Boltzmann Transport Equations for Nanoscience Applications

Zlatan Aksamija
Electrical and Computer Engineering Dept.
University of Wisconsin-Madison
Overview

• We want to understand electrical and thermal transport in nanoscale systems
• Simulate transport in nanotubes, nanoribbons, nanowires, etc.
  – Why BTE?
  – Derivation of the BTE
  – Classical vs. Quantum
  – Carbon Nanotubes
  – Simulation of 1D systems
Why Boltzmann Transport Eqn. (BTE)?

- Originally derived for a dilute gas of non-interacting particles
- Extended to the simulation of electron and phonon transport
- Particle motion treated classically as in the Liouville equation
- Particle interactions introduced through quantum-mechanical perturbation theory
- Very flexible, general, and powerful
- Can include many other important effects:
  - electron bandstructure
  - phonon dispersion
  - self-consistency (Poisson equation)
  - Electro-thermal transport
Distribution function

- Distribution function $f_{T}(r,k,t)$ represents the probability for a particle to occupy position $r$ with momentum $k$ at time $t$.
- Distribution function $f_{T}$ contains all the information about the transport in the system.
- From $f_{T}$ we can obtain average quantities like current, mobility, mean-free-path, etc.
- It is 7-D in general: 3-D spatial ($r$) + 3-D momentum ($k$) + time ($t$) dependence.
- In 1-D materials like CNTs and nanowires, space and momentum are 1-D, so $f_{T}$ is 3-D altogether.
Semi-classical vs. Quantum

- Semi-classical BTE treats particles as classical point particles
  - Includes scattering through Fermi’s Golden Rule
  - Assumes collisions are instantaneous
  - Position and momentum are independent and functions of time

- Quantum BTE is capable of including quantum transport effects
  - quasi-particle states
  - level shift and broadening
  - requires a straightforward modification to the scattering rates

- Wigner equation takes this another step further to include the effects of confining potentials
  - Add higher derivatives ($3^{rd}$, $5^{th}$, etc.) of the potential and distribution
Particles change state by 3 different mechanisms:

1. Motion in real space due to electron velocity
2. Acceleration in momentum due to electric field
3. Scattering due to phonons

Consider a small cube in combined x and k space:
Particles change state by 3 different mechanisms:

1. Motion in real space due to electron velocity

The net particle gain is the difference at the two faces times the velocity in the x direction:

\[
\frac{df(x, y, z, t)}{dt} = v_x [f(x, y, z, t) - f(x + dx, y, z, t)] \ dx
\]

In the limit of small dx this becomes:

\[
\frac{df(x, y, z, t)}{dt} = -v_x \frac{\partial f(x, y, z, t)}{\partial x}
\]
Particles change state by 3 different mechanisms:

1. Motion in 3D space:
   - In general 3-D space, when there is a spatial gradient to the electron distribution, electrons will travel from a region of higher density to region of lower density.
   - The gradient of the distribution points in the direction of greatest change, therefore direction of electron motion.
   - Therefore the rate of change of the distribution function (scalar!) is equal to the electron velocity (a vector!) dotted with the gradient (another vector!):

\[
\frac{\partial f_T(r, k, t)}{\partial t} = \nu(r) \cdot \nabla r f_T(r, k, t) = \frac{dr}{dt} \cdot \nabla r f_T(r, k, t)
\]
Particles change state by 3 different mechanisms:

1. Motion in real space:
   - Particle velocity is the time derivative of its position
     \[ v(k) = \frac{dr(t)}{dt} \]
   - Velocity can be obtained from the bandstructure or dispersion
     \[ v(k) = \frac{1}{\hbar} \nabla_k E(k, \mu), \quad v(q) = \nabla_q \omega(q, \mu) \]
   - Putting these together produces
     \[ \frac{\partial f_T(r, k, t)}{\partial t} = -\frac{1}{\hbar} \nabla_k E(k, \mu) \cdot \nabla_r f_T(r, k, t) \]
Particles change state by 3 different mechanisms:

