Quantum Results from Classical Molecular Dynamics

Jian-Sheng Wang

Department of Physics, National University of Singapore

Outline

- **Thermal transport problems**
- **Classical molecular dynamics (MD) for thermal transport – advantages and disadvantages**
- **Quantum “correction” after MD simulations**
- **QMD – classical MD with quantum baths**
  - Derivation & results
- **QMD to electron transport and electron-phonon interactions**
- **Outlook and conclusion**

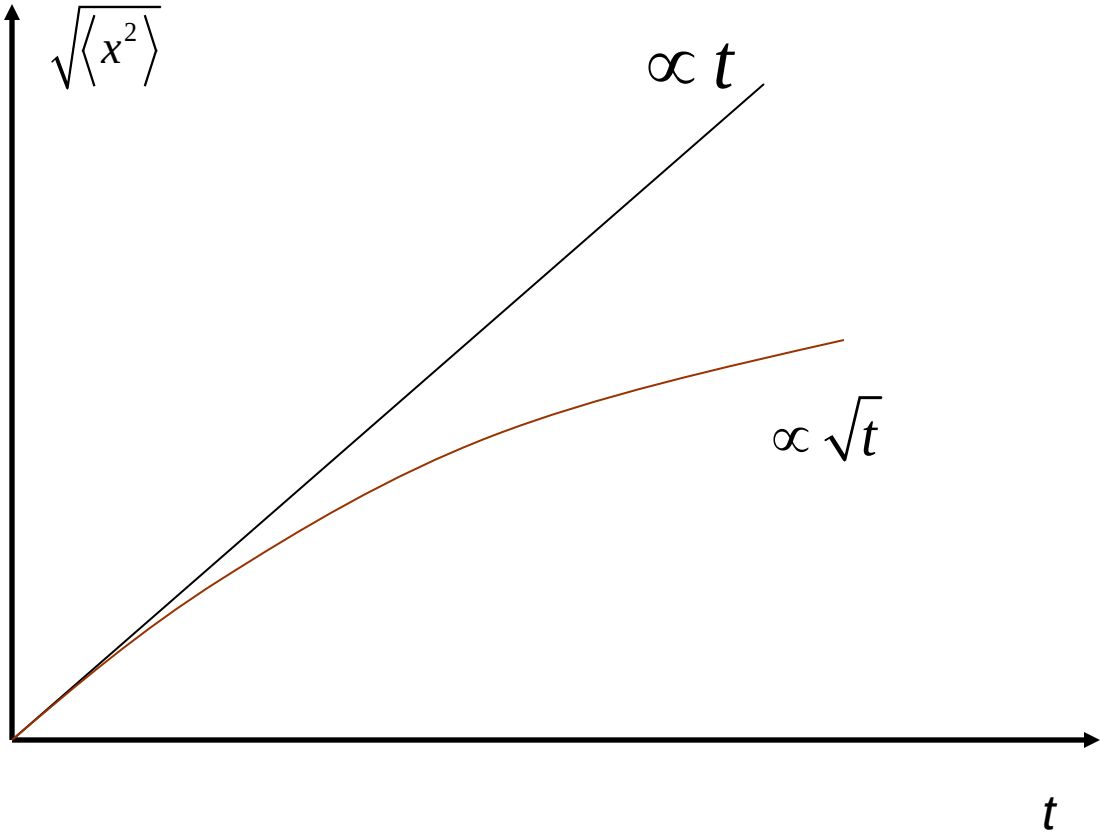
Fourier's law for heat conduction

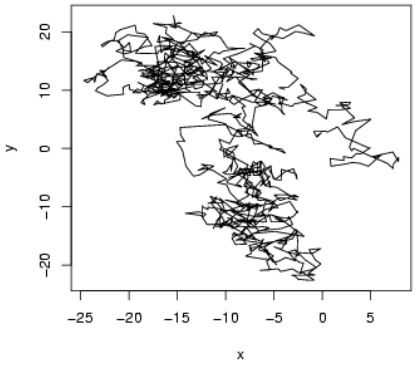
Fourier, Jean Baptiste Joseph, Baron (1768-1830)

$$\mathbf{J} = -\kappa \nabla T$$

$$\tilde{f}[\omega] = \int_{-\infty}^{+\infty} f(t)\, e^{i\omega t} dt$$

Diffusive transport vs ballistic transport

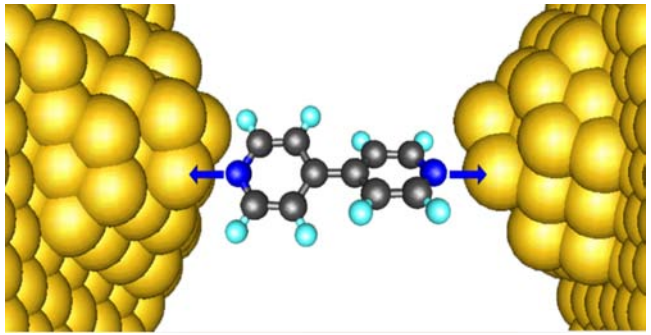




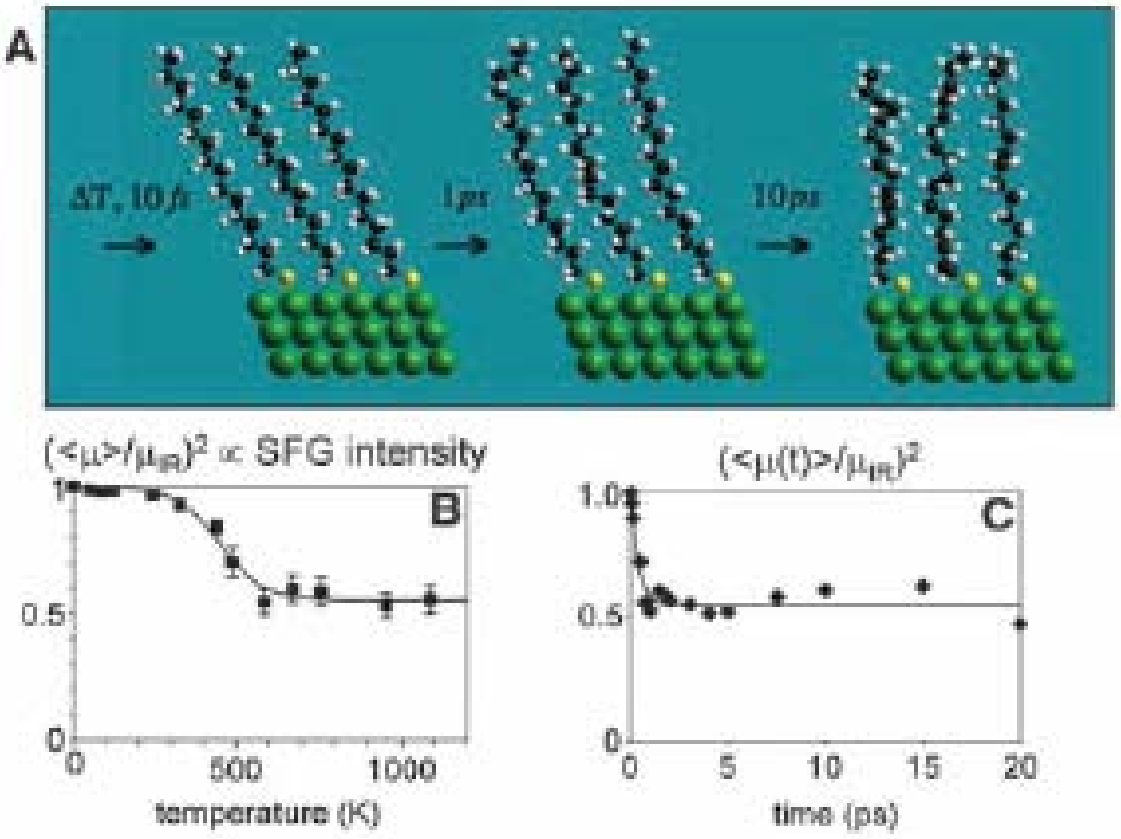
Thermal conductance

$$I = \left(T_L - T_R\right)\sigma$$

$$\kappa = \sigma \frac{L}{S}, \quad I = SJ$$



Experimental report of Z Wang et al (2007)



The experimentally measured thermal conductance is 50pW/K for alkane chains at 1000K. From Z Wang et al, Science 317, 787 (2007).

