

The Phonovoltaic Cell

The phonovoltaic (pV) cell is similar to the photovoltaic. It harvests nonequilibrium (hot) optical phonons, rather than photons, which are more energetic than the bandgap to generate power in a *p-n* junction. We develop an analytical model for the efficiency and figure of merit of a pV cell and show that a pV with an optical phonon resonant with the bandgap, much more energetic than the thermal energy, and coupled strongly with the electron substantially surpasses the thermoelectric efficiency. This analytic finding is examined through Monte-Carlo simulation of the Boltzmann transport equation and self-consistent hydrodynamic simulations. Graphene, one of few materials with an optical phonon much more energetic than the bandgap, the thermal energy, and strongly coupled to the electron, is examined as a potential pV material. Its bandgap is tuned through hydrogenation within density functional simulation. Then, its electron-phonon and phonon-phonon couplings and kinetics are investigated. Hydrogenation is shown to degrade the electron-phonon coupling, precluding its use as a pV material.

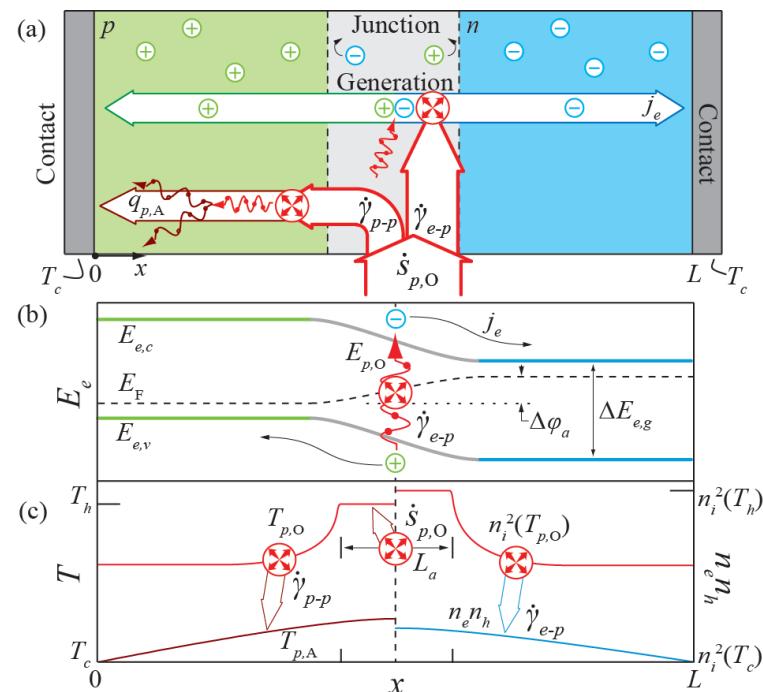


Figure 1. (a) The phonovoltaic cell, (b) energy diagram, and (c) nonequilibrium in optical and acoustic phonon temperatures and carrier concentration. An external source excites the optical phonon population in the active region, and the resulting nonequilibrium drives the generation of electrons and downconversion of optical into acoustic phonons. The junction separates the generated electron-hole pairs to create power, while the acoustic phonons conduct to the cold contacts.

