Super-slippery Carbon Nanotubes: Symmetry Breaking breaks friction

M. Dammjanović and T. Vuković and I. Milošević
Faculty of Physics, University of Belgrade, POB 368, Belgrade 11001, Yugoslavia
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The friction between the walls of multi-wall carbon nanotubes is shown to be extremely low in general, with important details related to the specific choice of the walls. This is governed by a simple expression revealing that the phenomenon is a profound consequence of the specific symmetry breaking: super-slippery sliding of the incommensurate walls. In this paper, the principles of tribology, offering a recipe for the lubricant selection are emphasized.

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Various possible applications of the carbon nanotubes motivated extensive investigations of their remarkable physical properties, from the mechanical to the optoelectronic ones. The symmetry based prediction of the extremely small friction between the walls of a double-wall tube (DWT) has been confirmed recently both by the thorough numerical analysis and the experiment. Here we give complete theoretical discussion of such a behavior. To this end we analyze the DWTs W-W (Tab. I). The wall W is (12,12); its radius is $D/2 \approx 4.7\text{Å}$. The wall W is one of the remaining tubes $(n_1, n_2)$. The first three with radii $D/2 \approx R^{in} = 4.7\text{Å}$, suite as the inner wall, and the last four with $D/2 \approx R^{out} = 11.57\text{Å}$, as the outer one. The first part of the paper gives the exhaustive insight to the variety of the interesting phenomena. Then the results are reconsidered to extract three general principles of tribology, offering a recipe for the lubricant selection are emphasized.

The friction between the walls of multi-wall carbon nanotubes is shown to be extremely low in general, with important details related to the specific choice of the walls. This is governed by a simple expression revealing that the phenomenon is a profound consequence of the specific symmetry breaking: super-slippery sliding of the incommensurate walls. In this paper, the principles of tribology, offering a recipe for the lubricant selection are emphasized.

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Firstly, we look for the potential $V(\varphi, z)$ produced by $W'$ at the arbitrary point $r = (D/2, \varphi, z)$. Since necessarily invariant under the symmetry group of $W'$, $V(\varphi, z)$ can be expanded in the basis of invariant functions, harmonics. The suitable basis invariant under the $U$-axis defined by $\Phi$ and $Z$ is $(M = 0, 1, \ldots; \omega \text{ real})$:

$$C_M^\omega(\varphi, z) = \cos(M(\varphi - \Phi) + 2\pi\omega(z - Z)),$$

There is unique combination of $C_M^\omega$ and $C_M^{-\omega}$, namely

$$A_M^\omega(\varphi, z) = C_M^\omega(\varphi, z) + C_M^{-\omega}(\varphi, z), \quad (M, \omega \geq 0),$$

invariant under the mirror planes through $U$. The roto-helical symmetries impose restrictions on $M$ and $\omega$; indeed, the invariance under $C_n$ and $(C_n^\omega |a/q)$ implies:

$$M = 0 \mod n, \quad (\text{rotations}),$$

$$Mr + \omega a = 0 \mod q \quad (\text{helical}).$$

The solutions of this and the other systems appearing
TABLE I: Family of DWTs $(n_1, n_2) - (12, 12)$. The row of $W = (n_1, n_2)$ gives: symmetry group of $W$ (line group $T^Q_1(a)D_n$, or $T^Q_1(a)D_{nh}$ for $W$ chiral or achiral) and of $W^{-1}(G_0)$, common solutions $X^M_{\omega'}$ of $\text{(3)}$ and $\text{(4)}$ in the form of $\text{(5)}$. For commensurate DWT $G_0 = T^Q_0(A)G_N$ (line group), $S_1 = \gamma = q/a, S_2 = T = Q/A$ and $S = \gamma'/T$. For incommensurate DWT $G_0 = C_N$ (point group), $S_1 = q, S_2 = G(q,q')$ and $S = qG(q,q')$. The translational periods $a$ and $A$ are in the units of $a_0$.