2. Acceleration in momentum due to electric field
   Again consider a small cube in k-space, and look at $k_x$ direction. The net gain is the difference at the two faces times the velocity in the $k_x$ direction:
   \[
   \frac{df(k_x, k_y, k_z, t)}{dt} = v_{kx} [f(k_x, k_y, k_z, t) - f(k_x + dk_x, k_y, k_z, t)]
   \]
   In the limit of small $dk_x$ this becomes:
   \[
   \frac{df(k_x, k_y, k_z, t)}{dt} = \frac{dk_x}{dt} \frac{\partial f(k_x, k_y, k_z, t)}{\partial k_x}
   \]
Particles change state by 3 different mechanisms:

2. Acceleration under the force of the electric field:
   - When an electric field $\mathbf{E}$ is applied to an electron, it produces an accelerating force $\mathbf{F} = -e\mathbf{E}$ on the electron.
   - Magnetic field can also be added $\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$
   - Analogous to $\mathbf{F} = ma = m\frac{dv}{dt} = \frac{d\mathbf{p}}{dt}$, we have:

     $$\frac{d\mathbf{k}}{dt} = \frac{1}{\hbar} \mathbf{F} = -\frac{e\mathbf{E}}{\hbar}$$

   - Therefore the rate of change of the distribution function (scalar!) is equal to the applied force $\mathbf{F}$ (a vector!) dotted with the gradient in momentum (another vector!): 

     $$\frac{\partial f_T(\mathbf{r}, \mathbf{k}, t)}{\partial t} = -\frac{e\mathbf{E}}{\hbar} \cdot \nabla_{\mathbf{k}} f_T(\mathbf{r}, \mathbf{k}, t)$$
Electrons change state by 3 different mechanisms:

3. Scattering in and out of a momentum state:
   - Can be derived by examining a small differential element in momentum space
   - Particles occupying a state $k$ with probability $f_T(k)$ can scatter out of $k$ with transition probability $S(k,k')$
   - Particles occupying a state $k'$ with probability $f_T(k')$ can scatter into state $k$ with transition probability $S(k',k)$

\[
S(k,k')f_T(k) \rightarrow S(k',k)f_T(k')\]
Electrons change state by 3 different mechanisms:

3. Scattering in and out of a momentum state:
   - Every scattering into \( \mathbf{k} \) increases the occupancy \( f_T(\mathbf{k}) \)
   - Every scattering out of \( \mathbf{k} \) decreases \( f_T(\mathbf{k}) \)
   - The net change in occupancy \( f_T(\mathbf{k}) \) is the in-scattering minus the out-scattering
   - For each state \( \mathbf{k} \), add up contributions from all other states \( \mathbf{k}' \)

\[
\frac{\partial f_T(\mathbf{k})}{\partial t} = \sum_{\mathbf{k}'} \left[ S(\mathbf{k}', \mathbf{k}) f_T(\mathbf{k}') - S(\mathbf{k}, \mathbf{k}') f_T(\mathbf{k}) \right]
\]
Degeneracy and exclusion

- Pauli’s Exclusion Principle tells us that only one electron can occupy a given state at a given time (ignoring spin).
- Because of exclusion, an electron can scatter into a state only if it is empty.
- To account for exclusion, we multiply the transition rate by the probability that the state is not occupied, given by \((1 - f_T(k))\).
- Finally we add all the contributions by summing over all the possible final states \(k'\)

\[
\frac{\partial f_{T'}(k)}{\partial t} = \sum_{k'} \left[ S(k', k) f_T(k') (1 - f_T(k)) - S(k, k') f_T(k) (1 - f_T(k')) \right]
\]

- This form referred to as “degenerate statistics”
Boltzmann Transport Eqn. (BTE)