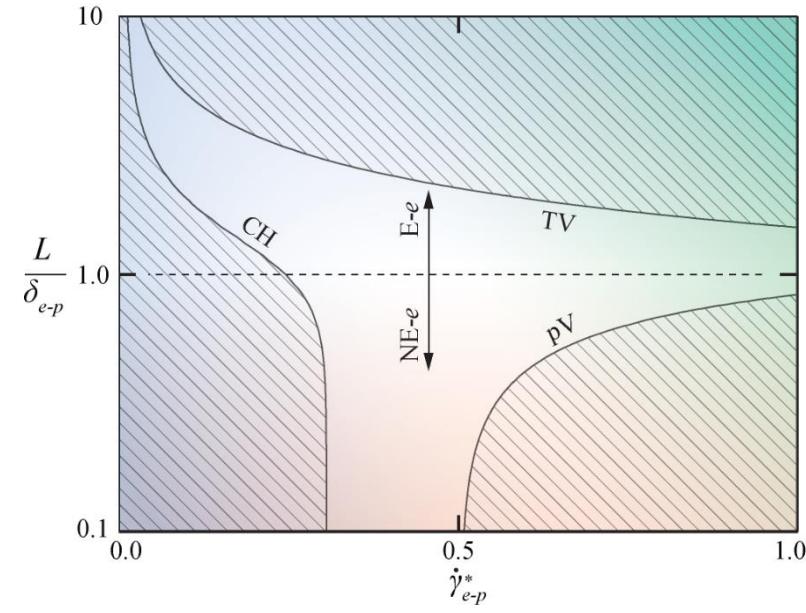


Figure 3. The phonovoltaic (pV), thermovoltaic (TV), and conduction hindered (CH) regimes. When the optical phonon equilibrates with both electron and acoustic phonon, the device operates as thermoelectric (TE), and is named a TV. When the acoustic phonon equilibrates with the optical phonon, but the electron does not, the device operates with negligible efficiency. Thus, the pV regime exists where there is no equilibrium (device length, L , smaller than the electron-phonon, δ_{e-p} , and phonon-phonon cooling length, $\delta_{p-p} = \gamma_{e-p}^* \delta_{e-p}$), the TE regime exists when $L > \delta_{e-p}$, and the CH regime exists where $\gamma_{e-p}^* \rightarrow 0$.

Efficiency of a Phonovoltaic Cell

The efficiency of the phonovoltaic shown in Fig. 1 is limited by the following: The degree of nonequilibrium, or Carnot efficiency (η_C),

$$\eta_C = 1 - T_c / T_{p,O},$$

where T_c and $T_{p,O}$ are the contact and optical phonon temperature; The fraction of hot optical phonons which produce electrons rather than acoustic phonons (γ_{e-p}^*)

$$\gamma_{e-p}^* = \gamma_{e-p} / (\gamma_{e-p} + \gamma_{p-p}),$$

where γ_{e-p} is the electron-phonon coupling and γ_{p-p} is the phonon-phonon coupling]; And the fraction of optical phonon energy which produces electron kinetic energy rather than potential energy ($\Delta E_{e,g}^*$)

$$\Delta E_{e,g}^* = \Delta E_{e,g} / E_{p,O},$$

where $\Delta E_{e,g}$ and $E_{p,O}$ are the bandgap and optical phonon energy. Thus, the figure of merit (Z_{pV}) and efficiency (η_{pV}) are

$$Z_{pV} = \gamma_{e-p}^* \Delta E_{e,g}^*, \quad \eta_{pV} < \eta_C Z_{pV}.$$

The efficiency is further reduced by the performance of the diode, largely related to $\Delta E_{e,g} / k_B T_c$. See Fig. 2 for the estimated efficiency. In addition, the pV cell requires nonequilibrium, i.e., a nanoscale device as shown in Fig. 3.