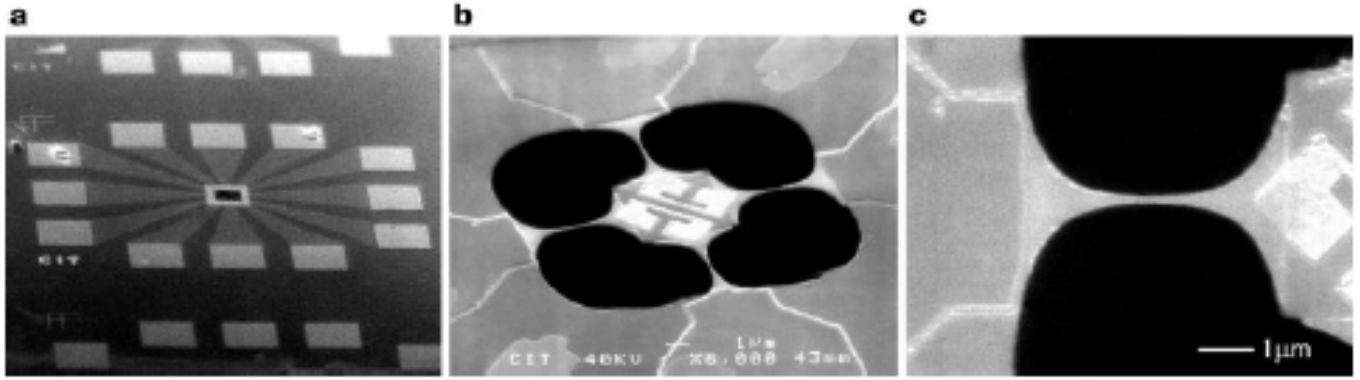
“Universal” thermal conductance in the low temperature limit

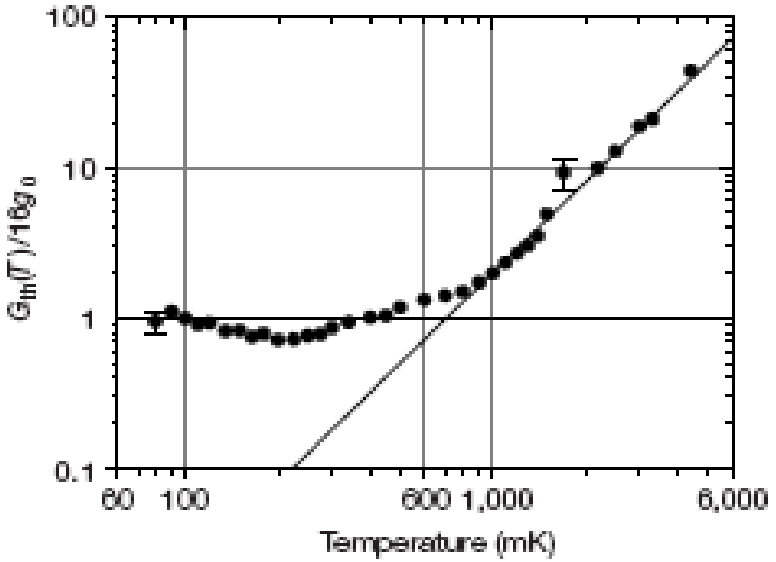
$$\sigma \simeq M \frac{\pi^2 k_B^2 T}{3h}$$

Rego & Kirczenow,
PRL 81, 232 (1998).

$M = 1$

Schwab et al experiments





From K Schwab, E A Henriksen, J M Worlock and M L Roukes, Nature, 404, 974 (2000).

Classical molecular dynamics

- **Molecular dynamics (MD) for thermal transport**
  - Equilibrium ensemble, using Green-Kubo formula
  - Non-equilibrium simulation
    - **Nosé-Hoover heat-bath**
    - **Langevin heat-bath**
    - **Velocity scaling heat source/sink**
- **Disadvantage of classical MD**
  - Purely classical statistics
    - **Heat capacity is quantum below Debye temperature**
    - **Ballistic transport for small systems is quantum**

Quantum corrections

- **Methods due to Wang, Chan, & Ho, PRB 42, 11276 (1990); Lee, Biswas, Soukoulis, et al, PRB 43, 6573 (1991).**
- **Compute an equivalent "quantum" temperature by**

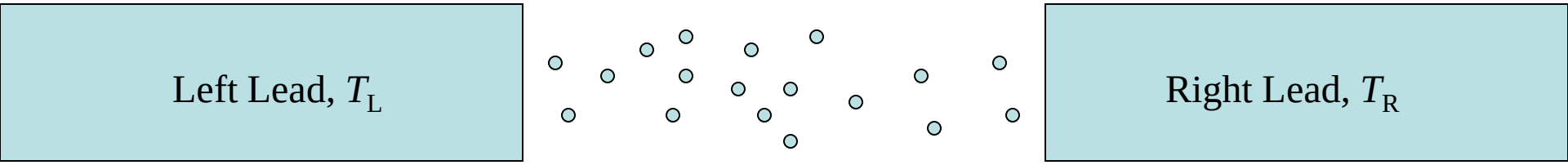
$$Nk_BT = \sum_{\omega} \hbar\omega \left(\frac{1}{\exp(\hbar\omega / k_B T_Q) + 1} + \frac{1}{2} \right) \qquad (1)$$

- **Scale the thermal conductivity by**

$$\kappa = \kappa_{\mathrm{MD}} \frac{dT}{dT_Q} \qquad (2)$$

- **But we have a criticism to this method**

Thermal conduction at a junction



semi-infinite leads serve as heat baths

Junction Part

Quantum heat-bath & MD

- **Consider a junction system with left and right harmonic leads at equilibrium temperatures T_L & T_R, the Heisenberg equations of motion are**

$$\ddot{u}_L = -K^L u_L - V^{LC} u_C,$$
$$\ddot{u}_C = F^C - V^{CL} u_L - V^{CR} u_R,$$
$$\ddot{u}_R = -K^R u_R - V^{RC} u_C$$

$$u = \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ u_j \\ \vdots \end{pmatrix} \qquad (3)$$

- **The equations for leads can be solved, given**

$$u_L(t) = u_L^0(t) + \int_{-\infty}^{t} g_L(t-t')V^{LC}u_C(t')dt', \qquad (4)$$

where

$$\left(\frac{d^2}{dt^2} + K^L\right)u_L^0(t) = 0, \quad \left(\frac{d^2}{dt^2} + K^L\right)g_L(t) = -\delta(t)I$$

Quantum Langevin equation for center

- **Eliminating the lead variables, we get**

$$\ddot{u}_C = F^C - \int_{-\infty}^{t} \Sigma(t-t')u_C(t')dt' + \xi_L + \xi_R \qquad (5)$$

where retarded self-energy and "random noise" terms are given as

$$\Sigma = \Sigma_L + \Sigma_R, \quad \Sigma_\alpha = V^{C\alpha} g_\alpha V^{\alpha C},$$
$$\xi_\alpha = -V^{C\alpha} u_\alpha^0, \quad \alpha = L, R \qquad (6)$$

(such idea for classical ensemble appears as early as in 1976, Adelman & Doll, JCP.)

Properties of the quantum noise

$$\left\langle \xi(t) \right\rangle = 0, \tag{7}$$

$$\left\langle \xi_L(t)\xi_L^{\dagger 0}(t') \right\rangle \overset{0}{=} V^{CL} \left\langle u_L(t)u_L(t')^T \right\rangle V^{LC}$$

$$= V^{CL} i\hbar g_L^{>}(t-t')V^{LC} = i\hbar \Sigma_L^{>}(t-t'),$$

$$\left\langle \xi_L^{\dagger}(t')\xi_L(t) \right\rangle^T = i\hbar \Sigma_L^{<}(t-t'), \tag{8}$$

$$\int_{-\infty}^{+\infty} \left\langle \xi_L^{\dagger}(t')\xi_L(t) \right\rangle^T e^{i\omega t} dt = i\hbar \Sigma_L^{<}[\omega] = -2\hbar f(\omega) \mathrm{Im}\,\Sigma_L[\omega] \tag{9}$$

For nonequilibrium Green's function (NEGF) notations, see JSW, Wang, & Lü, Eur. Phys. J. B, 62, 381 (2008).