| Tube | Line Group | $G_0$ | $X^M_{\omega'}$ | $S_1$ | $S_2$ | $S$ |
|------|------------|-------|-----------------|-------|-------|-----|
| (12,0) | $T^Q_1(\sqrt{3})D_{12h}$ | $C_{12}$ | $12^4$ | 24 | 24 | 24 |
| (7,7) | $T^Q_1(4)D_{7h}$ | $T^Q_1(1)C_1$ | $12^6$ | 14 | 1 | 336 |
| (11,2) | $T^Q_1(7)D_3$ | $T^Q_1(7)C_3$ | $1^760$ | 14 | 1/2 | 2352 |
| (12,12) | $T^Q_1(1)D_{12h}$ | | 24 |
| (17,17) | $T^Q_1(1)D_{7h}$ | $T^Q_1(1)C_1$ | $12^4$ | 34 | 1 | 816 |
| (18,16) | $T^Q_1(2)D_2$ | $C_2$ | $12^8$ | 868 | 4 | 5208 |
| (29,1) | $T^Q_1(7)D_3$ | $D_3$ | $12^6$ | 1742 | 2 | 20904 |
| (24,9) | $T^Q_1(2)D_3$ | $C_3$ | $12^8$ | 582 | 6 | 2328 |

latter on will be given in the form $(L, K = 0, \pm 1, \ldots)$

$$M = M^* L, \quad \omega = \omega^* K, \quad Y L + K = 0 \mod X, \quad (4)$$

with specified $M^* \omega^*, X$ and $Y$ ($G(X, Y) = 1$). In the rectangular 2D lattice with the periods $M^* \omega^*$, the allowed pairs $(M, \omega)$ form the sublattice $(0, 0)$, $(0, -\omega^* X)$, $(M^*, -\omega^* Y)$ and $(M^*, -\omega^* X + \omega^* Y)$. This cell with area $M^* \omega^* X$ contains only trivial solution $M = \omega = 0$. Particularly, $\text{(3)}$ is solved by $\text{(4)}$ for $\omega^* = a^{-1}, M^* = n, X = q/n$ and $Y = r$; the cell area is $\gamma = q/a$. This singles out the harmonics $G^M_{\omega'}$ and $A^M_{\omega'}$ of the chiral and achiral tubes. The harmonics $\omega^*$ and $z$-periods are $\phi/L$ and $a/|K|$; those with $M = n$ and $\omega = \pm a^{-1}$ are invariant under the roto-helical symmetries of $W$ only, while the others have $|L/K|$ times finer periodicity.

Consequently, the allowed $M$ and $\omega$ for $(12,12)$ tube,

$$M = 12L, \quad \omega = K/a_0, \quad L + K = 0 \mod 2, \quad (5)$$

single out the harmonics $A^M_{\omega'}$ in $\text{(4)}$. Further, for the $W$-wall we fix $\Phi = Z = 0$ ($x$-axis is chosen as the $U$-axis of $W$'). Therefore, one finds:

$$V(\varphi, z) = \sum_{tsu} V_C(r - r'_{tsu}) = \sum_{M, \omega \geq 0}^\prime \alpha^M_{\omega} A^M_{\omega'}(\varphi, z), \quad (6)$$

where the prime indicates the summation over the solutions of $\text{(3)}$ only. We calculate the potential by the left part of $\text{(4)}$ with $V_C$ being the Van der Waals type interatomic potential fitted to the $\pi^+$-bonding $\text{(3)}$. The sum over 82 monomers (41 elementary cells with 1968 atoms) is scanned in 41 x 41 points within $\varphi \in [0, \pi/6]$ and $z \in [0, 1]$. The fast Fourier transform yields the amplitudes $\alpha^M_{\omega = K} = 12L, (L, K = 0, \ldots, 20)$ on the right of $\text{(4)}$. The results for $R_{\text{in}}$ and $R_{\text{out}}$ are in Fig. $\text{2}$. As the potential $V(\varphi, z)$ practically does not vary on $10^{-4}$\AA scale (in the vicinity of $R_{\text{in}}$ and $R_{\text{out}}$) these plots refer to all the DWTs listed in Tab. $\text{1}$. Arbitrary constant $\alpha^0_0$ is set to zero. No aliasing occurs, the functions excluded by $\text{(3)}$ are with zero amplitudes, while the amplitudes of the harmonics rapidly decrease with $L$ and $K$, and become negligible (within the numerical error of $10^{-11}$meV) out of the depicted range. This property is nicely illustrated in the density plot (Fig. $\text{2}$) of the potential $V(\varphi, z)$: It is notably periodic only with the periods of the tube.

