Super-slippery carbon nanotubes

Symmetry breaking breaks friction

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Abstract. 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 is a Goldstone mode. Three universal principles of tribology, offering a recipe for lubricant selection are emphasized.

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1 Introduction

Various possible applications of the carbon nanotubes [1] motivate extensive investigations of their remarkable physical properties. Recently, the experiment [2] confirmed previous symmetry based [3] and numerical [4,5] predictions of the extremely small friction between the single-wall tubes forming a double-wall one (DWT). Here we present a complete theoretical discussion of such behavior. To this end we analyze seven DWTs W'-W (Tab. 1). The wall W' is (12,12); its radius is $D'/2 = 8.14$ Å. The wall W is one of the remaining tubes (n_1, n_2). The first three with radii $D/2 \approx R^{\text{in}} = 4.7$ Å, are suitable for the inner wall, and the last four with $D/2 \approx R^{\text{out}} = 11.57$ Å, as the outer one. The first part of the paper gives exhaustive insight into a variety of interesting phenomena. Then the results are reconsidered to extract three general principles profoundly relating interaction and symmetry, leading to the final conclusion: the reduction of friction is due to the incompatibility of the DWT walls symmetries.

2 Symmetry and interaction of the walls

Any single-wall tube (n_1, n_2) is completely determined by its symmetry group [3]. The U-axis maps the atom C_{000} to the second one C_{001}. Then the successive rotations C_n for the tube φ-period $\phi = 2\pi/n$ ($n = \mathcal{G}(n_1, n_2)$ where $\mathcal{G}$ is the greatest common divisor) yield the initial monomer with $2n$ atoms C_{0su} ($s = 0, \ldots, n-1$; $u = 0, 1$). Finally, the screw axis generator $(C_q^r | na/q)$ arranges the monomers helically, translating (for na/q) and rotating (through $2\pi r/q$) them along the z-axis. Here, q is the order of the isogonal group principle axis, a is the translational z-period and r is the integer related to the chirality.

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Let the x-axis of the coordinate system be rotated for Φ and translated for Z along the z-axis to coincide with the tube U-axis. Then the coordinates $\mathbf{r}_{tsu} = (D/2, \varphi_{tsu}, z_{tsu})$ of the tth monomer atom are:

$$\varphi_{tsu} = (-1)^u \varphi_0 + 2\pi(\frac{tr}{q} + \frac{s}{n}) + \Phi, \qquad (1a)$$

$$z_{tsu} = (-1)^u z_0 + t\frac{n}{q}a + Z, \quad t = 0, \pm 1, \ldots. \quad (1b)$$

Here $a_0 = 2.461$ Å, $\varphi_0 = \frac{n_1+n_2}{\pi D^2}a_0^2$, $z_0 = \frac{n_1-n_2}{2\sqrt{3}\pi D}a_0^2$.

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

$$C_\omega^M(\varphi, z) = \cos(M(\varphi - \Phi) + 2\pi\omega(z - Z)). \qquad (2a)$$

There is unique combination of C_ω^M and $C_{-\omega}^M$, namely

$$A_\omega^M(\varphi, z) = C_\omega^M(\varphi, z) + C_{-\omega}^M(\varphi, z), \quad (M, \omega \geq 0), \quad (2b)$$

invariant under the mirror planes through U. The invariance $C_n C_\omega^M(\varphi, z) = (C_q^r | na/q) C_\omega^M(\varphi, z) = C_\omega^M(\varphi, z)$ under the roto-helical symmetries restricts M and ω:

