Nanotube Electron Drag in Flowing Liquids

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We show that electric current can be generated in metallic carbon nanotubes immersed in liquids flowing along them. Molecular layers of the liquid coat the nanotube, slip along its surface, and excite there a phonon wind, which drags free carriers in the tube. The induced electric current should allow building of nanoscale detectors or power cells.

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Carbon nanotubes have extraordinary physical properties [1] leading to many potential applications [2]. They possess extremely stiff structures of a diamond strength [3], given by the graphene layers, rolled in various directions and diameters. In metallic or semiconducting nanotubes [4–6] electric current can be generated by an applied dc bias [7] or optically [8].

Recent studies show that the *skeletal construction* of nanotubes, highly accessible to external agents, could be efficiently used to vary their electronic structure in unconventional ways. In an excellent example [9], applied dc bias to a nanotube, immersed in a NaCl solution, attracts ions to its walls, depolarizes them, and thus changes the nanotube length. Carbon nanotubes immersed in polymers or liquids also have shifted spectra of their internal vibrations [10]. Therefore, one might ask if nanotubes could be sensitive and efficient *converters of signals* from the surrounding liquid or gaseous media. Such nanoscale detectors are largely demanding in microchemical and biological methods [11], where local dynamical effects are intensively studied.

It would be particularly attractive if nanotubes could detect *motion* in the surrounding liquid. Electric current in a layered electron gas can be induced, for example, by the exchange of momentum with a different electron gas, moving at a small distance. The effect, suggested decades ago [12], was realized only recently in low-dimensional structures [13]. Experiments show [14] that electrons in one layer are driven by hot longitudinal acoustical (LA) phonons emitted by electrons running in the adjacent layer, rather than by their fluctuating Coulomb forces [15]. Electrons can be also pumped by surface acoustic waves at interfaces [16] or by periodical opening of quantum dots in mesoscopic systems [17,18].

Motion of liquids in the vicinity of metallic nanotubes could be ideally detected by such electron driving. Fluids can wet [19] and coat the nanotube in a form of layers, which slip along it faster the farther they are from the tube [20]. Complexity of this solid-liquid interface should allow various driving mechanisms [21]. In the *mediated* regime, momentum from the moving liquid is transferred through the slipping layers to the nanotube momentum and to the quasimomentum of its phonons and other elementary excitations. The resulting phonon wind can drive free carriers in the nanotube, similarly as in other low-dimensional structures [14]. Fluctuating Coulombic fields of the molecules also *directly scatter* free carriers and drive them in pockets traveling in the tube coating. In Fig. 1, we show a scheme of the free carrier driving in a metallic nanotube immersed in a liquid.

The phonon driving of electrons is close in nature to thermoelectric effects. Even though metallic carbon nanotubes with an electron-hole symmetry should have a zero thermopower, experiments in nanotube ropes [22] reveal a holelike thermopower, related to doping by intermixed semiconducting tubes. Nanotubes immersed in liquids can be also effectively doped by the fluctuating molecular field [9]. Therefore, current could be induced in all types of pristine single wall metallic nanotubes (SWNT), as well as in multiwall metallic nanotubes (MWNT), where mostly electrons in the surface SWNT would be driven.

The free carriers which Coulombically scatter from the moving molecules would become partly localized in the sliding coating. We can see here an analogy with MWNT

