Bending vibrations of free and microdroplet-loaded graphene in the framework of the molecular dynamics method

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Abstract. Molecular dynamic (MD) modeling revealed that takes place swing up of transverse vibrations of graphene atoms with their transition to bending vibrations of membrane type. The amplitudes of such oscillations can reach large values, which considerably exceed the interatomic distances already for samples of micron sizes and amount to $10^{-2}$ from the length of the sample. The results of MD simulation were compared with the characteristic vibrational frequencies of graphene in the approximation of the tensioned membrane. The behavior of the graphene membrane during it loading with a liquid metal microdroplet has been considered also. Contact angles and relative stretching of the membrane outside and under the drop allow us to calculate the surface tension of the drop.

1. Introduction
Currently, great progress has been made in growing large graphene sheets [1]. At the same time, linear dimensions with respect to structurally perfect regions can reach hundreds of microns. This made it possible to use graphene as a material for a new type of terahertz oscillators [2]. We carried out molecular dynamic (MD) simulation of oscillations of large graphene clusters in order to study their stability with respect to large transverse amplitudes. The simulation was performed using the LAMMPS (large-scale atomic/molecular massively parallel simulator) program with applying Tersoff [3] and LCBOP [4] many-body potentials.

2. Graphene sheet vibrational dynamics
During the simulation, the system maintained a constant temperature using the Nose–Hoover thermostat [5]. The construction of dispersion curves according to the results of molecular dynamics simulation was performed using the method proposed by Kong Li et al [6]. Thus obtained dispersion curves are shown in figure 1.

The amplitude of thermal vibrations of graphene atoms can be found on the basis of the dispersion curves and the ratio

$$\langle u^2 \rangle = \frac{h}{2Nm} \sum_{q, \lambda} \varepsilon^*_{\alpha}(q, \lambda)\varepsilon_{\alpha}(q, \lambda) \coth \left( \frac{\hbar\omega_{\lambda}(q)}{2k_B T} \right),$$

(1)
Figure 1. Dispersion curves for graphene: solid line—Tersoff potential; dashed line—LCBOP; squares—experimental data.

Table 1. Comparison of elastic constants for graphene obtained by the MD method using the LCBOP potential with theoretical ab initio calculation [8] and experimental data for graphite.

| Elastic constants (N/m) | $C_{11}^{(2D)}$ | $C_{12}^{(2D)}$ | $C_{44}^{(2D)}$ | $C_{66}^{(2D)}$ |
|-------------------------|-----------------|-----------------|-----------------|-----------------|
| Simulation              | 330.64          | 73.36           | 0.02            | 128.64          |
| Theory [8]              | 358             | 60.4            | —               | 129             |
| Experiment [7]          | 355(5)          | 60.7(7)         | 1.34(1)         | 146(7)          |

where $m$ is mass of the carbon atom; $T$ is the temperature of the crystal; $\omega^2(q)$ and $\varepsilon_{\alpha}(q, \lambda)$ are the eigenvalues and eigenvectors of the dynamic matrix of the crystal $D_{ka,k'\beta}$:

$$\omega^2(q)\varepsilon_{\alpha}(q) = \sum_{k',\beta} D_{ka,k'\beta}(q)\varepsilon_{k'\beta}(q),$$

where the indices $\alpha, \beta$ correspond to the Cartesian projections of the vectors; $k$ and $k' = 1, 2, \ldots$ enumerate the basic carbon atoms inside the unit cell. In figure 2 shows the calculation of the amplitudes of thermal vibrations of graphene atoms in the harmonic approximation, found by relation (1).

As a result, we obtained that the amplitudes of transverse oscillations of atoms vary from 0.06 to 0.23 Å, with an increase in temperature from 300 to 2000 K.

For the transition from molecular dynamic calculations to the continuous limit describing by the theory of elasticity, we found elastic constants for graphene using the LAMMPS program (table 1), where we made the comparison with experimental data [7] for graphite using the relation $C_{ij}^{(2D)} = C_{ij}^{(3D)}h_1$, $h_1 = 3.35$ Å, and include ab initio theoretical calculations [8].

With the help of the LAMMPS program, we carried out MD simulation of the vibrational dynamics of graphene lattice containing 1600 carbon atoms with periodic boundary conditions with zero atoms shift in vertical direction. During the simulation, the temperature rose from
Figure 2. Results of calculating the temperature dependence of the root mean square (RMS) displacement of carbon atoms in the graphene lattice in the harmonic approximation: 1—the dispersion relation (1) is used; 2 and 3—the dispersion curve obtained by the MD method using the LCBOP and the Tersoff potentials, respectively.

Figure 3. Bending vibrations of the surface of a graphene cluster containing 1600 carbon atoms at the time $t = 0.5$ ps.

Bending vibrations of the surface of a graphene cluster containing 1600 carbon atoms at the time $t = 0.5$ ps.

