

## Orientalional Melting in Carbon Nanotube Ropes

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Using Monte Carlo simulations, we investigate the possibility of an orientational melting transition within a “rope” of carbon nanotubes. When twisting nanotubes bundle up during the synthesis, orientational dislocations or twistons arise from the competition between the anisotropic intertube interactions, which tend to align neighboring tubes, and the torsion rigidity that tends to keep individual tubes straight. We map the energetics of a rope containing twistons onto a lattice gas model and find that the onset of a free “diffusion” of twistons, corresponding to orientational melting, occurs at  $T_{\text{OM}} \approx 160$  K.

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Since their first successful synthesis in bulk quantity [1], “ropes” of single-wall carbon nanotubes have been in the spotlight of nanotube research. Recent experimental data indicate that carbon nanotube ropes exhibit an unusual temperature dependence of conductivity [2], magnetoresistance [3], and thermoelectric power [4]. Several physical phenomena have been suggested to cause the intriguing temperature dependence of conductivity behavior, such as twistons [5], orientational melting [6,7], weak localization [8], and Kondo effect [3]. The opening of a pseudogap near  $E_F$  in a bundle composed of (10, 10) tubes has been postulated to result from breaking the  $D_{10h}$  tube symmetry by the triangular lattice [6,9].

Nanotubes [10] and  $C_{60}$  “buckyball” molecules [11,12] are similar insofar as their interaction is weakly attractive and nearly isotropic when condensing to a solid. The small anisotropy of the  $C_{60}$  intermolecular potential drives the solid to an orientationally ordered simple-cubic lattice with four molecules per unit cell at low temperatures [13]. Only at  $T \approx 249$  K does the  $C_{60}$  solid undergo a transition to a face-centered cubic lattice. As confirmed by  $^{13}\text{C}$  nuclear magnetic resonance [14], this is an order-disorder phase transition, with  $C_{60}$  molecules spinning freely and thus becoming equivalent above 249 K. Unlike the  $C_{60}$  solid, very little is known about the equilibrium structure of bundled nanotubes beyond the fact that they form a triangular lattice [1]. In particular, nothing is known about the equilibrium orientation of the tubes within a rope. More intriguing still is the possibility of an orientational melting transition associated with the onset of orientational disorder within a rope.

In the following, we calculate the potential energy surface and the orientational order of straight and twisted tubes within a rope. We further postulate that realistic nanotube ropes contain orientational dislocations that have been frozen in as the tubes formed ropes at a finite temperature, the same way as dislocations are known to form in crystals. We map the energetics of a rope with dislocations onto a lattice gas model and find that the onset of orientational disorder, corresponding to a free axial diffu-

sion of twistons, should occur at  $T_{\text{OM}} \approx 160$  K in ropes containing various types of nanotubes.

In order to determine the orientational order and the rotational motion of tubes in a rope, we need to describe both the intertube interaction and the torsional strain within the individual tubes. Since the anisotropic part of the intertube interaction in a rope is weak and local, it can be well described by pairwise intertube (*not* interatomic) interactions. To describe the interaction between tubes in a rope as a function of their orientation, we use the parametrized linear combination of atomic orbitals (LCAO) formalism with parameters determined by *ab initio* results for simpler structures [15]. This technique has been successfully used to explain superconductivity arising from interball interactions in the doped  $C_{60}$  solid [16], the opening of a pseudogap near  $E_F$  in a (10, 10) nanotube rope [6,7], and the opening and closing of four pseudogaps during the librational motion of a (5, 5)@(10, 10) double-wall tube [17]. The total energy functional consists of a nonlocal band structure energy term and of pairwise interatomic interactions describing both the closed-shell repulsion and the long-range van der Waals attraction. A smooth cutoff function [18] has been implemented to keep the total energy continuous as the neighbor topology changes while tubes rotate. This energy functional correctly reproduces the exfoliation energy, the interlayer distance, and the  $C_{33}$  modulus of hexagonal (*AB*) graphite, as well as the energy barrier for interlayer sliding, corresponding to the energy difference between *AB* and *AA* stacked graphite.

