Cohesive Energy and Line Energy of Graphene

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Graphical Abstract
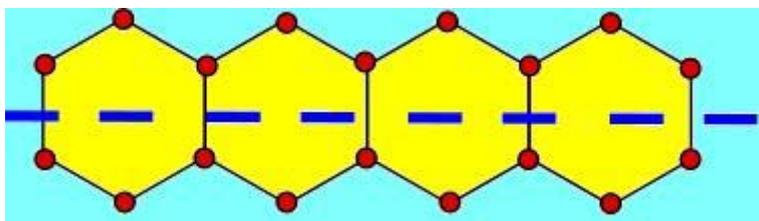
The rupture of σ-bonds in graphene
and calculation of cohesive energy

Cohesive Energy and Line Energy of Graphene

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ABSTRACT

A theory presented enables calculating the cohesive energy and line energy (the work of formation of the unit border line length) of graphene from the first principles, which also yields estimating the line tension of graphene at zero temperature. Contributions from chemical bonds and dispersion forces have been estimated separately to give the summary value 16.7×10^{-10} J m^{-1} for the line energy of graphene. The significance of line energy and line tension for the nanotube formation is discussed.

KEYWORDS

Graphene, cohesive energy, line energy, line tension, dispersion (van der Waals) forces.

In spite of the popularity of graphene, not all its properties have been discussed in the literature. This article acquaints with the line energy of graphene and exhibits how to calculate it. For three-dimensional crystalline solids possessing both faces and edges, line energy is typically of secondary importance as compared with surface energy. By contrast, for such a two-dimensional structure as graphene, line energy is a physical quantity of the same significance as surface energy for three-dimensional bodies. Surface energy (as an excess energy at the surface after formation a new surface) is simply deduced from cohesive energy in a condensed medium as half (because two surfaces appear after the rupture of a body) of cohesive energy per unit surface area. Similarly, turning to graphene, we can define line energy as half of the work of rupture of a graphene sheet along a straight line per unit line length in a vacuum at zero temperature. This is the same as half of cohesive energy between two half-planes of a graphene sheet per unit line length. The rupture of a two-dimensional solid in two parts includes two stages: the rupture of chemical bonds (if any) between adjacent particles along the rupture line and disjoining the two solid parts against long-ranged attractive forces beyond the limit of their action. If n is the number of chemical bonds per unit line length and u_b is the bond energy (the work needed for rupturing a bond), cohesive energy u_c and line energy ε are defined as

$$u_c = nu_b + u_c^1 \tag{1}$$

$$\varepsilon = (nu_b + u_c^1)/2 \tag{2}$$

where u_c^1 is the line cohesive energy (i.e. cohesive energy per unit line length) of long-ranged forces. Below, we consider the chemical bond and long-range contributions separately.

We begin with the contribution of chemical bonds, which is evident to be determined by the number of bonds ruptured per unit length of a rupture line. However, this number depends on the line direction within the graphene plane. This is exhibited in Fig. 1 where the net of graphene σ-bonds is depicted with the choice of three different directions. Lines 1, 2, and 3 are of the same length, but line 1 intersects 9 bonds, line 2 intersects 10 bonds, and line 3 even 17 bonds. Corre-
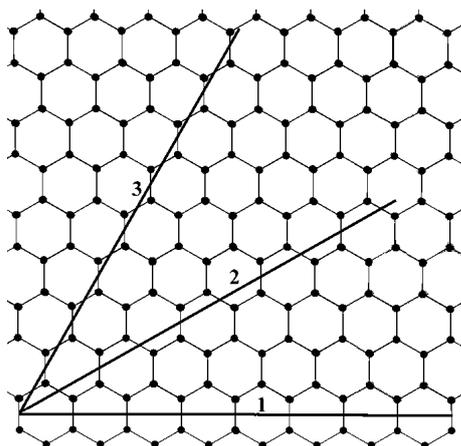
Fig. 1 Dependence of the chemical bond component of line energy on the line direction in the graphene plane: lines 1, 2, 3 of the same length intersect different numbers of chemical bonds.

spondingly, the chemical bond contribution to line energy will be largest for line 3. The direction corresponding to line 1 seems to be most favorable energetically and, if so, should be realized in nature. The fact that line 1 corresponds to the real graphene boundary has been recently confirmed by Z.-L. Li et al.[1] For the whole above reason, we choose the direction of line 1 for our calculations.