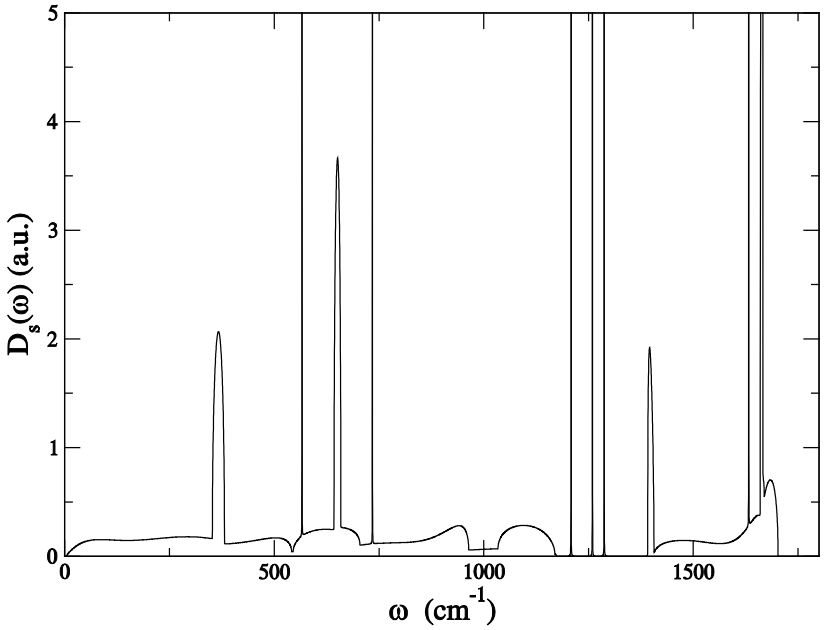
Quasi-classical approximation, Schmid (1982)

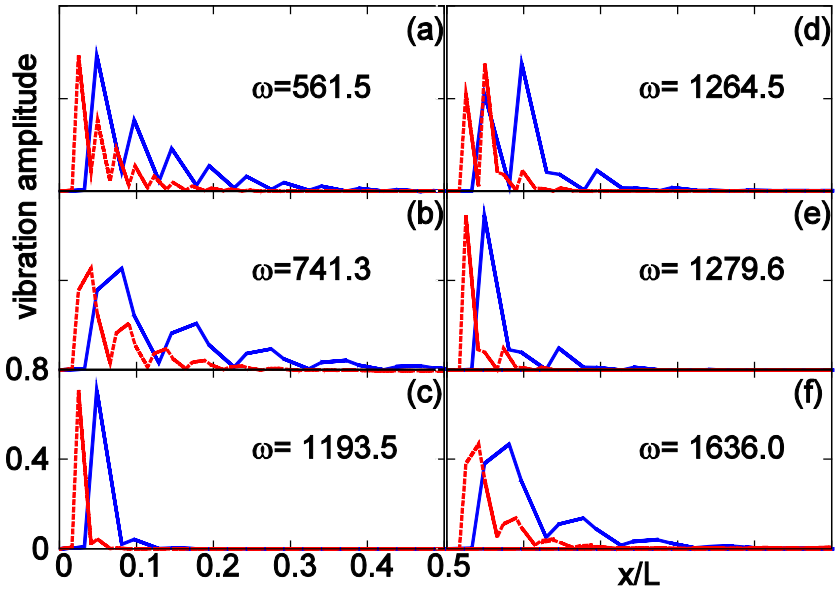
- Replace operators u_C & ξ by ordinary numbers

- Using the symmetrized quantum correlation, $i\hbar(\sum^{>} + \sum^{<})/2$ for the correlation matrix of ξ.

- For linear systems, quasi-classical approximation turns out exact! See, e.g., Dhar & Roy, J. Stat. Phys. 125, 805 (2006).

Delta singularities in self-energy





The surface density of states vs frequency for a 2 unit cell (8 atoms) wide zigzag graphene strip. The delta peaks are consistent with the localized edge modes shown on the left. JSW, Ni, Jiang, Phys. Rev. B 80, 224302 (2009).

Implementation

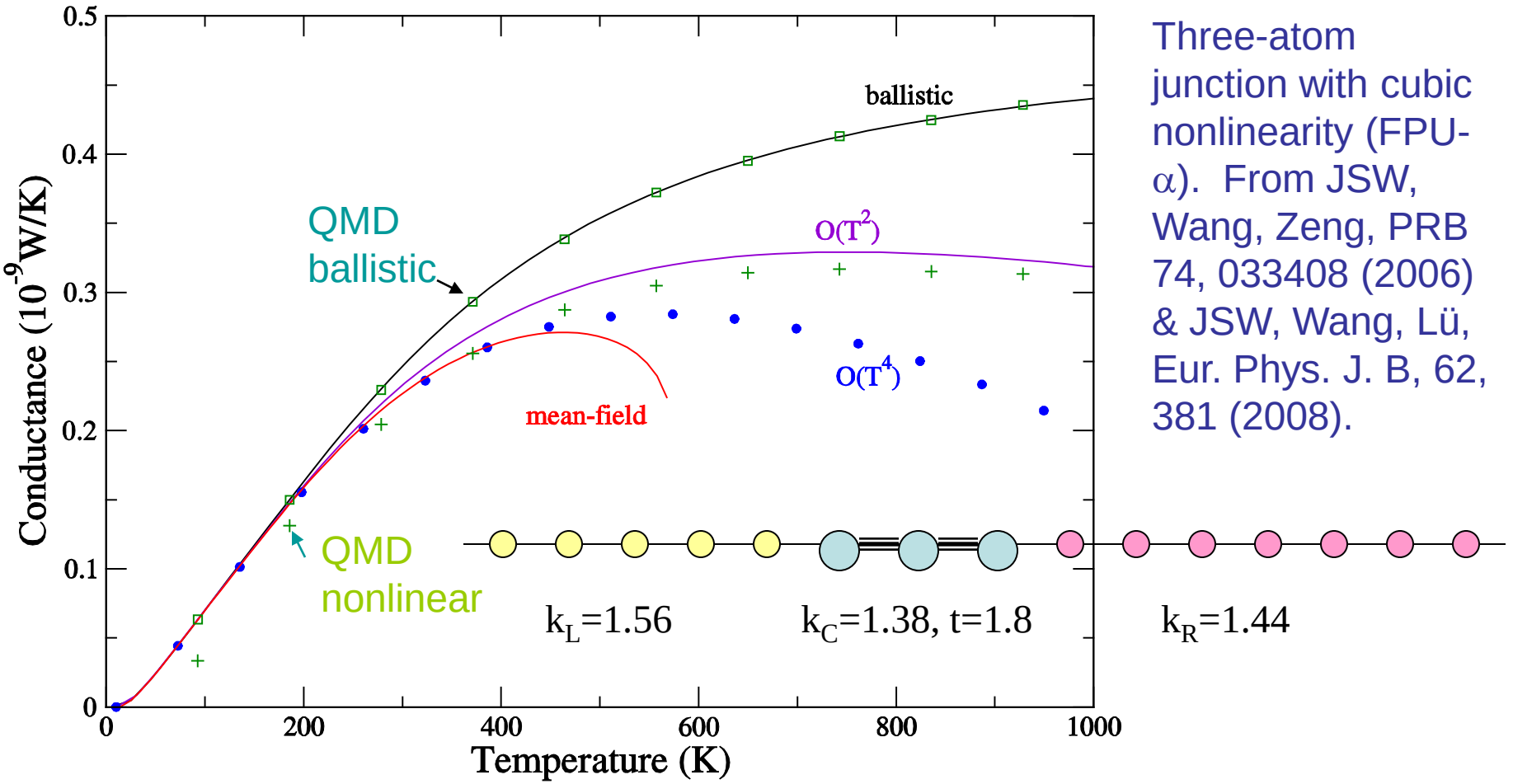
- **Generate noise using fast Fourier transform**

$$\xi(t = lh) = \frac{1}{hM}\sum_k \tilde{\xi}_k e^{-i\,2\pi lk/M} \qquad (10)$$

- **Solve the differential equation using velocity Verlet**
- **Perform the kernel integration using a simple rectangular rule**
- **Compute energy current by**

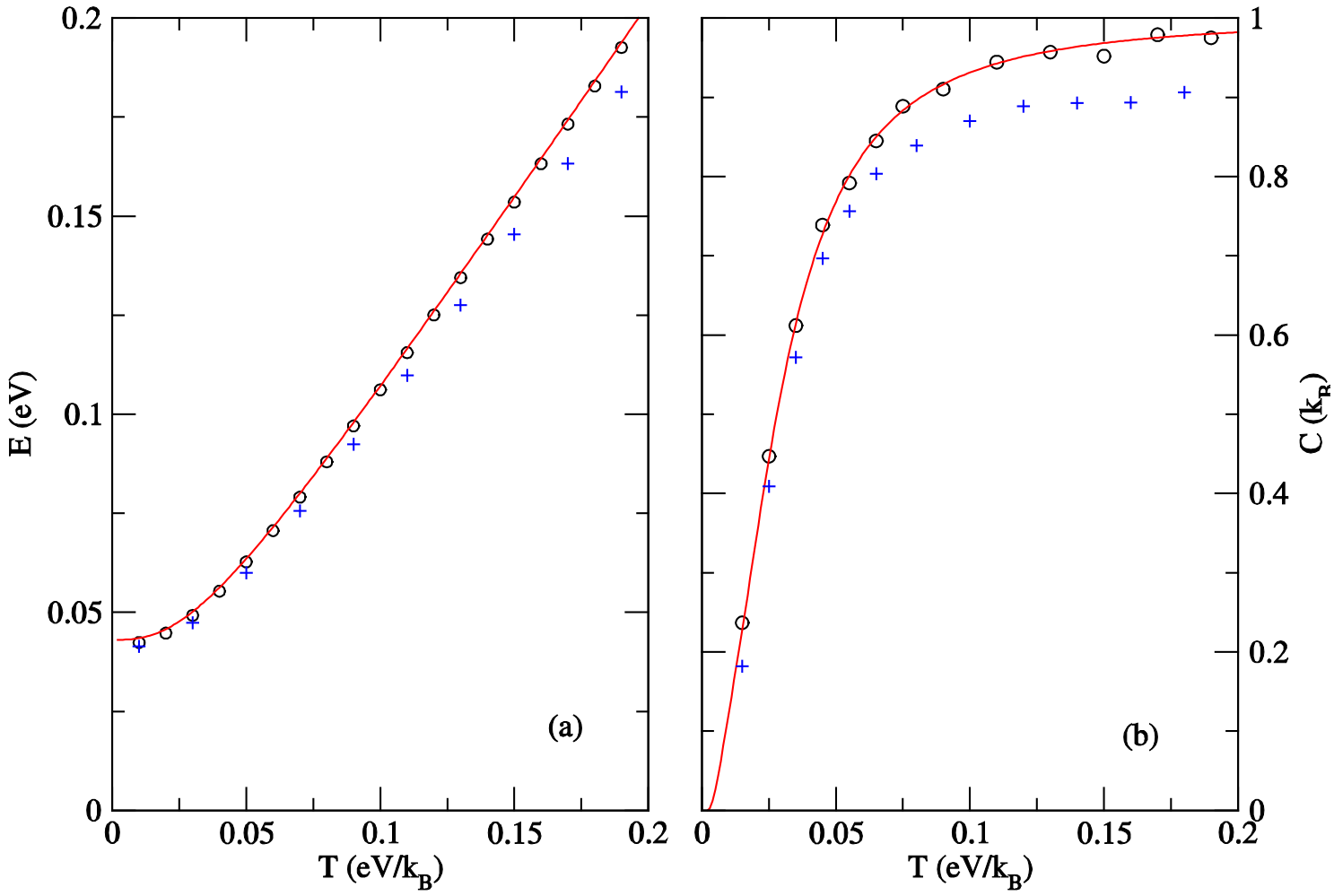
$$I_L = -\left\langle \frac{dH_L}{dt} \right\rangle = \left\langle \dot{u}_C^T \left(-\int_{-\infty}^{t} \Sigma_L(t - t')u_c(t')dt' + \xi_L \right) \right\rangle \qquad (11)$$

