Onsager reciprocal relations with broken time-reversal symmetry

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Outline

Onsager reciprocal relations are a cornerstone in nonequilibrium thermodynamics

As the other principles of thermodynamics, they introduce fundamental constraints on heat to work conversion

Breaking Onsager relations (typically, by a magnetic field) would allow, in principle, to have Carnot efficiency at finite power

We show that Onsager relations remain valid even in the presence of a generic magnetic field

The Nobel Prize in Chemistry 1968: From the award ceremony speech

"Professor Lars Onsager has been awarded this year's Nobel Prize for Chemistry (1968) for the discovery of the reciprocal relations, named after him, and basic to irreversible thermodynamics… Onsager's reciprocal relations can be described as a universal natural law…It can be said that Onsager's reciprocal relations represent a further law making possible a thermodynamic study of irreversible processes…It represents one of the great advances in science during this century.

According to Nico Van Kampen Onsager derived his reciprocal relations in a *"stroke of genius"*

Irreversible thermodynamic

Irreversible thermodynamics based on the postulates of equilibrium thermostatics plus the postulate of time-reversal symmetry of physical laws (if time t is replaced by $-t$ and simultaneously applied magnetic field $\boldsymbol{B}$ by $-\boldsymbol{B}$)

The thermodynamic theory of irreversible processes is based on the Onsager Reciprocity Theorem

Refs.: H. B. Callen, Thermodynamics and an introduction to thermostatics
S. R. de Groot and P. Mazur, Non-equilibrium thermodynamics

Thermodynamic forces and fluxes

Irreversible processes are driven by thermodynamic forces (or generalized forces or affinities) $\mathcal{F}_k$

Fluxes J_i characterize the response of the system to the applied forces

Entropy production rate given by the sum of the products of each flux with its associated thermodynamic force

$$\mathscr{S} = \mathscr{S}(U, V, N_1, N_2, \ldots) = \mathscr{S}(E_0, E_1, E_2, \ldots)$$

$$\frac{d\mathscr{S}}{dt} = \sum_k \frac{\partial \mathscr{S}}{\partial E_k} \frac{dE_k}{dt} = \sum_k \mathcal{F}_k J_k$$

Linear response

Purely resistive systems: fluxes at a given instant depend only on the thermodynamic forces at that instant (memory effects not considered)

$$J_i = \sum_j L_{ij}\mathcal{F}_j + \sum_{j,k} L_{ijk}\mathcal{F}_j\mathcal{F}_k + \ldots$$

Fluxes vanish as thermodynamic forces vanish

Linear (and purely resistive) processes:

$$J_i = \sum_j L_{ij}\mathcal{F}_j$$

L_{ij} Onsager coefficients (first-order kinetic coefficients) depend on intensive quantities (T,P,μ,...)

Phenomenological linear Ohm's, Fourier's, Fick's laws

Onsager reciprocal relations

Relationship of Onsager theorem to time-reversal symmetry of physical laws

Consider delayed correlation moments of fluctuations (without applied magnetic fields)

$$\delta E_j(t) \equiv E_j(t) - E_j, \quad \langle \delta E_j \rangle = 0,$$

$$\langle \delta E_j(t)\delta E_k(t+\tau)\rangle = \langle \delta E_j(t)\delta E_k(t-\tau)\rangle = \langle \delta E_j(t+\tau)\delta E_k(t)\rangle$$

$$\lim_{\tau\to 0}\left\langle \delta E_j(t)\frac{\delta E_k(t+\tau)-\delta E_k(t)}{\tau}\right\rangle = \lim_{\tau\to 0}\left\langle \frac{\delta E_j(t+\tau)-\delta E_j(t)}{\tau}\delta E_k(t)\right\rangle$$

$$\langle \delta E_j \delta \dot{E}_k\rangle = \langle \delta \dot{E}_j \delta E_k\rangle$$

Assume that fluctuations decay is governed by the same linear dynamical laws as are macroscopic processes

$$\delta \dot{E}_k = \sum_l L_{kl} \delta \mathcal{F}_l$$

$$\sum_l L_{kl} \langle \delta E_j \delta \mathcal{F}_l \rangle = \sum_l L_{jl} \langle \delta \mathcal{F}_l \delta E_k \rangle$$

