Thermodynamics of graphene

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Abstract

The 21st century has brought a lot of new results related to graphene. Apparently, graphene has been characterized from all points of view except surface science and, especially, surface thermodynamics. This report aims to close this gap. Since graphene is the first real two-dimensional solid, a general formulation of the thermodynamics of two-dimensional solid bodies is given. The two-dimensional chemical potential tensor coupled with stress tensor is introduced, and fundamental equations are derived for energy, free energy, grand thermodynamic potential (in the classical and hybrid forms), enthalpy, and Gibbs energy. The fundamentals of linear boundary phenomena are formulated with explaining the concept of a dividing line, the mechanical and thermodynamic line tensions, line energy and other linear properties with necessary thermodynamic equations. The one-dimensional analogs of the Gibbs adsorption equation and Shuttleworth–Herring relation are presented. The general thermodynamic relationships are illustrated with calculations based on molecular theory. To make the reader sensible of the harmony of chemical and van der Waals forces in graphene, the remake of the classical graphite theory is presented with additional variable combinations of graphene sheets. The calculation of the line energy of graphene is exhibited including contributions both from chemical bonds and van der Waals forces (expectedly, the latter are considerably smaller than the former). The problem of graphene holes originating from migrating vacancies is discussed on the basis of the Gibbs–Curie principle. An important aspect of line tension is the planar sheet/nanotube transition where line tension acts as a driving force. Using the bending stiffness of graphene, the possible radius range is estimated for achiral (zigzag and armchair) nanotubes.
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1. Introduction. Graphene: a two-dimensional solid in the three-dimensional space

Graphene is a monatomic allotropic modification of carbon. As an element of the graphite structure, graphene was under investigation since 1916 [1], and its first theory [2] was formulated in 1947 to explain the electronic properties of graphite. Attempts to exfoliate graphene from graphite began since 1990 while graphene had been considered theoretically as a self-sufficient object for decades (the term "graphene" arose in 1987 [3]). Experimentally, graphene was separated from graphite only in 2004 [4] to become one of the most famous substances in the history of science. This fame originates from a number of unique quantum, electrophysical, thermophysical, optical, and mechanical properties of graphene. The turn of speech "the most" is often used when characterizing graphene, and a vast literature has been devoted to this subject already including some monographs (e.g., [5]). Nevertheless, there is a direction in this ocean of literature that looks rather poor. This is the characterization of graphene from the point of view of surface science and, especially, of boundary thermodynamics. The goal of this paper is closing this gap. However, to elaborate the boundary thermodynamics of graphene, we have, first of all, to choose a method of consideration based on graphene properties.

Graphene is the thinnest and the most light-weight of known materials. Graphene is made out of carbon atoms tied, by σ- and π-bonds, in a honeycomb lattice. Fig. 1 shows the mutual positions of atoms and σ-bonds between them (of course, the depiction is purely symbolic; using one line does not mean a single C–C bond). The equilibrium length of the chemical bond between two adjacent atoms in graphene (we designate it as b) is $b = 0.142$ nm [6]. From this value and accounting for the hexagonal symmetry of the lattice, it is easy to calculate the surface concentration ρ (the number of atoms per unit area) as follows. If b is the hexagon side, the hexagon area is $(3\sqrt{3}/2)b^2$, and the number of hexagons per unit area

is $2/3\sqrt{3}b^2$. Each hexagon includes six carbon atoms, but each atom simultaneously belongs to three hexagons so that $\rho = 4/3$ $\sqrt{3}b^2 \approx 38.177$ nm^{-2}. With the carbon atomic mass 12.0107 and Avogadro's constant 6.022×10^{23}, this yields the surface density of graphene about 76.143×10^{-5} g m^{-2}. That means that 1 g of a graphene film possesses the area of 1313 m^2, which is enough to cover almost two football fields. As a majority of results of quantum-chemical estimations, the above ρ-value refers to zero temperature, and one can expect two-dimensional expansion of graphene with heightening temperature. Indeed, the molecular dynamics simulation, under the condition of suppressing out-of-plane fluctuations, yields the two-dimensional coefficient of thermal expansion $\alpha^{2D} = 5.51 \times 10^{-6}$K^{-1}, which remains constant up to 1000 K [7]. However, the real temperature behavior turns to be more complex. At heightening temperature, out-of-plane thermal fluctuations cause rippling the graphene sheet with its two-dimensional contraction, which corresponds to a negative value of α^{2D}.
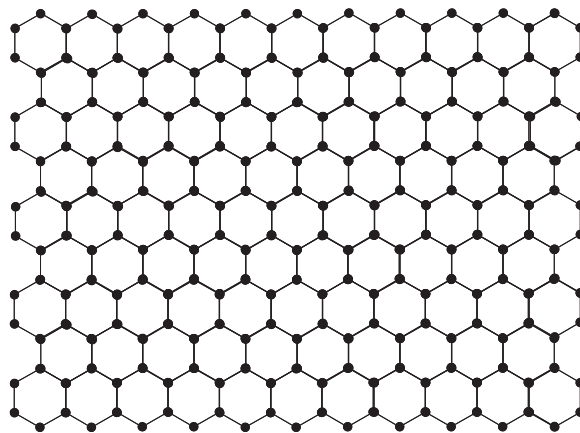

Fig. 1. The honeycomb lattice of graphene. Lines connecting carbon atoms symbolize real (not single) chemical bonds. The zigzag and armchair boundaries are shown as horizontal and vertical edges of a rectangular graphene sheet, respectively.