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Research paper

# Car–Parrinello molecular dynamics study of the melting behaviors of $n$-atom ($n = 6, 10$) graphene quantum dots

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ABSTRACT

First-principles molecular dynamics has been applied to inquire into the melting behaviors of $n$-atom ($n = 6, 10$) graphene quantum dots ($GQD_6$ and zigzag $GQD_{10}$) within the temperature range of $T$ = 0–500 K. The temperature dependence of the geometry of each quantum dot is thoroughly evaluated via calculating the related shape deformation parameters and the eigenvalues of the quadrupole tensors. Examining the variations of some phase-transition indicators such as root-mean-square bond length fluctuations and mean square displacements broadly proposes the value of $T_m = 70$ K for the melting point of $GQD_6$ while a continuous, two-stage phase transition has been concluded for zigzag $GQD_{10}$.



## 1. Introduction

Over the past decade, much studies have been focused on different, intriguing properties of two-dimensional nanomaterials [1–8], particularly on graphene because of spread spectrum of its applications in many diverse areas such as nanoelectronics, optoelectronics, bioelectronics, etc. [9], leading to rapidly-accumulating literature in the realm of low-dimensional systems as well. It has demonstrated excellent electronic, mechanical and optical characteristics including ultrahigh mobility, outstanding flexibility and stability, excellent thermal conductivity ($5000\ Wm^{-1}\ K^{-1}$), high transmittance within the visible infrared region, exceptional room-temperature electron mobility ($2.5 \times 10^5\ cm^2\ V^{-1}\ s^{-1}$), large specific surface area ($2630\ m^2\ g^{-1}$), a Young's modulus of about 1 TPa and intrinsic strength of 130 GPa [10–15]. Enjoying outstanding electrical conductivity, optical transparency, mechanical flexibility, and two-dimensionality has made it a promising candidate for transparent and conductive electrodes [16]. Unlike conventional metal electrodes, graphene has the advantage that its Fermi level, and therefore, its workfunction could be tailored by chemical doping or electrostatic gating [17,18], making it to be of great use in device applications such as high-efficiency chemically-doped solar cells and gate-controlled variable Schottky barrier devices [19,20]. It has also an optical absorption of about $\pi\alpha \approx 2.3\%$ in the infrared limit (with $\alpha$ the fine-structure constant), complete impermeability to any gases, and the ability to sustain extremely high densities of electric current (a million times larger than copper) [15]. It is a basic building block for graphitic materials of all dimensionalities, being wrapped into zero-dimensional fullerene or quantum dots, rolled into one-dimensional nanotubes, or stacked into three-dimensional graphite.

The technological drive for making electronic devices continuously smaller has some interesting consequences: it is now routinely possible to make small electron boxes in solid-state devices, containing an integer number of conduction electrons [21]. Such devices are usually operated as transistors via field-effect gates, called single-electron transistors. In semiconductor boxes, the number of trapped electrons could be reduced to zero, one, two, etc. Such semiconductor single-electron transistors are called quantum dots. Graphene quantum dots (GQDs) are zero-dimensional graphene nanoparticles with confined electrons in all the three spatial dimensions leading to quantization of their spectrum. They have excellent optical properties and biosecurity, exhibiting remarkable prospects in biomedical fields such as cell imaging and biosensors [22], also leading to state-of-the-art display technologies such as quantum dot light-emitting devices (QD-LED) [23].

In spite of the broad literature aforementioned, limited studies have been focused on GQDs in terms of thermodynamics. The thermodynamic properties of such systems could be of great importance particularly when they are tunnel-coupled to source and drain in transistors. Indeed, the need to meet the ever-increasing demand on making electronic devices much smaller in size–playing a vital role in many different areas such as nanotechnology and nanomedicine as well–could uncover the importance of such nanostructures. In the light of applying finite-temperature *ab initio* molecular dynamics computer simulations [24–27]–which has

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made significant contribution to much of our understanding of condensed-matter systems together with electronic-structure calculations based on density-functional theory (DFT) [28]–therefore, in the present work, the melting behaviors of $n$-atom ($n = 6, 10$) graphene quantum dots ($GQD_6$ and zigzag $GQD_{10}$) are going to be studied within the Car–Parrinello approach [29], allowing to sample thermal fluctuations by means of atomic trajectories generated with DFT forces [30].

## 2. Computational details

The density-functional molecular dynamics (DFMD) method introduced by Car and Parrinello has been applied to investigate the finite-temperature behaviors of $GQD_6$ and zigzag $GQD_{10}$ via adopting a self-consistent plane-wave pseudopotential approach [32] as implemented in Quantum ESPRESSO integrated suite [33]. The generalized gradient approximation [34] proposed by Perdew, Burke and Ernzerhof (PBE) [35] has been applied for the exchange and correlation functionals. Effects of the atomic core (non-valence electrons) have been described using a scalar-relativistic ultrasoft pseudopotential [36,37] generated by Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) pseudization method [38] with nonlinear core correction [39], while the valence shell is considered to be $2s2p$. The electron density is augmented through a Fourier interpolation scheme in real space [40]. For $GQD_6$ and zigzag $GQD_{10}$, respectively, the kinetic energy cut-offs of about 60 and 65 Rydberg (Ryd) for the wave functions, and 250 and 260 Ryd for the charge densities and the potentials have been found to be enough to reach energy convergence. Free cubic cells containing six atoms in a honeycomb array (Fig. 1(a)), and ten atoms in a graphene-like zigzag array (Fig. 1(b)) have been used under periodic boundary conditions with vacuum spaces of about 15 Å along the three spatial dimensions to decouple the weakest possible periodic interactions. Fixed-cell relaxations based on the Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimization method [41–43] have been applied on the atomic positions to find the relaxed ones in a way that the magnitude of each component of the total force on each atom drops to less than $7.35 \times 10^{-5}$ Ryd/Å. The forces in a Car–Parrinello molecular dynamics (CPMD) calculation are the partial derivative of the Kohn–Sham energy ($E^{KS}$) with respect to the nuclear positions ($\mathbf{R}_I$) and the Kohn–Sham orbitals ($\Phi_i$). The orbital forces are calculated as the action of the Kohn–Sham Hamiltonian ($H^{KS}$) on the orbitals:

$$F(\Phi_i) = -f_i H^{KS}\phi_i = -\frac{\delta E^{KS}}{\delta \phi_i^*}$$

with $\{f_i\}$ integer occupation numbers, whereas the forces associated to the nuclear degrees of freedom could be expressed as

$$\mathfrak{F}(\mathbf{R}_I) = -\frac{\partial E^{KS}}{\partial(\mathbf{R}_I)}$$

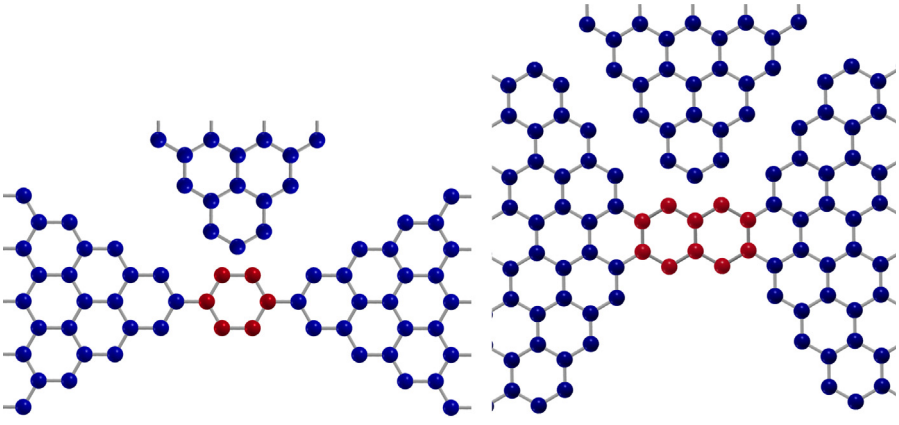
The corresponding Newtonian equations of motion for both the orbitals and nuclear positions could be obtained by the Car–Parrinello (CP) Lagrangian

$$\mathfrak{L}_{CP}\left[\mathbf{R}^N, \dot{\mathbf{R}}^N, \Phi_i, \dot{\Phi}_i\right] = \frac{1}{2}\sum_I M_I \dot{\mathbf{R}}_I^2 + \frac{1}{2}\sum_i \mu\langle\dot{\Phi}_i|\dot{\Phi}_i\rangle - \epsilon^{KS}\left[\Phi_i, \mathbf{R}^N\right]$$

with $\epsilon^{KS}$ the extended Kohn–Sham energy functional, and $M_I$ the ionic mass [44]. The fictitious electron mass (the inertia parameter assigned to the orbital degrees of freedom, $\mu$) in the CP Lagrangian, used to control the time evolution of the electronic degrees of freedom, is chosen to be 200 a.u. (200 times the mass of an electron) with mass cut-off of about 2.5 Ryd for the Fourier acceleration effective mass in order to prevent the quality of the simulations to be affected adversely and having minimized the electron drag effect. The nuclei evolve in time at a certain, instantaneous physical temperature $\propto \sum_I M_I \dot{\mathbf{R}}_I^2$. Although temperature is a collective effect and is mainly intelligible in dealing with macroscopic systems including large numbers of particles of the order of the Avogadro's number, the kinetic theory [45] providing a microscopic explanation of temperature based on the movements of the constituent particles enables DFMD simulations to apply temperature to few-particle systems through the equipartition theorem [46],

$$T = \frac{2\langle E\rangle}{3Nk_B}$$

with $N$ the number of constituent atoms and $k_B$ the Boltzmann constant. In the first CPMD simulations, respectively for $GQD_6$ and zigzag $GQD_{10}$, extended electronic minimizations of 480 and 725 femtoseconds (fs)–with time steps of about 0.19 and 1.45 fs to integrate the electronic and nuclear equations of motions–with fixed atoms and fixed cells are carried out in order to bring the electronic systems (electronic wave functions) on their ground states relative to the starting atomic configurations until the convergence of the kinetic energies associated to the fictitious electronic dynamics to a value less than $1 \times 10^{-7}$ Ryd, and the convergence of the total energies to those obtained from self-consistent-field calculations ($-70.831$ and $-118.530$ Ryd) are achieved. After having minimized the electrons, the canonical ($NVT$) CPMD simulations restarting with zero initial velocities are performed on nuclear degrees of freedom at different temperatures using the standard Verlet algorithm



(a) $GQD_6$ (b) zigzag $GQD_{10}$

**Fig. 1.** Schematics of hypothetical transistors based on (a) $GQD_6$ and (b) zigzag $GQD_{10}$, tunnel-coupled to source and drain–visualized by XCrySDen [31].