# First-principles calculation of the interlayer distance of the two-layer graphene

# First-Principles Calculation of the Interlayer Distance of the Two-Layer Graphene

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By using first principles calculations, we study the interlayer distance of the two-layer graphene. We use a recently developed van der Waals density functional theory (VDWDFT) as well as the local density approximation (LDA). Both methods give successful results for graphite; i.e. the calculated interlayer distances are comparable with the experimental value. We find that the interlayer distance of the two-layer graphene is close to that of graphite. We also find that the AA stacking structure of the two-layer graphene has higher energy than that of the AB stacking one and the layer distance of the AA stacking is larger than that of the AB stacking. It is thus suggested that the interlayer distance becomes somewhat large when the stacking deviates from the AB stacking.

Since a single-layer graphite called graphene was isolated from graphite,[1)] graphene has been attracting a wide scientific interests because of novel electronic properties. Graphene does not have a band gap and there is so called Dirac cone at the zone bound points where the Fermi level is located. The electronic properties of few-layer graphenes are different from that of the single-layer graphene and this difference raises scientific problems. In the case of the two-layer graphene, for an example, electric field opening of the band gap was theoretically predicted and experimentally confirmed.[2–7)] To study the electronic properties of few-layer graphenes, it is essential to clarify the interlayer distance but the distance is still unclear.

It was reported from high resolution transmission electron microscopy (TEM) observation that interlayer distances of double-layer graphitic carbon systems are up to 3.84 Å,[8)] and inter shell distances of multiwalled carbon nanotubes are in the range from 3.59 to 3.62 Å .[9)] These observed distances are larger than the interlayer distance of graphite (3.35 Å). First principles calculations based on the generalized gradient approximation (GGA) indicated that the interlayer distance of the two-layer graphene is larger than that of graphite.[10)] This result seems to be consistent with the above

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mentioned experimental results. However, the interaction between the nearest layer is a van der Waals type, so the validity of the GGA is unclear. Conventional DFT (local density approximation (LDA) and GGA) is usually insufficient to include van der Waals interaction, which is prominent in weakly bonded materials such as molecular crystal and many organic compounds.[11–13)]

In this study, we perform first principles calculations based on the LDA, GGA and van der Waals density functional theory (VDWDFT).[14,15)] We find that the interlayer distance of the two-layer graphene is close to that of graphite. We also find that the metastable AA stacking structure has larger interlayer distance than that of the AB stacking structure. Therefore, the deviation from the AB stacking is expected to enlarge the interlayer distance.

We perform first principles calculations by using the code PHASE [16)] in which the plane wave basis set and ultrasoft pseudopotential [17)] are employed. We use the LDA, GGA and VDWDFT. In the VDWDFT, we first perform self-consistent calculation where only the GGA exchange potential is included in the many body potential. Next we evaluate the total energy by using the following exchange-correlation energy:

$$E_{xc}^{vdW-DF} = E_{ex}^{GGA} + E_{c}^{LDA} + E_{c}^{nl}, \tag{1}$$

where $E_{xc}^{vdW-DF}$ , $E_{ex}^{GGA}$, and $E_{c}^{LDA}$ are the exchange-correlation energy in the VDWDFT, GGA exchange energy, and the LDA correlation energy, respectively. $E_{c}^{nl}$ is the nonlocal correlation energy which is expressed as

$$E_{c}^{nl} = \frac{1}{2}\int d\mathbf{r}_i d\mathbf{r}_k \rho(\mathbf{r}_i)\phi(\mathbf{r}_i,\mathbf{r}_k)\rho(\mathbf{r}_k), \tag{2}$$

where $\phi(\mathbf{r}_i,\mathbf{r}_k)$ is a nonlocal function and $\rho$ is the electron density obtained from the above mentioned self-consistence calculation.

In the calculation of graphite, we use the rectangular lattice in which four atoms in each layer are contained. The maximum kinetic energy of the plane waves is 36 rydberg and $10\times10\times10$ k-point mesh in the full Brillouin zone (BZ) is used. In the calculation of the two-layer graphene, we use the repeated slab model where the length of the the vacuum region is 10.58 Å and the k-point mesh in the full Brillouin zone is $10\times10\times1$. We apply the least square fourth or fifth order polynomials fitting to the function of the total energy over the interlayer distance. Based on the result of this fitting, we determine the equilibrium interlayer distance and the interlayer binding energy ($\epsilon$) which is the difference between the energies for the equilibrium layer distance and the infinite layer one.

We first carry out LDA calculations of the graphite having the AB stacking structure. Our calculated interlayer distance is 3.35 Å ; therefore our calculation well reproduce the experimental value (3.35 Å).[18)] We note that our calculated value is comparable with a previous calculation based

on the LDA (3.33 Å).[19] The energy of the AB stacking structure is 11.0 meV/atom lower than that of the AA stacking structure (Table I). The interlayer distance (3.60 Å) of the AA stacking structure is larger than the corresponding value of the AB stacking structure (3.35 Å). Our results for the graphite are consistent with those of the past LDA calculations, i.e., it was also shown that the AB stacking structure has a lower energy than that of the AA stacking structure and that the interlayer distance of the AB stacking is smaller than that of the AA stacking.[20]

Next we perform VDWDFT calculations to evaluate the interlayer distance of the graphite. We find that the interlayer distance of the AB stacking structure is 3.50 Å, which is close to previously calculated result based on the VDWDFT (3.59 Å).[21] Our result is somewhat larger than that of the experimental value (3.35 Å). This small overestimation seems to be reasonable because it was reported that the VDWDFT tends to overestimate the equilibrium distance. [22] The energy of the AB stacking structure is 3.80 meV/atom lower than that of the AA stacking structure (Table I). As well as the LDA calculations, the VDWDFT calculations lead to the conclusion that the interlayer distance of the AA stacking structure (3.65 Å) is larger than that of the AB stacking structure (3.50 Å).