With fixed position of $W$-wall, the $W'$-$W$ relative position and mutual interaction are determined by $\Phi$ and $Z$ of the $W$-wall $U$-axis. The interaction is the sum of the potential $\text{(3)}$ values in the positions $\text{(4)}$ of $W$ atoms:

$$V(\Phi, Z) = \sum_{M, \omega \geq 0}^\prime \sum_{tsu} \alpha^M_{\omega} A^M_{\omega'}(\varphi_{tsu}, z_{tsu}). \quad (7)$$

For the infinite $W$-wall the summation over $u$, $s$ and $t$ easily gives the interaction per the $W$-wall atom:

$$v_\infty(\Phi, Z) = \sum_{M, \omega \geq 0}^\prime \cos(M\Phi + 2\pi\omega Z) \times \alpha^M_{\omega} \cos(M\varphi_0 + 2\pi\omega z_0). \quad (8)$$

Here the double prime restricts the summation to $M$ and $\omega$ satisfying simultaneously $\text{(3)}$ and $\text{(4)}$ for the $W$-wall parameters. This means that the interaction is mediated only by those $W$-harmonics which are also invariant under the roto-helical symmetries of $W$. Then the allowed $M$, $\omega$ values (solutions of the system $\text{(3)}$-$\text{(5)}$) are given by $\text{(7)}$ with $Y = 1$ and $M^*, \omega^*$ and $X$ listed in Tab. $\text{1}$. The absolute value of the constants in the second line of $\text{(3)}$ roughly determines variation of $v(\Phi, Z)$. Thus, the corrugation $\text{(3)}$ over atom is small whenever the constant $M^* \omega^* X$ is large; large $M$ and $\omega$ indicate small $|\alpha^M_{\omega}|$.

For the incommensurate ($\alpha'/a$ irrational) walls $\omega^* = 0$. Consequently the mediating harmonics are constant along $Z$, yielding $Z$-dependent $v_\infty$. Further, $M^* = qG(q,q') (X = 1$ imposes no restriction). The ideal infinite walls slide along the tube axis exactly without friction, while the rotational friction oscillates with the $\Phi$-period $2\pi/M^*$. Fig. $\text{2}$ presents the calculated interaction $v_\infty(\Phi)$ for the $(12,0)$ wall; its $\Phi$-period is $\phi'/2$. In all other cases $M^*$ is rather large, allowing only very high $M$ of the mediators; their amplitudes are beyond the accessible numerical precision and the computed interaction vanishes, indicating small friction. In the commensurate cases $M^*$ is large: the $\Phi$-dependence of the interaction stems from the harmonics with extremely small amplitudes, giving negligible rotational friction. The calculated interaction is only $Z$ dependent (Fig. $\text{2}$), with the $Z$-period $\alpha'/2$ (since $w' = 2$). Particularly, for the $(11,2)$ wall $X = 7$. This additionally forbids all the numerically significant harmonics: $(11,2)$-$(12,12)$ walls friction is extremely weak.

