Nanoscale Energy Conversion by Selective Electron Emission:
A New Paradigm or Maxwell's Demon Revisited?

Energy and Nanotechnology: Strategy for the Future

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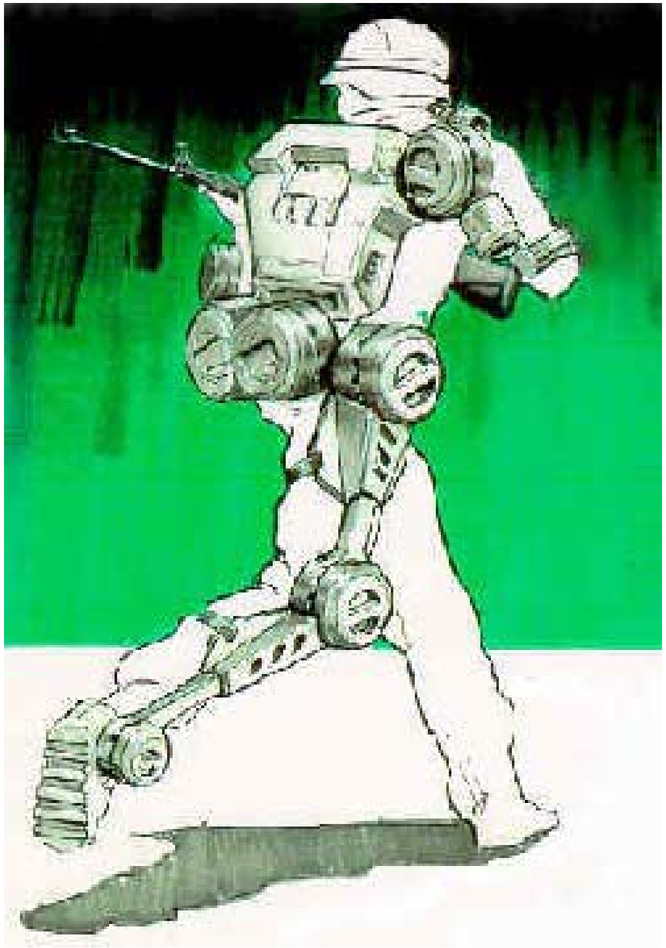
Outline

- Direct energy conversion
- Energy transport in electron emission processes
  - Thermal-field emission
  - Thermionic emission
- Conclusions

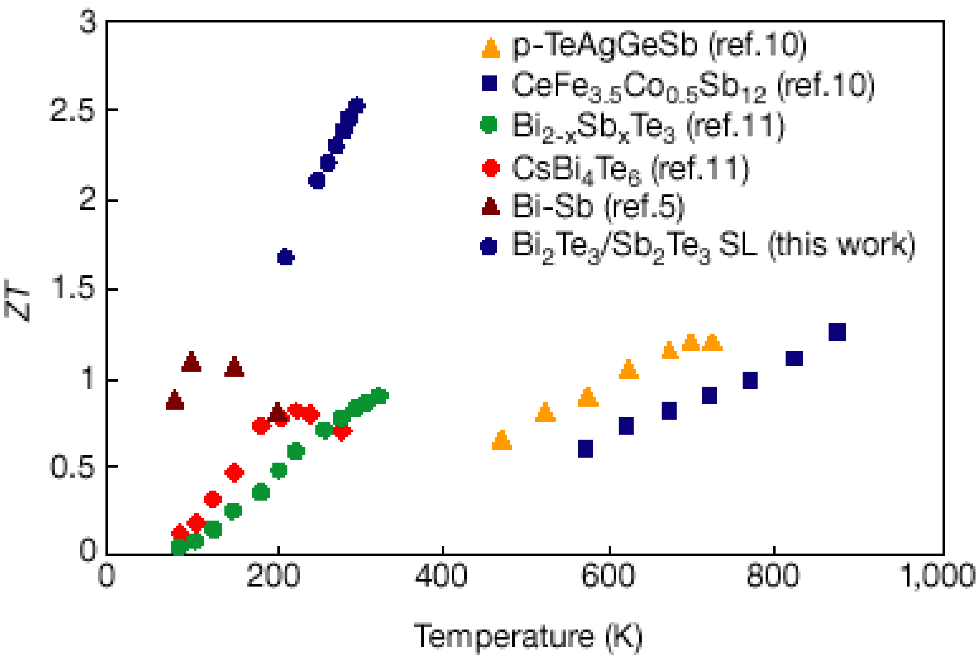
Direct Energy Conversion

- Direct thermal-electrical conversion eliminates moving parts
  - Enhanced reliability
  - Traditionally low conversion efficiency
- Short-term opportunities
  - Solar-thermal power generation
  - Man-portable power generation and cooling
  - Electronics cooling
  - Radioisotope power generation
- Longer-term opportunities
  - Topping cycles for fossil fuel plants
  - Bottoming cycles for fuel cells, exhaust systems