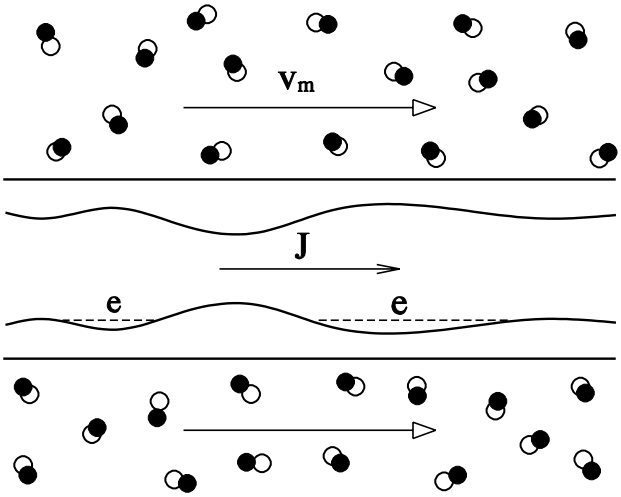

FIG. 1. Scheme of a metallic nanotube immersed in a liquid, flowing along it with a bulk velocity v_m. The molecules, denoted by pairs of circles for different atoms, coat the nanotube in a form of slipping layers, which generate a phonon wind in the tube. This wind and fluctuating Coulomb fields from the molecules drive free carriers in the nanotube.

in "the air," where intertube coupling opens a pseudogap at the Fermi level [23], leading to a fractionally quantized conductivity [24]. A similar pseudogap could form and spatially fluctuate in a metallic nanotube immersed in liquids, since the coating layers, fluctuating in real space, effectively act as separate SWNT in MWNT. In the moving liquid, *fluctuating potential pockets* in the pseudogap travel along the tube and drag the free carriers.

We try to describe these complex driving mechanisms in a (10,10) armchair carbon nanotube [25], with a metallic structure and Fermi level E_F shifted by doping. The simplified model Hamiltonian is

$$H = \sum_{\alpha;k} \pm\hbar k v_F c^{+}_{\alpha,k} c_{\alpha,k} + \sum_q \hbar\omega_q b^{\dagger}_q b_q + H_{e-p} + \sum_{k,q} [V^p_m(k, k-q, t) b^{\dagger}_k b_{k-q} + \text{H.c.}] + \sum_{k,\bar{k}} [V^e_m(k, \bar{k}, t) c^{+}_{1\mp,k} c_{2\pm,\bar{k}} + \text{H.c.}], \quad (1)$$

where summation over wave vectors k extends in the 1D Brillouin zone of the tube. The index $\alpha = \pm 1, \pm 2$ denotes the bands, with the sign indicating the direction of the intraband velocity [7] $v_F \approx 1$ nm/fs (see Fig. 2). The second and third terms denote the phonon Hamiltonian and electron-phonon coupling [26,27]. The fourth and fifth terms represent scattering of phonons and electrons by the fluctuating potential of the medium V^p_m and V^e_m.

The last two source terms induce the electric current $J = J_{e-p} + J_{e-l}$, due to driving of carriers by the generated phonon wind (J_{e-p}) and by the carrier localization in the sliding coating (J_{e-l}). Here, we assume, for simplicity, that in the mediated driving only LA phonons are transferring momentum from the liquid to the quasimomentum of the free carriers. We discuss this driving first, and start by estimating the liquid induced quasimomenta in the phonon bath.

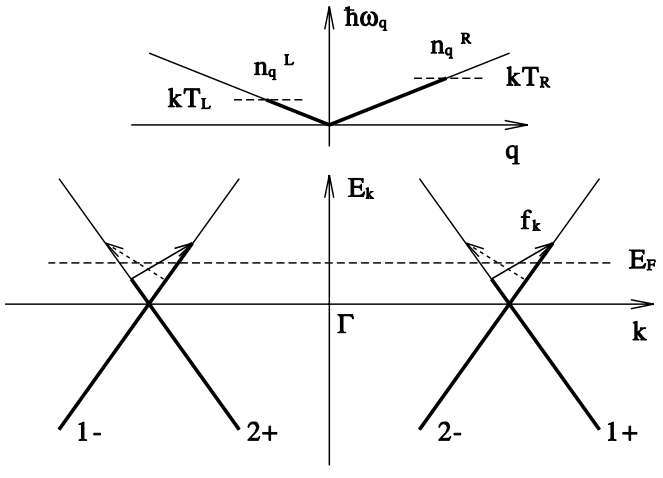

FIG. 2. Electronic structure of the lowest bands in carbon nanotube (10,10), where the Fermi level E_F is shifted up by dopants or the liquid. The populated regions of the carrier distribution f_k are drawn by tick lines. The unbalance in f_k is induced by the phonon population $n^{R,L}_q$ with different temperatures T_R, T_L for the right and left propagating LA phonon winds, as shown schematically in the inset.