Assume that the fluctuation of each thermodynamic force is associated only with the fluctuation of the corresponding extensive variable

$$\langle \delta E_j \delta \mathcal{F}_l \rangle = -k_B \delta_{jl}$$

Onsager relations: $L_{jk} = L_{kj}$

Onsager-Casimir relations

Onsager reciprocal relations reflect at the macroscopic level the time-reversal symmetry of the microscopic dynamics, invariant under the transformation:

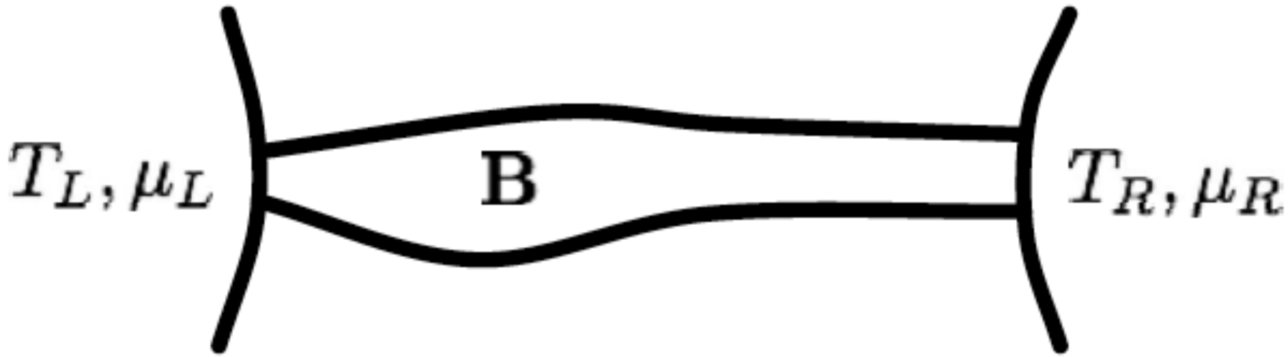
$$\mathcal{T}(\boldsymbol{r},\boldsymbol{p},t) \equiv (\boldsymbol{r},-\boldsymbol{p},-t) \quad \Rightarrow \quad L_{jk} = L_{kj}$$

With an applied magnetic field one instead obtains Onsager-Casimir relations:

$$\mathcal{T}_{\boldsymbol{B}}(\boldsymbol{r},\boldsymbol{p},t,\boldsymbol{B}) \equiv (\boldsymbol{r},-\boldsymbol{p},-t,-\boldsymbol{B}) \quad \Rightarrow \quad L_{jk}(\boldsymbol{B}) = L_{kj}(-\boldsymbol{B})$$

but in principle one could violate the Onsager symmetry: $L_{jk}(\boldsymbol{B}) \neq L_{kj}(\boldsymbol{B})$

Carnot efficiency at finite power with breaking Onsager symmetry?



$$\begin{cases} J_e = L_{ee}(\mathbf{B})\mathcal{F}_e + L_{eh}(\mathbf{B})\mathcal{F}_h \\ J_h = L_{he}(\mathbf{B})\mathcal{F}_e + L_{hh}(\mathbf{B})\mathcal{F}_h \end{cases}$$

$$\mathcal{F}_e = \Delta V/T \quad (\Delta V = \Delta\mu/e)$$

$$\mathcal{F}_h = \Delta T/T^2$$

$$\Delta\mu = \mu_L - \mu_R$$

$$\Delta T = T_L - T_R$$

B applied magnetic field or any parameter breaking time-reversibility such as the Coriolis force, etc.