$$M = 0 \mod n, \qquad \text{(rotations)}, \qquad (3a)$$

$$Mr + \omega na = 0 \mod q \qquad \text{(helical)}. \qquad (3b)$$

All the solutions of this type of system of equations are

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

for $L, K = 0, \pm 1, \ldots$ and the integer constants M^*, ω^*, X and Y ($\mathcal{G}(X, Y) = 1$). In the rectangular 2D lattice with the periods M^* and ω^*, the allowed pairs (M, ω) form the sublattice with the cell $(0, 0)$, $(0, -\omega^*X)$, $(M^*, -\omega^*Y)$ and $(M^*, \omega^*X - \omega^*Y)$. This cell with area $M^*\omega^*X$ contains only the trivial solution $M = \omega = 0$. Particularly, (3)
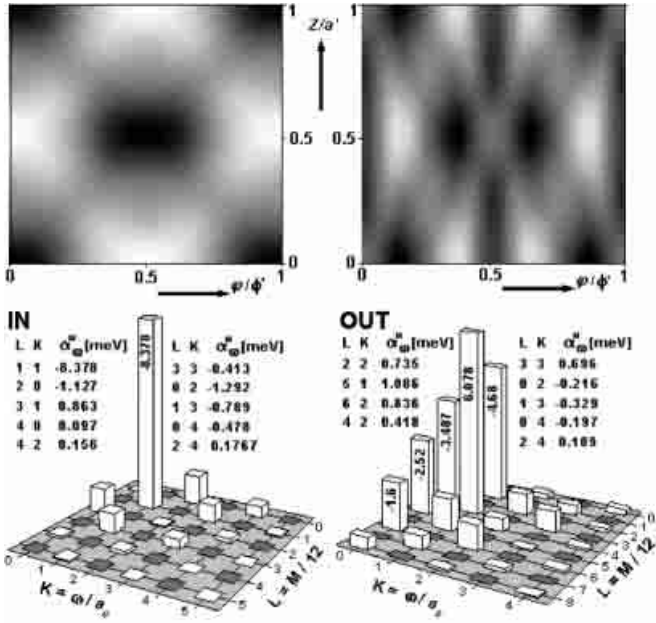
Fig. 1. The potential $V(\varphi,z)$ of (12,12) at $\rho = R^{\text{in}}$ (left) and $\rho = R^{\text{out}}$ (right) within the φ- and z-periods ϕ' and a', with the expansion amplitudes α_ω^M below.

is solved by (4) for $\omega^* = a^{-1}$, $M^* = n$, $X = q/n$ and $Y = r$ and the cell area is $\gamma = q/a$. This singles out the harmonics C_ω^M and A_ω^M of the chiral and achiral tubes. The harmonics φ- and z-periods are ϕ/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 ω for (12,12) tube,

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

single out the harmonics $A_\omega'^M$ in (2b). Further, for the W′ wall we fix $\Phi = Z = 0$ (x-axis is chosen as the U-axis of W′). Therefore, one finds:

$$V(\varphi,z) = \sum_{tsu} V_C(\mathbf{r} - \mathbf{r}'_{tsu}) = \sum_{M,\omega \geq 0}' \alpha_\omega^M A_\omega'^M(\varphi,z), \quad (6)$$

where the prime indicates the summation over the solutions of (5) only. We calculate the potential using the left part of (6) with V_C being a Van der Waals type inter-atomic potential fitted with a $\pi^\perp$-bonding [5]. The sum over 82 monomers (41 elementary cells with 1968 atoms) is scanned in 41×41 points within $\varphi \in [0, \pi/6)$ and $z \in [0, 1)$. The fast Fourier transform yields the amplitudes $\alpha_{\omega=K}^{M=12L}$ ($L, K = 0, \ldots, 20$) on the right of (6). The results for R^{in} and R^{out} are shown in Figure 1. As the potential $V(\varphi,z)$ practically does not vary on the 10^{-1} Å scale (in the vicinity of R^{in} and R^{out}) these plots refer to all the DWTs listed in Table 1. Arbitrary constant α_0^0 is set to zero. No aliasing occurs, the functions excluded by (5) have zero amplitudes, while the amplitudes of the harmonics rapidly decrease with L and K, and become negligible (within the numerical error of 10^{-10} meV) out of the depicted range. This property is nicely illustrated