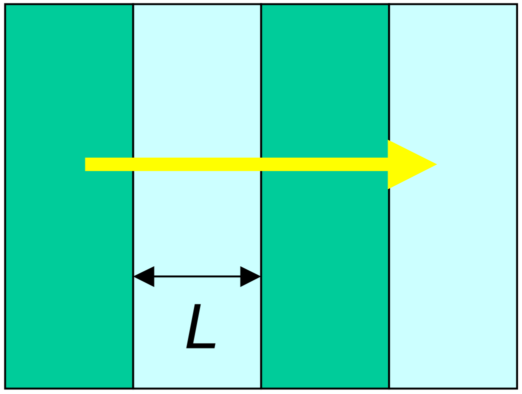


Nanoscale Thermoelectrics

- Figure of merit *ZT*
  - Indicates thermodynamic efficiency
  - Typical bulk values *ZT*~1
  - Enhanced by nanoscale spatial confinement
- Measured *ZT* = 2.4 for 10Å/50Å Bi_2Te_3/Sb_2Te_3 superlattices (Venkatasubramanian et al., 2001)
  - Coefficient of performance approximately 2-3 for room temperature refrigeration
- Nanowires (Hicks and Dresselhaus, 1993)
  - Extrapolation of model to ZT~4



Thin-film superlattice

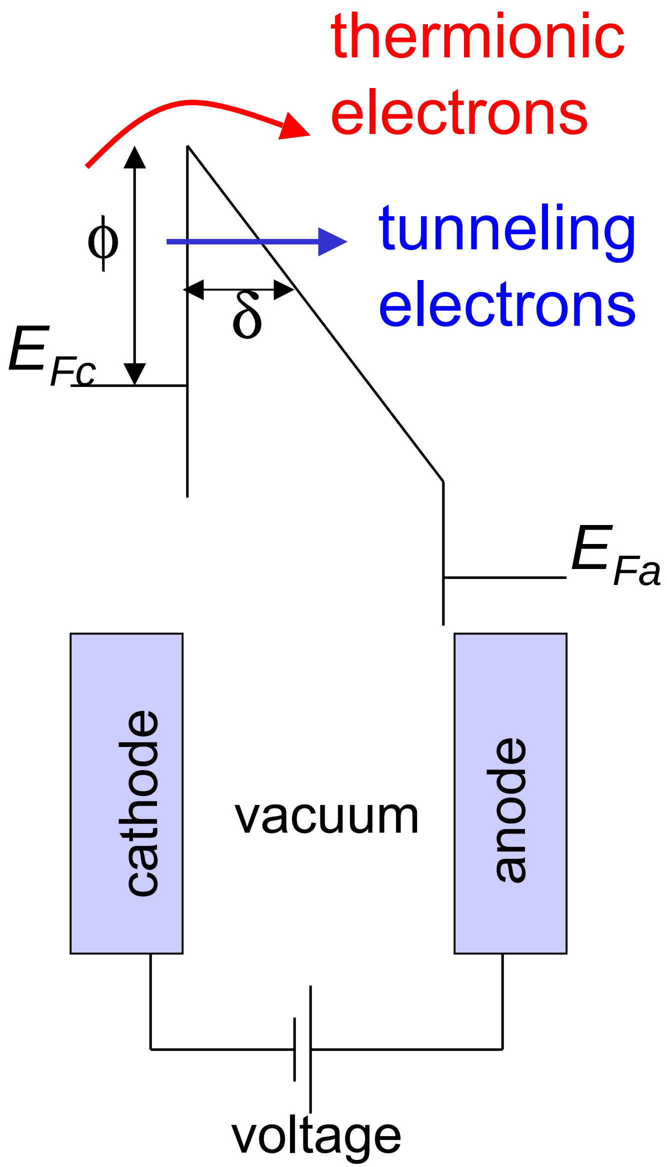


Electron Emission Processes

- Electron can emit over potential barriers (thermionic emission), OR
- They can tunnel through them (field emission)
- First studied in detail by Fowler and Nordheim (1928) for metal-vacuum-metal structures
- Emission is a strong function of field strength
- Tunneling probability

