Flow-induced voltage and current generation in carbon nanotubes

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Abstract

New experimental results, and a plausible theoretical understanding thereof, are presented for the flow-induced currents and voltages observed in single-walled carbon nanotube samples. In our experiments, the electrical response was found to be sublinear – nearly logarithmic – in the flow speed over a wide range, and its direction could be controlled by an electrochemical biasing of the nanotubes. These experimental findings are inconsistent with the conventional idea of a streaming potential as the efficient cause. Here we present Langevin-equation based treatment of the nanotube charge carriers, assumed to be moving in the fluctuating field of ions in the flowing liquid. The resulting "Doppler-shifted" force-force correlation, as seen by the charge carriers drifting in the nanotube, is shown to give a sublinear response, broadly in agreement with experiments.

Single-walled carbon nanotubes (SWNT) in contact with a flowing liquid provide a unique microfluidic system that offers a large interfacial area of intimate atomic contact between the liquid and the solid substrate. This can lead to a strong coupling of the charge carriers in the nanotube to the particles in the flowing liquid, more so if the liquid is polar or ionic in character. The effect of this coupling is expected to be further enhanced due to charge carrier entrainment because of the quasi-one dimensionality of the conducting nanotubes. Recently, the flow of a variety of liquids over SWNT bundles was studied experimentally,

otubes are kept in their place by a supporting insulating substrate. The electrical signal is measured along the flow direction (u_L) as shown Fig. 1. The other experimental details are as in [1]. A sensor with a minimal contact resistance of $\sim$25Ω (found from four- probe measurements) was used in the experiments so that the short-circuit current could be measured. The short-circuit current (open-circuit voltage) was measured by connecting the microammeter (millivoltmeter) across the SWNT sample. The resistance (two-probe) of the device, measured with the sensor dipped in the liquid was found to be $\sim$ 70 Ω. Figure 2 shows the dependence of the induced voltage and current on the flow velocity u_L. The solid line is a fit to the empirical relation $I = \alpha_I \log(\beta_I\ u_L + 1)$, with $\alpha_I = 0.02\mu A$ and $\beta_I = 4.8 \times 10^4 s/cm$. The voltage also fits the empirical relation $V = \alpha_V \log(\beta_V\ u_L + 1)$, where $\alpha_V = 1.4\mu V$ and $\beta_V = 4.8 \times 10^4 s/cm$. It can readily be seen that $\alpha_V = \alpha_I \times R$, i.e., the resistance encountered is precisely the resistance (2 probe) of the device. This is an important point to note: if an electrokinetic mechanism were operating, the resistance obtained would have been orders of magnitude higher, i.e., equal to that of the electrolyte ($\sim 0.1 M\Omega$)[5]. This in itself rules out quite decisively the electrokinetic mechanism of voltage generation. Next, we consider the measured direction of the flow induced current with respect to the flow direction as a function of the bias voltage V_B (see inset of Fig.3). This potential biases the SWNT with respect to the Au-reference electrode immersed in the flow chamber close to sample as shown in the inset of Fig.(3). The dependence of the sign and the magnitude of the flow-induced voltage on V_B for an aqueous solution of 0.01 M KCl (conductivity 1.4 mS/m) and for a fixed flow speed of 0.04 cm/s is shown in Fig.(3). It is seen that the flow-induced signal is positive, i.e., s /

nanotube charge carriers by the liquid flow. The dependence of the flow-induced signal on the concentration of different types of ions in the liquid is, however, found to be complicated

satisfies $u_D/\tau_D = (u_L - u_D)/\tau_L$ giving

$$u_D = u_L/(1 + \tau_L/\tau_D). \tag{1}$$

Equation (1) is merely a restatement of the condition of frictional force-balance in the steady state. It would appear to give an induced short-circuit current (equivalently, an open circuit voltage via the nanotube resistance) along the nanotube which is linear in the flow velocity. The nonlinearity is, however, really hidden in the u_L dependence of the relaxation time τ_L that we will now try to make explicit. It may be noted here that we are assuming, for simplicity, a uniform liquid flow without the hydrodynamic complications of a no-slip boundary condition.