Table 1. DWTs family W-(12, 12). The row of W= (n_1, n_2) gives: symmetry groups LG of W ($\mathbf{T}_q^r(a)\mathbf{D}_n$ or $\mathbf{T}_q^r(a)\mathbf{D}_{nh}$ for W chiral or achiral) and $\mathbf{G}_\cap$ of W-W′, common solutions $X_\omega^{M^*}$ of (3) and (5) in the form of (4), cell areas S_1 and $S_\cap$ of the harmonics of LG and $G_\cap$ and the breaking rate S. For commensurate DWT $\mathbf{G}_\cap = \mathbf{T}_Q^R(A)\mathbf{C}_N$ (line group), $S_1 = \gamma = q/a$, $S_\cap = \Gamma = Q/A$ and $S = \gamma\gamma'/\Gamma$. For incommensurate DWT $\mathbf{G}_\cap = \mathbf{C}_N$ (point group), $S_1 = q$, $S_\cap = \mathcal{G}(q, q')$ and $S = qq'\mathcal{G}(q, q')$. The periods a and A are in units of a_0.

W	LG (line group)	$\mathbf{G}_\cap$	$X_{\omega^*}^{M^*}$	S_1	$S_\cap$	S
(12,0)	$\mathbf{T}_{24}^1(\sqrt{3})\mathbf{D}_{12h}$	$\mathbf{C}_{12}$	1_0^{24}	24	24	24
(7,7)	$\mathbf{T}_{14}^1(1)\mathbf{D}_{7h}$	$\mathbf{T}_1^1(1)\mathbf{C}_1$	1_2^{168}	14	1	336
(11,2)	$\mathbf{T}_{98}^{45}(7)\mathbf{D}_1$	$\mathbf{T}_1^1(7)\mathbf{C}_1$	7_2^{168}	14	$\frac{1}{7}$	2352
(12,12)	$\mathbf{T}_{24}^1(1)\mathbf{D}_{12h}$			24		
(17,17)	$\mathbf{T}_{34}^1(1)\mathbf{D}_{17h}$	$\mathbf{T}_1^1(1)\mathbf{C}_1$	1_2^{408}	34	1	816
(18,16)	$\mathbf{T}_{868}^{51}(\sqrt{651})\mathbf{D}_2$	$\mathbf{C}_2$	1_0^{5208}	868	4	5208
(29,1)	$\mathbf{T}_{1742}^{1683}(\sqrt{2613})\mathbf{D}_1$	$\mathbf{C}_1$	1_0^{20904}	1742	2	20904
(24,9)	$\mathbf{T}_{582}^{317}(\sqrt{291})\mathbf{D}_3$	$\mathbf{C}_3$	1_0^{2328}	582	6	2328

in the density plot (Fig. 1) 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 positions the mutual interaction are determined by Φ and Z of the W-wall U-axis. The interaction is the sum of the potential (6) values in the positions (1) of W atoms:

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

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

$$v_\infty(\Phi, Z) = \sum_{M \geq 0, \omega}'' \cos(M\Phi + 2\pi\omega Z) 2\alpha_{|\omega|}^M \cos(M\varphi_0 + 2\pi\omega z_0). \quad (8)$$

Here the double prime restricts the summation to M and ω satisfying simultaneously (5) and (3) 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-ω values (solutions of the system (3–5) are given by (4) with $Y = 1$ and M^*, ω^* and X as listed in Table 1. The absolute value of the constants in the second line of (8) roughly determines the variation of $v(\Phi, Z)$, i.e. the corrugation [5] per W-atom. Obviously, this is small whenever the area $M^*\omega^*X$ is large: large M and ω indicate small $|\alpha_\omega^M|$.