For the finite $W$-wall with $m$ monomers, the interaction is also obtained from $\text{(4)}$. The horizontal symmetry
The second line in (9) apparently suggests

\[ \frac{1}{m} \]

other walls finite walls mediators (8), giving of the corrugation/atom quasi-oscillations. However, for the wall (12,0), and \( v_0 = v_{\infty} \), infinite wall mediators (12,17) this effect (as it usually) is of great significance for any \( m \) only the infinite wall mediators are important.

giving the complete theoretical insight to the diverse observed phenomena (8) and predicting some new subtle effects, the presented analysis itself may be of interest in tribology. Yet, it can be further deepen by a profound interpretation based on symmetry, which is a cornerstone of the perormed harmonic analysis. To this end, we subdivide the main results of the analysis into the three general principles. As the first produced by an isolated system, invariant under the symmetry group of \( W' \). Otherwise some measurement would identify different system \( W' \). So, \( W' \)-produced potential \( V(r) \) is invariant function, and can be expanded over a basis of harmonics only; all but the lowest harmonics are invariant under supergroups of the \( W' \) symmetry group (finer periods \( \omega \), \( \omega > 1 \) remarked below (8)). B: the harmonic with large supergroups have small extreme amplitudes. Finally, low harmonics decrease and rapidly become negligible as \( M \) increases. The external field \( V \) affects the system \( W \) only by the minimal part of \( V \) invariant under the symmetry of \( W' \). This, only takes the projection of \( V \) to the subspace of the \( W' \)-harmonics counts, while the contribution of the orthogonal part vanishes. Indeed, the interaction is mediated only by those \( W' \) harmonics that are additionally invariant under the roto-helical symmetries of the other wall. Even for them, from (3) follows that \( A_0^W \) of \( W' \) is orthogonal to all \( C_0^W \) of \( W \) unless \( M = M' \) and \( \omega = \omega' \). Therefore the projected \( A_0^{W'} \) is \( C_{0,\omega}(\varphi, z) \cos(M\Phi \pm \omega Z) \). Due to the \( W' \)-wall invariance of \( C_0^M \), its value is the same \( C_{0,\omega}^{W'}(\varphi_0, z_0) \) over all the \( W \) atoms \( C_{\infty,0} \). This completely explains (8).

Taken together, A and C show that the symmetries of the interacting systems \( W' \) and \( W \) restrict their interaction only to the \( W' \)-harmonics having invariant parts with respect to the \( W \)-wall symmetry. This is performed in two consecutive steps. Firstly, the roto-helical symmetries of the \( W' \) and \( W \) walls are collected into the subgroups \((L^{(1)}-)type (8) G \) and \( G' \) of mutually commuting elements. This enables the choice of the harmonics of \( G' \) being either harmonics of \( G \) (becoming mediators) or orthogonal to them (giving no contribution). Secondly, as the parities (\( U \)-axes) do not commute, they select (for each of the symmetry groups) the linear combinations \( \{ \) of \( G^- \) and \( G^- \) harmonics, which are not mutually orthogonal. The parities thus influence the interaction by the cosine terms which dump the mediators amplitudes in (8). Analogously, the first line in (8) is also the dumping cosine, while the second one is the sum of \( C_{\infty,0} \) values.

![Diagram](image.png)

**FIG. 2:** The corrugation/atom dependence of the \( W \)-wall monomer number for the considered DWWTs. Inset: \( v_\infty(\Phi) \) for the wall (12,0), and \( v_\infty(Z) \) for (7,7) and (17,17) for the other walls \( v_\infty(\Phi, Z) \) is below the precision.

Analysis of (8) reveals quite interesting phenomena. The second line in (8) apparently suggests \( 1/m \) dumping of the corrugation/atom quasi-oscillations. However, both the numerator and denominator vanish for the infinite walls mediators (8), giving \( m \)-independent terms which are summed in \( v_\infty \). The additional exclusively finite wall mediators give the dumped oscillations superposed to \( v_\infty \), as transparent from Fig. 3. Although numerically \( v_\infty \) may vanish, really it is only small, and the total corrugation always increases with \( m \). For the (7,7) wall only the infinite wall mediators are numerically recorded, while for (17,17) they prevail by several orders of magnitude. Since they are with \( M = 0 \), the rotational friction is almost negligible for any \( m \). On the contrary, for (12,0) the rotational friction is dominant. For the other tubes the infinite wall mediators are not recorded, making both rotational and translational friction components significantly oscillating with \( m \) and approaching to zero. Peculiarity of the commensurate cases is that whenever \( m \) is multiple of \( qA/na \), i.e. when the ring length is multiple of the \( W-W' \) translational period \( A \), all the numerators vanish. Only the infinite wall mediators contribute and \( v_m = v_{\infty} \), infinite wall corrugation/atom is exactly regained by this sharp resonant effect! This is illustrated in Fig. 2 for (18,12) wall: \( v_{\infty} \) vanishes and ring moves spatially almost freely (when \( m \) is an odd multiple \( \times (9) \) corrugation is small but observable). For (7,7) and (17,17) this effect (as it usually) is of great significance for any \( m \) only the infinite wall mediators are important.