(we assume $T_L > T_R, \;\; \mu_L < \mu_R$)

Onsager and transport coefficients

$$G = \left(\frac{J_e}{\Delta V}\right)_{\Delta T=0} = \frac{L_{ee}}{T}$$

$$K = \left(\frac{J_h}{\Delta T}\right)_{J_e=0} = \frac{1}{T^2}\frac{\det \boldsymbol{L}}{L_{ee}}$$

$$S = -\left(\frac{\Delta V}{\Delta T}\right)_{J_e=0} = \frac{1}{T}\frac{L_{eh}}{L_{ee}}$$

$$\Pi = \left(\frac{J_h}{J_e}\right)_{\Delta T=0} = \frac{L_{he}}{L_{ee}}$$

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Fundamental aspects of steady-state conversion of heat to work at the nanoscale

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Constraints from thermodynamics

POSITIVITY OF THE ENTROPY PRODUCTION:

$$\dot{\mathscr{S}} = \mathfrak{F}_e J_e + \mathfrak{F}_h J_h \geq 0 \quad \Rightarrow \quad \begin{aligned} &L_{ee} \geq 0 \\ &L_{hh} \geq 0 \\ &L_{ee}L_{hh} - \frac{1}{4}(L_{eh} + L_{he})^2 \geq 0 \end{aligned}$$

ONSAGER-CASIMIR RELATIONS:

$$L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B}) \quad \Rightarrow \quad \begin{aligned} &G(\mathbf{B}) = G(-\mathbf{B}) \\ &K(\mathbf{B}) = K(-\mathbf{B}) \\ &\Pi(\boldsymbol{B}) = TS(-\boldsymbol{B}) \end{aligned}$$

Breaking Onsager symmetry: $\Pi(\boldsymbol{B}) \neq TS(\boldsymbol{B})$

[that is, $L_{eh}(\boldsymbol{B}) \neq L_{he}(\boldsymbol{B})$], [or $S(\mathbf{B}) \neq S(-\mathbf{B})$]

Both maximum efficiency and efficiency at maximum power depend on two parameters

$$x = \frac{L_{eh}}{L_{he}} = \frac{S(\boldsymbol{B})}{S(-\boldsymbol{B})}$$

$$y = \frac{L_{eh}L_{he}}{\det \boldsymbol{L}} = \frac{G(\boldsymbol{B})S(\boldsymbol{B})S(-\boldsymbol{B})}{K(\boldsymbol{B})}T$$

$$\eta_{\max} = \eta_C \, x \, \frac{\sqrt{y+1}-1}{\sqrt{y+1}+1}$$

At $B = 0$ there is time-reversibility and:

asymmetry parameter $x = 1$

the efficiency only depends on $y(x=1) = ZT$

Output power at maximum efficiency

$$P(\bar{\eta}_{\max}) = \frac{\bar{\eta}_{\max}}{4} \frac{|L_{eh}^2 - L_{he}^2|}{L_{ee}} \mathfrak{F}_h$$

When time-reversibility is broken, <u>within linear response</u> it is not forbidden from the second law to have simultaneously Carnot efficiency and non-zero power.

Terms of higher order in the entropy production, beyond linear response, will generally be non-zero. However, irrespective how close we are to the Carnot efficiency, we could in principle find small enough forces such that the linear theory holds.

[G.B., K. Saito, G. Casati, PRL **106**, 230602 (2011)]

Reversible part of the currents

$$J_i^{\text{rev}} = \sum_{j=e,h} \frac{L_{ij} - L_{ji}}{2} \mathfrak{F}_j$$

$$J_i^{\text{irr}} = \sum_{j=e,h} \frac{L_{ij} + L_{ji}}{2} \mathfrak{F}_j$$

The reversible part of the currents does not contribute to entropy production

$$\dot{\mathscr{S}} = \mathfrak{F}_e J_e + \mathfrak{F}_h J_h = J_e^{\text{irr}} \mathfrak{F}_e + J_h^{\text{irr}} \mathfrak{F}_h$$

Possibility of dissipationless transport?