In a simple caricature of the real situation then, consider the ionic density in the liquid, fluctuating thermally and flowing past the nanotube at a mean velocity $u_L\hat{\mathbf{z}}$, producing thereby a fluctuating couloumbic potential $\phi(\mathbf{r}, t)$, at a point $\mathbf{r}$ at time t. We are, of course, interested in the case of $\mathbf{r}$ lying on the z axis i.e., $\mathbf{r} = (0, 0, z)$ (in the 1D nanotube). For the space-time correlation function $\langle\phi(0, 0)\phi(\mathbf{r}, t)\rangle \equiv G_0(\mathbf{r}, t)$ in the mean rest frame of the ions, the charge carriers in the nanotube see this correlation Galilean boosted to $G(\mathbf{r}, t) \equiv G_0(\mathbf{r} - \hat{\mathbf{z}}vt, t)$ with $v = u_L - u_D$. This Galilean boost (Doppler shift) is the key physical point of our treatment. At $u_L = 0$, the fluctuation-dissipation theorem (FDT) tells us that the coefficient of the zero-frequency friction to the motion of the charge carriers in the nanotubes, arising from the ionic thermal fluctuations, is proportional to the time integral of this on-site force-force correlation function. If we *assume* this relation even for $u_L \neq 0$ we have

$$1/\tau_L = 1/(m_e k_B T) \int_{-\infty}^{\infty} \langle eE_z(\mathbf{r} - \hat{\mathbf{z}}vt, t) eE_z(r, 0)\rangle dt. \tag{2}$$

Here E_z is the z-component of the coulombic (electric) field due to the ions; m_e is the mass of the charge carrier with e the electronic charge; k_B is the Boltzman constant, and T the absolute temperature. We re-write the right hand side of Eqn.(2) in Fourier ($\mathbf{q}$)- space, expressing the above force-force correlator in terms of the ionic charge-densities $\rho(\mathbf{r}, t)$ using $E_z(\mathbf{q}, t) = -iq_z\phi(\mathbf{q}, t)$ and $-q^2\phi(\mathbf{q}) = e\rho(\mathbf{q}, t)/\epsilon$, where ϵ is the solvent dielectric constant, and obtain straightforwardly

$$\frac{1}{\tau_L} = \frac{1}{m_e k_B T}\left(\frac{4\pi e^2}{\epsilon}\right)^2 \rho_0 \int \frac{d\mathbf{q}}{(2\pi)^3}\left(\frac{q_z^2}{q^4}\right)\left(\frac{q^2}{q^2 + \kappa^2}\right)\left(\frac{2/\tau_q}{(vq_z)^2 + (1/\tau_q)^2}\right) \tag{3}$$

$$= \frac{\rho_0}{4\pi m_e D\kappa k_B T}\left(\frac{4\pi e^2}{\epsilon}\right)^2 \frac{1}{x}\left(1 - \frac{2}{x} + \frac{1}{x^2}\log\left|1 - x^2\right| - \frac{1}{x^2}\log\left|\frac{1 - x}{1 + x}\right|\right) \tag{4}$$

where $x = v/D\kappa$, and ρ_0 is the mean ionic number density. In Eqns. (3) and (4) we have used the Debye -screened form for the static charge structure factor $S_q^0 = \langle \rho_q \rho_{-q} \rangle = q^2/(q^2 + \kappa^2)$ with screening length κ^{-1} as the inverse of the Debye screening length and a diffusive form $1/\tau_q = Dq^2$ [7] with D the ionic diffusion constant. It can be seen at once that Eqn.(4) , taken in conjunction with Eqn.(2), gives a drift velocity u_D(and therefore the short-circuit current) as a sublinear function of the flow velocity u_L. This sublinearity is a generic feature of this mechanism, and is clearly seen in inset of Fig.(2) in which we have plotted the induced

of its Fourier transform $C_q(t)$ yields

$$u_D \;=\; \frac{1}{\zeta^2}\int_{-\Lambda}^{\Lambda}\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\int_0^\infty \mathrm{d}t\langle e^{iq_z[z(t)-z(t')]}\rangle iq_z C_q(t) \tag{7}$$

where Λ is an ultraviolet cut-off of the order of an inverse ionic diameter. As in the preceding heuristic treatment, let us take the correlation $C_q(t)$ of the ions to be the Galilean boost, with velocity u_L, of an equilibrium correlation function $C_q^0(t)$, with a relaxation time τ_q:

$$C_q(t) = C_q^0(t)e^{-iq_z u_L t} \equiv C_q^0 e^{-iq_z u_L t}e^{-t/\tau_q}, \tag{8}$$

