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Adhesive tape exfoliation: why it works for Graphene

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Abstract –Single crystal graphite can be cleaved by the use of an adhesive tape. This was also the initial route for obtaining Graphene, a graphite slab one layer thick. In this note a few simple and fun considerations are presented in an attempt to put some light on why this procedure is successful. In particular on the nature of the surprisingly small number of repetitive steps that are needed in order to obtain a single layer slab. Two frameworks for exfoliation are investigated, parallel exfoliation involving repetitive simultaneous cleaving, the other, serial exfoliation, which involves the repetitive cleaving of a single chunk of graphite. For both cases, parallel and serial exfoliation, it is investigated how many generations of cleavages are needed. An approximate model with the probability distribution expressed as a simple closed form is presented and compared with the simulations.

Introduction. – Graphene holds significant promise for elucidating lower dimensional phenomena as well as being a key material that has the potential to unleash a new avalanche of technological developments [1,2]. Hence, not surprisingly graphene has attracted much attention as is the case for emerging materials with similar properties based on other elements, e.g. BN [3]. The initial isolation of Graphene invoked fabrication through repetitive cleaving with the use of an adhesive tape [4], and it enabled pioneering studies relating to the conductivity of Graphene [4], suspension of graphene [5], and nano particle channeling [6].

The apparent astronomical size of Avogadro's number when compared with every day's countable phenomena, such as the number of apples in a tree is well know. Hence, it might at first seem implausible that a single layer of graphite can be obtained through indiscriminating repetitive cleaving of a single graphite crystal or highly oriented pyrolytic graphite. Nonetheless, we now know that this is the case [4].

A typical slab of graphite, lets say 0.3 mm thick, contains about 10^6 atomic layers. How many times does one need to cleave the slab with the use of adhesive tape to obtain a single layer [4] or to obtain a slab with 300 or fewer layers being approximately 1000 Å thick [7]?

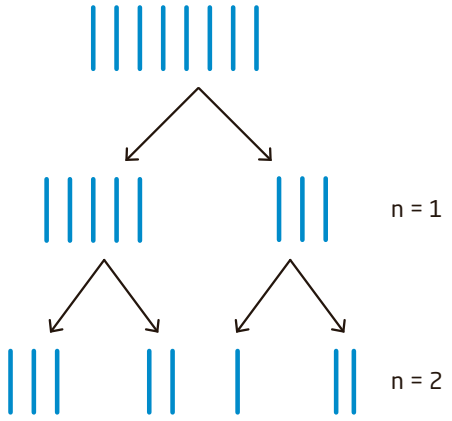

Fig. 1: Schematic depiction of what is denoted parallel exfoliation strategy here. The vertical bars indicate individual planes of honeycomb-ordered carbon atom. At each generation of cleavages all the graphite slabs are subdivided into two new slabs. The procedure is repeated in parallel until the first occurrence of a single layer.

The phenomenon that a thickness can grow with an integer power of 2 is common knowledge and is often illustrated with a sheet of paper repeatedly folded over itself. If this was the structure of graphite it would need

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to be unfolded about 20 times to obtain a one layer thick sheet, and 13 times to obtain a slab being 300 layer thick. For repetitive exfoliations, it will be shown below that yet smaller number of cleaving attempts will be needed. Two strategies will be presented: parallel exfoliation and serial exfoliation.

Parallel Exfoliation. – The basic assumptions regarding the exfoliation is that the adhesion of the tape is strong in the sense that cleavage is assumed never to take place at the tape but always between two adjacent honeycomb layers of graphite, and that a cleavage is equally likely to take place between any set of adjacent graphite planes. The principle of parallel exfoliation is depicted in Figure 1. Each cleavages generation is preformed simultaneous.

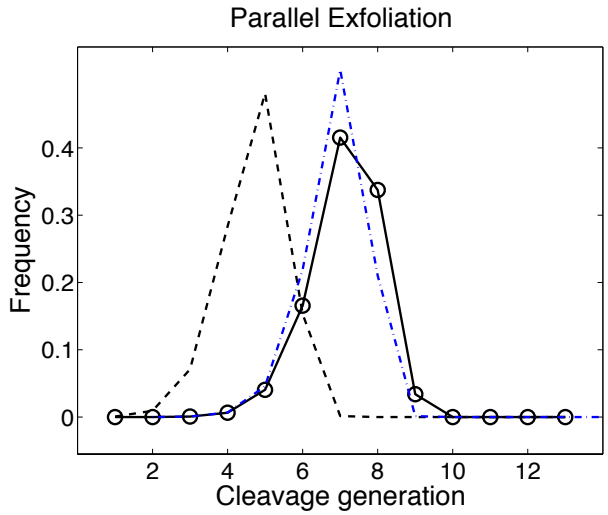

Fig. 2: The points (circles) on the solid line show the result of a numerical simulation of parallel exfoliations. In total, the simulation is averaged over 10^5 run. The relative occurrence, i.e. the fraction of the simulations which succeeded in n steps is shown as a function of the cleavage generation. The dashed line most far to the left indicates the resulting curve for obtaining a slab of 300 or less layers, rather than obtaining a single layer. The blue dashed-dotted line is the result obtained under the approximative assumption of stochastic independence, see Equation (11). It should be compared to the solid line to the right.