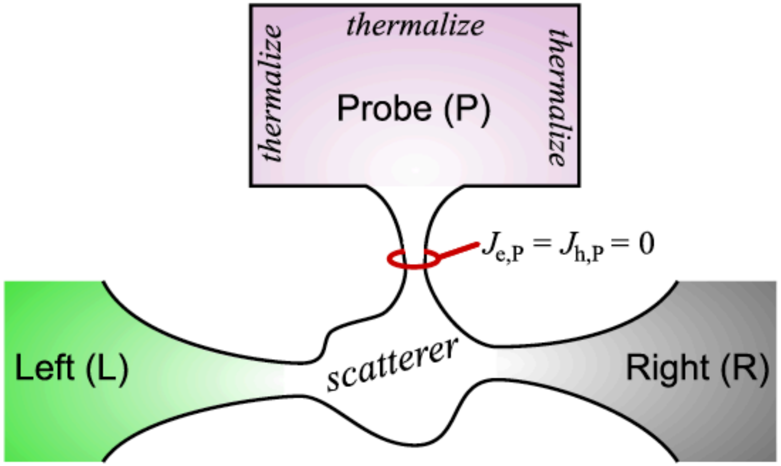
[K. Brandner, K. Saito, U. Seifert, PRL **110**, 070603 (2013)]

How to obtain asymmetry in the Seebeck coefficient?

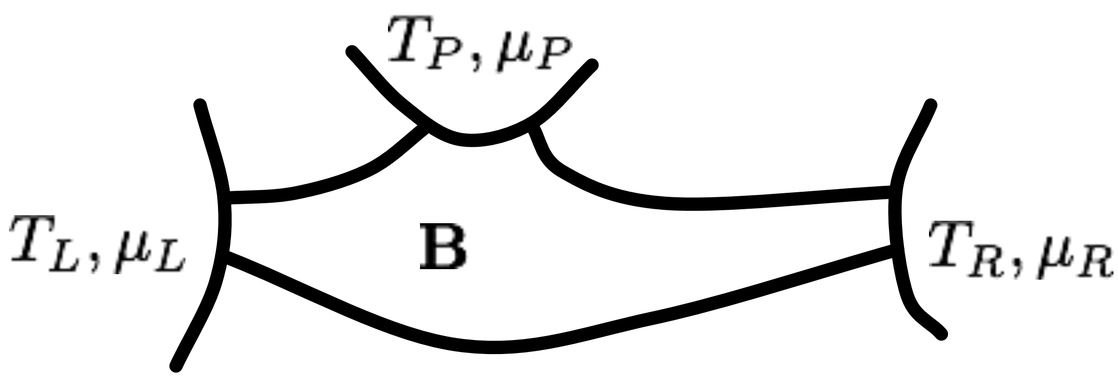
For non-interacting systems, due to the symmetry properties of the scattering matrix ⇒ $S(\mathbf{B}) = S(-\mathbf{B})$

This symmetry does not apply when electron-phonon and electron-electron interactions are taken into account

Let us consider the case of partially coherent transport, with inelastic processes simulated by **"conceptual probes"** mimicking inelastic scattering (Buttiker, 1988).



Non-interacting three-terminal model



P probe reservoir

$$T_L = T + \Delta T,\ T_R = T$$
$$\mu_L = \mu + \Delta\mu,\ \mu_R = \mu$$
$$T_P = T + \Delta T_P$$
$$\mu_P = \mu + \Delta\mu$$

Charge and energy conservation:

$$\sum_k J_{e,k} = 0,\ \sum_k J_{u,k} = 0 \qquad (J_{h,k} = J_{u,k} - (\mu/e) J_{e,k})$$

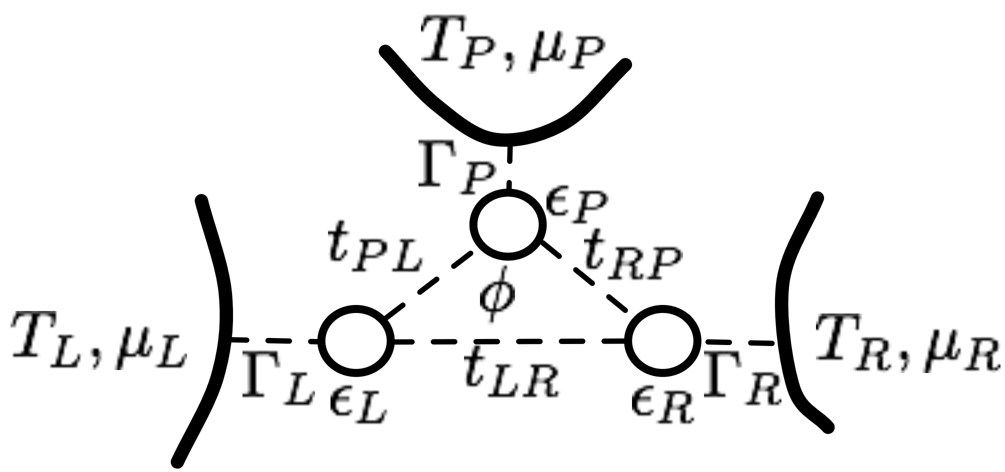
Entropy production (linear response):

