Modeling the destruction of realistic nanotube emitters: Relative role of charging and temperature

Savas Berber and David Tománek
Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824-2320, USA
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To discriminate between the effect of charge and temperature as the main cause of structural changes in nanotube-based field-electron emitters, we performed molecular dynamics simulations of charged single- and multiwall carbon nanotubes under realistic conditions. Our results indicate that cap-terminated nanotubes disintegrate abruptly under critical emission conditions. Disintegration, involving either desorption of cap fragments or a transformation into carbon chains and graphitic flakes, occurs prior to melting and is accelerated by Coulomb repulsion that destabilizes the charged tip.

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The use of carbon nanotubes[1,2] as field-electron emitters[3–5] is considered as very promising for a number of commercial applications, including field emission displays,[6] cathode-ray tubes,[7] x-ray sources,[8] sensors,[9] and electron sources for electron microscopes.[10,11] Apart from their high aspect ratio, which provides large field enhancement, the most important advantage of carbon nanotubes is their structural stability, thanks to the rigidity of the sp^2 bond.[2] One of the main limitations of conventional field emitters, consisting of sharp metal tips, lies in the shape instability of the tip exposed to the large electric fields used for field emission. Carbon nanotubes, on the contrary, should not change their shape, unless the applied field exceeds a critical value. Previous calculations have addressed field-electron emission from nanotubes,[12,13] but not the structural changes occurring beyond the stability limit. Key issues regarding the disintegration process, including the microscopic decay mechanism and the relative role of heat and Coulomb destabilization, have never been addressed. In view of the applications mentioned, it is important to establish the stability limit and decay mechanism by studying the structural evolution of carbon nanotube tips in large fields.

Here, we present a theoretical study of structural changes in carbon nanotubes during electron emission in extremely large applied fields beyond ≈ 10 V/μm. Molecular dynamics (MD) simulations of nanotubes subject to large fields and high temperatures suggest that disintegration occurs prior to the onset of melting and is accelerated by the Coulomb repulsion that destabilizes the charged tip.

The observed changes in the emitter structure were interpreted by structure optimization and molecular dynamics studies of nanotubes under conditions mimicking what happens in the experiment. We specifically accounted for changes in the electronic structure and the Coulomb repulsion in the tip region, which carries a net charge due to the applied field, and temperature increase during the electron emission process. The electronic structure and total energy of the nanotube under emission conditions were described using a parametrized linear combination of atomic orbitals Hamiltonian, which had been applied successfully to related processes, including fusion of nanotubes[14] and melting of fullerenes.[15] This real-space method, augmented by Coulomb repulsion terms, was found particularly suited to describe the bond weakening caused by occupation of antibonding states as well as net electrostatic repulsion in the charged tip region. Structural evolution at nonzero temperatures was investigated using microcanonical and canonical[16,17] molecular dynamics simulations.

Under typical operating conditions of field-electron microscopes, where no structural changes occur for short times at field values of $\lesssim 10$ V/μm, we found our results to agree well with self-consistent local density functional calculations using norm-conserving pseudopotentials, as implemented in the SIESTA code.[18] The self-consistent approach is impractical for realistic systems, since an adequate description would involve very long nanotube segments[13] and suffer from convergence problems and an excessive demand on computer resources.

To understand the origin of structural changes in nanotubes during field-electron emission, we performed structure optimization and molecular dynamics simulations for (5,5) and (10,10) single-wall and (5,5)@(10,10) double-wall nanotubes, all terminated by caps, at different applied fields and temperatures. Since the energy barrier for field detaching the cap by ideal cleavage is considerable even in narrow nanotubes,[19] we conclude that the destruction process is very different from ideal cleavage and requires molecular dynamics calculations for an adequate description. We expect our molecular dynamics simulations to discriminate between the relative importance of temperature and excess charge and thus to decide the dominant decay mode under particular conditions.