Consider a system of densely packed nanotubes in two layers separated by $d = 20$ nm of water. We assume that water flows between the layers with a velocity linearly falling from the value $v_m = 1$ cm/s, in the center, to zero, at the layers, giving the gradient at the nanotube wall $\partial v_x/\partial y = 10^6$ s^{-1}. The flow is *laminar,* since the Reynolds number [28] $\text{Re} = (d/2) v_m \rho/\mu = 10^{-4}$ is much smaller than the critical value $\text{Re} \approx 2000$, where $\rho = 10^3$ kg/m^3 is the water density and $\mu \approx 10^{-3}$ Pa s is the viscosity of water. The medium acts on a unit surface of the tubes by the force $\mathcal{F} = \mu \partial v_x/\partial y = 10^3$ N/m^2. We obtain that a nanotube with the length $l = 1$ μm and periphery 10 nm is driven by the friction force $F \approx 10$ pN.

The force F transfers a momentum p to the nanotube by microscopical scattering events. The momentum p is partly transferred to the nanotube body directly, and partly it is transferred to *asymmetrically* generated quasimomenta $q \neq 0$ of its phonons and other excitations [21]. The resulting average quasimomentum is shared with electrons and later also transferred to the nanotube body by "umklapp" processes. The quasimomentum generation is influenced by the nanotube coating. Its layers give the tube a rough surface, covered by defects, additive molecules, clusters, or small islands [20]. The defect boundaries, exposed to the unidirectional flow of molecules, differently absorb momentum from the liquid, and inject phonons with a nonzero average quasimomentum into the nanotube. Here, we simplify the picture, and assume that *all* the transferred momentum p results in the phonon wind. Then, for the phonon umklapp time $\tau_{\text{um}} \approx 10$ ps [29], the steady-state quasimomentum density in the phonon bath is $p_{\text{fric}} = (F/l)\tau_{\text{um}} \approx 0.6$ ps eV/nm^2.

While the dragged free electrons can be modeled by a shifted Fermi sea, a similar shift cannot be implemented in the hot-phonon population, because of the singularity in the Bose-Einstein distribution n_q at low q. Instead, we can assume [30] that two phonon winds propagate left and right, and have *different temperatures* T_L, T_R. For simplicity, we consider one LA phonon mode with the dispersion $\omega_q = c\,|q|$ ($c \approx 5$ km/s). Then the two distributions are $n^{L,R}_q = 1/(e^{\hbar\omega_q/kT_{L,R}} - 1)$, where L (R) holds for $q < 0$ ($q > 0$). The temperatures T_L, T_R can be interpreted with the help of a thermopower driving, where differently heated sample contacts maintain microscopic temperatures in each region of the nanotube which is ballistic for phonons. The difference of these temperatures in two such neighboring regions can be identified with the molecular driven difference $\Delta T = T_R - T_L$.

In Fig. 2 we show the lowest bands of the (10, 10) tube with a Fermi level E_F shifted up; the LA phonon populations $n^{L,R}_q$ are schematically shown in the inset. The electron distribution f_k, with populated regions emphasized by thick lines, is unbalanced on the branches with velocities $\pm v_F$ due to the presence of the hot-phonon wind, induced by the flowing liquid. The scattering of electrons is

increased if their energy and quasimomentum is simultaneously increased (decreased). Moreover, for $E_F > 0$ the strength of transitions for negative electron energies (holes) is weaker than for positive energies, due to the Pauli blocking, so the current can be generated.

The temperatures $T_{L,R}$ in the model distribution $n_q^{L,R}$ can be obtained by setting the quasimomentum density $p_{\rm fric}$ induced by the molecular friction equal the quasimomentum density $p_{\rm tot}$ in the phonon bath

$$p_{\rm tot} = \frac{1}{l_0} \sum_{q>0} \hbar q (n_q^R - n_q^L). \qquad (2)$$

Here, the sum is performed over momentum states in a tube of a unit length l_0. For the above values we find the difference $\Delta T = T_R - T_L \approx 5$ K for $T_{\rm equil} = 300$ K.