To determine the interaction between a pair of aligned ( $n, n$ ) nanotubes, we first define the orientational angles  $\varphi_1$  and  $\varphi_2$  for these tubes by the azimuthal angle of the center of a particular bond with respect to the connection line between adjacent nanotube axes, as shown in Fig. 1(a). For each ( $\varphi_1, \varphi_2$ ) pair, we calculate the intertube interaction using a fine mesh of 800  $k$  points sampling the one-dimensional irreducible Brillouin zone. Because of the high symmetry of the system, the interaction energy  $\Delta E(\varphi_1, \varphi_2)$  is periodic in  $\varphi_1$  and  $\varphi_2$ , with a period  $\Delta\varphi = 360^\circ/n$ . With the simple variable

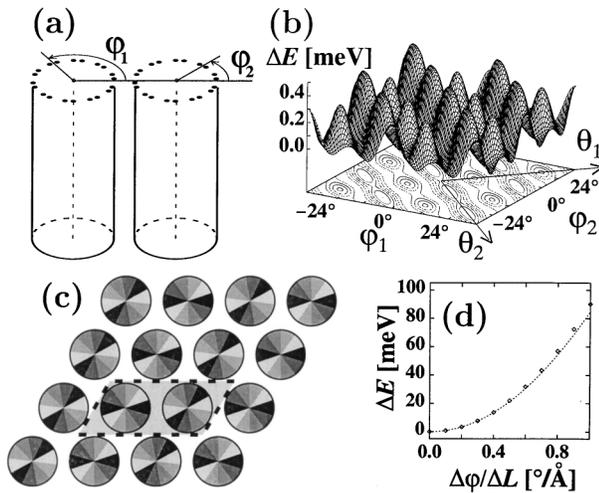


FIG. 1. (a) Definition of the orientational angles  $\varphi_1$  and  $\varphi_2$  of two aligned nanotubes. (b) Interaction energy *per atom* between two (10,10) carbon nanotubes at equilibrium distance as a function of the tube orientations. (c) Top view of the equilibrium structure of bundled interacting nanotubes, with a two-tube unit cell. (d) Torsion energy *per atom* within an individual (10,10) nanotube.

transformation  $\theta_1 = \varphi_1 + \varphi_2$  and  $\theta_2 = \varphi_1 - \varphi_2$ , the interaction energy  $\Delta E$  can be simply expanded in harmonic functions of  $\theta_1$  and  $\theta_2$ , with the same period  $\Delta\theta = 360^\circ/n$ . The resulting potential energy surface, displayed in Fig. 1(b) for a pair of (10,10) nanotubes, shows a maximum corrugation of only  $\Delta E_{\max} \approx 0.5$  meV/atom.

The equilibrium geometry of bundled (10,10) nanotubes can be found by optimizing the total energy  $E$  with respect to the orientations of all individual tubes [19]. Because of the high level of orientational frustration in a triangular lattice of (10,10) nanotubes with  $D_{10h}$  symmetry, the potential energy surface  $E(\varphi_1, \varphi_2, \dots)$  is very complex. We determine the global minimum of  $E(\varphi_1, \varphi_2, \dots)$  by applying the Metropolis Monte Carlo algorithm to an infinite system of straight nanotubes in a  $(2 \times 2), (4 \times 4), \dots, (8 \times 8)$ , superlattice, with unit cells containing between 4 and 64 nanotubes. Independent of the unit cell size, we find that the global energy minimum corresponds to a two-dimensional oblique lattice with two tubes per unit cell, shown in Fig. 1(c). In equilibrium, the orientations  $\varphi_1, \varphi_2$  of the two tubes within this unit cell satisfy the condition  $\theta_1 = \varphi_1 + \varphi_2 = 12^\circ$  and  $\theta_2 = \varphi_1 - \varphi_2 \approx \pm 9.71^\circ$  within the range  $-18^\circ \leq \theta < +18^\circ$ .