where C_q^0 is the equilibrium equal-time correlation function of the force fluctuations. This form, despite its undeniable limitations, is the simplest way to capture the basic physics of ions moving past the nanotube, and admits an essentially analytical treatment. As before, the force-force correlation C_q^0 can be expressed in terms of the ionic charge-density correlation, which is known as an input from the liquid state(dilute ionic solution) theory, namely that $C_q^0 \propto (q_z^2/q^4)S_q^0$ with the ionic charge structure factor $S_q^0 = q^2/(q^2+\kappa^2)$. Note the factor (q_z^2/q^4) arising from the gradient $(\partial/\partial z)$ and the Laplacian(∇^2) in q- space. Replacing $z(t)$ in Eqn.(7) by its mean $u_D t$ for simplicity, we obtain the compact expression

$$u_D = v\alpha\int_{-\Lambda}^{\Lambda}\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left(\frac{1}{q_z^2v^2+\tau_q^{-2}}\right)\left(\frac{q_z^2}{q^2+\kappa^2}\right), \tag{9}$$

for the drift velocity of the charge carriers in the nanotube, where as before $v = u_L - u_D$, α is a lumped constant of proportionality that depends on the parameters of the liquid-state correlation function input used above. With the ultraviolet cut-off (Λ) set to infinity, and [7] with $1/\tau_q = Dq^2$, Eqn. (9) has precisely the form of Eqn.(1) taken in conjunction with the Eqn.(4), allowing us thereby to identify the integral on its right-hand side essentially with τ_D/τ_L. This gives us an expression for the flow-speed dependence of τ_L, and thus finally an analytic expression for the charge drift velocity (u_D) as a function of the liquid flow velocity (u_L). This reaffirms our heuristic argument given at the beginning.

We close by summarizing the main points of our work. First, on the experimental side, we have clearly shown that the liquid flow produces not only a voltage (i.e., not merely a capacitive charging), but a short-circuit current as well in the nanotube; that both have a sublinear dependence on the imposed flow-speed; and that the voltage/current ratio corresponds to the nanotube sample resistance. These observations are incompatible with an electrokinetic origin for the (electronic) current in the nanotube. On the theoretical side,

we have proposed a theory wherein the current is essentially a statistical consequence of the flow-induced asymmetry in the correlation of the ions, in the ambient fluid as seen by the charge carriers in the nanotube. Importantly, our theory predicts in general a sublinear behavior for the electrical response, with a linear regime at only the smallest values of imposed flow. The extended logarithmic regime seen in experiments can presumably be rationalized in detail with particular forms for the correlation function (C_q^0) and the relaxation time (τ_q), as inputs to be taken from the liquid state (dilute ionic solution) theory. Moreover, a realistic treatment will require taking into account details of the complex, hydrophobic, inter-nanotube micro-fluidic environment of our mat samples. Thus, very specifically, the no-slip boundary condition would imply a decreasing velocity of the flow nearer the nanotube (the shear flow).This decrease in the flow velocity will,however,be offset by the corresponding increase in its effectiveness(via the screened coulombic forcing) closer to the interface.The resulting levelling is expected to broaden the sublinear response and thus improve agreement with the experiment. Our main point, however, is that the experiments show sublinear behavior, which is inconsistent within existing theories of flow-induced voltages and currents in nanotubes, and that our approach naturally and inevitably leads to strong sublinearity. Finally, we emphasize that the flow-induced asymmetry of the random fluctuations is key to the charge-carrier drift (drag) mechanism in our theory. In this broad sense our approach here subsumes the asymmetric fluctuating ratchets invoked earlier [1] in a general way. In this connection, reference must be made to the idea of a drag (shear) induced by the relative motion between material surfaces, where the Doppler shifted and aberrated photonic fluctuations, e.g. zero-point photons, have been invoked very effectively [9, 10] . We would also like here to add that more than one mechanisms could very well be at work in these systems. For example, in a recent publication Persson et al [11] have invoked a combination of frictional stick-slip and barrier-hopping to explain the observed phenomenon of flow-induced voltages in SWNT. The one we propose here seems particularly robust and general, and we look forward to experimental tests, especially of the predicted saturation of the electrical response at high flow speeds.