In the honeycomb lattice of graphene (Fig. 1), the hexagon side length (we denote it as *b*) is $b = 0.142$ nm. As it follows from the geometry of Fig. 1, the distance between σ-bonds in the direction chosen is 0.246 nm. Hence, the number of σ-bonds per unit length is $n \approx 4.065 \times 10^9 \, \mathrm{m}^{-1}$. Of course, the rupture of σ-bonds (which are simply more convenient for depicting in drawings) is always accompanied by rupturing π-bonds with accounting for the delocalization energy. So we need the total bond energy for our calculations. To find the bond energy u_b, we note that, since the σ-bond length for graphene (0.142 nm) and for benzene (0.140 nm) is almost the same, we can simply use the well-known total bond energy of benzene $u_b = 490$ kJ mole$^{-1} = 8.135 \times 10^{-19}$ J for estimating the cohesive energy of graphene. Taking these numerical values for *n* and u_b, we obtain the chemical bond contribution to cohesive energy

$$nu_b = 33.069 \times 10^{-10} \, \mathrm{J \, m}^{-1}.$$

It remains to calculate the contribution of long-ranged forces. In the case of graphene, the long-ranged forces are dispersion forces. Their significance for graphene systems have been multiply discussed in the literature,[2–5] but estimations made concerned the interaction of parallel layers of gra-

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phene and substrates. By contrast, we consider two in-plane parts of a single graphene layer. We perform calculations using the Lennard-Jones pair potential[6–8]

$$\varnothing(R) = 4\varepsilon_{CC}\left[\left(\frac{\sigma_{CC}}{R}\right)^{12} - \left(\frac{\sigma_{CC}}{R}\right)^{6}\right], \quad \varepsilon_{CC} = 0.4396 \text{ kJ mol}^{-1}, \quad \sigma_{CC} = 0.3851 \text{ nm} \tag{3}$$

where R is the distance between two interacting carbon atoms. Summing up over all interacting pairs can be replaced by integration, and, assuming the matter density to be constant, one proceeds to a continuum model as an approximation for a real solid where matter is distributed discretely. The possibility and validity of such approximation was lively discussed when formulating a theory of graphite,[9–11] and Brennan was first to state that that the interaction between graphite layers should be estimated only by discrete summation, whereas each layer taken separately (i.e. graphene) can be considered as a continuum. We follow this approach and this approximation.
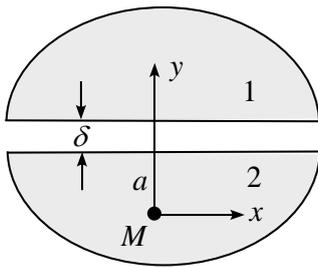
Fig. 2 The interaction between a single molecule at point M in the half-plane 2 and the half-plane 1 as a whole; δ is a minimum possible distance for dispersion forces taken as the initial gap between the two half-planes and a is the distance from point M to the gap.