We can estimate the steady-state electron distribution f_k in the presence of LA phonons with the distributions $n_q^{L,R}$. The distribution f_k^- in the band 1_- (2_-), coupled to the distribution f_k^+ in the band 2_+ (1_+), can be obtained from the Boltzmann equation with the electron-phonon scattering [31,32]. For simplicity, we evaluate the linear rate of change of f_k^- in equilibrium

$$\frac{\partial f_k^-}{\partial t} = \frac{2\pi}{\hbar} \sum_{q<0} |g(q)|^2 \, \delta(\varepsilon_k^- - \varepsilon_{k+q}^+ + \hbar\omega_q) \{(n_q^L + 1) f_{k+q}^{0+} (1 - f_k^{0-}) - n_q^L f_k^{0-} (1 - f_{k+q}^{0+})\}$$
$$+ \frac{2\pi}{\hbar} \sum_{q>0} |g(q)|^2 \, \delta(\varepsilon_k^- - \varepsilon_{k-q}^+ - \hbar\omega_q) \{n_q^R f_{k-q}^{0+} (1 - f_k^{0-}) - (n_q^R + 1) f_k^{0-} (1 - f_{k-q}^{0+})\} \qquad (3)$$

for the crossed band energies $\varepsilon_k^\pm = \mp \hbar v_F (k - k_0) > 0$; for $\varepsilon_k^\pm < 0$ we exchange the emission/absorption factors $n_q^{R,L} \leftrightarrow (n_q^{R,L} + 1)$ and interchange $\sum_{q<0} \leftrightarrow \sum_{q>0}$. The different steepness of the electron and phonon dispersion relations allows us to limit to the above two situations. In Eq. (3) we use the Fermi-Dirac distribution $f_k^{0\pm} = 1/(e^{\varepsilon_k^\pm / k_B T} + 1)$ in the bands $\pm$, and the band-independent phonon coupling $g(q) \approx C_{e-p}\sqrt{|q|}$. We include transitions between the nearest crossed bands, as shown in Fig. 2, and neglect intraband (forward) scattering, which does not relax current. Transitions to the crossed bands with opposite k are active practically only in the carrier relaxation, which is therefore used in J_{e-p} with a twice shorter momentum relaxation time [33] τ_k [see (4)].

The electric current J_{e-p} can be calculated from the steady-state change $\delta f_k = f_k - f_k^0$ of the electron population in the presence of the phonon wind. Assuming that carriers relax their quasimomenta (branch velocity in 1D) with the equilibrium time τ_k, we obtain $\delta f_k \approx \dot{f}_k \tau_k$, where we use the linear rate of change in (3). The time τ_k^- in the band 1_- (2_-) can be expressed similarly as $\dot{f}_k^-$. For $\varepsilon_k^\pm > 0$ it is equal to ($T_R = T_L = T$)

$$(\tau_k^-)^{-1} = \frac{2\pi}{\hbar} \sum_{q<0} |g(q)|^2 \, \delta(\varepsilon_k^- - \varepsilon_{k+q}^+ + \hbar\omega_q) \{(n_q + 1) f_{k+q}^{0+} + n_q (1 - f_{k+q}^{0+})\}$$
$$+ \frac{2\pi}{\hbar} \sum_{q>0} |g(q)|^2 \, \delta(\varepsilon_k^- - \varepsilon_{k-q}^+ - \hbar\omega_q) \{n_q f_{k-q}^{0+} + (n_q + 1)(1 - f_{k-q}^{0+})\}, \qquad (4)$$

while for $\varepsilon_k^\pm < 0$ we make the exchanges as in Eq. (3). Since only the backscattering is considered here, this τ_k is identical with the electron decay time [7]. Transitions to the next crossed bands can be included as in (3). At room temperatures, the τ_k thus obtained are only weakly dependent on k, as expected for LA phonon scattering [32].