A numerical simulation with $N = 10^6$ layers parallel exfoliated n times determined from the first occurrence of a single layer. In the simulation for which the results are shown in Figure 2 parallel exfoliation was initiated 10^5 times in order to obtain good statistics. Depicted is frequencies of the needed number of cleaves generations to obtain a single layer of graphite. Remarkable, with only 8 or less attempts of cleaving there is a 96 % probability for having obtained a single layered slab.

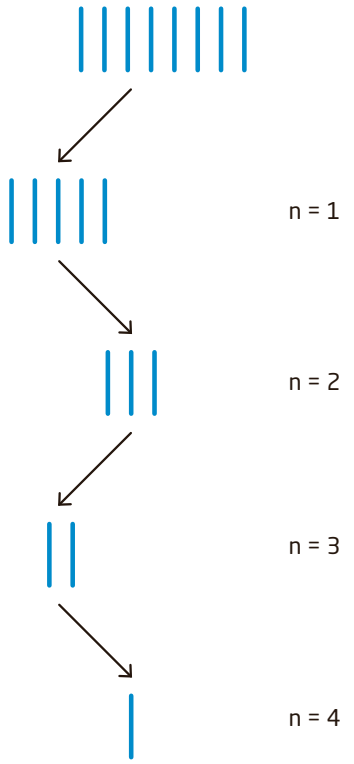

Fig. 3: The principle of serial exfoliation. After each consecutive cleaving of the graphite crystal only one slab is maintained. This is done without use of intelligent choice, e.g. by random, or always to the same side, or alternating to the right and left. In the programmed algorithm the selection is always to the same side.

Serial Exfoliation. – The parallel method discussed the previous section is not as straightforwardly experimentally as it might seems. Therefore here is considered a simple serial cleavage strategy where, at random, just one slab is maintained after each cleaves, see Figure 3 for a schematic explanation. For serial exfoliation with an initial crystallite of graphite with N planes, the probability P_1 for obtaining a single layer after the first attempt of cleaving is

$$P_1 = \frac{2}{N-1} \, . \tag{1}$$

The probability P_2 after the second attempt of cleaving is

$$P_2 = (1 - P_1) \, \frac{1}{N-3} \left(1 + \sum_{i=2}^{N-3} \frac{2}{i} \right) \, . \tag{2}$$

The sum can be expressed as

$$P_2 = \frac{2\Psi(N-2) + 2\gamma - 1}{N-1} \tag{3}$$

where $\Psi(x)$, the Digamma function, is the logarithmic derivative of the Gamma function $\Gamma(x)$ and γ is Euler's

constant. With each cleavage generation, a summation of the summation is added and the complexity of the term is similarly increased. In this communication, the calculations are performed by a numerical simulation in a similar manner to what was the case for parallel exfoliation. Figure 4 shows the frequency for the number of repeated attempts of cleaving which is needed to obtain a single layer thick slab. Here, it can be seen that with 18 or less attempts of cleaving, there is 95 % chance to obtain a sheet of graphene and the mean value is less than 14.

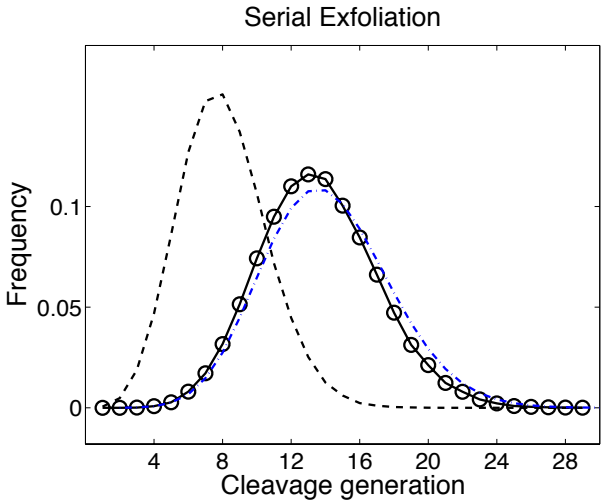

Fig. 4: The result of a numerical simulation of serial exfoliations is plotted as points (circles). The frequencies are calculated from the result of 10^5 simulations as the fraction of the simulations which succeeded in n steps (y-axis). Here, n indicates the number of attempts of cleaving which in this case is equally to the cleavage generation. The dashed line indicates the resulting curve for obtaining a slab of 300 or less layers, rather than obtaining a single layer. The blue dashed-dotted line shows the result of the approximative modeling, see Equation (8).