- Particles are conserved so rate of change in time has to equal the change due to scattering.
- Therefore we simply equate the two rates to obtain the BTE:

\[
\frac{df_T(r, k, t)}{dt} = \left( \frac{df_T(r, k, t)}{dt} \right)_{\text{scat.}}
\]

- The sum can be converted to an integral in the limit of small \(dk\).
- This makes the BTE a difficult integro-differential equation.

\[
\frac{\partial f_T(r, k, t)}{\partial t} - \frac{eE(r)}{\hbar} \cdot \nabla_k f_T(r, k, t) + \frac{1}{\hbar} \nabla_k E(k, \mu) \cdot \nabla_r f_T(r, k, t) = \\
\frac{\Omega}{(2\pi)^3} \int d^3k' [S(k', k)f_T(k')(1 - f_T(k)) - S(k, k')f_T(k)(1 - f_T(k'))]
\]
“Shorthand” BTE

- The BTE can be derived quickly by starting with the semiclassical assumption and applying the chain rule
- Start by noting the distribution function $f_T$ is a function of position $r$, momentum $k$, and time $t$
- Assume $r(t)$ and $k(t)$ are independent and only functions of time
- REMINDER: Chain rule in 1-D and n-dimensions

$$\frac{df(g(t))}{dt} = \frac{\partial f(g)}{\partial g} \frac{dg(t)}{dt} \quad \frac{df(g(t))}{dt} = \nabla_g f(g) \cdot \frac{dg(t)}{dt}$$

- Apply the chain rule to obtain the complete time derivative:

$$\frac{df_T(r, k, t)}{dt} = \frac{\partial f_T(r, k, t)}{\partial t} + \nabla_r f_T(r, k, t) \cdot \frac{dr}{dt} + \nabla_k f_T(r, k, t) \cdot \frac{dk}{dt}$$
Interpreting the BTE:

The BTE is saying that probability is conserved along the path of the particle

- Use Taylor expansion in phase space:

\[
\begin{align*}
f_T(r + dr, k + dk, t + dt) &= f_T(r, k, t) + \frac{\partial f_T(r, k, t)}{\partial t} dt + \nabla_r f_T(r, k, t) \cdot dr + \nabla_k f_T(r, k, t) \cdot dk \\
&+ \frac{df_T(r, k, t)}{dt} dt + \nabla_r f_T(r, k, t) \cdot \frac{dr}{dt} + \nabla_k f_T(r, k, t) \cdot \frac{dk}{dt}
\end{align*}
\]
Interpreting the BTE:

The BTE is saying that probability is conserved along the path of the particle

- Recognize the expression for total time derivative
- Substitute in the conservation equation:

\[
f_T(r + dr, k + dk, t + dt) =
\]

\[
f_T(r, k, t) + dt \left( \frac{f_T(r,k,t)}{dt} \right) = f_T(r, k, t) + dt \left( \frac{f_T(r,k,t)}{dt} \right)_{scat}.
\]
Interpreting the BTE:

The BTE is saying that probability is conserved along the path of the particle:

- Particles will move in space according to their velocity:
  \[ dr = \frac{dr(t)}{dt} \, dt = v(k) \, dt \]

- Particles change momentum according to the forces acting on them
  \[ dk = \frac{dk}{dt} \, dt = -\frac{eE(r)}{\hbar} \, dt \]

- Particles can scatter from a momentum state \( k \) into another momentum state \( k' \) due to interactions with phonons, photons, plasmons, impurities, boundaries, etc.
Solving the BTE

• The BTE poses tremendous computational burdens due to high dimensionality (7-D=3-D space+3-D momentum + time)
• In order to solve it, we must simplify:
  – Consider momentum space only (homogeneous/bulk materials)
    • Iterative methods, spherical harmonics expansions, Rode’s Method
  – Consider real space only
    • Moments of the BTE, Hydrodynamic equations, Drift-Diffusion
  – Assume distribution is near equilibrium
    • Relaxation time approximation, Analytical methods
  – Only consider samples of the $f(r,k,t)$
    • Monte Carlo method for device simulation
  – Consider 1-D systems (produces a 3-D problem)
    • Good for carbon nanotubes, silicon nanowires, etc.
Transport simulation in Carbon Nanotubes