$$\dot{\mathscr{S}} = {}^t\boldsymbol{\mathcal{F}}\mathbf{J} = \sum_{i=1}^{4} J_i \mathcal{F}_i$$

$${}^t\mathbf{J} = (J_{eL}, J_{hL}, J_{eP}, J_{hP})$$

$${}^t\boldsymbol{\mathcal{F}} = \left(\frac{\Delta\mu}{eT}, \frac{\Delta T}{T^2}, \frac{\Delta\mu_P}{eT}, \frac{\Delta T_P}{T^2}\right)$$

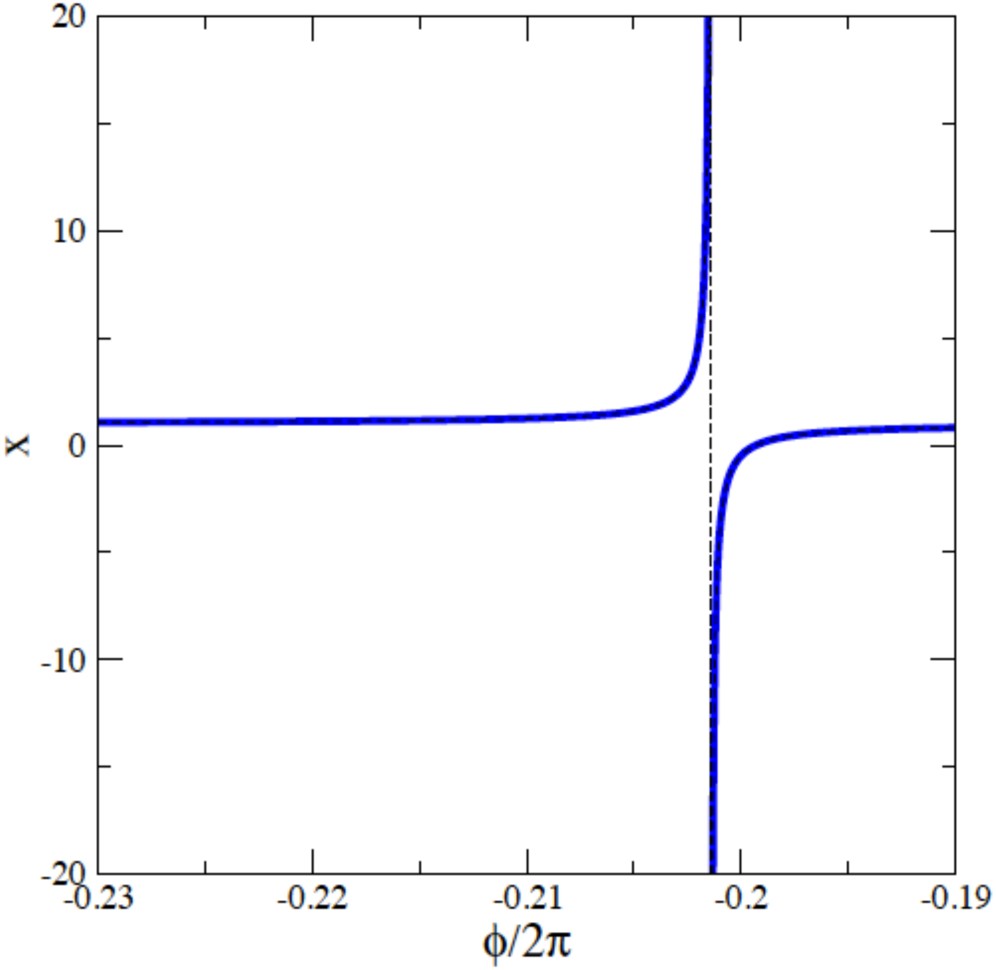
Illustrative three-dot example



