A quantum theory of triboelectricity

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We propose a microphysical theory of the triboelectric effect, the off-equilibrium process by which rubbing separates charge across the interface between two surfaces. Surface electrons are treated as an open system, weakly coupled by tunneling to two baths, corresponding to the bulk materials. We show that work can be extracted from the motion-induced population inversion of fermions, thus extending and generalizing Zel’dovich’s theory of bosonic superradiance. We argue that this is consistent with the basic phenomenology of triboelectrification and triboluminescence.

INTRODUCTION

The term electricity was coined from the ancient Greek ἐλεκτρόν for amber, a solid material that charges if rubbed with silk or fur. Triboelectrification, the separation of electric charges by rubbing two surfaces together, was reported in antiquity, but there is still no satisfactory theory for it. This is connected to the fact that the microphysics of dry friction remains poorly understood, due to its essentially off-equilibrium nature. In the 6th century BCE, the pre-Socratic philosopher Thales of Miletus pointed to magnets and amber as evidence for “a soul or life even to inanimate objects” [1, 2]. The Bohr–van Leeuwen theorem establishes that classical physics cannot explain the observed properties of magnetic materials [3]. It is less widely appreciated that classical electrodynamics is insufficient to account for triboelectricity.

Consider the triboelectric generator shown schematically in Fig. 1. The inner cylinder of material A rotates about its axis with angular velocity \( \Omega \). For the right choice of material B in the outer, hollow cylinder, a voltage is established between A and B, which can sustain a current \( I \) through an external circuit. The circuit’s classical electromotive force \( E \) vanishes by the Maxwell-Faraday law:

\[
E \equiv \oint \mathbf{E} \cdot d\mathbf{s} = -\frac{d}{dt} \int \mathbf{B} \cdot d\mathbf{a} = 0,
\]

as there is no significant variation of the net magnetic flux through the plane of the circuit. Thus, at the interface between the two materials A and B, electrons are being transported against the net electric potential difference by a non-conservative force, effectively acting as a negative resistance. The power for this evidently comes from the motor that spins the cylinder A, but how that mechanical energy is converted into electrical work calls for further explanation.

The dynamics of work extraction from a quantum system coupled to an external disequilibrium has, in recent years, become a subject of considerable practical and theoretical interest in quantum thermodynamics [4]. In 1971, Zel’dovich described an irreversible process, later dubbed “superradiance”, by which the kinetic energy of a moving dielectric can be partially converted into coherent radiation [5, 6]. This theoretical result played a key role in the development of black-hole thermodynamics and it provides a useful guide to a broad class of active, irreversible processes; see, e.g., [7, 8]. As in a laser, superradiance depends on population inversion, which in the case of rotational superradiance comes from the disequilibrium associated with the bath’s macroscopic motion. Work may then be extracted from the population-inverted states through stimulated emission, while generating entropy in the bath [9].

There is no fermionic superradiance because the Pauli exclusion principle prevents stimulated emission. However, the motion-induced population inversion of fermions can sustain a macroscopic current between two baths coupled to those fermionic states. Such a process has not, to our knowledge, been considered theoretically before, although the authors of [10] noted the presence of Fermi surfaces of singularities in the Green’s functions of fermions in the background of a charged black hole. Here we argue that it offers a plausible theory of triboelectricity, including such remarkable phenomena as the generation of X-rays by peeling ordinary adhesive tape. [11, 12]

OPEN SYSTEM

We consider the surface electrons as an open quantum system, weakly coupled to two baths corresponding to the bulk materials A and B. In accordance with the setup shown in Fig. 1, we assume cylindrical symmetry so that each electron mode, both in the surface and in the bulk, is labeled by the common magnetic quantum number \( m \). The remaining quantum numbers will be labelled by \( \sigma \) and \( \kappa \). We work in units such that \( \hbar = 1 \). The formalism

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and notation will be very similar to those used to describe rotational superradiance in [9].