Comparison of QMD with NEGF



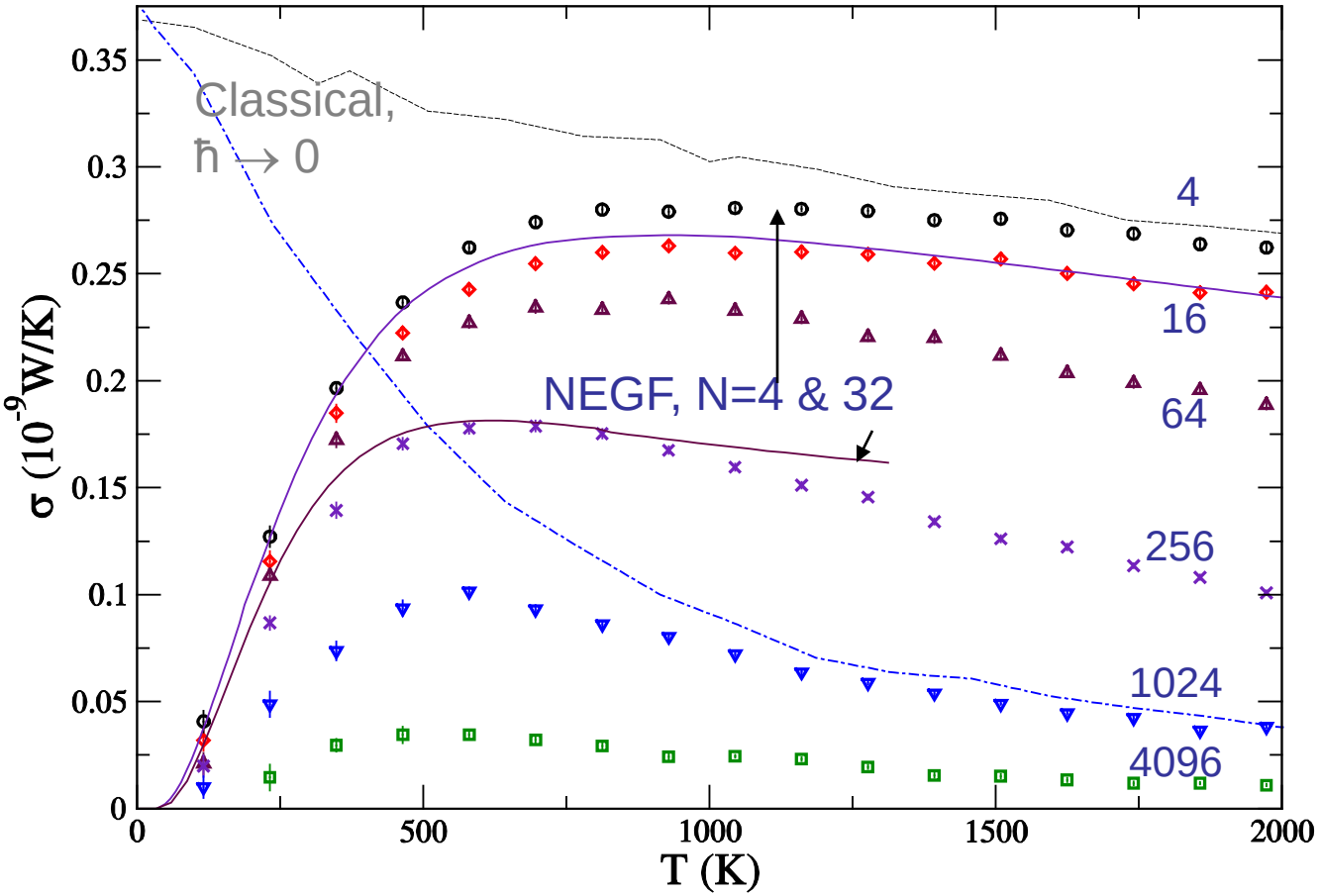
Three-atom junction with cubic nonlinearity (FPU-α). From JSW, Wang, Zeng, PRB 74, 033408 (2006) & JSW, Wang, Lü, Eur. Phys. J. B, 62, 381 (2008).

Equilibrium simulation



1D linear chain (red lines exact, open circles QMD) and nonlinear quartic onsite (crosses, QMD) of 128 atoms. From Eur. Phys. J. B, 62, 381 (2008).

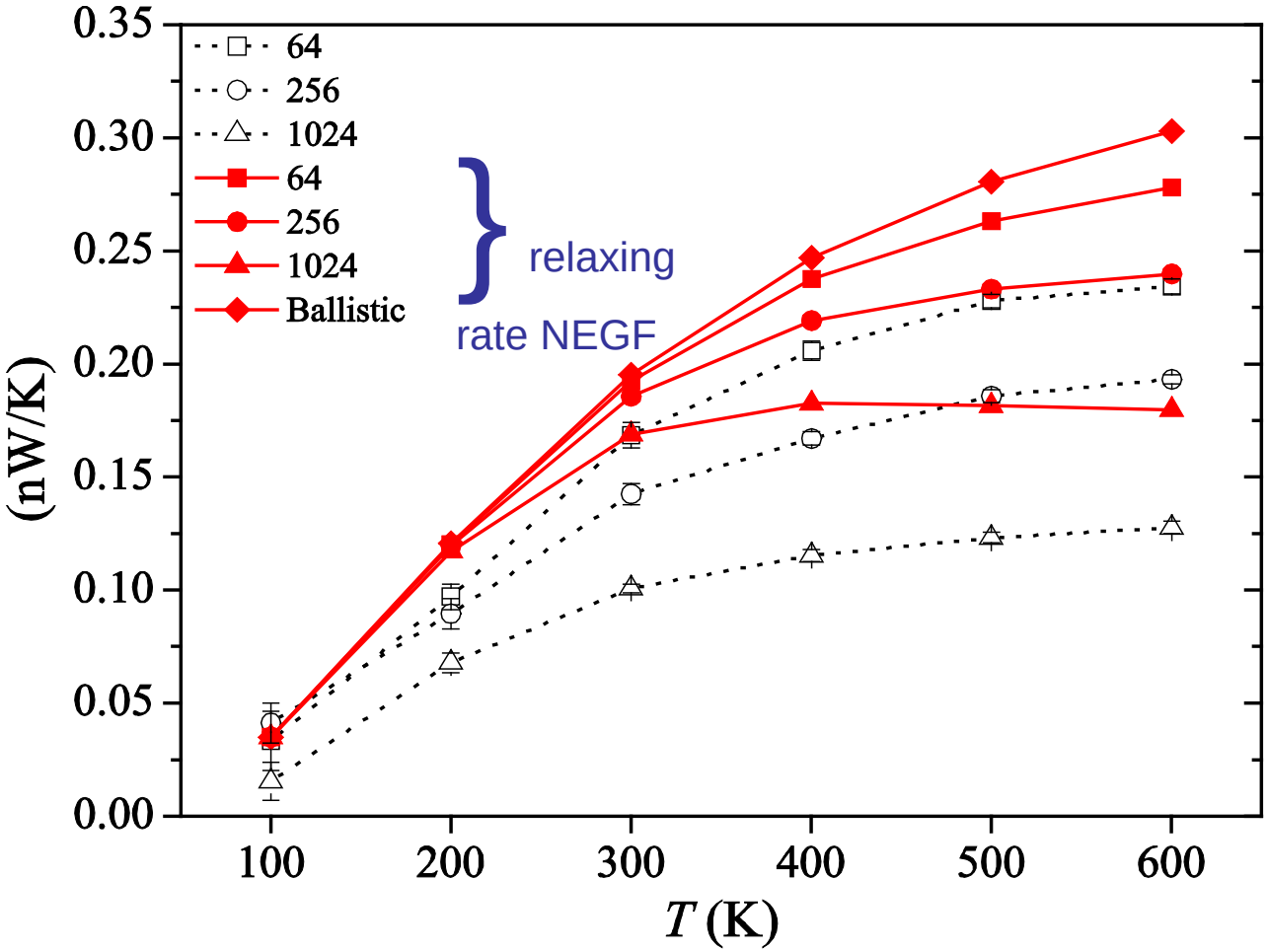
From ballistic to diffusive transport



1D chain with quartic onsite nonlinearity (Φ^4 model). The numbers indicate the length of the chains. From JSW, PRL 99, 160601 (2007).