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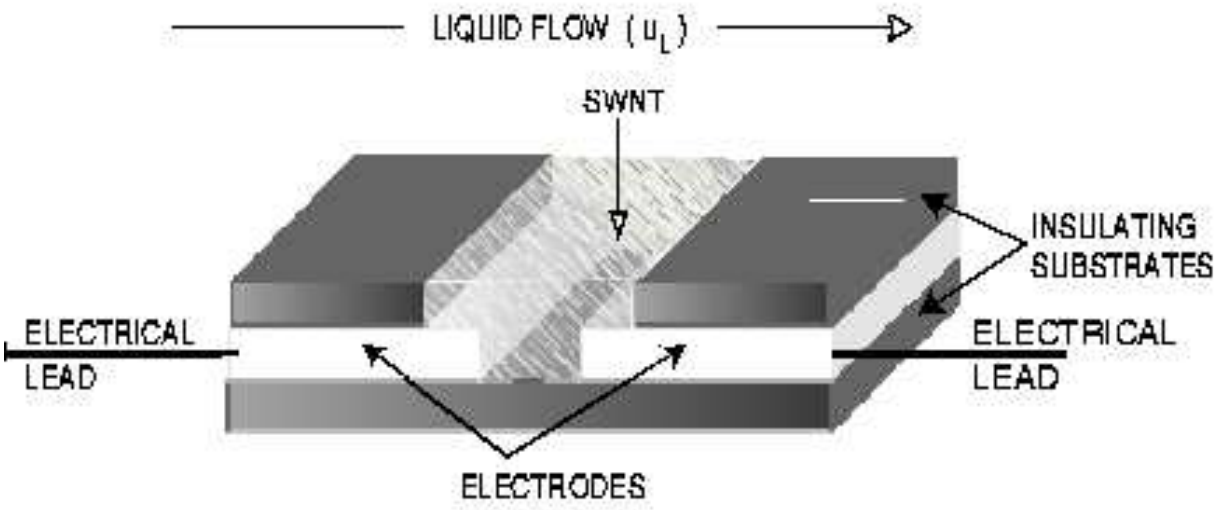

FIG. 1: Schematic sketch of the nanotube flow sensor placed along the flow direction(u_L). SWNT bundles are packed between two metal electrodes. The insulating substrate keeps the SWNT in place. The electrical leads are taken out from the metal electrodes.