At rest, the system Hamiltonian is the sum of terms of the form

$$H_0^a = \sum_{\sigma,m} \omega_a(\sigma,m) c_{\sigma,m}^\dagger c_{\sigma,m}$$

for \(x = a, b\), with \(a\) corresponding to the surface attached to material \(A\), and \(b\) corresponding to the surface attached to material \(B\). Meanwhile, the Hamiltonians for the baths are of the form

$$H_0^X = \sum_{\kappa,m} \omega_X(\kappa,m) c_{\kappa,m}^\dagger c_{\kappa,m}$$

for \(X = A, B\).

If the material \(A\) rotates with an angular velocity \(\Omega\) small enough that its internal states are not excited by the rotation, then we have effective Hamiltonians

$$H_\Omega^a = \sum_{\sigma,m} [\omega_a(\sigma,m) - m\Omega] c_{\sigma,m}^\dagger c_{\sigma,m}$$

(4)

and

$$H_\Omega^b = \sum_{\kappa,m} [\omega_B(\kappa,m) - m\Omega] c_{\kappa,m}^\dagger c_{\kappa,m}$$

(5)

The sign of \(\Omega\) in Eqs. (4) and (5) is arbitrary and has been chosen for later convenience, as in [9].

We consider a weak interactions between the surface electrons and each of the two baths:

$$H_X^\tau = \sum_{\kappa,\sigma,m} g_X^{\tau}(\kappa,\sigma,m) c_{\kappa,m}^\dagger c_{\sigma,m} + \text{h.c.}$$

(6)

where the \(g_X^{\tau}\)'s correspond to tunneling amplitudes. Interactions between the \(a\) and \(b\) surface electrons are neglected. The total Hamiltonian for our model is

$$H_{\text{tot}} = H_\Omega^a + H_0^b + H_A^b + H_0^b + H_A^a + H_B^a + H_B^b.$$  (7)

KINETIC EQUATIONS

The occupation numbers for the surface electron states are:

$$n_x(\sigma,m) = \langle c_{\sigma,m}^\dagger c_{\sigma,m} \rangle.$$  (8)

In the limit of weak coupling between the system and the baths, we may compute the decay rates \(\gamma_{\uparrow}^{xX}\) using the Fermi golden rule [13, 14]. The pumping rates \(\gamma_{\uparrow}^{xX}\) are related to the decay rates by the Kubo-Martin-Schwinger (KMS) condition. Omitting the quantum numbers, the corresponding kinetic equation may be written as

$$\dot{n}_x = \gamma_{\uparrow}^{XA} + \gamma_{\uparrow}^{XB} - (\gamma_{\uparrow}^{XA} + \gamma_{\uparrow}^{XB} + \gamma_{\uparrow}^{\downarrow A} + \gamma_{\uparrow}^{\downarrow B}) n_x.$$  (9)

Let us define

$$n_X(y) = \frac{1}{e^{\beta(y - \mu_X)} + 1},$$

(10)

where \(\mu_X\) is the chemical potential of the corresponding bulk material in equilibrium.

By the Fermi golden rule, the rate of decay of the \(a\) surface electrons into the bath \(A\) is

$$\gamma_{\uparrow}^{aA}(\sigma,m) = 2\pi[1 - n_A(\omega_a(\sigma,m))] g_{A}^{\tau2}(\sigma,m),$$

(11)

where

$$g_{A}^{\tau2}(\sigma,m) = \sum_\kappa |g_{A}^{\tau}(\kappa,\sigma,m)|^2 \delta(\omega_a(\sigma,m) - \omega_B(\kappa,m)).$$

(12)

For the pumping rate we have, by the KMS condition,

$$\gamma_{\uparrow}^{aA}(\sigma,m) = 2\pi n_A(\omega_a(\sigma,m)) g_{A}^{\tau2}(\sigma,m) = e^{-\beta(\omega_a(\sigma,m) - \mu_A)} g_{A}^{\tau2}(\sigma,m).$$

(13)