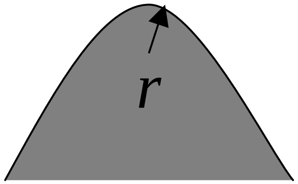
$$T \propto e^{-\delta}$$

$$\delta = \text{local barrier thickness}$$

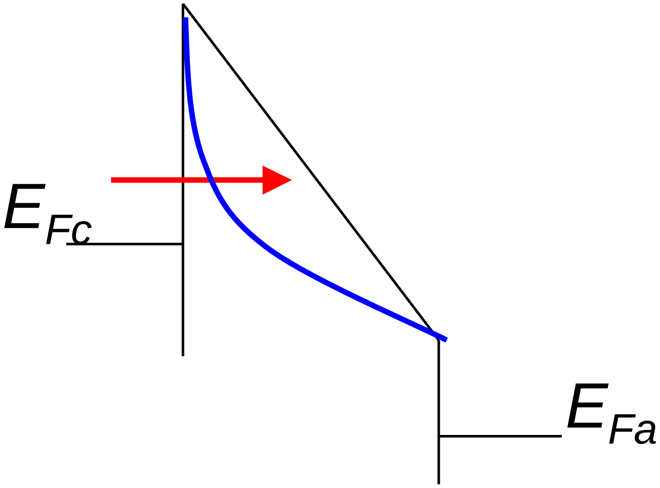


Geometric Field Enhancement

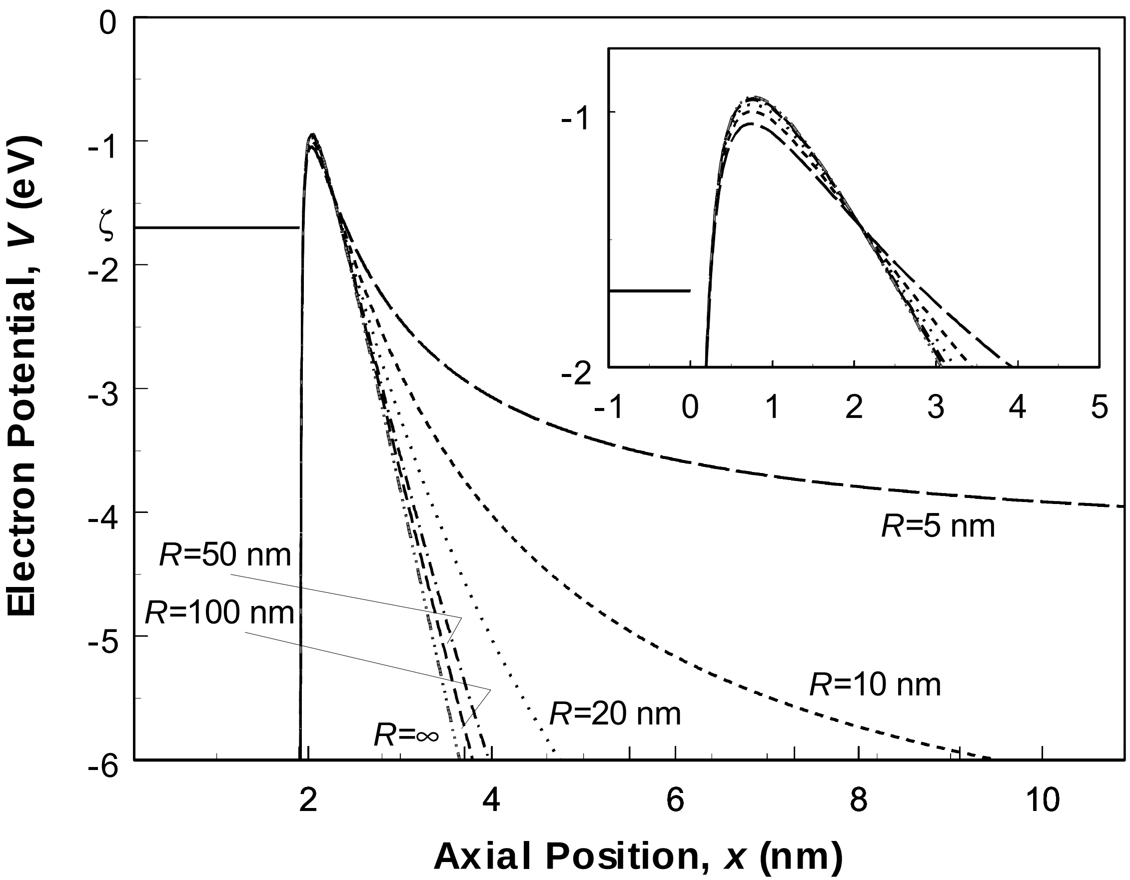
- Spindt (1968) created micron-sized metallic tips to enhance field emission
  $F_{local} = \beta F_{ave} \sim F_{ave} / r$
  β = Field enhancement factor