$$H_S = \sum_k \epsilon_k c_k^\dagger c_k + (t_{LR} c_R^\dagger c_L e^{i\phi/3} + t_{RP} c_P^\dagger c_R e^{i\phi/3} + t_{PL} c_L^\dagger c_P e^{i\phi/3} + \text{H.c.})$$

Asymmetric structure, e.g.. $\epsilon_L \neq \epsilon_R$

Asymmetric Seebeck coefficient



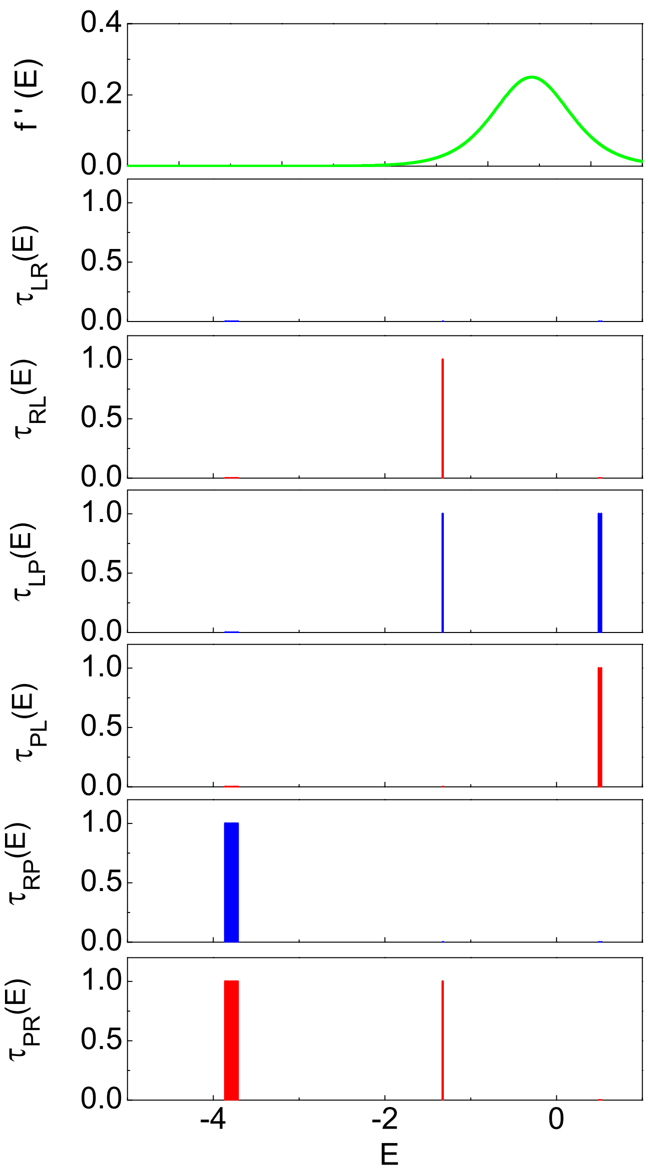
$$x(\phi) = \frac{L'_{12}(\phi)}{L'_{21}(\phi)} = \frac{S(\phi)}{S(-\phi)} \neq 1$$