- CNT bandstructure and Density-of-States (DOS)
- CNT phonon dispersion
- 1-D BTE for CNTs
- Upwind Discretization
- Stability and Boundary Conditions (BCs)
- Poisson Equation (self-consistent potentials)
- Scattering Rates
- Linear Analytic method
- Results and Future Work
Single-walled Carbon Nanotubes

- CNTs are rolled-up sheets of monolayer graphene
- Have many interesting properties:
  - Extremely strong
  - Great thermal conductors
  - High optical phonon frequency
  - Can be both semiconducting or metallic depending on how the graphene sheet is rolled up (zig-zag, armchair, chiral)
- Potential applications as
  - FET devices
  - Interconnects
  - Sensors
  - Cooling solutions
  - Filters, etc.
CNT Bandstructure

• In general, bandstructure is obtained by solving the stationary Schroedinger equation for the periodic atomic potential
• CNT Bandstructure obtained by zone folding tight-binding graphene data according to:

\[ k_z f = k \frac{K_2}{\| K_2 \|} + \mu K_1 \quad \mu = 0, 1, \ldots, N - 1 \]

• N is the number of atoms in the unit cell, and k is the CNT wave-vector
• K_1 and K_2 are reciprocal basis vectors of the honeycomb lattice
• This allows a simple and sufficiently accurate treatment of electronic structure
• Other methods, including *ab initio*/*DFT* possible
CNT Bandstructure

- Graphene bandstructure can be computed using tight-binding by solving the secular equation:

\[ \det [H - ES] = 0 \]

- \( E \) is the energy we are solving for, and \( H \) and \( S \) are given by:

\[
H = \begin{pmatrix}
\epsilon_{2p} & tf(k) \\
ťf(k)^* & \epsilon_{2p}
\end{pmatrix}, \quad S = \begin{pmatrix}
1 & sf(k) \\
ťf(k)^* & 1
\end{pmatrix}
\]

- Momentum dependence enters through the form factor \( f(k) \)
- Parameters \( s \) and \( t \) are the overlap and transfer integrals, and are computed from first-principles calculations.
- Typical values are: \( \epsilon = 0 \), \( s = 0.129 \), and \( t = -3.033 \) eV.
CNT Bands and DOS results

- Results for a (10,10) metallic tube
- Note the bands crossing at zero energy. These will contribute most to electronic transport.
- Often only this portion is taken into account.
- Also note the non-zero density of states around Fermi level
- This makes the nanotube metallic (states available for transport even in equilibrium).
Electron velocities

- Metallic (10,10) tube
- Velocity given by the gradient of the dispersion:

\[ v(k, \mu) = \frac{1}{\hbar} \frac{dE(k, \mu)}{dk} = \frac{1}{\hbar} \frac{1}{b_{1,2}T} b_{1,2}^T (H^i - ES^i) b_{1,2} \]

- Velocity highest near Fermi level \( E_F \). This is the typical value of around \( 8.1 \times 10^5 \) m/s.
CNT Phonon dispersion

- Obtained by zone-folding the graphene dispersion
- Force Constant approach by fitting to measured data
- Factors due to bending of the graphene sheet into a tube
- High density of optical (OP) and zone-boundary (ZB) modes
- Strong interaction between electrons and OP and ZB modes
CNT Phonon velocities

- Phonon group velocities also obtained from the gradient of the dispersion:

\[ v_g(q, \mu) = \frac{d\omega(q, \mu)}{dq} \]

- Optical modes have flat dispersion giving rise to low group velocities
- Optical modes contribute little to thermal transport
1D Boltzmann Transport Eqn. (BTE)