Here we carry out first principles calculations of the two-layer graphene. First we use the LDA and find that the interlayer distance of the two-layer graphene of the AB stacking structure (3.35 Å) is the same as the corresponding value of the graphite. We also study the AA stacking structure and find that its energy is 6.0 meV/atom higher than that of the AB stacking structure. The calculated interlayer distance (3.60 Å) is larger than that of the AB stacking (3.35 Å) as shown in Table II.

We next employ the VDWDFT in the calculation of the two-layer graphene. We find that interlayer distance of the AB stacking structure (3.49 Å) is close to than the corresponding value of the graphite (3.50 Å). We also study the AA stacking structure and find that its energy is 3.0 meV/atom higher than that of the AB stacking structure. As well as the LDA calculation, the VDWDFT calculation gives the result that the interlayer distance of the AA stacking (3.65 Å) is larger than that of the AB stacking (3.49 Å) as shown in Table II.

We here study the interlayer binding energy ($\epsilon$) of the AB stacking structure of graphite. The LDA and the VDWDFT give the energies of 30.5 and 31.0 meV/atom, respectively. Our value based on the LDA is comparable with those of the previous LDA calculations (20-30 meV/ atom). [23–26] The estimated values based on the LDA (30.5 meV/atom) and the VDWDFT (31.0 meV/atom) are close to previously experimental values (22-52 meV/atom)[27,28] (Table I) .

Next we study the interlayer binding energies of the two-layer graphene. The values based on the LDA and the VDWDFT are 16.5 meV/atom and 17.5 meV/atom, respectively (Table II). Therefore, we conclude that the interlayer binding energy of the two-layer graphene is smaller than that of graphite.

As mentioned above, our LDA and VDWDFT calculations show that the interlayer distance of the two-layer graphene having the AB stacking structure is very close to that of the graphite having the same stacking. On the other hand, a previous GGA calculation showed that the interlayer distance of the two layer graphene (3.58 Å) is larger than that of the graphite (3.26 Å).[10] We perform GGA calculations by using the primitive cell and $18 \times 18 \times 1$ k-point mesh. These conditions are similar to those in the previous calculation.[10] We do not find a stable structure; i.e. the two-layer graphene is not bound. In any case, the GGA is not suitable for calculations of van der Waals systems.

Based on the results of our LDA and VDWDFT calculations in this study, we conclude that the interlayer distance of the metastable AA stacking structure of the two-layer graphene is somewhat larger than that of the AB stacking structure. Therefore, it is suggested that the interlayer distance becomes large when the stacking deviates from the AB stacking. We also find that the interlayer distances of graphite and the two-layer graphene are very close. So, it is suggested that the deviation from the AB stacking in two-layer graphitic systems leads to the layer distances which are larger than that of the graphite. This deviation from the AB stacking is expected to occur in the case of double wall and multiwall carbon nanotubues since the two nearest neighbor tubes have different radii.

In summary, we have carried out first principles DFT calculations using the LDA, GGA and the VDWDFT to investigate the interlayer distance of the two-layer graphene. We found that the interlayer distance is the same as that of the graphite. The binding energy of the graphite was found to be larger than that of the two-layer graphene. The interlayer distance of the metastable AA stacking structure of the two-layer graphene is larger than that of the AB stacking structure . It is thus suggested that the interlayer distance becomes somewhat large when the stacking deviates from the AB stacking.

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**Table I.** Calculated results of the graphite. $d_{AB}$ ($d_{AA}$) represents the layer distance of the AB (AA) stacking. $\Delta E$ is the difference between the energies of the AB and AA stacking structures. $\epsilon_{AB}$ and $\epsilon_{AA}$ are the interlayer binding energies of the AB stacking and AA stacking structures, respectively.

| | $d_{AB}$ (Å) | $d_{AA}$ (Å) | $\Delta E$/atom (meV) | $\epsilon_{AB}$ (meV) | $\epsilon_{AA}$ (meV) |
|---|---|---|---|---|---|
| LDA | 3.35, 3.33[a] | 3.60 | 11.0 | 30.5 | 19.5 |
| VDWDFT | 3.50, 3.59[b] | 3.65 | 3.80 | 31.0 | 27.2 |
| Expt. | 3.35[c] | | | | |
| | [a] *Ref*. 19. | [b] *Ref*. 21. | [c] *Ref*. 18. | | |

**Table II.** Calculated results of the two-layer graphene. $d_{AB}$ ($d_{AA}$) represents the layer distance of the AB (AA) stacking. $\Delta E$ is the difference between the energies of the AB and AA stacking structures. $\epsilon_{AB}$ and $\epsilon_{AA}$ are the interlayer binding energies of the AB stacking and AA stacking structures, respectively.

| | $d_{AB}$ (Å) | $d_{AA}$ (Å) | $\Delta E$/atom (meV) | $\epsilon_{AB}$ (meV) | $\epsilon_{AA}$ (meV) |
|---|---|---|---|---|---|
| LDA | 3.35 | 3.60 | 6.0 | 16.5 | 10.5 |
| VDWDFT | 3.49 | 3.65 | 3.0 | 17.5 | 14.5 |

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