For an isolated nanotube in a field, depicted in Fig. 1(a), the induced excess charge density on the surface σ is related

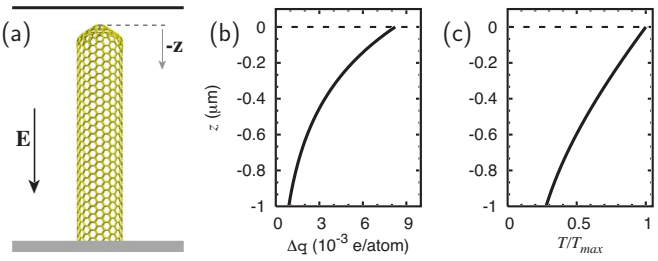

FIG. 1. (Color online) Distribution of excess charge and temperature in a carbon nanotube electron emitter under realistic emission conditions. (a) Schematic picture of the nanotube emitter in a uniform electric field $E(z)$. The position z is given with respect to the nanotube tip. (b) Excess charge density along the tube based on results from Ref. 13. (c) Typical steady-state temperature profile of a self-heating nanotube emitter, with the highest temperature T_{max} at the tip.

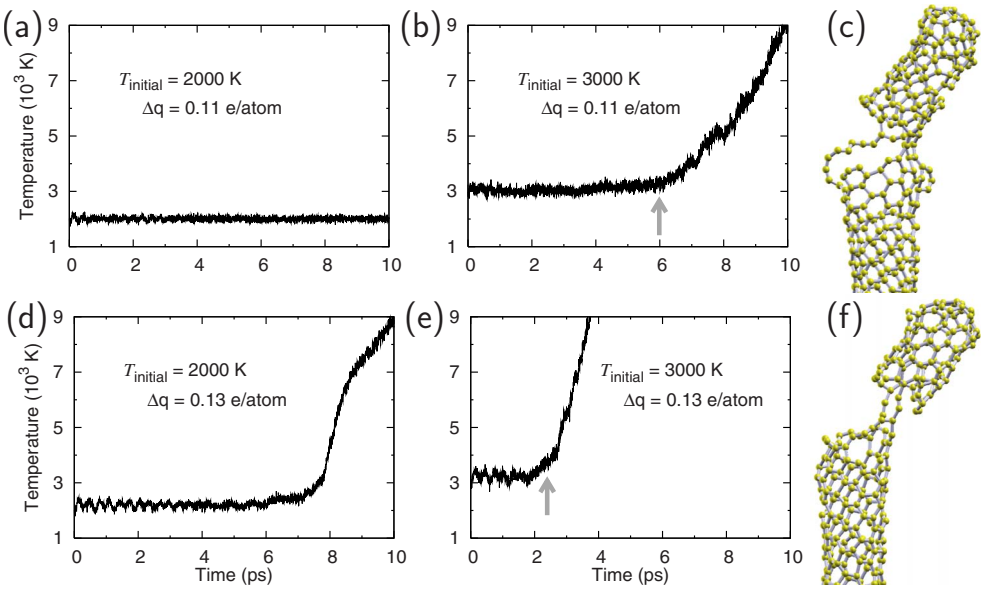

FIG. 2. (Color online) Time evolution of the kinetic temperature T during microcanonical molecular dynamics simulations of charged, hot nanotube emitters. Results for low excess charge $\Delta q=0.11e$/atom in (a) and (b) are compared to results for $\Delta q=0.13e$/atom in (c) and (d). Results for the low initial temperature $T_{initial}=2000$ K in (a) and (d) are compared to those for hotter tubes with $T_{initial}=3000$ K. Structural snapshots at the point of destruction, indicated by an arrow in (b) and (e), are presented in (c) and (f), respectively.

to the local electric field $E \approx \sigma/\epsilon_0$. This charge density is the highest near the exposed tip and decays exponentially from the tip with the decay length of ≈ 0.5 μm,[13] as seen in Fig. 1(b). In the region within 10 nm from the tip, where structural changes occur due to the higher temperature, the change in the excess charge is below 2% and thus can be ignored.