- Electron BTE (1D):

\[
\frac{\partial f_T(x, k, t)}{\partial t} + \frac{eF}{\hbar} \frac{d}{dk} f_T(x, k, t) + v(k, \mu) \frac{d}{dx} f_T(x, k, t) = \frac{\Omega}{2\pi} \int \frac{dk'}{2\pi} \left[ S(k', k) f_T(k') (1 - f_T(k)) - S(k, k') f_T(k) (1 - f_T(k')) \right]
\]

- Sum converted to an integral in the limit of small dk.
- RHS looks like a standard 2D advection equation.
- Can apply standard discretization techniques.
Upwind Discretization

- Determine direction of differencing based on the sign of velocity and field at each (j,k) point

\[
f_{j,k}^{n+1} = f_{j,k}^n - \frac{f_{j,k}^n - f_{eq,j,k}^n}{\tau_k} \text{ relaxation time}
\]

\[
- \frac{1 + \text{sgn}(v_k)}{2}\nu_k(f_{j,k}^n - f_{j,k-1}^n) - \frac{1 - \text{sgn}(v_k)}{2}\nu_k(f_{j,k+1}^n - f_{j,k}^n)
\]

\[
- \frac{1 + \text{sgn}(F_j)}{2}\nu_j(f_{j,k}^n - f_{j-1,k}^n) - \frac{1 - \text{sgn}(F_j)}{2}\nu_j(f_{j+1,k}^n - f_{j,k}^n)
\]

- Constant \(\tau_k\) is the “relaxation time” computed from the scattering rate integral over all k
Stability and BCs

- Explicit time-stepping places a restriction on step-size $\Delta t$ dependent on the discretization:

$$\left| \frac{eE}{\hbar} \right| \frac{\Delta t}{\Delta k} < 1$$

$$|v_{max}| \frac{\Delta t}{\Delta x} < 1$$

- For $\Delta x \sim 1$nm, $\Delta t \sim 1$fs
- This is comparable to the relaxation time (10~50fs)
- Relaxation time poses another limitation on the timestep ($\Delta t \ll \min_{k}(\tau_{k})$)
- Periodic BCs in momentum (lattice is periodic)
- Homogenous Neumann BCs in space (quasi-equilibrium)
- Fermi-Dirac initial condition (start off with equilibrium)
Poisson Equation

- Charge and current can be obtained from

\[ \rho(t, x) = e \int f(x, k, t) dk \]
\[ I(x, t) = e \int v(k) f(x, k, t) dk \]

- Solve the Poisson equation for the potential along the tube

\[ V_{j+1}^n - 2V_j^n + V_{j-1}^n = \frac{\Delta x^2 \rho_j^n}{\epsilon} \]

- Boundary conditions given by applied potentials
- Extend to full 3-D Poisson for semiconducting CNTs
CNT Scattering Rates

- Scattering rates derived from quantum-mechanical “Fermi’s Golden Rule”
- Coupling potentials between electrons and phonons given by Bardeen’s Deformation Potential theory
- Acoustic rates have a factor of $q$ squared:

$$\frac{1}{\tau(k_i, \mu_i)} = \sum_{k_f, \mu_f} \frac{\hbar D_{ac}^2}{2 \rho \omega_{q, \mu_p}} \left[ q^2 + \left( \frac{2 \mu_p}{D} \right)^2 \right] \left( N_{q, \mu_p} + \frac{1}{2} \mp \frac{1}{2} \right) \delta \left( E(k_i, \mu_i) - E(k_f, \mu_f) \pm \omega_{q, \mu_p} \right)$$

- The signs depend on absorption or emission of a phonon.
- The $\delta$ function controls energy conservation
- Can be replaced by a Lorentzian to allow collisional broadening
CNT Scattering Rates