- Field enhancement is predicted by electrostatic theory



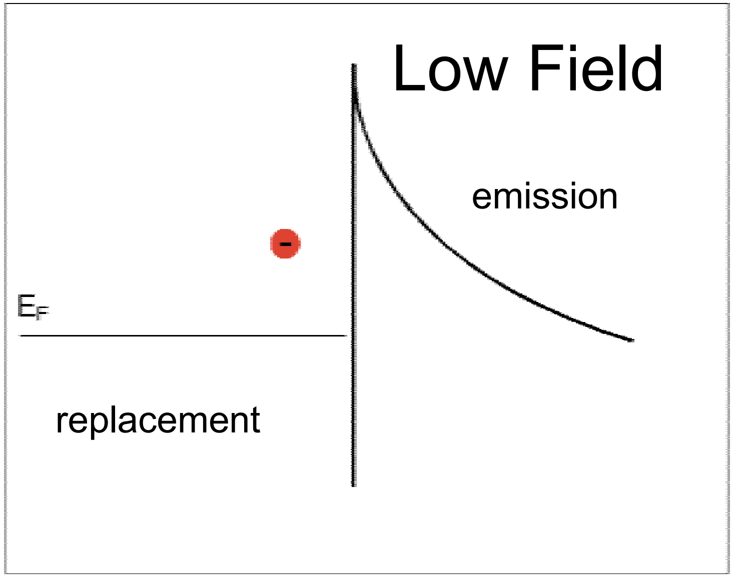
Nanoscale Effects on Emission

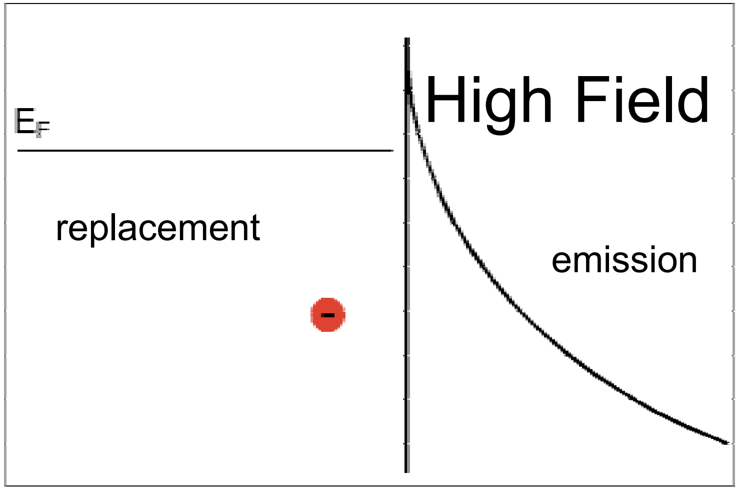


Effect of emitter radius on potential profile as a function of position from emitter and emitter radius. All profiles produce the same current density, J = 10 A/cm^2. ϕ = 1.7 eV. T = 300 K. (Fisher, 2001)

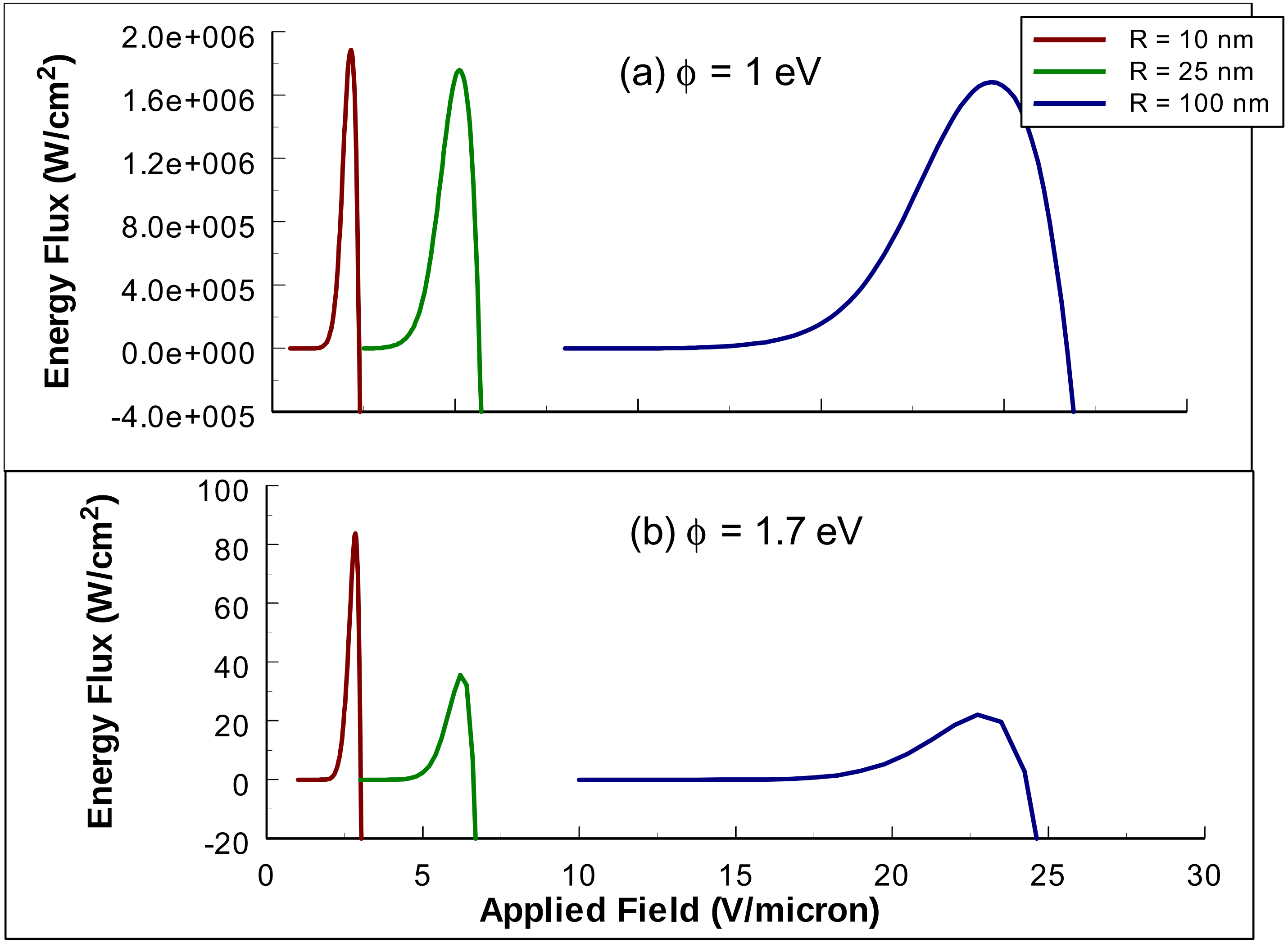
Energy Exchange

- Average emitted electron energies from moments of emission integral
  - Can be higher or lower than replacement electrons, depending on the field strength and curvature
- Replacement electrons from charge conservation and availability of states