Even though the energy barrier  $\Delta E \leq 0.5$  meV per atom for a free rotation in a pair of tubes, shown in Fig. 1(b), appears small, the barrier to rotate an entire tube, that is completely straight and rigid, is unsurmountable. In the following, we postulate that tube rotations in a rope are still possible in view of the finite, albeit large value of the tube torsion constant. To determine the torsional strain within an isolated, twisted (10,10) tube, we combined the LCAO method mentioned above with the recursion

technique [20]. This approach has been used successfully to describe the dynamics of fullerene melting [21], the growth of multiwall nanotubes [22], and the dynamics of a “bucky-shuttle” memory device [23]. Our calculations, shown in Fig. 1(d), suggest that the torsional energy is harmonic up to a strain of  $\Delta\varphi/\Delta L \approx 1^\circ/\text{\AA}$ . Within this harmonic regime, the torsional energy *per atom* can be well represented by the expression  $\Delta E = \kappa(\Delta\varphi/\Delta L)^2$ , with  $\kappa \approx 2.58 \times 10^{-2}$  meV/(rad<sup>2</sup>/\AA<sup>2</sup>). Since the number of atoms in the tube is proportional to the total tube length  $\Delta L_{\text{tot}}$ , the total torsional energy of the tube is inversely proportional to the total tube length for a given total twist angle  $\Delta\varphi_{\text{tot}}$ , and hence becomes vanishingly small for a long tube.

To study the possibility of orientational melting in a nanotube rope, we first consider an unrealistic model system of bundled (10,10) tubes consisting of torsionally decoupled axial segments of 20 atoms, resembling rigid “rings” or “disks.” The interaction between two adjacent disks in neighboring tubes is the value  $\Delta E$  of Fig. 1(b), multiplied by the number of atoms in the disk. Absence of axial coupling makes this system equivalent to a two-dimensional triangular lattice of disks with one (orientational) degree of freedom per disk. Results of Monte Carlo simulations of orientational melting in  $(2 \times 2), (4 \times 4)$ , and  $(6 \times 6)$  superlattices with 4, 16, and 36 such tubes per unit cell, respectively, are shown in Fig. 2. To ensure proper phase space sampling even at low temperatures, each data point represents an ensemble average taken over  $\geq 10^5$  Monte Carlo steps *per degree of freedom*. Results for the temperature dependence of the total energy per degree of freedom, shown in Fig. 2(a), suggest that an orientational melting transition should occur at  $T_{\text{OM}} \approx 55$  K. This transition becomes more pronounced with increasing unit cell size in the superlattice. The sharp peak in the temperature dependence of the corresponding specific heat data, shown in Fig. 2(b), suggests this phase transition to

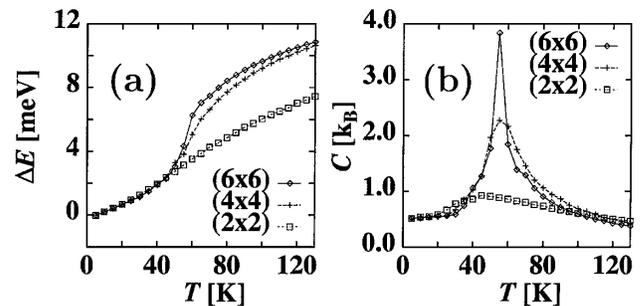


FIG. 2. Temperature dependence of (a) the total energy  $\Delta E$  and (b) the specific heat  $C$  *per degree of freedom* in model  $(m \times m)$  superlattices of interacting (10,10) nanotubes with *zero torsional rigidity*. Each nanotube is modeled by a chain of torsionally decoupled, rigid segments (“disks”) containing twenty atoms, each representing one orientational degree of freedom. In this model system, orientational melting occurs at  $T \geq T_{\text{OM}} \approx 55$  K.

be of first order. At low and at high temperatures, the specific heat per degree of freedom approaches the classical value  $C = 0.5k_B$ .