Due to the shift of the energies in in Eq. (4), for the rate of decay of a surface electrons into the bath \(B\) we have

$$\gamma_{\uparrow}^{aB}(\sigma,m) = 2\pi[1 - n_B(\omega_a(\sigma,m) - m\Omega)] g_{B}^{\tau2}(\sigma,m;\Omega),$$

(14)

where

$$g_{B}^{\tau2}(\sigma,m;\Omega) = \sum_\kappa |g_{B}^{\tau}(\kappa',\sigma,m)|^2 \times \delta(\omega_a(\sigma,m) - m\Omega - \omega_B(\kappa,m)).$$

(15)

The pumping rate is given by the modified KMS relation

$$\gamma_{\uparrow}^{aB}(\sigma,m) = e^{-\beta(\omega_a(\sigma,m) - m\Omega - \mu_B)} g_{B}^{\tau2}(\sigma,m).$$

(16)

Thus, when

$$m\Omega > \omega_a(\sigma,m) - \mu_B$$

(17)

the corresponding state exhibits population inversion \((\gamma_{\uparrow}^{aB} > \gamma_{\uparrow}^{aA})\), making it possible to extract electrical work. A similar analysis gives us \(\gamma_{\downarrow}^{bX}\) and \(\gamma_{\downarrow}^{bX}\).
TRIBOCURRENT

In the steady state (ṅ_a = 0), Eq. (19) implies that

\[ n_a = \bar{n}_a \equiv \left( \frac{\gamma^{aA}_\uparrow + \gamma^{aB}_\uparrow}{\Gamma^a} \right) \]

where

\[ \Gamma^a \equiv \gamma^{aA}_\uparrow + \gamma^{aA}_\downarrow + \gamma^{aB}_\uparrow + \gamma^{aB}_\downarrow. \]

For each channel (σ, m), the number of electrons per unit time that flow from A to a is

\[ j_a = \gamma^{aA}_\uparrow - \frac{\gamma^{aA}_\uparrow + \gamma^{aB}_\uparrow}{\Gamma^a} \bar{n}_a. \]

By Eqs. (29) and (18), this can be re-expressed as

\[ j_a = \gamma^{aA}_\uparrow - \frac{\gamma^{aA}_\uparrow + \gamma^{aB}_\uparrow}{\Gamma^a} \bar{n}_a. \]

The current that flows from B to b (which in the steady state equals the current from b to A) is then

\[ j_b = \gamma^{bB}_\uparrow - \frac{\gamma^{bB}_\uparrow + \gamma^{bB}_\uparrow}{\Gamma^b} \bar{n}_b \]

As illustrated in Fig. 2, the total electric current from A to B is

\[ J = -e \sum_{\sigma, m} j_a(\sigma, m) - \sum_{\sigma', m} j_b(\sigma', m). \]

By Eqs. (13) and (14) we have that

\[ \gamma^{aA}_\uparrow \gamma^{aB}_\downarrow \sim n_A(\omega_\uparrow, \sigma, m)[1 - n_B(\omega_\downarrow, \sigma, m) - m\Omega]. \]

As the ratio μ/k_BT for ambient temperature is \( \approx 10^2 \), we replace the Fermi-Dirac distributions by step functions, \( n_X (y) \sim H(\mu_X - y) \), giving

\[ \gamma^{aA}_\uparrow \gamma^{aB}_\downarrow \sim \chi_{\mu_B + m\Omega, \mu_A}(\omega_\sigma, \sigma, m), \]

where \( \chi_E \) is the indicator function of the set E. Thus, only surface modes of electrons satisfying

\[ m\Omega < \mu_A - \mu_B \]

contribute to the tribocurrent \( j_a \) in Eq. (21), so that \( j_a > 0 \). By a similar reasoning we find that only modes satisfying

\[ m\Omega > \mu_A - \mu_B \]

contribute to \( j_b \) in Eq. (24) and therefore \( j_b > 0 \). The sign of \( J \) in Eq. (25) depends on the relative magnitude of the positive quantities \( \gamma^{aA}_\uparrow \gamma^{aB}_\downarrow / \Gamma^a \) and \( \gamma^{bA}_\downarrow \gamma^{bB}_\uparrow / \Gamma^b \), controlled by the coupling between surface and bulk electrons in the respective materials.