• Zone Boundary:

\[
\frac{1}{\tau(k_i, \mu_i)} = \sum_{k_f, \mu_f} \frac{\hbar D_{ZB}^2}{2\rho \omega_{q,\mu_p}} \left( N_{q,\mu_p} + \frac{1}{2} + \frac{1}{2} \right) \delta (E(k_i, \mu_i) - E(k_f, \mu_f) \pm \omega_{q,\mu_p})
\]

• Optical rate:

\[
\frac{1}{\tau(k_i, \mu_i)} = \sum_{k_f, \mu_f} \frac{\hbar D_{OP}^2}{2\rho \omega_{q,\mu_p}} \left( N_{q,\mu_p} + \frac{1}{2} + \frac{1}{2} \right) \delta (E(k_i, \mu_i) - E(k_f, \mu_f) \pm \omega_{q,\mu_p})
\]
Broadening

• When the scattering rate is high ($\delta \sim k_B T$) transitions can occur between perturbed “quasi-particle” states
• This is described by the particle “self-energy”
• For simplicity assume self-energy is pure imaginary (no level shift, only broadening).
• Replace $\delta$-function with a Lorentzian distribution
• Can add self-consistency by using optical theorem:

$$\delta_{k,\mu} = -\frac{\hbar}{2} \text{Im} \Sigma(k, \mu) = \frac{\hbar}{2\tau(k, \mu)}$$

• Take into account initial and final state broadening:

$$\delta = \delta(k_i, \mu_i) + \delta(k_f, \mu_f)$$
Broadening

- Replace δ-function with a Lorentzian distribution

\[ \delta \left( E(k_i, \mu_i) - E(k_f, \mu_f) \pm \hbar \omega(q, \mu_p) \right) \]

\[ \frac{1}{\pi} \frac{\delta}{\delta^2 + \left( E(k_i, \mu_i) - E(k_f, \mu_f) \pm \hbar \omega(q, \mu_p) \right)^2} \]

- This makes numerical calculation of scattering rate (relaxation time) easier
- Energy no longer conserved exactly, only on the average
Linear Analytic Method

- Break integral apart into many small segments in $k$
- Expand energies to 1$^{\text{st}}$ order and integrate analytically over each small segment in k-space
- Add up contributions form all segments in k-space

$$
\int dk \frac{1}{\pi} \delta^2 + \left( E(k_i, \mu_i) - E(k_f, \mu_f) \pm \hbar \omega (q, \mu_p) \right)^2
$$

$$
= \sum_{k_f, \mu_f} \int_{dk} \frac{1}{\pi} \delta^2 + \left( \Delta E + \hbar v(k_f)(k - k_f) \right)^2
$$

$$
= \sum_{k_f, \mu_f} \frac{1}{\pi \hbar v(k)} \left( tan^{-1} \frac{\hbar v(k_f)dk - \Delta E}{\delta} + tan^{-1} \frac{\hbar v(k_f)dk + \Delta E}{\delta} \right)
$$
Results: IV curves for (10,10) SWNT

- Current saturates around 25\(\mu\)A due to onset of strong optical scattering
- Resistance scales linearly with length in the low-field regime (interconnect applications)
Comments and Extensions

• Extends naturally to many other 1-D systems:
  – Carbon Nanoribbons (CNRs) are candidates for future FET devices
  – Semiconducting CNTs show interesting current up-kick
  – Rough Si nanowires show great potential for energy harvesting
• Phonon (thermal) transport is treated with a similar discretization scheme (no interaction with the electric field)
• Non-equilibrium transport can be explored in detail
• Thermo-electric properties can be simulated
• This requires coupling through scattering integrals (for each k sum over all k’, expensive ~1hr/tstep)
• Possible efficient parallel implementation
References

• “Semiconductor Transport” by David K. Ferry, Taylor&Francis (2000), chapter 3
• “An Introduction to the Theory of the Boltzmann Equation” by Stewart Harris, Dover Publications
• “Basic Semiconductor Physics” by Chihiro Hamaguchi, Springer (2001), chapter 6