To address orientational melting in a realistic (10, 10) nanotube rope, we add the proper torsional coupling between the disks, according to our results in Fig. 1(d). Monte Carlo simulations analogous to those described above showed no indication that initially straight nanotubes would start to perform a “ratcheting twisting motion,” corresponding to orientational melting in the rope, up to 4000 K when individual nanotubes should disintegrate structurally. We have also found that the large mass and high bond stiffness essentially inhibit any global or local axial sliding motion within the rope below this high structural melting temperature.

The key to the understanding of orientational melting is to consider the energetics and dynamics of orientational dislocations in the system. Consider two nanotubes which, under synthesis conditions, show a total twist  $\Delta\varphi_{\text{tot}} \geq 36^\circ$  over the entire tube length, at the negligible cost in total energy of  $\approx 0.1$  eV for a 100  $\mu\text{m}$  long tube. As these tubes bundle up during annealing, at least two orientationally aligned domains form within the tube pair, separated by an orientational dislocation. Similar twists of up to  $1^\circ/\text{nm}$ , associated with such orientational dislocations, have been recently observed by electron diffraction in nanotube ropes [24]. Such solitons may move rather freely along the tube axes, but cannot be annihilated if the paired tubes are infinitely long, or if they bundle up to a double torus [25].

The equilibrium geometry of these frozen-in twistons is given by the competition between the anisotropic intertube interactions, which tend to align neighboring tubes, and the torsion rigidity that tends to keep individual tubes straight. The formation of twistons is a general phenomenon that is independent of tube chirality. The energetics and dynamics of twistons is well represented by mapping the Frenkel-Kontorova model onto the orientational degrees of freedom of a triangular lattice of chains. In bundled (10, 10) nanotubes, the orientation  $\varphi(z)$  of individual tube layers near the dislocation is well reproduced by the function  $\varphi(z) = \varphi_0 + \Delta\varphi\{1 + \exp[(z - z_0)/w]\}^{-1}$ , with the typical values  $\Delta\varphi \approx 36^\circ$  and  $w \approx 30$  Å. Such dislocations, which can be either left or right handed, show a total twist of  $36^\circ$  that extends across a very long tube segment of  $\approx 250$  Å in the axial direction, thus resulting in a very small twisting deformation of only  $\approx 0.18^\circ$  per tube layer.

The energy cost of  $\Delta E \approx 5$  eV to create such a twiston, given by the energy difference between ropes containing one or no dislocation, is relatively high. Whereas this energy makes a spontaneous creation of twistons or left-/right-handed twiston pairs within a rope unlikely even at high temperatures, there are only two other scenarios to change their total number. Twistons could “slide off” the end, thus negligibly modifying the total number of twistons in very long ropes. The other scenario involves

the annihilation of left-/right-handed twiston pairs which is most likely to occur just after synthesis, as no activation energy is often associated with this process. Since the number of left- and right-handed twistons is likely to differ, the dynamics will eventually be dominated by the remaining twistons of one handedness. For the pairs of left-/right-handed twistons separated by large distances, presence of orientational dislocations in adjacent tubes will impose an activation barrier onto its annihilation and reduce the probability of this process.

In the following, we thus focus our attention on a system with a constant number of twistons of the same handedness and the onset of their mobility. The dynamics of the entire system is limited to a subspace of the configurational space, where the number of twistons on each tube is fixed. We notice that the axial motion of a twiston corresponds to a finite tube rotation in that given segment, and that the energetics of a rope containing twistons can be mapped onto a lattice gas model of twistons moving along individual tubes. The small potential energy barriers associated with an “up”- and a “down”-moving twiston passing each other in adjacent tubes depend on the orientation of the other surrounding tubes, and are evaluated by the total energy expression above. We correlate the onset of orientational melting in the rope with depinning and a completely free “diffusion” of twistons within the tubes.