An approximate model. – Let us consider a continuous form of the problem, one where a real number x_1 is chosen indiscriminately in the interval $[0, L]$ at the first iteration. At the second iteration a real number x_2 is chosen in the interval $[0, x_1]$ and so on. Henceforward, this determines the sequence $\{x_i\}$.

The probability density function $f_1(s)$ for x_1 to have the value s is

$$f_1(s) = \frac{1}{L} \tag{4}$$

where $s \in [0, L]$. The probability density function $f_n(s)$ can be iteratively expressed with the use of the function $f_{n-1}(s)$. For $f_2(s)$, the probability that x_2 is equal to s is

$$f_2(s) = \int_s^L \frac{1}{u} f_1(u)du = \frac{1}{L}[\ln(L) - \ln(s)] \ . \tag{5}$$

By induction we obtain the following probability distribution for the possible values of x_n:

$$f_n(s) = \frac{[\ln(L) - \ln(s)]^{n-1}}{L(n-1)!} \ . \tag{6}$$

The probability that $x_n \in [0, \Delta]$ and that all of the preceding values $x_1, x_2, .., x_{n-1} \in [\Delta, L]$ can be calculated as

$$P_n = \int_0^\Delta f_n(s)ds \cdot \left[1 - \int_0^\Delta f_{n-1}(s)ds\right] \tag{7}$$

We are now ready to make a comparison to the simulation results presented earlier. A comparison of results from a model with real valued x_i to the results of a simulation which allowed only for a discrete set of integer numbers will be approximative and requires some choices. We will proceed by setting $L = N$ and using the approximation of evaluating the integrals at the discrete point $\Delta = 2$. Here, the choice of two, rather than one, is made in order to address for the fact that in the simulation study graphene was allowed to form at both ends of the current slab of graphite layers and not just at one end. The set of probabilities are

$$P_n \simeq 2\frac{[\ln(L) - \ln(2)]^{n-1}}{L(n-1)!} \cdot [1 - 2\frac{[\ln(L) - \ln(2)]^{n-2}}{L(n-2)!}] \ . \tag{8}$$

With this set of derived approximative probabilities $\{P_i\}$ a normalization factor of 1.08 is needed for their sum to proper add to unity. The results are depicted on Figure 4 as the blue dashed-dotted curve. The average number of generations is 13.6 for the simulation and 14.1 for blue dash-dotted curve. If the curve had been calculated from the $\Delta = 1$ values the average number of generations for the model would have been 14.8 and the curve would be correspondingly sifted.

From the above calculated P_n we can estimate the probability Q_n for not obtaining graphene after n or fewer attempts.

$$Q_n = 1 - \sum_{i=1}^{n} P_i \ . \tag{9}$$

Let us briefly revisit the case of parallel exfoliation and make an estimate of the probability W_n for not obtaining graphene after n or fewer attempts. Assuming stochastic independence which in this case is an approximation we have

$$W_n = Q_n^{(2^{n-1})} \ . \tag{10}$$

Hence, for parallel exfoliation we have the approximative probabilities Z_n for obtaining graphene after n attempts

$$Z_n = W_{n-1} - W_n \tag{11}$$

with $Z_1 = P_1$. They estimated probabilities are depicted in Figure 2 as the blue dashed-dotted line. The mean number of generations for the simulation is 7.2, while for the Z_i distribution it is 6.9 generations.The relative small shift towards lower numbers reflects that the assumed stochastic independence is not strictly obeyed.

Conclusion. – Provided that we could guide the positions of a cleavage we would need only one of them and in practice probable work with just two. The remarkable result in this note is that only about 7 or 13 indiscriminate positioned attempts of cleaving are needed in order to obtain a layer of graphene, where the number of cleaves depends on the chosen strategy. This is despite the fact that a typical small crystal of graphite contains about 10^6 layers of carbon atoms. The results of the simulation are approximatively described by a simple continuous model. The relative small number of cleavage generations needed to obtain graphene can be understood from the rapid change of the functional form of the successive probability density functions, see Equation (6).

For real physical crystals, a cleavage can jump between layers, e.g. by involving a step [8, 9]. In such cases even shorter exfoliation sequences will lead to fractions of sheets which is only one atomic layer thick and refined selection methods have been developed [10]. There are many open questions associated with the cleaving of graphite. For example, how does the strength of the Van der Waals interactions distribute themselves on an atomic scale during the dynamical process of cleaving? Is there an analogy to fingering [11] and cavitation [12] which are both seen in debonding [13–15] when a viscous fluid is involved? Are the presented results relevant for other dimensions than two, such as one dimensional random cleaving of biomolecules, e.g. the decay of DNA. This could perhaps contribute to our understanding of the distribution between shorter and longer fragments in old DNA [16].

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