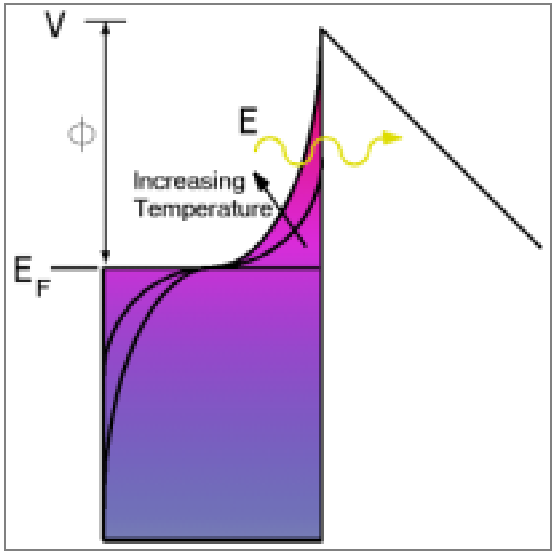
Predicted Net Energy Flux

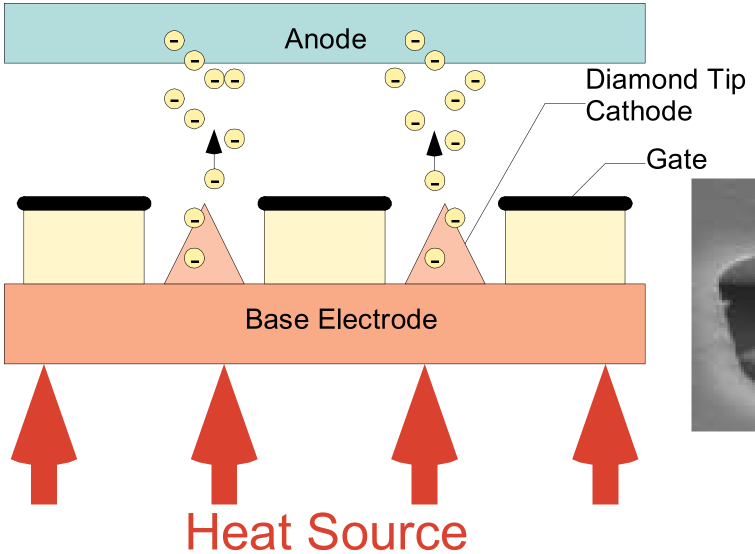


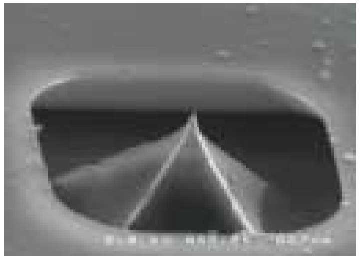
Emission energy flux from the cathode as a function applied field *F*, emitter characteristic radius *R*, and work function ϕ. (a) ϕ = 1 eV. (b) ϕ = 1.7 eV. Each part shows curves for three emitter radii, *R* = 10, 25, and 100 nm. Temperature *T* = 300 K. (Fisher and Walker, 2002)

Thermionic Emission

- Observed first by Edison (1880s)
- Current density derived by Richardson (1912)
- Thermal-to-electrical power generation
  - Low-energy-replacement electrons excited by heat source
  - Heat applied to a nanostructured substrate
  - Electrons excited to higher energy states
  - High energy electrons emitted to anode
  - Energy is dissipated across a load