Using the Lennard-Jones potential, the energy U_M of interaction between a single molecule located at point M at a distance a from the edge of half-plane 2 (Fig. 2) and half-plane 1 as a whole is

$$U_M = -4\varepsilon_{CC}\rho\int_{a+\delta}^{\infty} dy \int_{-\infty}^{\infty}\left[\frac{\sigma_{CC}^{12}}{(x^2+y^2)^6} - \frac{\sigma_{CC}^6}{(x^2+y^2)^3}\right]dx = \frac{3\pi\rho\varepsilon_{CC}\sigma_{CC}^6}{8(a+\delta)^4}\left[\frac{21\sigma_{CC}^6}{80(a+\delta)^6} - 1\right] \tag{4}$$

where ρ is the number of carbon atoms per unit area; x and y are Cartesian coordinates with the origin at point M, x being directed along and y across the gap between the half-planes. Computing the whole interaction energy for the two half-planes per unit gap length (the layer of unit length and thickness da of half-plane 1 containing ρda molecules), we obtain

$$U = \int_0^{\infty} U_M \rho da = \frac{\pi\varepsilon_{CC}\sigma_{CC}^6\rho^2}{8}\left[\frac{7\sigma^6}{80\delta^9} - \frac{1}{\delta^3}\right]. \tag{5}$$

This is not a final result because the length δ is not yet determined. Indeed, we cannot set $\delta = 0.142$ nm since this quantity refers to σ-bonds and not to dispersion forces. Moreover, this length falls into the repulsive region for dispersion forces, so that, just after the rupture of σ-bonds, the system instantaneously passes (with increasing δ) to a stable state corresponding to dispersion forces. This stable state is obvious to correspond to a minimum of U, and the δ-value needed is found from the condition $dU/d\delta = 0.$ This yields

$$\frac{\delta}{\sigma_{\mathrm{CC}}} = \left(\frac{21}{80}\right)^{1/6} \approx 0.800181, \quad \delta \approx 0.308 \text{ nm}. \tag{6}$$

Substituting this result in Eqn (5), we arrive at the expression for the interaction energy

$$U = -\frac{\pi}{12}\left(\frac{80}{21}\right)^{1/2} \varepsilon_{\mathrm{CC}} \sigma_{\mathrm{CC}}^3 \rho^2 . \tag{7}$$

Cohesive energy per unit line length only differs in sign from Eqn (7), so we have

$$u_{\mathrm{c}}^{\mathrm{l}} = \frac{\pi}{12}\left(\frac{80}{21}\right)^{1/2} \varepsilon_{\mathrm{CC}} \sigma_{\mathrm{CC}}^3 \rho^2 \approx 0.511\,\varepsilon_{\mathrm{CC}} \sigma_{\mathrm{CC}}^3 \rho^2 . \tag{8}$$

With the above numerical values $\varepsilon_{\mathrm{CC}} \approx 72.99 \times 10^{-23}$ J, $\sigma_{\mathrm{CC}} = 3.851 \times 10^{-10}$ m, $\rho = 38.177 \times 10^{18}$ m^{-2}, this yields $u_{\mathrm{c}}^{\mathrm{l}} = 3.1 \times 10^{-11}$ J m^{-1}, which makes about only 1% for the contribution of dispersion forces as compared with the contribution of chemical bonds. The total line cohesive energy of graphene looks numerically as 33.4×10^{-10} J m^{-1}. Correspondingly, we have for the line energy of graphene analytically

$$\varepsilon = \frac{1}{2}nu_{\mathrm{b}} + \frac{\pi}{24}\left(\frac{80}{21}\right)^{1/2} \varepsilon_{\mathrm{CC}} \sigma_{\mathrm{CC}}^3 \rho^2 \tag{9}$$

and numerically $\varepsilon = 16.7 \times 10^{-10}$ J m^{-1}.

To comment this result, we have, first of all, to caution a reader against confusing two important notions: line energy ε and line tension κ (line free energy). Since energy and free energy become equal at zero temperature, we can say that we have also calculated the line tension of graphene at zero temperature (when $\varepsilon = \kappa$). The temperature dependence of line tension is mainly induced by

entropy, and this effect is significant with respect to the contribution of long-ranged forces. How-

ever, in our case, the contribution of long-ranged forces turns to be negligible as compared with

chemical bonds, and this allows us to hope that the effect of chemical bonds is also great with re-

spect to the influence of temperature. In other words, we can hope that the result obtained for line

energy could be also valid for the line tension of graphene within a more or less wide temperature

range.