The main source of temperature increase in the nanotube emitter is self-heating during electron emission. Similar to the amount of excess charge, also the temperature increase is caused by a higher emission current in a larger external field. Considering a 1 μm long emitter exposed to the field of 14 V/μm,[13] the basis of the data in Fig. 1, each emitted electron should locally deposit (14 eV$-\phi$) into the nanotube tip, where ϕ is the work function. This excess heat is carried away by thermal conduction to the anchor point of the nanotube and, to a minor degree, by black-body radiation. Convection does not contribute to cooling, since the emitter is in vacuum. In steady state, cooling must locally compensate heating all over the structure. Starting from the heated tip, the heat flux through each nanotube segment must thus be equal and constant. With a finite, temperature dependent thermal conductivity, this assumption leads to the temperature profile along the nanotube emitter shown in Fig. 1(c).

In Fig. 2, we present MD simulation results for an ≈ 40 Å long C_{290} nanotube emitter, modeled by a C_{230} segment of a (5,5) nanotube with terminating domes at both ends. After equilibrating the system at initial temperature values ranging from 0 to 3000 K using a Nosé-Hoover thermostat, we followed its time evolution using microcanonical MD. Since the total energy and the number of atoms N are conserved in the simulation, changes in the potential energy U, related to structural transitions, mirror changes in the kinetic energy K in the center-of-mass reference frame. We relate K to the kinetic temperature T by $K=(3/2)Nk_BT$ and monitor the time evolution of the effective temperature to identify structural transitions related to decay. In particular, onset of fragmentation is reflected in a raise of T, caused by the charged, mutually repelling fragments gaining kinetic energy.

With no excess charge, we expect an onset of disorder at all nanotube emitter atoms close to the melting temperature of large fullerenes and graphite in the range of 3000–4000 K.[15] As seen in Figs. 2(a) and 2(b) for the low excess charge value $\Delta q=0.11e$/atom, there is no indication of instability at 2000 K, but a clear indication of decay at 3000 K. The snapshot of the nanotube emitter at the point of decay near 6 ps, depicted in Fig. 2(c), suggests a local fracture that is very different from a molten neutral structure.

Even a modest increase in the excess charge to $\Delta q=0.13e$/atom destabilizes the nanotube at 2000 K, as seen in Fig. 2(d), and speeds up the decay process at 3000 K, as seen in Fig. 2(e). The decay process at this higher value of Δq also leads to a more abrupt detachment of the cap region, as depicted in Fig. 2(f). Our results thus show that emitter decay is affected both by temperature and excess charge in the tip region.

To get further insight into the relative role of temperature and excess charge on the decay process, we need to consider the probability of its occurrence, which is $\exp(-\Delta U/k_BT)$, with ΔU referring to the activation barrier needed for the structural change. We first investigate the effect of excess charge Δq on the stability of the nanotube emitter at $T=0$. In Fig. 3(a), we show the average atomic binding energy in the C_{290} nanotube emitter as a function of the excess charge. With an increasing amount of excess charge, the intrinsic stability of the system gradually decreases by the rising Coulomb repulsion to the point where isolated charged fragments become more stable than the charged nanotube. The destabilizing effect of Δq is partly to populate antibonding orbitals,