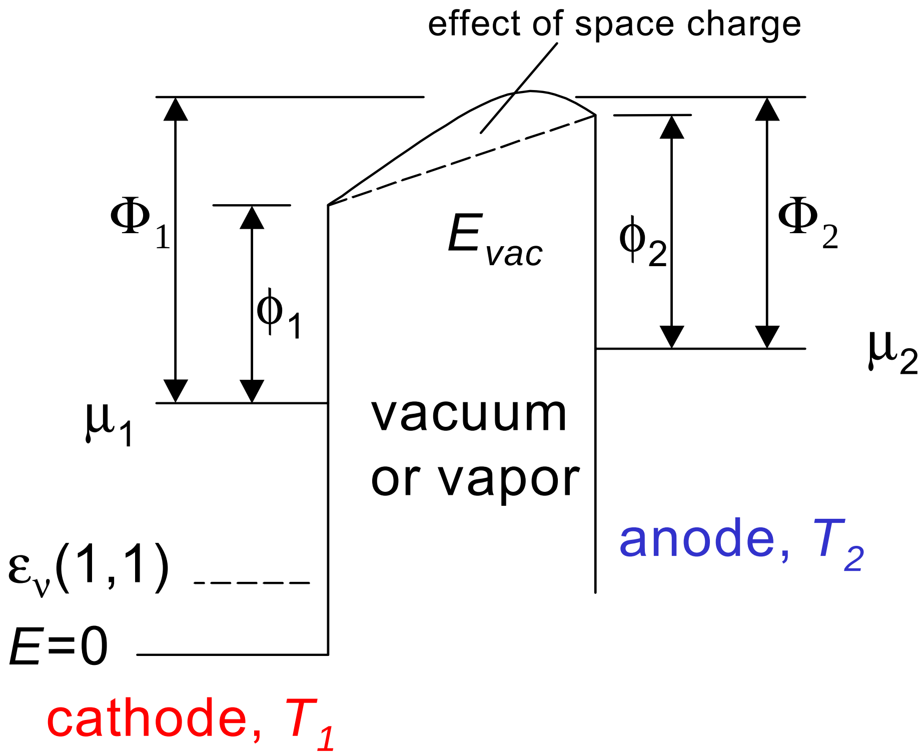






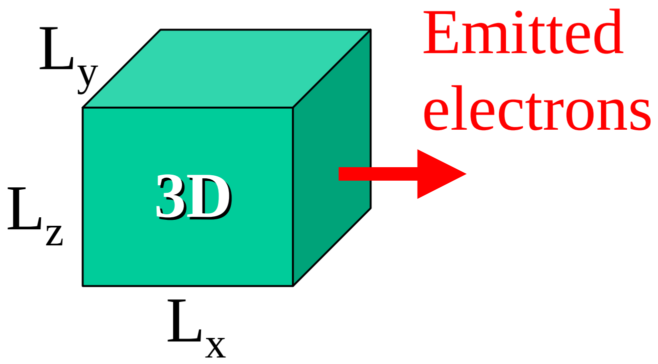
Thermionic Device Operation

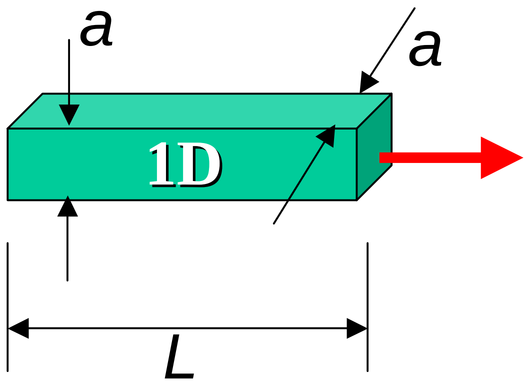
- Electrons thermally excited above the chemical potential μ according to the Fermi-Dirac distribution function
- At a material surface, electrons may escape the material if their energy exceeds the work function
- Additional potential barriers exist due to space charge and generated voltage



Electron motive diagram for a thermionic power generation diode, with $T_1 > T_2$.

Quantum Confinement Effects





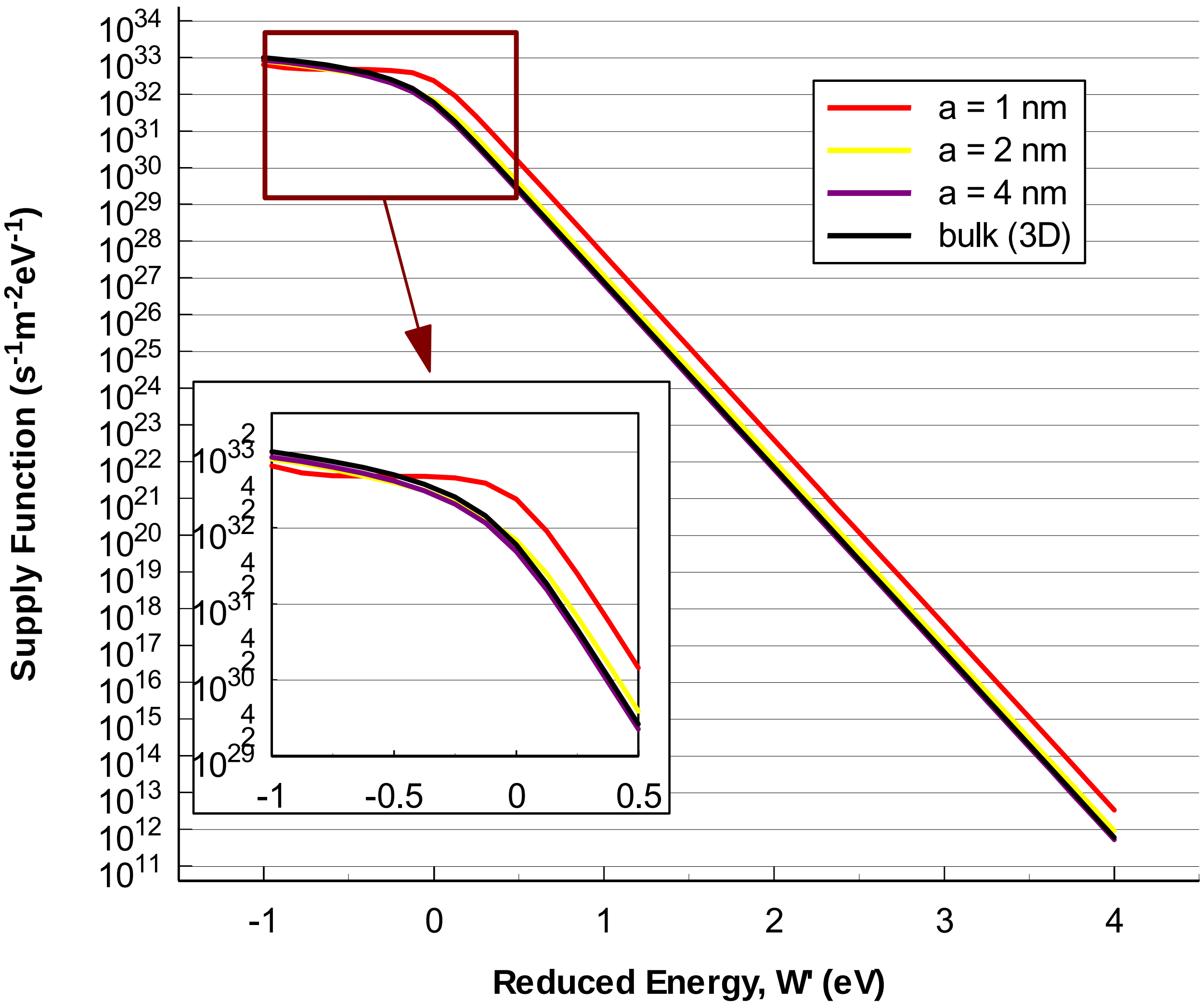
- Confinement influences energy states of electrons