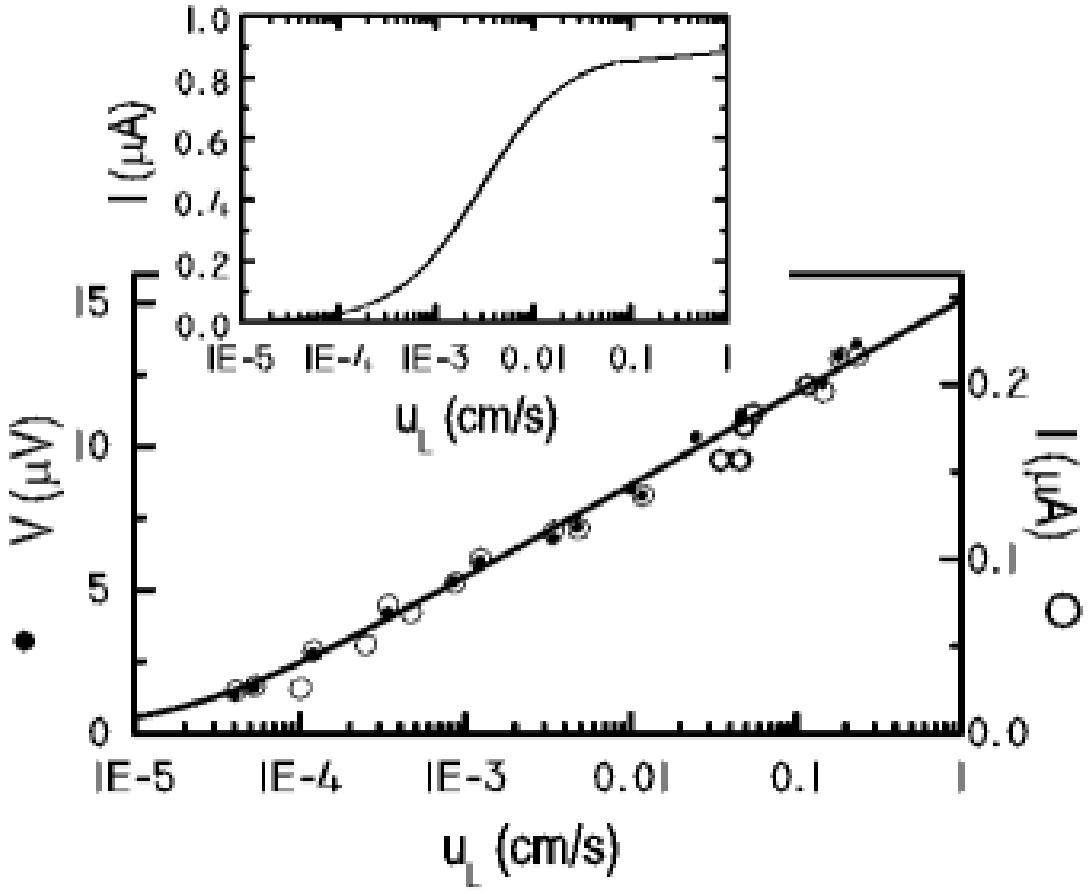

FIG. 2: Voltage (full circles) and current (open circles) as functions of flow speed u_L. The solid line is a fit to the logarithmic function as explained in the text. Inset shows the theoretical plot of current ($I = neu_D A$) versus flow speed based on Eqn.(1,4) for typical choice of parameters: T=300K; ϵ=80(CGS units); $D\kappa = 10^{-4}$ cm/s; $\tau_D = 10^{-16}$ s; $\rho_0 = 10^{13}$ cm^{-3}; charge carrier density in nanotubes ($n = 10^{18}$ cm^{-3}); cross-sectional-area (A) $= 10^{-3}$ cm^2. The strong sublinearity is clearly seen.

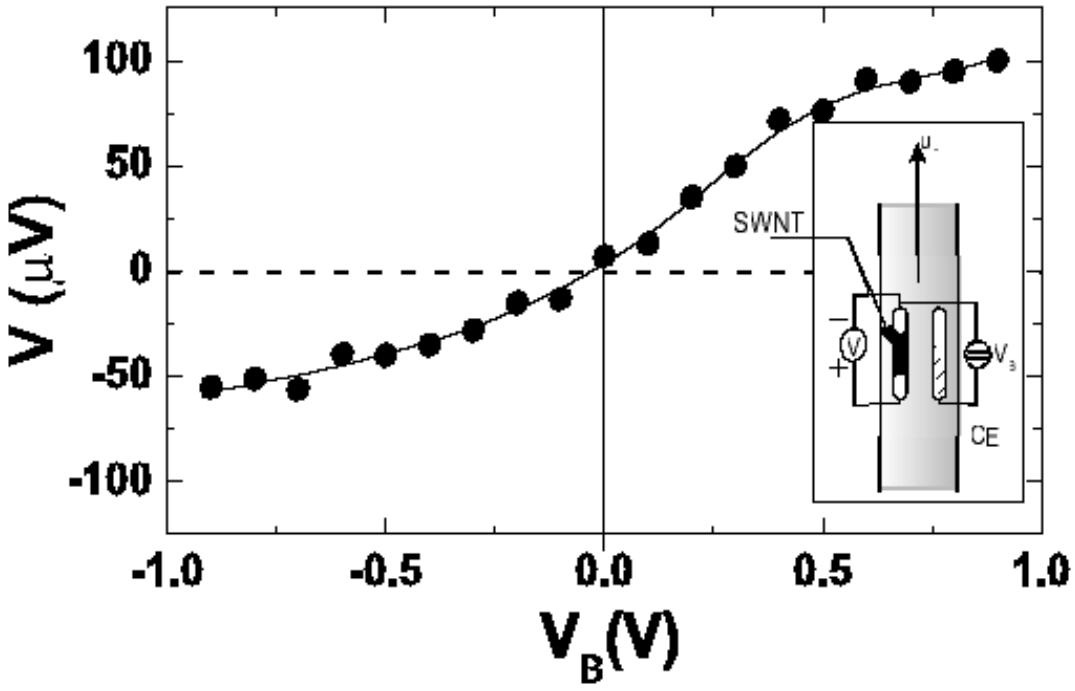

FIG. 3: Flow-induced voltage as a function of bias V_B. Inset: schematic of electrochemical biasing of the nanotubes; CE is the counterelectrode.The solid line is a guide to the eye