Given the complete theoretical insight to the diverse observed phenomena (8) and predicting some new subtle effects, the presented analysis itself may be of interest in tribology. Yet, it can be further deepen by a profound interpretation based on symmetry, which is a cornerstone of the performed harmonic analysis. To this end, we subdivide the main results of the analysis into the three general principles. As the first produced by an isolated system, invariant under the symmetry group of \( W' \). Otherwise some measurement would identify different system \( W' \). So, \( W' \)-produced potential \( V(r) \) is invariant function, and can be expanded over a basis of harmonics only; all but the lowest harmonics are invariant under supergroups of the \( W' \) symmetry group (finer periods \( \omega \), \( \omega > 1 \) remarked below (8)). B: the harmonic with large supergroups have small extreme amplitudes. Finally, low harmonics decrease and rapidly become negligible as \( M \) increases. The external field \( V \) affects the system \( W \) only by the minimal part of \( V \) invariant under the symmetry of \( W' \). This, only takes the projection of \( V \) to the subspace of the \( W' \)-harmonics counts, while the contribution of the orthogonal part vanishes. Indeed, the interaction is mediated only by those \( W' \) harmonics that are additionally invariant under the roto-helical symmetries of the other wall. Even for them, from (3) follows that \( A_0^W \) of \( W' \) is orthogonal to all \( C_0^W \) of \( W \) unless \( M = M' \) and \( \omega = \omega' \). Therefore the projected \( A_0^{W'} \) is \( C_{0,\omega}(\varphi, z) \cos(M\Phi \pm \omega Z) \). Due to the \( W' \)-wall invariance of \( C_0^M \), its value is the same \( C_{0,\omega}^{W'}(\varphi_0, z_0) \) over all the \( W \) atoms \( C_{\infty,0} \). This completely explains (8).

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at different monomers (when the ring symmetry group $D_n$ acts on a single atom, a single monomer is obtained; consequently, the $D_n$-harmonic $C_{\Omega}^M$ has constant value only along a single monomer).

Hence, only the mutually commuting symmetries produce the rarefaction of the mediators (explicated by the double primes in (6) and (1)). The corrugation is mainly determined by the phenomenological harmonic amplitudes (reflecting the nature and intensity of the interatomic forces), i.e. by the commutative symmetries of the walls, selecting the corresponding mediators. Still, all the symmetries contribute to the fine tuning of the interaction: the dumping factors and the mediators values at the atoms result in the interaction position dependence. Just this causes the friction.

Clearly, the rarefaction is the most important effect. Its estimation in terms of the commuting groups quite profoundly clarifies the interplay between symmetry and friction. According to the note after (4), the cell area of the wall harmonic sublattice is $\gamma = q/a$. This quantity directly measures the roto-helical symmetry: the more symmetric the wall is, the severer are the restrictions (Alternatively, since all W-atoms are obtained by the action of its symmetry group on $C_{900}$, their linear $z$-density measures the order of the group; and $\gamma$ is the half of this density.) Further, the area $S = M^* \omega^* X$ points to the lowest mediators, giving the estimate of the inverse friction. Simple inspection of Tab. 1 in the commensurate cases shows that $S = \gamma^*/\Gamma$, where $\Gamma = Q/A$ measures the DWT symmetry group. The established result in the form $S = |G \otimes G'|/|G_0|$ (the order of the direct product is $|G \otimes G'| = |G||G'|$) means that $S$ is the symmetry breaking rate from the group $G \otimes G'$ to the actual DWT symmetry group $G_\gamma = G \cap G'$. And, $G \otimes G'$ is the symmetry group of the non-interacting systems: independently performed transformations of $G$ and $G'$ preserve the system energy.