BASIC PHENOMENOLOGY

According to Eqs. (28) and (29), as \( |\mu_A - \mu_B| \) increases under a net charging fewer modes contribute to the \( j_a \) in Fig. 2 giving the charging, while more modes contribute to the opposing current. This may explain why triboelectrification is usually observed only when two materials that are well separated in the “triboelectric series” are rubbed against each other [15]. Moreover, it may also explain why the net current between the rubber belt and the metal brush is opposite at the two terminals of a Van de Graaff generator, where the respective brushes are identical except for voltage (see, e.g., [16]). One may also expect inhomogeneous charging, with patches of positive and negative charge of size comparable to the macroscopic scale of roughness, \( \approx 1 \mu m \), as reported in [17].

Let \( (k_z, k_m) \) be the cylindrical components of the wave vector and let \( k_F \) be the maximum value of \( \sqrt{k_z^2 + k_m^2} \), corresponding to the Fermi wave vector for the surface electrons. In terms of the linear speed \( V_s = |\Omega R| \) with which the surface of material A slides against the surface of material B in Fig. 1

\[ |m\Omega| = k_m V_s \leq k_F V_s. \]

By Eqs. (28), (29), and (30),

\[ e\phi_{oc} = |\mu_A - \mu_B| \text{ at zero current} \lesssim \hbar k_F V_s, \]

where \( \phi_{oc} \) is the tribovoltage, and where we have reintroduced \( \hbar \). This result applies also to systems without cylindrical symmetry. For \( k_F \simeq 10^{10} m^{-1} \) and \( V_s \simeq 1 m/s \), the tribovoltage is therefore \( \phi_{oc} \lesssim 10^{-5} V \).

The generator of Fig. 1 cannot exceed this bound on the voltage. However, if triboelectrification is followed by a rapid mechanical separation of the charged surfaces, the voltage will be increased accordingly. If the distance between the charged surfaces grows from interatomic to meter scale, the resulting voltage will be \( \lesssim 10^5 V \), as in a Van de Graaff generator [16]. If the distance goes from interatomic to \( \approx 10 \mu m \) scale, the energy of the electrons can be in the visible range (\( \gtrsim 1 eV \)). On triboluminescence, see [18] and references therein.

The surface charge density generated by peeling adhesive tape increases strongly with the peel rate [19]. The surface charge density \( \approx 10^{10} \text{e/cm}^2 \) reported in [12] may
be consistent with our theory, supposing that the maximum velocity of slippage between the dissimilar materials in contact is larger, by a couple of orders of magnitude, than the average peel rate \( \approx 10^{-2} \text{ m/s} \). The X-ray bursts produced by the peeling are preceded by a further hundredfold increase in the charge density, in a process connected with macroscopic stick-slip oscillations \[12\]. Such acoustic oscillations can enhance the effective \( m \Omega \) in the exponential of Eq. \[16\], pumping the \( \phi_{oc} \) by another two or three orders of magnitude.

**DISCUSSION**

Other authors have interpreted triboelectricity as resulting from the generation of phonons by the mechanical rubbing between the two materials \[20\]. The consumption of mechanical power in dry friction seems to require the generation of phonons that then thermalize in the bulk \[21\], and it is possible that some of these phonons could contribute to the tribocurrent by assisting electron tunneling, thus enhancing the effective \( \chi_g \)'s in Eq. \[6\].

On the other hand, the tribocurrents \( j_x \) in Fig. \[2\] might contribute to power consumption even when dry friction is not accompanied by significant net charging.

It remains to be seen whether the theory proposed here can describe the detailed triboelectric properties of materials. Many other questions about the microphysics of dry friction remain open. For instance, one possibility that might be considered is whether the slow wear observed when polished surfaces rub against each other could have something to do with the motion-induced tunneling of ions.

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