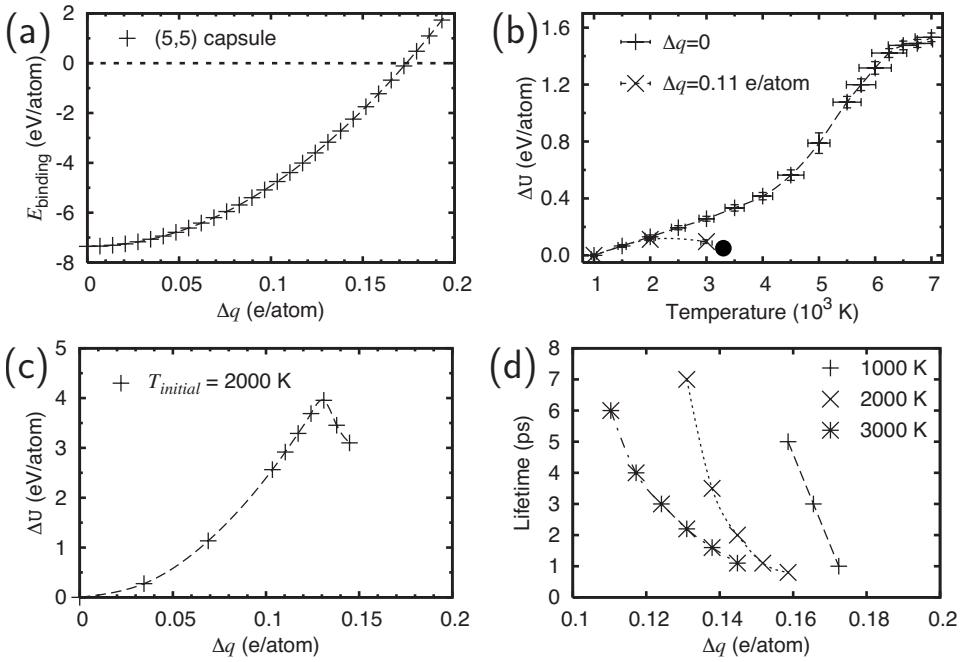

FIG. 3. (a) Average binding energy in a model nanotube emitter as a function of the excess charge Δq. (b) Dependence of the relative potential energy $\Delta U(T)$ of this system on the temperature T with respect to the value at $T=1000$ K. ● marks the point of disintegration. (c) Dependence of the relative potential energy $\Delta U(\Delta q)$ of this system on the excess charge Δq with respect to the value for the neutral system obtained in the long-time limit of molecular dynamics simulations with the initial temperature $T_{initial}=2000$ K. (d) Expected lifetime of the emitter as a function of the excess charge Δq for different initial temperatures.

but mainly to increase the Coulomb repulsion, proportional to Δq^2. Thus, the excess charge, occurring as Δq^2 in the exponent of the probability expression, plays a far more dramatic role in the disintegration process than the temperature. Our results for the binding energy as a function of Δq suggest a spontaneous Coulomb explosion at $T=0$ to occur for net excess charge $\Delta q \gtrsim 0.17e$/atom. At lower values of Δq, the nanotubes will still disintegrate, but the process will be delayed and thermally activated.

To complement our results in Fig. 3(a), we next investigate a purely thermal disintegration at $\Delta q=$const. In Fig. 3(b), we display the change of the potential energy ΔU as a function of temperature using time averages from molecular dynamics simulations for the values of ΔU and T. For a charge neutral system, we observe an initial linear increase of ΔU with the expected classical slope of $(3/2)k_B$. In the temperature range between 4000 and 6000 K, there is a well-formed step in $\Delta U(T)$, reminiscent of a phase transition in this finite system.[15] With no Coulomb repulsion present, the molten phase persists up to much higher temperatures as a contiguous structure that is constantly changing shape.

More interesting is to observe the behavior of this emitter carrying $\Delta q=0.11e$/atom. The results, shown by the symbols × and connected by a dotted line in Fig. 3(b), suggest a spontaneous disintegration at the rather low temperature $T \approx 3000$ K.

In Fig. 3(c), we revisit the stability of charged nanotube emitters, shown in Fig. 3(a) for $T=0$, for structures initially thermalized at the moderate temperature $T_{initial}=2000$ K. This is also the temperature value, where the behavior of uncharged and charged nanotube emitters starts deviating in Fig. 3(b). The results of our microcanonical MD simulations, depicting the expectation value of $\Delta U(t \to \infty)$, suggest a nearly quadratic dependence of ΔU on Δq, similar to the behavior in Fig. 3(a) at low values of Δq. Nanotube emitters charged with $\Delta q \gtrsim 0.13e$/atom, still stable at $T=0$, disintegrate into fragments at $T \approx 2000$ K. The gain in kinetic energy of mutually repelling fragments translates into a reduction of ΔU in this regime.

Finally, we combined the results of our MD simulations to learn more about the expected lifetime of a nanotube emitter as a function of the excess charge and temperature. Our results, displayed in Fig. 3(d), summarize our general finding that disintegration is accelerated at high temperatures and large values of the excess charge. The lifetime is characterized by the survival probability of the structure, given by $1-\exp(-\Delta U/k_BT)$, throughout a succession of attempts occurring with the attempt frequency $\nu \approx 10^{13}$ s^{-1}. Polynomial fits of our results at constant temperature values ranging from 1000 to 3000 K, shown in Fig. 3(d), allow an extrapolation to experimentally relevant lifetimes. To destabilize the nanotube emitter at $T \approx 3000$ K in roughly 1 μs, it should carry a mere excess charge $\Delta q \gtrsim 0.011e$/atom, only slightly larger than the maximum charge expected in nanotube emitters under steady-state conditions, as discussed in Fig. 1(b) and Ref. 13. At lower temperatures, we expect nanotubes carrying the same excess charge to survive much longer.