Results of a Monte Carlo simulation for the orientational melting transition in a (10, 10) nanotube rope containing twistons are presented in Fig. 3. We consider a  $(6 \times 6)$  superlattice of nanotubes with a fixed number of orientational dislocations on each tube. The energy of this system is given by the positions of these twistons within each periodically repeated unit cell containing 36 tubes with 5000 layer segments discretizing the axial direction. This system with nominally 180 000 degrees of freedom is mapped onto a lattice gas of twistons in the following way. Out of the 36 tubes per unit cell, we select twelve nonadjacent tubes, each containing a single twiston that can move axially. The remaining tubes in the unit cell have eight such orientational dislocations frozen in. Their positions are equally spaced over the tube axes, but axially offset in adjacent tubes.

The temperature dependence of the total energy of this classical system, shown in Fig. 3(a), shows a slope that is initially small close to  $T = 0$ , then becomes large within the temperature range  $0 < T \lesssim 500$  K, and finally becomes small. The corresponding specific heat data, shown in Fig. 3(b), begin with the classical value  $C = 0.5k_B$  at low temperatures and peak at  $T_{\text{OM}} \geq 160$  K. We have observed that ropes consisting of different types of tubes, such as (10, 10) and (9, 9), with different numbers of twistons, show a very similar behavior in spite of their significantly different ground state geometries and potential energy surface topologies. The nature of the orientational melting transition at  $T_{\text{OM}}$  is illustrated in Fig. 3(c). The two snapshots of the geometry, taken at  $T = 500$  K,

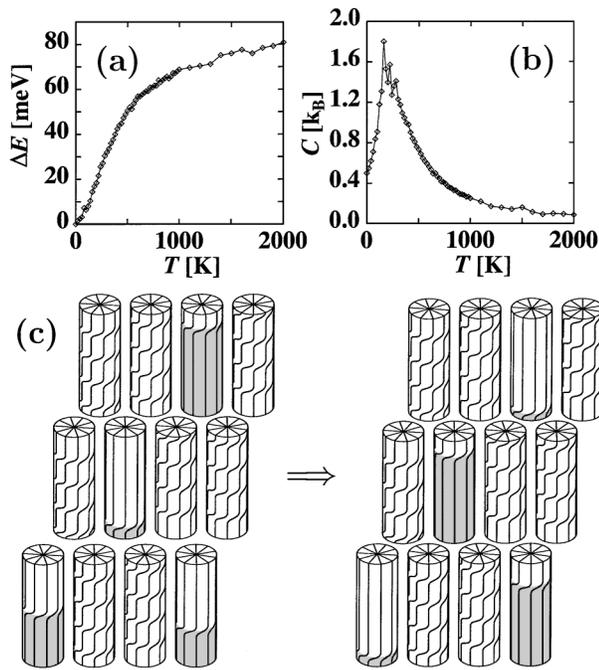


FIG. 3. Temperature dependence of (a) the total energy  $\Delta E$  and (b) the specific heat  $C$  per degree of freedom in a realistic rope consisting of interacting tubes of finite rigidity. (c) Illustration of the microscopic process of orientational melting in an exaggerated perspective. The two views depict the position of orientational dislocations at different points in time at  $T = 500$  K. The axial motion of the twistons, indicating orientational melting, is highlighted by the changing grey-shaded sections in four of the tubes.

indicate that above  $T \approx T_{OM}$ , frozen-in twistons become depinned and diffuse relatively freely along the tube axes, as indicated by the changing gray-shaded sections in the tubes. Since these twistons are important scattering centers for electrons, their depinning may significantly affect the transport in these one-dimensional systems at  $T \approx T_{OM}$  that may play the role of  $T^*$  in Ref. [2].

In summary, using Monte Carlo simulations, we have investigated the possibility of an orientational melting transition within a “rope” of carbon nanotubes. We postulate that during the synthesis, as twisting nanotubes bundle up, orientational dislocations or twistons arise from the competition between the anisotropic intertube interactions, which tend to align neighboring tubes, and the torsion rigidity that tends to keep individual tubes straight. We have mapped the energetics of a (10, 10) nanotube rope containing such twistons onto a lattice gas model and find that the onset of a free “diffusion” of twistons, corresponding to orientational melting, should occur at  $T_{OM} \geq 160$  K.

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