoms, half of which can be occupied by H-atoms lying on the chosen side of graphene.

Thus,

$$S_{g} = k_{B} \ln \Omega$$

$$\approx k_{B} \left[ \frac{1}{2} n_{g} \ln \left( \frac{1}{2} n_{g} \right) - \frac{1}{2} n_{g} - \frac{1}{2} n_{1} \ln \left( \frac{1}{2} n_{1} \right) + \frac{1}{2} n_{1} - \frac{1}{2} (n_{g} - n_{1}) \ln \left( \frac{1}{2} (n_{g} - n_{1}) \right) + \frac{1}{2} (n_{g} - n_{1}) \right]$$

$$= -\frac{1}{2} k_{B} \left( n_{1} \ln \frac{n_{1}}{n_{g}} + (n_{g} - n_{1}) \ln \frac{n_{g} - n_{1}}{n_{g}} \right)$$
(24)

Now, Eq. 9 reduces to

$$G = (1 + c_{v})k_{B}(n_{0} - n_{1})T$$

$$-(n_{0} - n_{1})k_{B}T\left(\ln T^{\frac{5}{2}} + \ln \frac{V}{n_{0} - n_{1}} + 69.22\right)$$

$$+\Lambda(\varepsilon_{H_{2}} - \varepsilon_{0})\int Cdx^{2} - \frac{1}{2}a^{2}\Lambda\varepsilon_{d}\int (\nabla C)^{2}dx^{2}$$

$$+\frac{1}{2}k_{B}T\left(n_{1}\ln \frac{n_{1}}{n_{g}} + (n_{g} - n_{1})\ln \frac{n_{g} - n_{1}}{n_{g}}\right)$$
(25)

The chemical potential of the system is given by<sup>7</sup>

$$\mu = \frac{\delta G}{\delta C}$$

$$= \Lambda \left[ \varepsilon_{H_2} - \varepsilon_0 - k_B T \left( c_v + 2 - 69.22 - \ln T^{\frac{5}{2}} - \ln \frac{V}{n_0 - n_1} \right) + a^2 \varepsilon_d \Delta C + \frac{1}{2} k_B T \ln \frac{n_1}{n_g - n_1} \right]$$

$$= \Lambda \left[ \varepsilon_{H_2} - \varepsilon_0 - k_B T \left( -64.72 - \ln \frac{k_B T^{\frac{7}{2}}}{P} \right) + a^2 \varepsilon_d \Delta C + \frac{1}{2} k_B T \ln \frac{n_1}{n_g - n_1} \right]$$
(26)

In our study, we choose a simple gradient system to describe the dynamic behavior of the hydrogen absorption

$$\frac{\partial C}{\partial t} = -\mu$$

$$= \Lambda \left[ -\varepsilon_{H_2} + \varepsilon_0 - a^2 \varepsilon_d \Delta C - k_B T \left( 64.72 + \ln \frac{k_B T^2}{P} \right) - \frac{1}{2} k_B T \ln \frac{n_1}{n_g - n_1} \right]$$
(27)

After rescaling time by  $\Lambda$ , Eq. 27 becomes

$$\frac{\partial C}{\partial t} = -\varepsilon_{H_2} + \varepsilon_0 - \varepsilon_d \Delta C - k_B T \left( 64.72 + \ln \frac{k_B T^2}{P} \right)$$

$$-\frac{1}{2} k_B T \ln \frac{C_{Avg}}{1 - C_{Avg}}$$
(28)

Now we can integrate the model system to find the equilibrium solutions. One set of conditions is to keep the pressure and the temperature of the ambient gas to be fixed. Under such conditions, either all sites are occupied or vacant. The solid line of Fig. 4 shows the phase boundary between parameters for which hydrogen is absorbed and desorbed from graphene. The corresponding results from atomistic computations have been reported in Ref. 6, and are shown by the dashed line. There is qualitative (and reasonably good quantitative) agreement between the phase boundaries.

The more interesting problem is what happens when the number of  $H_2$  molecules is fixed and the initial pressure is close to the transition line. Then, as the hydrogen is partially absorbed, the external pressure drops below the transition, and the absorption stops. The issue then is what are the patterns of absorption? Figure 5 shows some examples of H-absorbed states.

## **Concluding Remarks**

In conclusion, we have noted that the atomistic computations of hydrogen absorption on graphene agree with a simple Ising type model, and have used this observation to introduce a thermodynamic model for the process, that can be used for computations of H-absorption on a large scale. We used the model system to calculate the phase boundary between graphene and graphane.

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**Fig. 4.** Thermodynamic equilibrium lines when the initial concentration is  $4.8 \times 10^{-8}$ .

Our model<sup>28</sup> does not exhibit bistability, and hence there are no stable graphane/graphene boundaries on a large scale. However, such boundaries were shown to exist in atomistic calculations.<sup>8</sup> These atomistic calculations did not consider long-wavelength instabilities that can destabilize the interface. We would like to point out that our continuum generalization of the Ising model used the lowest order spatial derivatives. In principle, we could have introduced a continuum model containing higher order derivatives, which would have reduced to the same identical discrete Ising model. The stability of graphene/graphane boundaries may be different in these models. In the absence of experimental results on the stability of domains of graphane in graphene, it is difficult to determine which system best models the experiment.

In our computations, we also assumed that the graphene sheet does not experience crumpling.<sup>9-11</sup> However, suspended graphene sheets are known to exhibit crumpling at a microscopic scale,<sup>12,13</sup> as can be inferred on general grounds.<sup>14</sup> The computations outlined in the paper will need to be modified to account for such surface roughening.

Our model can be used to calculate long-term dynamics of hydrogen absorption on graphene, and to determine if graphene can be used as a practical means for hydrogen storage for mobile applications. Specifically, Figure 5 can be used to identify external conditions under which hydrogen can absorb or desorb from the graphene sheet.

Recent studies have shown that decoration with metal atoms appears to enhance the hydrogen storage capacity of graphene.<sup>5</sup> Our thermodynamic approach can be easily extended to these situations as well. All that is needed is the energy of a small number of configurations whose energies are computed from atomistic calculations.



Fig. 5. The maximum loadings that can be reached at different initial pressures.

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