Our results discussed so far were obtained for cap-terminated (5,5) nanotube segments with a high length-to-diameter aspect ratio. The vibration spectrum of these systems is dominated by axial stretching and bending modes that cause local stress accumulation and thus initiate fragmentation. For the sake of comparison, we investigated the vibration modes also in the wider (10,10) nanotubes of the same length. Associated with the smaller aspect ratio, we found a significant fraction of radial modes that caused axial unzipping in addition to the vibration modes mentioned above. Since there is no energy gain associated with axial unzipping, such defects heal readily and do not contribute directly to the nanotube emitter destruction. Thus, it is essential to use high aspect ratio systems when describing the disintegration process of nanotube emitters.

We also simulated the destruction of $(5,5)@(10,10)$ dome-closed double-wall nanotube emitters under extreme

conditions. As long as the outer wall was intact, it screened the electric field inside and caused no charge accumulation on the inner tube.[12] Only after the outer tube had been severely damaged, the inner tube acquired excess charge and was destroyed. In general, we expect the destruction of multiwall nanotube emitters also to progress sequentially from the outside in.

The advantage of molecular dynamics simulations is to offer detailed insight into the destruction dynamics in slow motion. Because of the short time step of 0.5 fs and limitations in computer resources, our total simulation times are limited to typically a few picoseconds. This is much shorter than experimentally relevant periods, making it hard to observe rare events. To overcome these limitations, we speeded up the dynamics by increasing the excess charge and temperature beyond the experimentally relevant values. These results, in combination with considerations based on statistical mechanics, were used to judge the long-time behavior of nanotube emitters under extreme conditions.

We have found that under steady-state conditions occurring during regular field-electron emission, excess charge accumulation and heating in the tip region do not cause damage to the emitter on the time scale of the MD simulations. With no excess charge, heat should melt the system uniformly, rather than inducing abrupt fracture observed in the experiment.[10,11] On the other hand, even at low temperatures, fluctuations in the excess charge occurring during the emission process may excite low-frequency vibrations, such as the head-shaking motion reported previously,[3] by changing the Coulomb repulsion. These vibrations are not only a heat source, but also, with the help of inertia and collective motion of the tip atoms, capable of locally increasing stress and thus destroying nanotube electron emitters prior to their melting.

Our simulations suggest that the preferred failure mode of carbon nanotube emitters is to detach the capped nanotube end, leaving an open-ended nanotube behind. Charged graphitic fragments, which detach from the open nanotube edge, subsequently disintegrate into smaller substructures. Carbon chains, attached to the tube,[4] are hard to observe in transmission electron microscopy (TEM), but occur commonly in our simulations, as seen in Fig. 2(c).

In situ TEM observations during electron emission[10,11] suggested that all structural changes in carbon nanotubes occurred abruptly, unlike in metal tip field emitters, which gradually self-sharpen in an applied field. We find this scenario in agreement with our simulation results, which suggest that degradation at high temperatures is assisted by the Coulomb repulsion in the charged tip region, causing an abrupt fracture at large values of the emission current.

Whereas our simulations have been performed for perfect nanotubes, it is likely that the failure is triggered at structural defects in real nanotube emitters. Defects, which could be either intrinsic or induced by ion bombardment during the field emission process,[20] are known to cause charge accumulation,[5] thus accelerating the disintegration.

In conclusion, we performed molecular dynamics simulations of charged single- and multiwall carbon nanotube electron emitters under realistic conditions to discriminate between the effect of charge and temperature as the leading cause of destruction. We found that cap-terminated nanotubes should disintegrate abruptly at high emission current values. Disintegration, involving either desorption of cap fragments or a transformation into carbon chains and graphitic flakes, occurs prior to melting and is accelerated by the Coulomb repulsion that destabilizes the charged tip.

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