For the incommensurate (a'/a irrational) walls, $\omega^* = 0$. Consequently the mediating harmonics are constant along Z, yielding Z-independent v_∞. Further more $M^* = qq'/\mathcal{G}(q, q')$ ($X = 1$ imposes no restriction). An ideal infinite wall slides along the tube axis *exactly* without friction, while the rotational friction oscillates with the Φ-period $2\pi/M^*$. Figure 2 presents the calculated interaction $v_\infty(\Phi)$ for the (12,0) wall with Φ-period of $\phi'/2$. In all other cases M^* is rather large, allowing only very high M of the mediators so their amplitudes are beyond the accessible numerical precision and the computed interaction vanishes, indicating small friction. In the commensurate
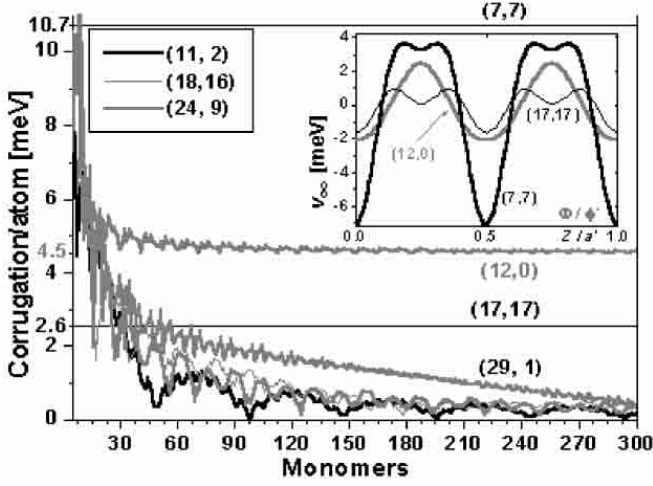
Fig. 2. The corrugation per atom dependence of the W-wall monomer number for the considered DWTs. Inset: $v_\infty(\Phi)$ for the wall (12,0), and $v_\infty(Z)$ for (7,7) and (17,17) (for the other walls $v_\infty(\Phi, Z)$ is below the precision).

cases M^* is large: the Φ-dependence of the interaction stems from the harmonics with extremely small amplitudes, giving negligible rotational friction. The calculated interaction is only Z dependent (Fig. 2), with the Z-period $a'/2$ (since $w^* = 2$). In particular, for the (11,2) wall $X = 7$. This additionally forbids all the numerically significant harmonics so (11,2)-(12,12) walls friction is extremely weak.

For the finite W-wall with m monomers, the interaction is also obtained from (7). The horizontal symmetry axis of W is in the middle of the ring: $\Phi_m = \Phi + \frac{2\pi r}{q}\frac{m-1}{2}$ and $Z_m = Z + \frac{na}{q}\frac{m-1}{2}$. The summation over u, s and $t = 0, \ldots, m-1$ gives:

$$v_m(\Phi, Z) = \sum_{M \geq 0, \omega}'' \cos(M\Phi_m + 2\pi\omega Z_m)$$
$$\times 2\alpha_{|\omega|}^M \cos(M\varphi_0 + 2\pi\omega z_0) \frac{\frac{1}{m}\sin(\pi m \frac{rM+na\omega}{q})}{\sin(\pi \frac{rM+na\omega}{q})} . \quad (9)$$

The double prime here restricts the summation to the solutions of the system (3a–5) for $M^* = nn'/N$, $\omega^* = 1/a'$, $X = 2$ and $Y = n/N$, with $N = \mathcal{G}(n, n')$. In fact, since the ring W has only rotational symmetries, this again restricts the interaction mediators to the common roto-helical harmonics. The infinite-wall mediators, also satisfying (3b) are only a portion of these.