$$E_{3D} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

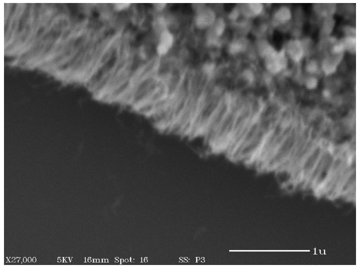
$$E_{1D} = \frac{\hbar^2}{2m}\left(k_x^2\right) + \frac{\left(\frac{\hbar\pi}{a}\right)^2}{2m}(n_y^2 + n_z^2), \qquad n_{y,z} = \text{integer}$$

Electron Supply Function

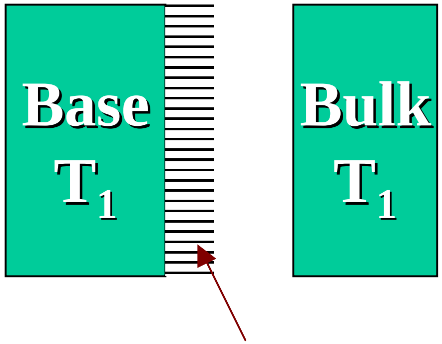
- Supply function gives number of electrons striking the emitting surface per unit time, area, and energy
- Noticeable increase in high-energy supply function for 1 nm quantum wire
- Larger wires are similar to bulk