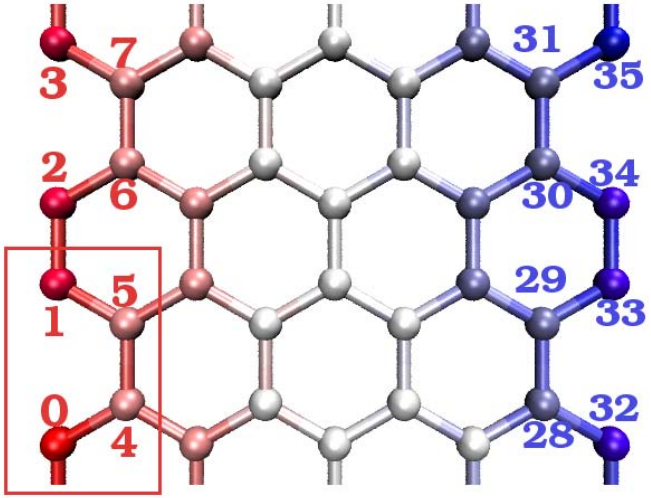
$$\sigma = \kappa \frac{S}{L}, \quad J = -\kappa \nabla T$$

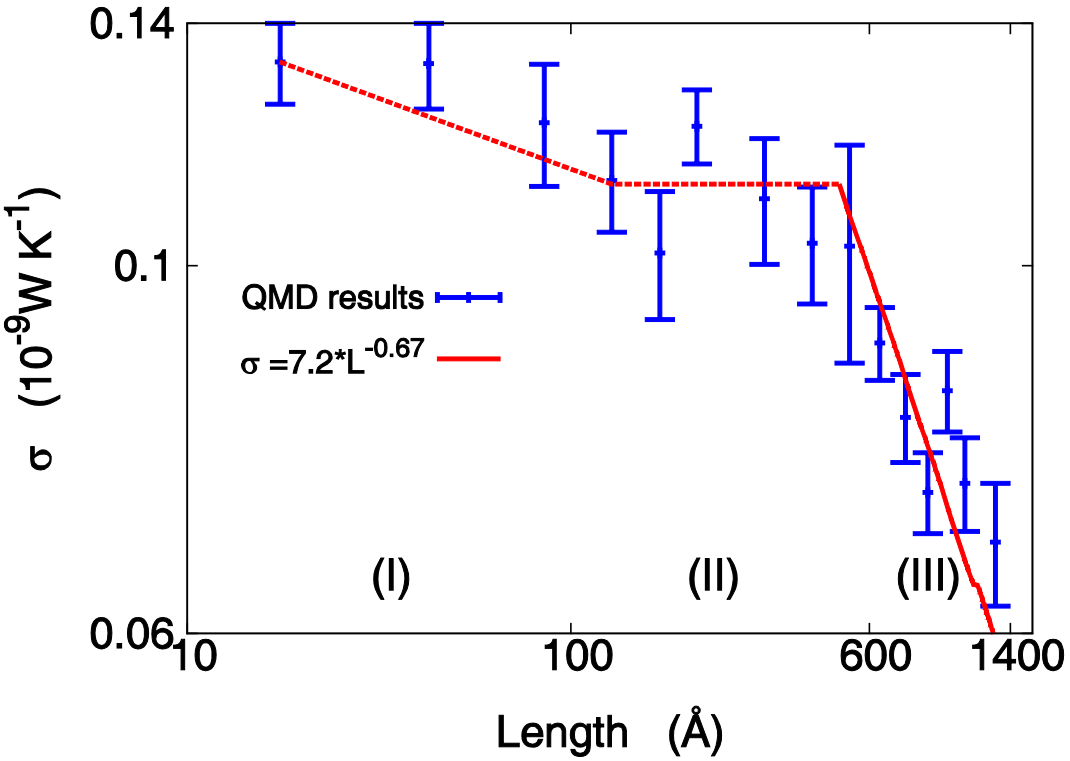
FPU-β model



It is not clear whether QMD over or under estimates the nonlinear effect. From Xu, JSW, Duan, Gu, & Li, PRB 78, 224303 (2008).

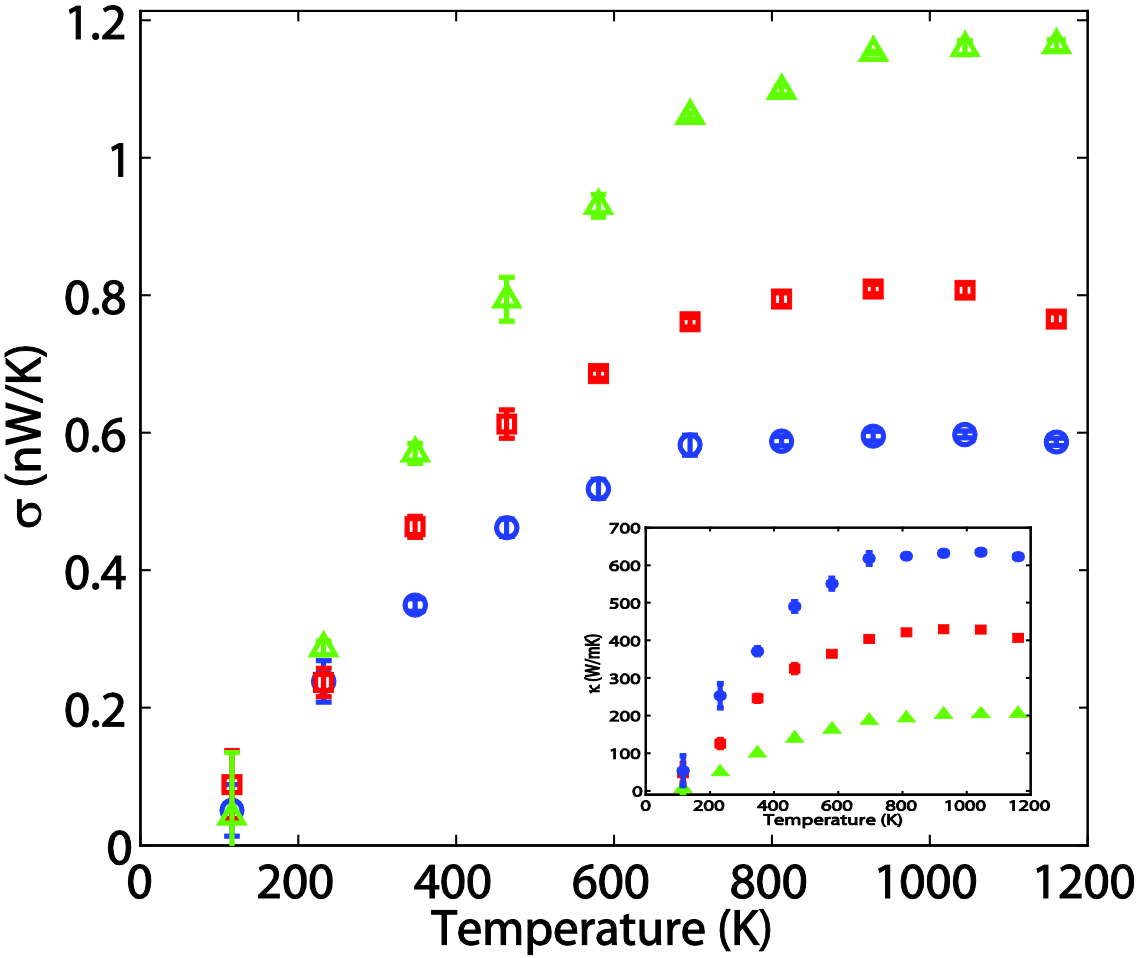
Conductance of graphene strips





Sites 0 to 7 are fixed left lead and sites 28 to 35 are fixed right lead. Heat bath is applied to sites 8 to 15 at temperature T_L and site 20 to 27 at T_R. JSW, Ni, & Jiang, PRB 2009.