Quite interesting phenomena follow from (9). In the second line in (9) the quasi-oscillations of the corrugation per atom are damped by $1/m$. However, both the numerator and denominator vanish for the infinite walls mediators (8), giving m-independent terms which are summed in v_∞. The additional exclusively finite wall mediators give the damped oscillations superimposed onto v_∞ as is obvious from Figure 2. Although numerically v_∞ may vanish, in reality it is always 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 dominate by several orders of magnitude. Since $M = 0$,

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, and both rotational and translational friction components significantly oscillate with m and finally approach zero. A peculiarity of the commensurate cases is that whenever m is a multiple of qA/na, *i.e.* when the ring length is a multiple of the W-W′ translational period A, all the numerators vanish. Only the infinite wall mediators contribute and $v_m = v_\infty$: the infinite wall corrugation per atom is exactly regained by this sharp resonant effect! This is illustrated in Figure 2 for an (11,2) wall: v_{98k} vanishes and the ring moves coaxially almost freely (if m is an odd multiple of 49, corrugation is small but observable). For (7,7) and (17,17) this effect (at m even) is not significant since for any m only the infinite wall mediators are important.

3 Symmetry breaking

The performed symmetry based harmonic analysis explains all the observed phenomena [2,3,5]. Yet, it reveals a quite profound interrelation of symmetry and interaction. To enlighten this, we summarize the main points of Section 2 into the three general principles.

A: the field produced by an isolated system W′ is invariant under the symmetry group of W′. Otherwise some measurement would identify a different symmetry group. So, the W′-produced potential $V(\mathbf{r})$ is an invariant function, which is expanded in harmonics only. All but the lowest harmonics are invariant under supergroups of the W′ symmetry group (finer periods for M, $|\omega| > 1$ remarked below (4)).

B: the harmonics with large supergroups have small expansion amplitudes. Really, $|\alpha_\omega^M|$ sharply decreases and rapidly becomes negligible with M and ω.

C: the external field V effects the system W only by the maximal part of V which is invariant under the symmetry of W. Thus, only the projection of V on 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 W. Even for them, from (2) it follows that $A_\omega'^{M'}$ of W′ is orthogonal for all C_ω^M of W unless $M = M'$ and $\omega = \pm\omega'$. Therefore the projected $A_\omega'^{M'}$ is $C_{\pm\omega}^M(\varphi, z)\cos(M\Phi \pm \omega Z)$. Due to the W-wall invariance of C_ω^M, it has the same value $C_\omega^M(\varphi_0, z_0)$ over all the W atoms C_{tsu}, giving immediately (8). Analogously, the first line in (9) is the damping cosine and the second one is the sum of C_ω^M values at different monomers. Acting on each atom, the ring symmetry group $\mathbf{D}_n$ gives a monomer only, and a $\mathbf{D}_n$-harmonic C_ω^M has a constant value.

From A and C it follows that the symmetries of W′ and W restrict their interaction only to the W′-harmonics which have invariant parts with respect to the W-wall symmetry. This is realized in two steps. Firstly, since the roto-helical symmetries of the W and W′ walls form mutually commuting subgroups $\mathbf{G}$ and $\mathbf{G}'$ (of $\mathbf{L}^{(1)}$-type,

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[3]), the harmonics of $\mathbf{G}'$ can be chosen to be either harmonics of $\mathbf{G}$ (becoming mediators) or orthogonal to them (giving no contribution). Secondly, noncommuting U and U' select out the linear combinations (2) of $\mathbf{G}$- and $\mathbf{G}'$-harmonics, which are not mutually orthogonal. The parities thus introduce the cosine factors in (8) and (9) which damp the mediator amplitudes. Generally, the reduction of the mediators (indicated by the double primes) is caused by the mutually commuting symmetries only. These are the primary determinants of the interaction scale (selecting the mediators amplitudes gives the nature of the interatomic forces). Still, all the symmetries contribute to fine tuning. The damping factors and the mediator values (scaled by the amplitudes!) at the atoms cause position dependence of the interaction, and this is the origin of friction.