The practical significance of line energy and line tension is evinced, for example, in the process

of transition graphene sheet/nanotube. At the formation of a nanotube out of a graphene sheet, two

sheet edges disappear, which yields energy gain (per unit nanotube length) 2ε under adiabatic and

2κ under isothermal conditions for the process. Taking into account that the bending stiffness of

graphene is very small,[12] we can say that both line energy and line tension practically play the role

of a driving force for the nanotube formation. At the same time, chemisorption and, largely, chemi-

cal doping of the graphene sheet edges[13] are direct methods of influencing line energy and line ten-

sion and can lead to a significant change or even to reversal of the situation when nanotubes roll out

into a sheet.[14] Remembering the said above about the direction dependence of line energy, we can

add that the choice of direction at cutting a graphene sheet, is also a method of influencing line en-

ergy and line tension.

In conclusion, let us discuss in short some points not taken into account in our calculations. The

first is a the possible role of the zero vibrational energy. This quantity refers to each carbon atom at

zero temperature and is defined as $h\nu/2$ where h is the Planck constant and ν is vibrational fre-

quency. This factor was not taken into account in our theory, but it does exist because the rupture of

a chemical bond inevitably changes the oscillation frequency. The problem of the influence of

boundary condition on the zero energy has already been brought up in the modern physics.[15] How-

ever, in the absence of numerical results, we can use only general arguments. Except the case of he-

lium, the zero energy is generally accepted to be considerably smaller than the energy of intera-

tomic interaction because the zero energy does not prevent solidification. This is also valid for mo-

lecular crystals when interatomic interactions are reduced to dispersion forces, and this means that the energy of dispersion forces overcounts the zero energy. In addition, not the zero energy itself but only its increment is to be compared with the interatomic interaction energy. Thus, speaking about the influence of the zero energy on the line energy value, we can expect a correction smaller than that estimated for van der Waals forces.

The second point that was not touched upon in our calculations is the process of relaxation of a graphene sheet after its rupture. The rupture of chemical bonds leads to a small shift of the boundary atoms location (boundary reconstruction) and, therefore, to a change in line energy. Generally, the degree of boundary reconstruction of matter depends on the matter compressibility. The standard procedure of estimating surface or line energy as halve of cohesive energy implies the relaxation stage to be inessential. Strictly speaking, this corresponds to the case of a rigid body. So we can say that we have calculated the chemical bonds and dispersion forces contributions to the line energy of graphene within the model of a rigid two-dimensional solid. Proceeding to real graphene needs a certain relaxation correction. A priori, a relaxation correction for graphene should be smaller than for three-dimensional solids for two reasons. First, graphene is the most rigid among all solids, and, as was already mentioned, increasing rigidity lowers the effect of relaxation. Second, graphene is a two-dimensional solid. The boundary force field is much weaker for two-dimensional solids as compared with three-dimensional solids of the same nature, and this should lead to lowering the boundary relaxation effect in two-dimensional bodies. Indeed, *ab initio* quantum mechanical calculations of the boundary relaxation for graphene sheets[16] yielded only small effects for symmetrical sheets of hexagonal symmetry. At a finite temperature, rectangular sheets exhibited some boundary reconstrucrion only at the sheet corners and practically no effect for a smooth boundary. Especially noticeable effect was attained for sheets of irregular shape, with buckling at the edge, which means deviations from the two-dimensional structure (this can be related to puckering aromatic rings in the energy-gradient field[17]). It is hard to say what was the relaxation effect for the graphene line energy in the latter case. However, we dealt with an infinite rectilinear graphene

boundary with no corners and at zero temperature to say that the unrelaxed line energy calculated above practically coincides with the relaxed one.

Acknowledgements

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