Zigzag (5,0) carbon nanotubes



Temperature dependence of the thermal conductance (and conductivity) for lengths 4.26 (green), 12.8 (red) and 25.6 (blue) nm, respectively. JSW, Ni and Jiang, PRB 2009.

Electron transport & phonons

- **For electrons in the tight-binding form interacting with phonons, the quantum Langevin equations are (set $\hbar = 1$)**

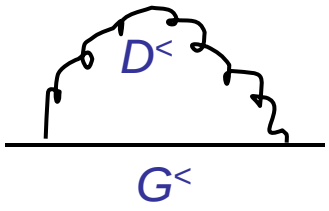
$$i\dot{c} = Hc + \int_{-\infty}^{t} \Sigma(t-t')c(t')dt' + \xi + M^k u_k c, \tag{12}$$

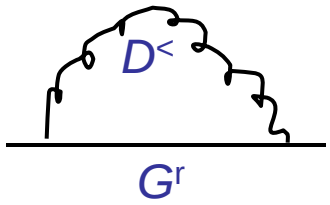
$$\ddot{u} = -Ku - \int_{-\infty}^{t} \Pi(t-t')u(t')dt' + \eta - c^{\dagger}Mc \tag{13}$$

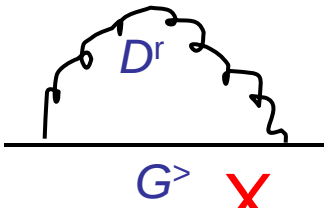
$$\left\langle \xi(t)\xi(t')^{\dagger\dagger} \right\rangle = i\Sigma^{>}(t-t'), \quad \left\langle \xi\ (t')\xi(t) \right\rangle^{T} = -i\Sigma^{<}(t-t'), \tag{14}$$

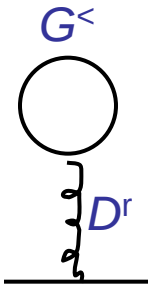
$$\left\langle \eta(t)\eta(t')^{\dagger} \right\rangle = i\Pi^{>}(t-t'), \quad \left\langle \eta(t')\eta^{T}(t) \right\rangle^{T} = i\Pi^{<}(t-t') \tag{15}$$

Quasi-classical approximation & NEGF

$\Sigma^{<}_{n} = i$ 

$\Sigma^{r}_{n} = i\{$ 

$+$ 

X
$-$ 

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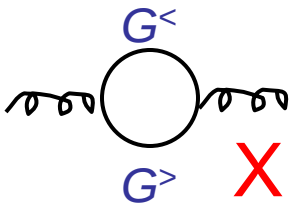
$\Pi^{<}_{n} = -i$ 

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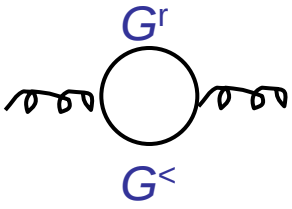
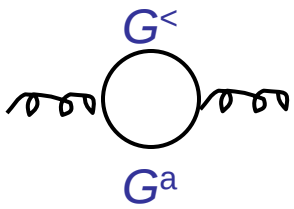
$\Pi^{r}_{n} = -i\{$ 

$+$ 

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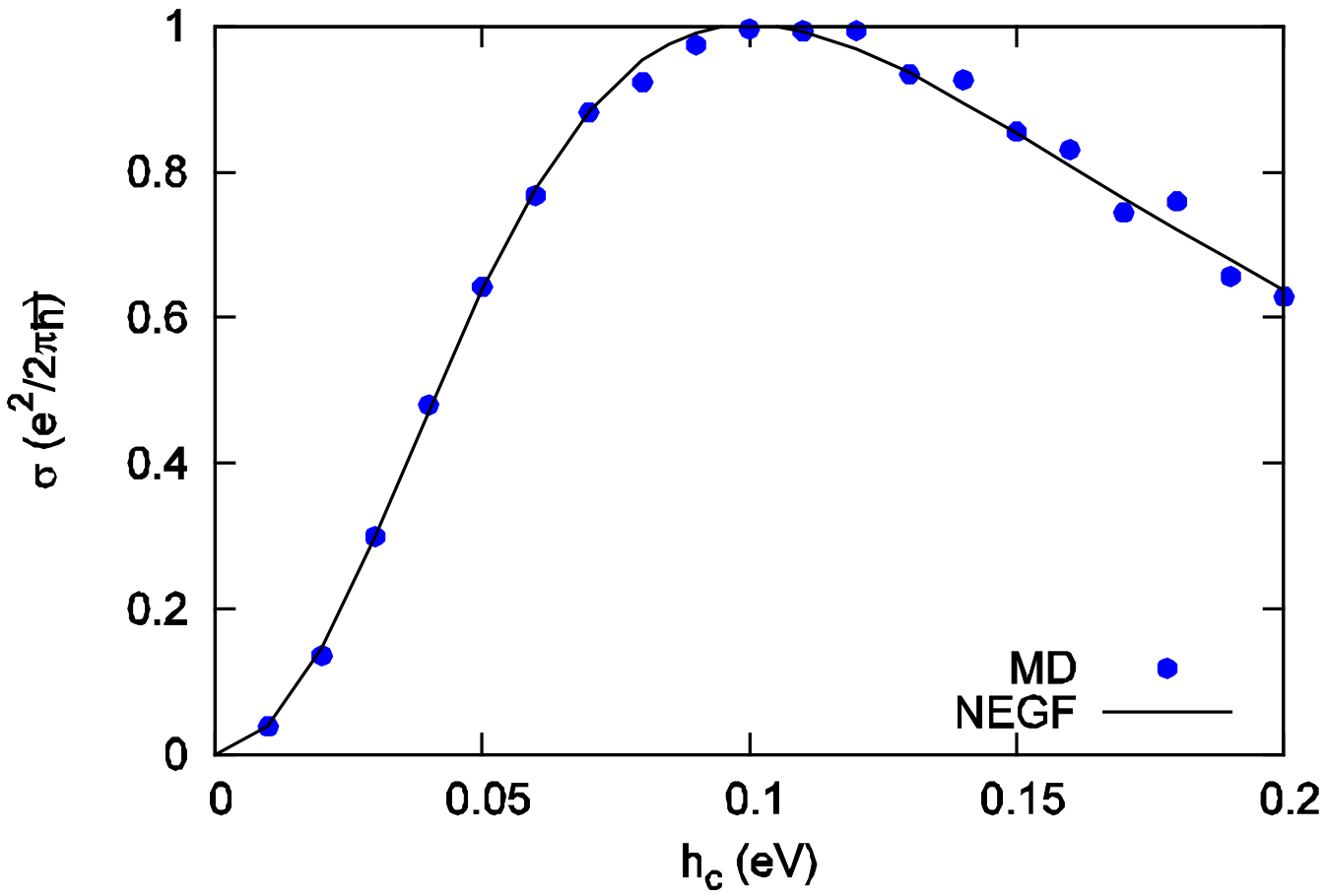
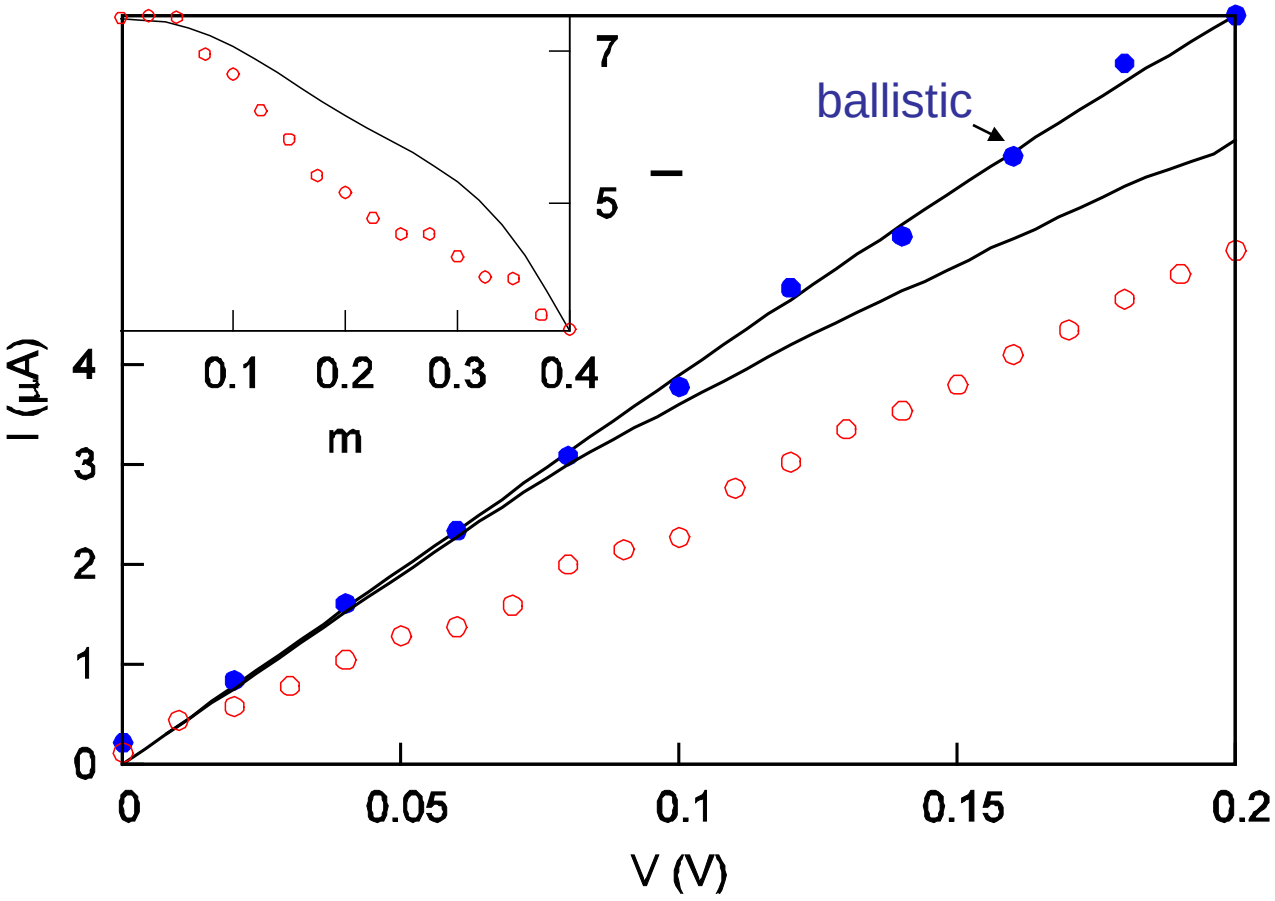
To lowest order in coupling M, quasi-classical approximation is to replace all $G^{>}$ by $-G^{<}$.