As we have shown, the interaction itself imposes a specific symmetry breaking. In the usual manner this produces $S = |G||G'|/|G_0|$ equivalent minima in the total energy (recall Jahn-Teller-effect, crystal phase transitions, particle physics symmetry breaking). While the minima density increases with the breaking rate, the variation of energy between them, proportional to the mediators amplitudes, decreases according to the principle B. In the extreme cases the energy is constant along some paths. This Goldstone super-slippery mode of the incommensurate walls is the phason of the incommensurate phase transitions. Even then the remaining pure rotational friction reflects the breaking of the rotational symmetry. The $z$-independent mutual interaction ($\omega = 0$) makes the walls effective symmetry groups $C_{\Omega}^r$ and $C_{\eta}^r$ (isogonal to $G'$ and $G$), with the intersection $C_{G(q,q')}$, and breaking rate $qq'/\phi(q,q')$. For the incommensurate DWT this equals $M^*$ for (3) (Tab. 1), giving the first allowed mediator ($M^*, 0$). With $M^* = 12$ for ($12,0$)-($12,12$) the walls therefore interact through the $W$-harmonic with $L = M/n' = 2$. Theoretically, this is the lowest possible DWT mediator, yielding the maximal rotational $W-W'$ friction. To conclude: in the view of the one-to-one correspondence of the single-wall tubes to their symmetry groups, the symmetries of the walls are to the large extent incompatible; the tremendous symmetry breaking and harmonics rarefaction leaves the mediating harmonics with very small amplitudes.

The performed analysis and conclusions are essentially general, and refer also to other structures with different type of symmetries [3]. For example, for DWT with both walls incomplete, the corrugation should decrease with the rotational symmetry breaking rate $\eta^*/N$. While $A$ and $C$ are purely group theoretical (the proof is based on the group averages), $B$ is phenomenological. Its elaboration is beyond the scope of this letter. Note that only its global validity is expected: the amplitude of the harmonics may locally increase (e.g. $|\alpha_1| > |\alpha_2|$ for $D/2 = R_{\text{min}}^\text{int}$), revealing the complex structure of the system or some hidden symmetry of the potential.

Several remarks we add at the end. The minima of the potential (1) determine the equilibrium positions of the W-wall. For the achiral walls minima of $v_\infty$ (Inset of Fig. 2) show that such DWTs have mirror planes $\mathbb{3}$. Linear and angular momentum quantum numbers of the vibrational modes of the rotational and translational walls displacements are $k = m = 0$; such modes can be detected by Raman scattering. Their frequencies may be estimated expanding the potential at minima $\mathbb{3}$. For the considered sufficiently long DWTs the maximal ones are given by the Inset of Fig. 2: the rotational $\omega_0^{(12,0)} \approx 21 \text{cm}^{-1}$, and two translational $\omega_2^{(7,7)} \approx 151 \text{cm}^{-1}, \omega_2^{(17,17)} \approx 85 \text{cm}^{-1}$. The others (almost) frictionless degrees appear as the (almost) acoustic modes. This may be a hint to test the friction by the Brillouin scattering. Combined with the described resonant corrugation effect, this can facilitate the experimental identification of the walls of the sample tubes. Finally, the rotational and translational displacements are in general coupled in two helical normal modes, corresponding to the maximal and minimal gradient of the mediators. This interesting (and possibly applicable) screwing effect may be estimated within the presented framework.

* Electronic address: yqoq@afrodita.rcub.bg.ac.yu
URL: http://www.ff.bg.ac.yu/qef/qse.e.htm

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