300 to 2000 K using the Nose–Hoover thermostat [5]. Simulation has shown that, along with small displacements of neighboring carbon atoms, bending vibrations of the whole plane of the graphene as a whole occur. The amplitudes of such oscillations can exceed the interatomic distances in the graphene lattice and make up to $10^{-2}$ of the sample length. One of the results of such simulation is shown in figure 3.

As the temperature rises to 2000 K, the amplitude of these oscillations reaches 0.5 Å (figure 4), which is two times higher than the results of calculations using formula (1), based on the harmonic approximation.

The large transverse atomic displacements amplitude shown in figure 3 corresponds to bending vibrations of the entire graphene surface. The buildup of bending graphene vibrations to anomalously large amplitudes, found in experiment [2].

Experimentally the graphene plane bending vibrations with anomalously large amplitudes were first observed in [2]. A graphene sheet with order a one micron size experienced bending vibrations with amplitudes up to 5 nm under the thermal and electrostatic effects from the scanning tunneling microscope (STM) needle. Figure 5 shows the time dependence of the transverse coordinates of a separately selected carbon atom participating in bending vibrations of the graphene plane at a temperature $T = 300$ K.
Figure 4. The amplitude of transverse displacements of the graphene surface depending on the temperature, obtained by the MD method using the Tersoff potential.

Figure 5. The transverse coordinates of one of the carbon atoms in the bending vibrations process of the graphene plane.

To determine the spectrum of the characteristic frequencies of transverse vibrations of carbon atoms in the case when there are bending vibrations of the graphene plane, we use the discrete Fourier transform for the time dependence of the transverse coordinate $z(t)$ shown in figure 5. Figure 6 shows the Fourier modulus components corresponding to the dominant overtones of bending vibrations.
Figure 6. Absolute values of Fourier components for the main overtones of bending vibrations of the graphene plane, obtained by using the Tersoff potential.

3. The relationship between MD modeling of graphene sheet vibrations with bending oscillations of a thin elastic plate

It is of interest to compare the result of the MD simulation of the final graphene cluster with the result of solving the corresponding problem in the continuous limit using the elastic constants from Table 1. To this aim, we simulated the oscillations of graphene sheet with fixation of carbon atoms along its perimeter. In this case, the oscillations will represent a superposition of standing waves. The graphene sheet for calculation was formed from 3600 carbon atoms arranged in rectangular with sides $a = 78 \text{ Å}$, $b = 128 \text{ Å}$.

The oscillation equation of a graphene membrane has the form [9]

$$D \nabla^4 \zeta(x, y) - \omega^2 \rho_s h_g \zeta(x, y) = \left( N_x \frac{\partial^2 \zeta(x, y)}{\partial x^2} + N_y \frac{\partial^2 \zeta(x, y)}{\partial y^2} \right),$$

(3)

where $\rho_s = 2.27 \times 10^{-6} \text{ kg/m}^2$ is the surface mass density for graphene; $D$ is the bending stiffness of the plate

$$D = \frac{E h_g^3}{12(1 - \mu^2)},$$

(4)

where $E$ is the Young’s modulus and $\mu$ is the Poisson ratio [10]; $h_g = 0.87 \text{ Å}$ is equivalent thickness for graphene [9]; $N_x$ and $N_y$ are initial longitudinal stresses $N_{x,y} = E h_g \varepsilon_{x,y}$, $\varepsilon_x$ and $\varepsilon_y$ are strains in $x$ and $y$ directions respectively. To find the frequencies by formula (3), we used the values of the constant $E h_g = 245 \text{ N/m}$ and $\mu = 0.41$ from [9].

For the oscillation frequencies of a rectangular membrane with sides $a$ and $b$ fixed at the edges takes place the relation

$$\omega_{mn} = \pi^2 \left( \frac{m^2}{a^2} + \frac{n^2}{b^2} \right) \sqrt{\frac{D}{\rho_s h_g}} \sqrt{1 + \frac{1}{\pi^2 D} \frac{N_x \left( \frac{m}{a} \right)^2 + N_y \left( \frac{n}{b} \right)^2}{\left( \frac{m}{a} \right)^2 + \left( \frac{n}{b} \right)^2}},$$

(5)

where $m$ and $n$ are harmonics defined by integer numbers.
4. Vibrations of graphene sheet loaded by metallic droplet

We have carried out molecular dynamics simulation of system graphene sheet–metal drop upon its surface. The graphene sheet and piece of iron were spatially separated each other at initial moment. The system was heated above iron melting temperature. During this process, graphene sheet and liquid iron droplet come together due to atomic attraction and formed the oscillating system (figure 8). To describe the interaction between iron-iron and carbon-iron systems we used the MEAM potential [12].

The vibrational spectrum of a graphene sheet loaded with an iron drop containing 150 atoms was found as described above and is shown in figure 9.