Ballistic electron transport, NEGF vs QMD



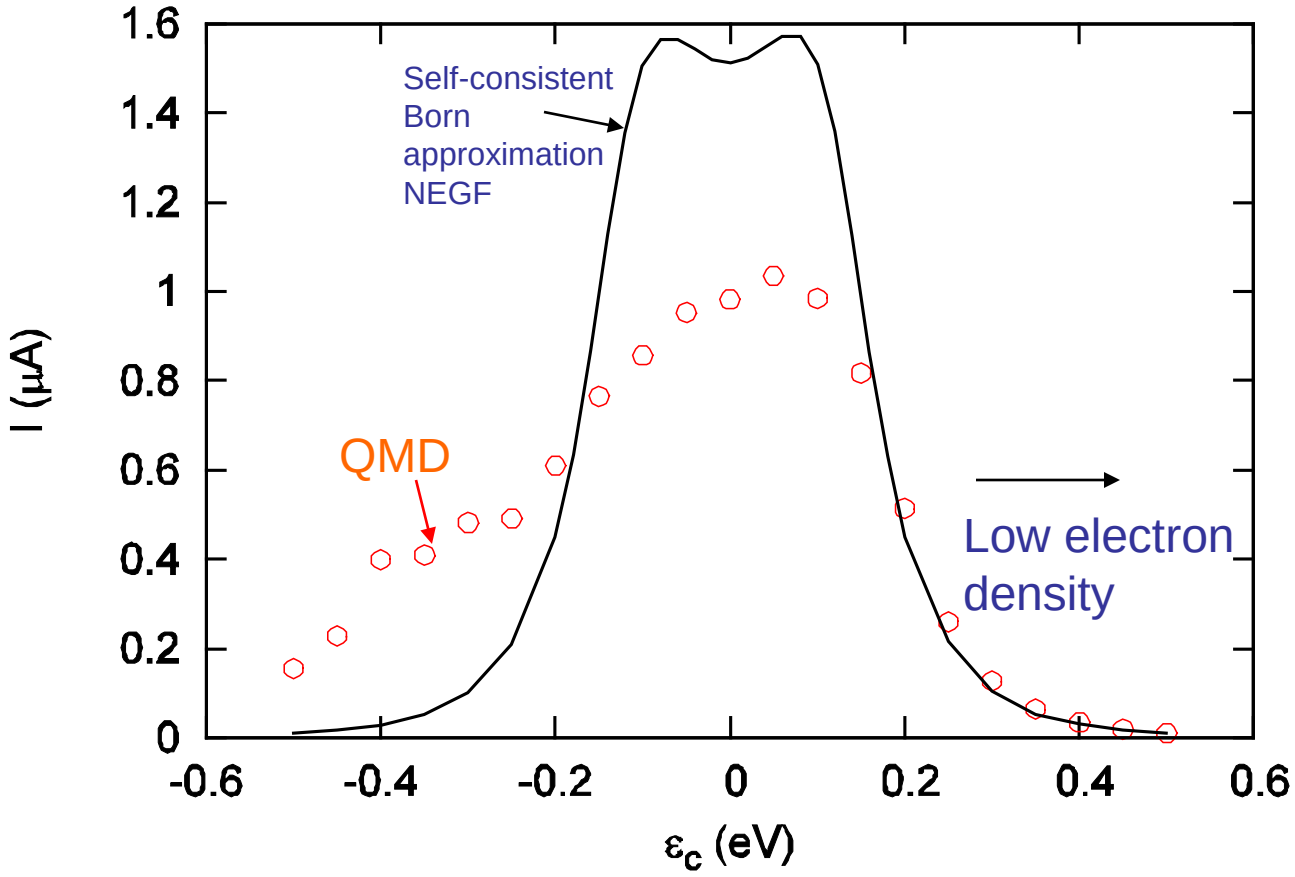
Nearest neighbor hopping model with two sites in the center, lead hopping $-h_l = 0.1$ eV, varying the center part hopping term. From Lü & JSW, arXiv:0803.0368. For NEGF method of electron-phonon interaction, see Lü & JSW, PRB 76, 165418 (2007).

Strong electron-phonon interactions

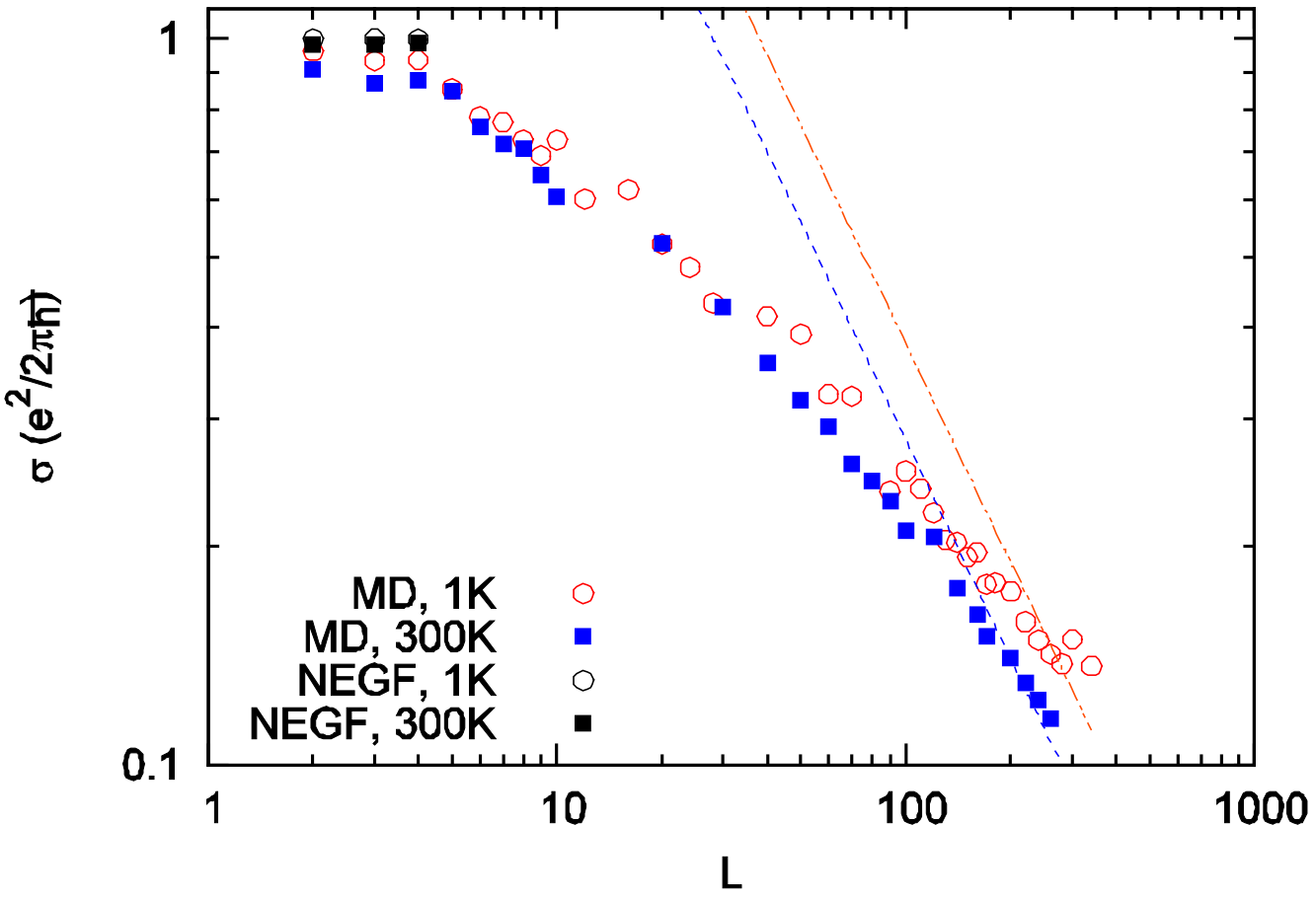


Two-center-atom model with Su, Schrieffer & Heeger electron-phonon interaction. Lines are NEGF, dots are QMD. From Lü & JSW, J. Phys.: Condens. Matter, 21, 025503 (2009).