In Fig. 3 we show the steady-state change of the electron population $\delta f_k^- \approx \dot{f}_k^- \tau_k$, calculated from (3)–(4) as a function of the separation $\Delta k = k - k_0$ of wave vectors from the crossings in the band 2_- (1_-). We use the values $T_{\rm equil}$ and ΔT, obtained from the molecular drag. For $E_F = 30$ meV, the density of excited carriers in band 2_- (1_-) is $\Delta n = \frac{1}{l_0} \sum_k \delta f_k^- \approx 0.55 \times 10^{-6}$ nm^{-1}; opposite population changes of the same size are induced in the bands 2_+ (1_+).

From the hot-phonon induced population Δn we can finally evaluate the electron current

$$J_{e-p} = \frac{2e}{l_0} \sum_{\alpha,k} v_F^\alpha \delta f_k^\alpha \approx 8 e v_F \Delta n. \qquad (5)$$

For the above parameters, we obtain $J_{e-p} \approx 0.7$ nA, which changes roughly linearly with the size of the arguments E_F, $T_{\rm equil}$ and ΔT. A densely packed layer of nanotubes of the width $w = 1$ mm would generate the total current $I \approx 1$ mA. More precise values could be obtained if the heat produced at various levels and other losses in the system were included in the modeling. The size of this current could allow one to study local dynamical effects in liquids or consider a power conversion.

A liquid at rest can also modify the *conductivity* σ of the nanotube, partly due to the Coulomb scattering of electrons from the molecules. This change is a precursor for generation of the current J_{e-l}, induced by carrier localization in the fluctuating dots when the liquid moves. The closer these dots are to the nanotube, the slower they move, but the more *they* localize carriers and thus contribute to this "cog-wheel pumping." Consider that a fraction r_l of free carriers at the Fermi energy is localized in the moving dots; an equivalent picture is that the free carriers are driven in the fraction r_l of time. The resulting

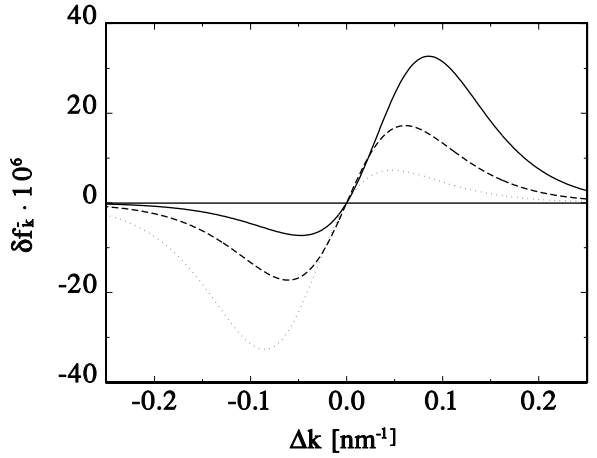

FIG. 3. The steady-state change of the electron population δf_k^- as a function of Δk in the band 2_- (1_-) calculated for $T_{\text{equil}} = 300$ K and $\Delta T = 5$ K. The solid, dotted, and dashed lines correspond to the Fermi levels $E_F = 30, 0, -30$ meV. The two situations with $E_F \neq 0$ give nonzero currents J_{e-p} in opposite directions.

current in the nanotube is $J_{e-l} \approx 2\, e\, v_m\, n_{\text{free}}\, r_l$. At room temperatures, about 1% of carriers in the Brillouin zone can be free, from which, for an optimistic guess $r_l \approx 0.1$, about 0.01 electron/nm become localized in the moving dots. The electrons follow the nearest coating layers, located at a distance $\approx$1 nm, with the speed $v \approx 0.1$ cm/s. The resulting current $J_{e-l} \approx 3$ fA is by 5 orders of magnitude smaller than J_{e-p} driven by nonequilibrium phonons, and thus can be neglected.

In summary, we have shown that electric current can be generated in metallic carbon nanotubes immersed in liquids flowing along them. Free nanotube electrons are mostly driven by hot phonons in the tube walls, induced by the friction of the moving liquid. The induced drag current is large enough to study liquid-flow phenomena on the nanoscale. Other tribo-effects can be observed in different types of nanotubes, liquid or gaseous environments, or system configurations.

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