Sample Solution to HW1

15.Mar.2024

Q1 Surface tension of graphene and graphene stacks

1. Surface tension of single layer graphene

   We first calculate the interaction potential between 2 graphene layers. Consider 1 carbon atom on one side of the graphene layer:

$$\phi_{\mathrm{C-SLG}} = \int_0^\infty -\frac{\beta_{\mathrm{CC}}}{r^6} 2\pi\sigma z \mathrm{d}z \tag{1}$$

   where $z = d\tan\theta$ is the radius in the other graphene plane, and $r = d/\cos\theta$. Since graphene has hexagonal unit cell with lattice parameter a, and two carbon atoms per unit cell, we have: $\sigma = 2/(\frac{\sqrt{3}}{2}a^2)$. Replacing $\mathrm{d}z = d/\cos^2\theta\mathrm{d}\theta$, we have:

$$\begin{aligned}\phi_{\mathrm{C-SLG}} &= \int_0^{\pi/2} -\frac{\beta_{\mathrm{CC}}}{d_0^6}\cos^6\theta \cdot 2\pi d_0 \tan\theta\sigma \cdot \frac{d_0}{\cos^2\theta}\mathrm{d}\theta \\ &= \int_0^{\pi/2} -\frac{2\pi\beta_{\mathrm{CC}}\sigma}{d_0^4}\cos^3\theta\sin\theta\mathrm{d}\theta \\ &= -\frac{2\pi\beta_{\mathrm{CC}}\sigma}{4d_0^4}(-\cos^4\theta)\Big|_0^{\pi/2} \\ &= -\frac{\pi\beta_{\mathrm{CC}}\sigma}{2d_0^4}\end{aligned} \tag{2}$$

   Since the density on the first graphene layer is also σ, and the surface tension is half the absolute value of adhesion energy, we get the surface energy of graphene as:

$$\gamma_{\mathrm{G1}} = -\frac{\phi_{\mathrm{C-SLG}}\sigma}{2} = \frac{\pi\sigma^2\beta_{\mathrm{CC}}}{4d_0^4} \tag{3}$$

2. Adhesion energy of graphene stacks

   Let's first calculate the total potential of system (m, n). Since in part 1, we have seen that the interaction between 2 sheets $\phi(1,1) \propto -d_0^{-4}$, the **total potential** is actually a summation between stacked layers separated by δ, hence

$$\phi(m,n) = -\frac{\pi\sigma^2\beta_{\mathrm{CC}}}{2}\underbrace{\sum_{j=0}^{m-1}}_{\mathrm{A}}\underbrace{\sum_{i=0}^{n-1}}_{\mathrm{B}}\frac{1}{(\delta + d_0(i+j))^4} \tag{4}$$

The work of adhesion $\Delta W_{\mathrm{AB}}(m,n)$ is just $-\phi(m,n)$:

$$\Delta W_{\mathrm{AB}}(m,n) = \frac{\pi\sigma^2\beta_{\mathrm{CC}}}{2} \sum_{j=0}^{m-1} \sum_{i=0}^{n-1} \frac{1}{(\delta + d_0(i+j))^4} \tag{5}$$

As can be seen from the equation, regardless of the layer numbers m and n, the work of adhesion always has power law of d_0^{-4}.

3. Surface tension of graphite

   With $\delta = d_0$ one can further simplify the previous formula by factoring out the distance d_0. The surface tension of graphite is thus $\gamma_{\mathrm{G}\infty} = \frac{1}{2}\Delta W_{\mathrm{AB}}(\infty,\infty)$:

$$\gamma_{\mathrm{G}\infty} = \frac{\pi\sigma^2\beta_{\mathrm{CC}}}{4d_0^4} \sum_{j=0}^{\infty} \sum_{i=1}^{\infty} \frac{1}{(i+j)^4} \approx 1.202\gamma_{\mathrm{G}1} \tag{6}$$

   which indicates that the surface tension of graphite is only sightly larger than single layer graphene, due to the short-range feature of the vdW interaction.

4. Estimation of β_{CC}

   Using Eq. 6, we get a value of 1.24×10^{-78} J·m^6. or equivalently 7.75 eV·Å^6, for β_{CC}.

5. Energy to cleave n-layer graphene sheets

   The energy required to cleave an n-layer graphene sheet corresponds to the work of adhesion between the n-layer sheet and graphite. Thus, we can simply apply Eq. 5 by setting m to a large number (e. g. 1000) to emulate graphene and n to the sheet's number of layers.

img/hw1_q1_5.pdf

Figure 1: Work normalized by area ΔW_{AB} required to cleave an n-layer graphene sheet from graphite as a function of n.