QMD is exact in low electron density limit



Ballistic to diffusive



Electronic conductance vs center junction size *L*. Electron-phonon interaction strength is *m*=0.1 eV. From Lü & JSW, arXiv:0803.0368.

Electrons as a heat bath (Lü, Brandbyge, et al, based on path-integral formulism)

$$\ddot{u} = F^C + F_e - \int_{-\infty}^{t} \Pi(t-t')u(t')dt'$$

$$- \int_{-\infty}^{t} \Sigma_e(t-t')u(t')dt' + \eta + \xi_e$$

A simplified QMD?

- **Consider the following Langevin equation for lattice vibration [Keblinski & JSW, unpublished; see also Buyukdagli, et al, PRE 78, 066702 (2008); Ceriotti, et al, JCTC (2010)]:**

$$\ddot{u} = -Ku - \gamma\dot{u} + \xi(t), \tag{16}$$

$$\left\langle \xi(t) \right\rangle = 0, \quad \left\langle \xi(t)\xi(t')^T \right\rangle = c(t)\, I, \tag{17}$$

$$\tilde{c}[\omega] = \int_{-\infty}^{+\infty} c(t) e^{i\omega t} dt = 2\gamma\hbar\omega \left[f(\omega) + \frac{1}{2} \right] \tag{18}$$

- **then in the limit of small damping ($\gamma \to 0$), the energy of the vibrational modes is given exactly as that of the corresponding quantum system.**

Conclusion & outlook

- **QMD for phonon is correct in the ballistic limit and high-temperature classical limit**
- **Much large systems can be simulated (comparing to NEGF)**
- **Quantum corrections in dynamics?**
  - Solve a hierarchical set of Heisenberg equations (Prezhdo et al, JCP)
  - Two-time dynamics (e.g., Koch et al, PRL 2008)?
  - Can we treat the noises ξ & η as operators (i.e. matrices) thus restore $\sum^{>} \neq \sum^{<}$?

Collaborators/students

- Baowen Li
- Pawel Keblinski
- Jian Wang
- Jingtao Lü
- Jin-Wu Jiang
- Eduardo Cuansing
- Nan Zeng
- Saikong Chin
- Chee Kwan Gan
- Jinghua Lan
- Yong Xu

- Lifa Zhang
- Xiaoxi Ni
- Bijay Kumar Agarwalla
- Thingna Juzar Yahya

Definitions of Phonon Green's functions

$$D^{r}_{jk}(t,t') = -i\theta(t-t')\left\langle [u_j(t),u_k(t')] \right\rangle,$$

$$D^{a}_{jk}(t,t') = i\theta(t'-t)\left\langle [u_j(t),u_k(t')] \right\rangle,$$

$$D^{>}_{jk}(t,t') = -i\left\langle u_j(t)u_k(t') \right\rangle,$$

$$D^{<}_{jk}(t,t') = -i\left\langle u_k(t')u_j(t) \right\rangle,$$

$$D^{t}(t,t') = \theta(t-t')D^{>}(t,t') + \theta(t'-t)D^{<}(t,t')$$

Relation among Green's functions

$$D^r - D^a = D^> - D^<,$$

$$D^t + D^{\bar{t}} = D^> + D^<,$$

$$D^t - D^{\bar{t}} = D^r + D^a,$$

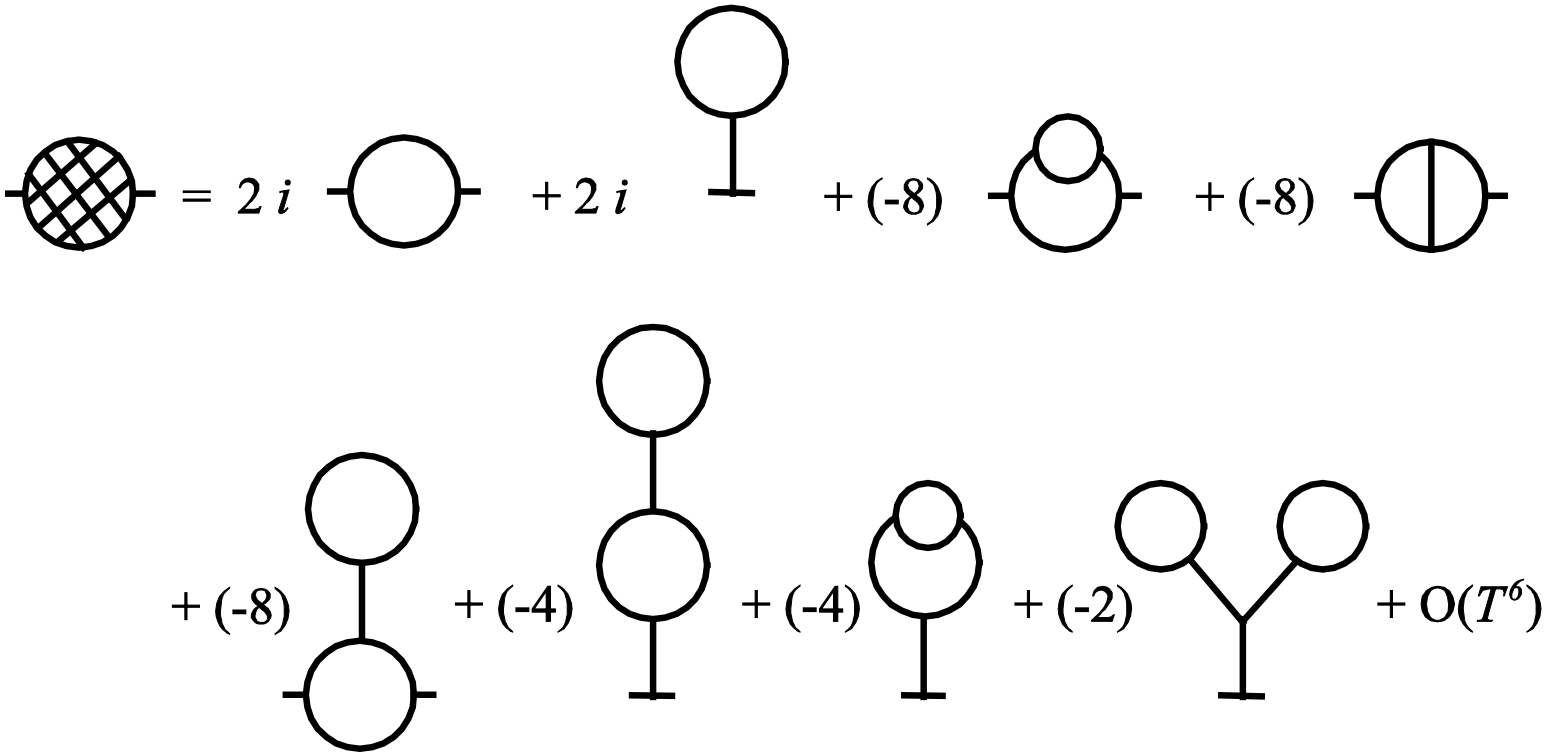
$$D^r = \left(D^a\right)^\dagger$$

$$D^r = D^t - D^<$$

$$D^< = f(\omega)\left[D^r - D^a\right]$$

$$f(\omega) = \frac{1}{e^{\hbar\omega/(k_B T)} - 1}$$

Self-energy Feynman diagrams



From self-energy to Green's functions, to heat current

$$G^r = \frac{1}{(\omega + i\eta)^2 - K^C - \Sigma^r - \Sigma_n^r},$$

$$G^< = G^r(\Sigma^< + \Sigma_n^<)G^a,$$

$$I_L = -\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\omega \mathrm{Re}\,\mathrm{Tr}\left(G^r\Sigma_L^< + G^<\Sigma_L^a\right)$$