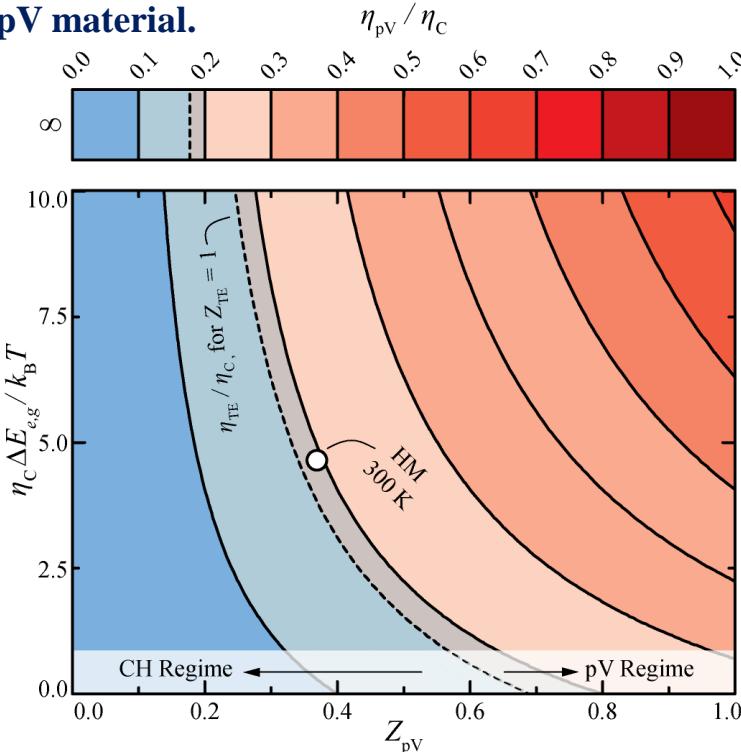


Figure 2. The pV efficiency. Significant nonequilibrium and a bandgap much larger than the thermal energy are required to outperform a TE with $Z_{TE} T = 1$. For $T \rightarrow 0$, the pV cell achieves $\eta_{pV} = \eta_C Z_{pV}$. When $\Delta E_{e,g} \rightarrow 0$, the pV cell approaches $\eta_{pV} = 0.25 \eta_C Z_{pV}$.

Tuning the bandgap of Graphene

While it has been suggested that arbitrary strain tunes the bandgap of graphene, tight-binding results and newer DFT results show that extreme strain is required to break the graphene symmetry and open a bandgap. Here, we use partial hydrogenation to open and tune the bandgap of graphene within DFT, as shown in Fig. 4. Hydrogenation opens a gap by transforming the sp² hybridization of graphene into the sp³ hybridization of, e.g., diamond.

At these concentrations, the graphene phonon dispersion remains relatively undisturbed, while adding the phonon modes of graphane (fully hydrogenated graphene), which includes 400 meV hydrogen vibrations and 160 meV diamond-like carbon vibrations.

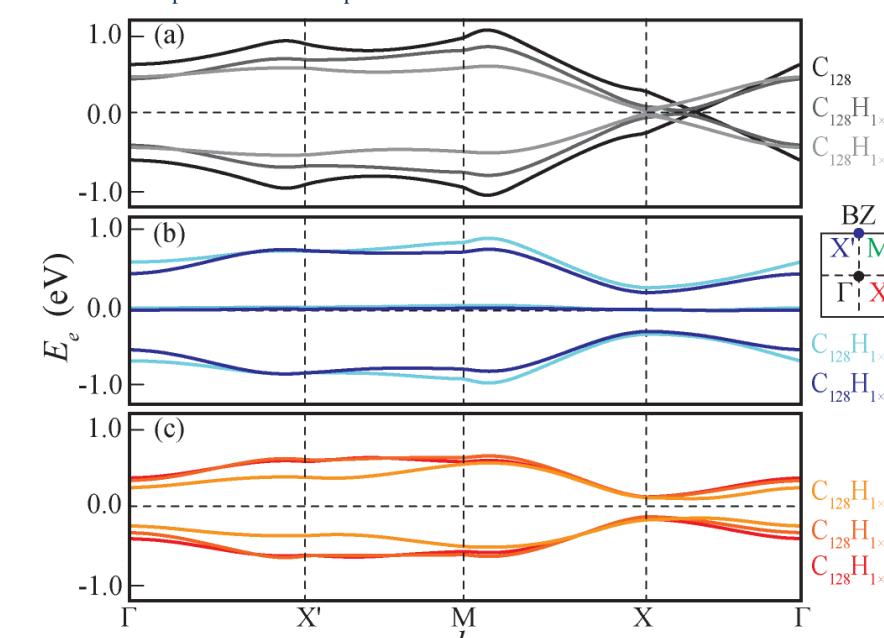


Figure 4. Variations in the bandstructure of graphene after hydrogenation. At low hydrogen concentrations, the Dirac point shifts towards X from Γ . Odd hydrogen atoms add a defect band with a large gap to the first conduction and first valence bands. Moderate hydrogen concentration (24 H : 128 C) opens a narrow gap around 200 meV wide.