To explain the absence of high frequencies in the spectrum of graphene loaded by a metal droplet (see figure 9), we pass from the approximation of the elastic plate to the approximation of the loaded membrane. This means the possibility of neglecting the bending stiffness $D$ in equation (3). Significant bending of the graphene plane takes place close to the base of the
Figure 8. Scheme of tension forces acting on the drop edge at the point of contact between the three phases.

Figure 9. The absolute values of the Fourier components of the main overtones of the bending vibrations of the graphene plane loaded with an iron microdrop are obtained using the MEAM potential.

droplet, however, carbon atoms turn out to be bound to iron atoms and do not contribute to the change in elastic energy, which is causing by both stretching and bending of graphene. However, starting from a certain distance from the droplet center $r_1$, the graphene tension $N_x$, $N_y$ becomes significantly less than near the droplet and become independent from the position. In this case, the bending energy of a graphene can be neglected for surface vibrations with small amplitudes. This corresponds to the limit $D \to 0$ in formula (3), we have the following frequency spectrum

$$
\nu_{mn} = \nu_0 \sqrt{n^2 \frac{N_y}{N_x} + \frac{a^2 m^2}{b^2}},
$$

(6)
where
\[ \nu_0 = \frac{1}{2a} \sqrt{\frac{N_x}{\rho_s}}. \]  
(7)

We also use the approximation that \( N_x = N_y = T \), and comparing the experimentally obtained frequency \( \nu = 0.016 \) THz of the mode \( m = 1, n = 1 \), we obtain \( T = 0.038 \) N/m. The vertical displacements satisfy the equation for a membrane with tension \( T \):

\[ \Delta \zeta + \frac{\omega^2 \rho_s}{T} \zeta = 0. \]  
(8)

Considering the circular part of the graphene surface under a drop of radius \( r_1 \) defined above, we write the equation for the vertical displacements of the drop

\[ 2\pi r_1 T \left( \frac{\partial \zeta}{\partial r} \right)_{r=r_1} = -\omega^2 M \zeta. \]  
(9)

Such a problem was considered for a circular membrane loaded with a disk in [13]. Relation (9) can be considered as boundary conditions for equation (8). The second boundary condition is the vanishing of the vertical displacement \( \zeta \) at the outer boundary of the membrane. It allows one to obtain the frequency spectrum of loaded membrane. One can also get a rough estimate for the frequency of droplet vertical displacement by assuming that

\[ \left( \frac{\partial \zeta}{\partial r} \right)_{r=r_1} \approx \frac{2\zeta}{r_1}, \]  
(10)

it gives

\[ \nu \approx \sqrt{\frac{T}{\pi M}} = 0.029 \text{ THz}. \]  
(11)

This frequency also appears in a computer experiment as the third peak in the spectrum in figure 9.

5. Determining the surface tension of metal droplets using their planting on a graphene sheet

By measuring the membrane tension close to the droplet and the wetting contact angles shown in figure 8, one can determine it surface tension writing the equilibrium conditions on the droplet boundary with graphene surface (Young equation)

\[ \sigma \cos \theta + \tau_2 \cos \theta_{12} = \tau_1, \]  
(12)

where \( \tau_1 \) and \( \tau_2 \) are the tension of the graphene sheet outside and under the drop, \( \sigma \) is the surface tension of the drop, indexes 1 and 2 correspond to graphene and droplet respectively. In our case, the graphene lattice extensions outside and under the drop \( \varepsilon = \delta x_1/\delta x_2 \) with good accuracy is equal to the tensions ratios \( \tau_1/\tau_2 \). As a result, the Young equation gives

\[ \sigma = \frac{\tau_1}{\cos \theta} \left( 1 - \frac{1}{\varepsilon \cos \theta_{12}} \right). \]  
(13)

For the case when iron droplet heated up to \( T = 1913 \) K the MD simulation gives angles \( \theta = 60^\circ \), \( \theta_{12} = 3^\circ \) and \( \varepsilon = 0.11 \). We assume that \( \tau_1 = Eth_{g} = 245 \) N/m and get that iron surface tension \( \sigma = 1.18 \) J/m\(^2\). At the same temperature the macroscopic iron sample has the surface tension \( \sigma_0 = 1.85 \) J/m\(^2\) [14]. A two-fold discrepancy in the result is apparently due to the incorrectness of the potential we used to describe the interaction between carbon and iron atoms.
6. Conclusions

MD simulation shows that for graphene starting from a certain temperature, bending vibrations with large amplitudes take place. The frequencies of these oscillations are well described in the approximation of a thin elastic plate with elastic constants getting from MD simulation.

Oscillations of graphene loaded by a metal drop, which partially wetting it, binding carbon atoms under it, is well described in the approximation of a loaded membrane. An approach is proposed for determining the surface tension of liquid metal droplets by measuring the contact angles and deformation parameters obtained by MD simulation of metal droplet heating on the graphene surface.

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