The profound relationship between symmetry and friction suffices to estimate the primary rarefaction effect in terms of the commuting subgroups. The cell area of the wall harmonic sublattice is $\gamma = q/a$ (remark after (4)). This quantity directly measures roto-helical symmetry. The larger symmetry gives severer restrictions (3) and sparser harmonics. (Alternatively, since all W-atoms are obtained by the action of its symmetry group on C_{000}, their linear z-density equal to 2γ, measures the order of the group [3].) Further, the area $S = M^*\omega^*X$ points to the lowest mediators, inversely estimating the friction. Inspection of Table 1 in the commensurate cases shows that $S = \gamma\gamma'/\Gamma$, where $\Gamma = Q/A$ measures the DWT symmetry group. The established result in the form $S = |\mathbf{G} \otimes \mathbf{G}'|/|\mathbf{G}_\cap|$ (the order of the direct product is $|\mathbf{G} \otimes \mathbf{G}'| = |\mathbf{G}||\mathbf{G}'|$) means that S is the symmetry breaking rate from the group $\mathbf{G} \otimes \mathbf{G}'$ to the actual DWT symmetry group $\mathbf{G}_\cap = \mathbf{G} \cap \mathbf{G}'$. And, $\mathbf{G} \otimes \mathbf{G}'$ is the symmetry group of the non-interacting W-W$'$ pair. Independently performed transformations of $\mathbf{G}$ and $\mathbf{G}'$ preserve the system energy. In this sense the interaction itself imposes a symmetry breaking. As usual (Jahn-Teller-effect, crystal phase transitions, particle physics symmetry breaking), this produces $S = |\mathbf{G}||\mathbf{G}'|/|\mathbf{G}_\cap|$ equivalent minima in the total energy. The density of minima increases with the breaking rate, while the mediator amplitudes, and thus the energy variation, decreases according to principle B. In the limit, in the incommensurate cases, the energy is constant along some path and the wall motion is super-slippery along it. This is a Goldstone mode like phason in 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, $\mathbf{C}_{q'}$ and $\mathbf{C}_q$ (isogonal to $\mathbf{G}'$ and $\mathbf{G}$), with the intersection $\mathbf{C}_{\mathcal{G}(q,q')}$, and breaking rate $qq'/\mathcal{G}(q,q')$. For the incommensurate DWT this equals M^* following from (8) (Tab. 1), giving the first allowed mediator $(M^*, 0)$. For the (12,0–12,12) walls $M^* = 24$ and they interact by the W$'$-harmonic with $L = M/n' = 2$. This is the lowest possible DWT mediator, which produces the maximal rotational W-W$'$ friction. In fact, due to the one-to-one correspondence of the single-wall tubes to their symme-

try groups, the symmetries of the walls are quite incompatible. The symmetry breaking and harmonics reduction are very strong, giving the mediating harmonics with very small amplitudes.

4 Concluding remarks

Theoretical analysis completely explaining the diversity of observed phenomena [2,3,5] and revealing some new subtle effects is presented. Its importance for tribology is emphasized by the generality of the symmetry arguments, which can refer to other structures with different type of symmetries [6]. For example, for DWT with both walls incomplete, the corrugation should decrease with the rotational symmetry breaking rate nn'/N. The underlying principles A and C are purely theoretical (the proof is based on the group averages), while B is phenomenological. Note that only its global validity is expected: the amplitude of the harmonics may locally increase (e.g. $|\alpha_1^{36}| > |\alpha_1^{12}|$ for $D/2 = R^{\text{out}}$) due the complex structure of the system or some hidden symmetry of the potential.

We add several remarks at the end. The minima of the potential (8) determine the equilibrium positions of the W-wall. For the achiral walls minima of v_∞ (inset of Fig. 2) show that such DWTs have mirror planes [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 by expanding the potential at a minim [7]. For sufficiently long DWTs under consideration, the maximum modes are given by the inset of Figure 2: the rotational $\omega_\Phi^{(12,0)} \approx 21$ cm^{-1}, and two translational $\omega_Z^{(7,7)} \approx 151$ cm^{-1}, $\omega_Z^{(17,17)} \approx 85$ cm^{-1}. The others (almost) frictionless degrees appear as (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 maximum and minimum gradient of the mediators. This interesting (and possibly applicable) screwing effect may be estimated within the presented framework.

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