Toy Example: Isothermal Power Generation

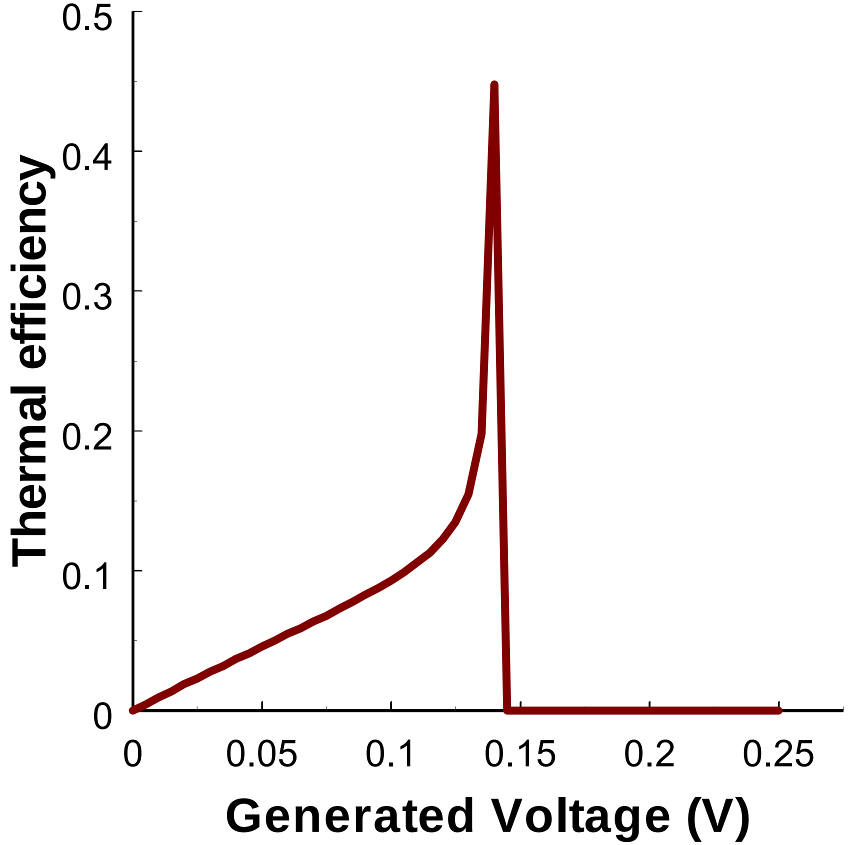


aligned CNT array

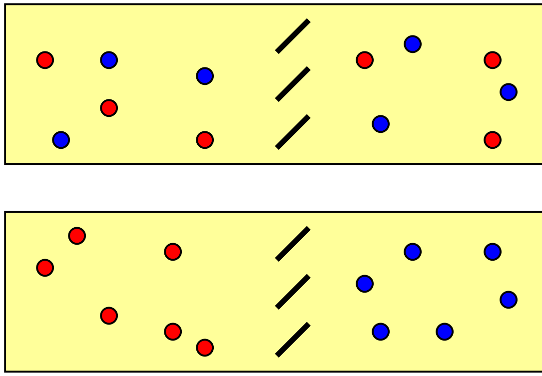


array of closely packed, aligned nanowires

- 2[nd] law of thermodynamics requires null thermal efficiency
- Simple theory predicts net power generation



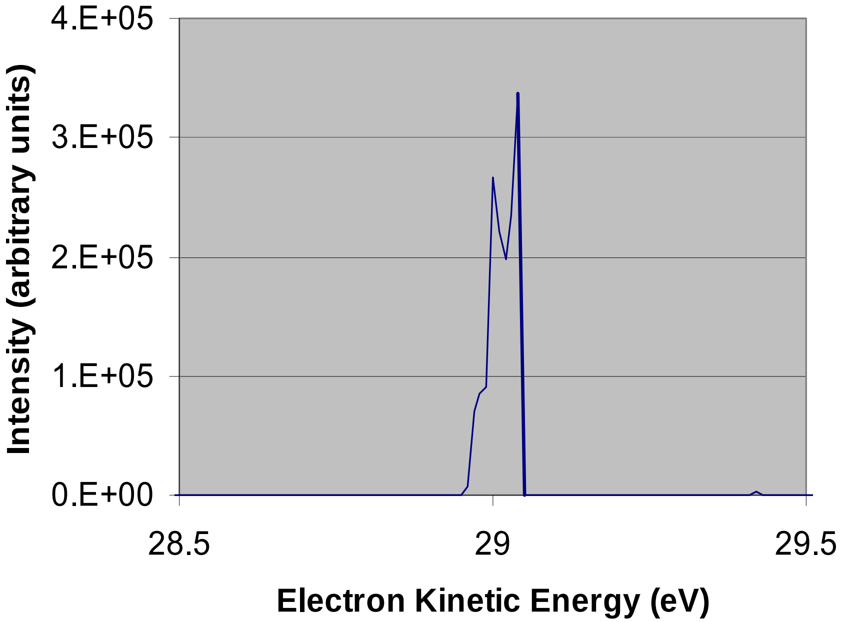
Is This Notion Possible?



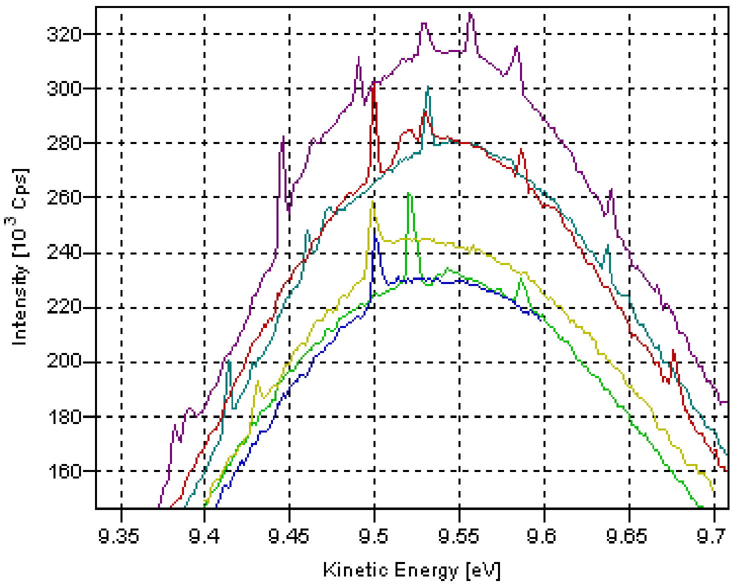
- Concept is similar to Maxwell's demon
  - High-energy particles separated from low energy particles by a lossless "shutter"
- Can nanomaterials serve as such separators?
  - Many unknowns
    - Nature of interfacial transport from 3D to 1D
    - Interactions among quantum wires
    - Internal loss (scattering) mechanisms
  - Answer: probably not, but…
    - Perhaps we can approach 2^{nd} law limits differently

Experimental Characterization

- Emitted electron energy distribution measurements
  - Room temp field emission from diamond nanotip



  - Thermionic emission from nanocrystalline diamond (T ≈ 970-980°C)



Prospects for Energy Conversion

- Direct energy conversion still in niche markets
  - Broader application will require higher efficiencies
  - Manufacturing economies of scale not competitive
- Nanoscale materials
  - All concepts require low work functions
  - Materials development required in surface science, combinatorial materials, controlled synthesis
- Many challenges
  - Understanding of transport at interfaces between bulk and confined materials
  - Non-uniform material behavior → must scale up from nano to macro
- Potential for exceptional performance
  - Generally high power density
  - Helpful Quantum Effects?

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