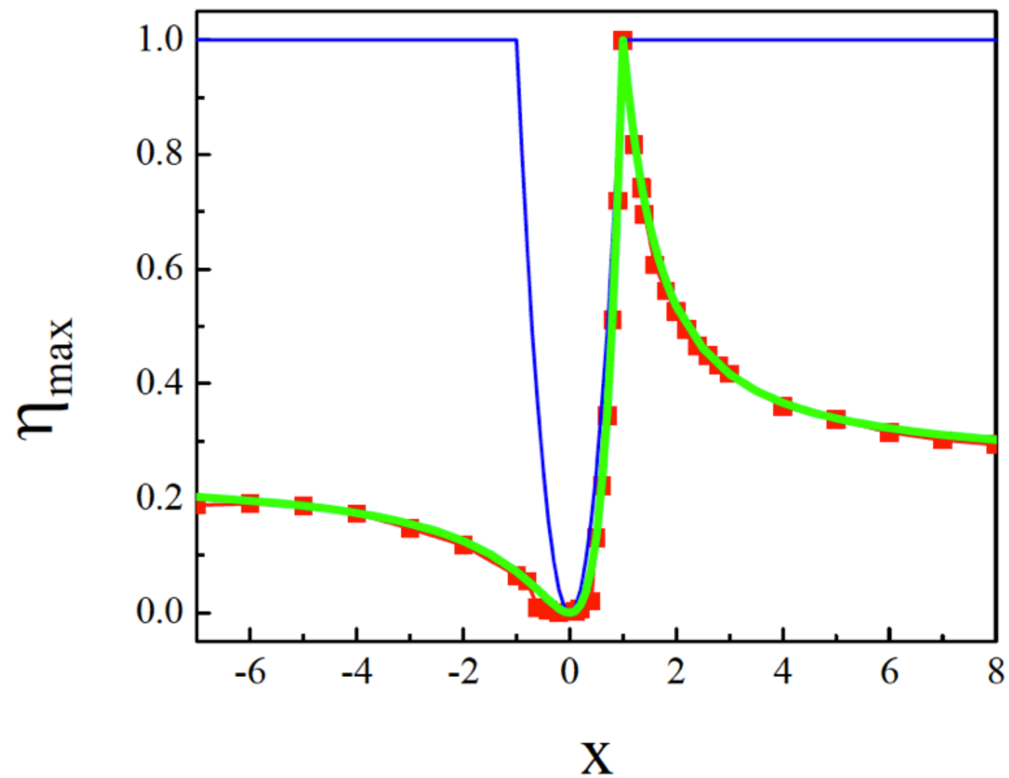
[K. Saito, G. B., G. Casati, T. Prosen, PRB **84**, 201306(R) (2011)]

[see also D. Sánchez, L. Serra, PRB **84**, 201307(R) (2011)]

Non-interacting three-terminal bound

$$\sum_i \tau_{ij}(E) = \sum_j \tau_{ij}(E) = 1$$



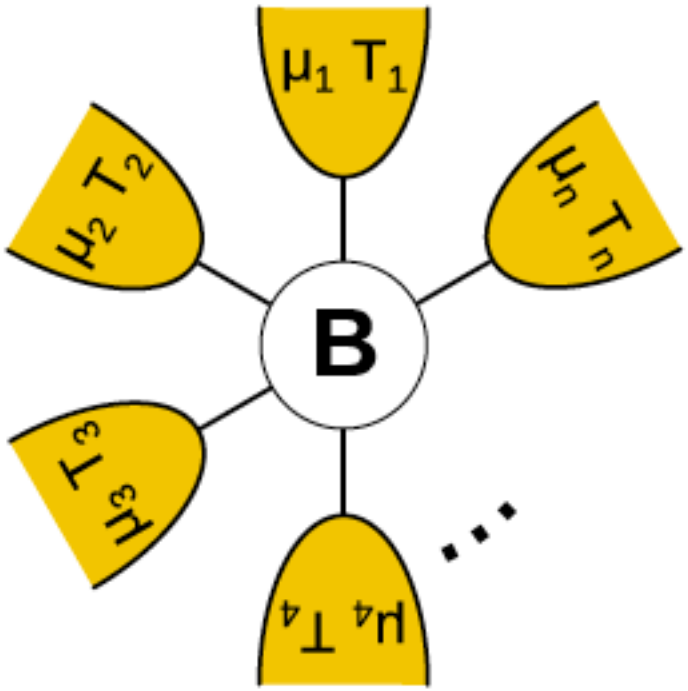


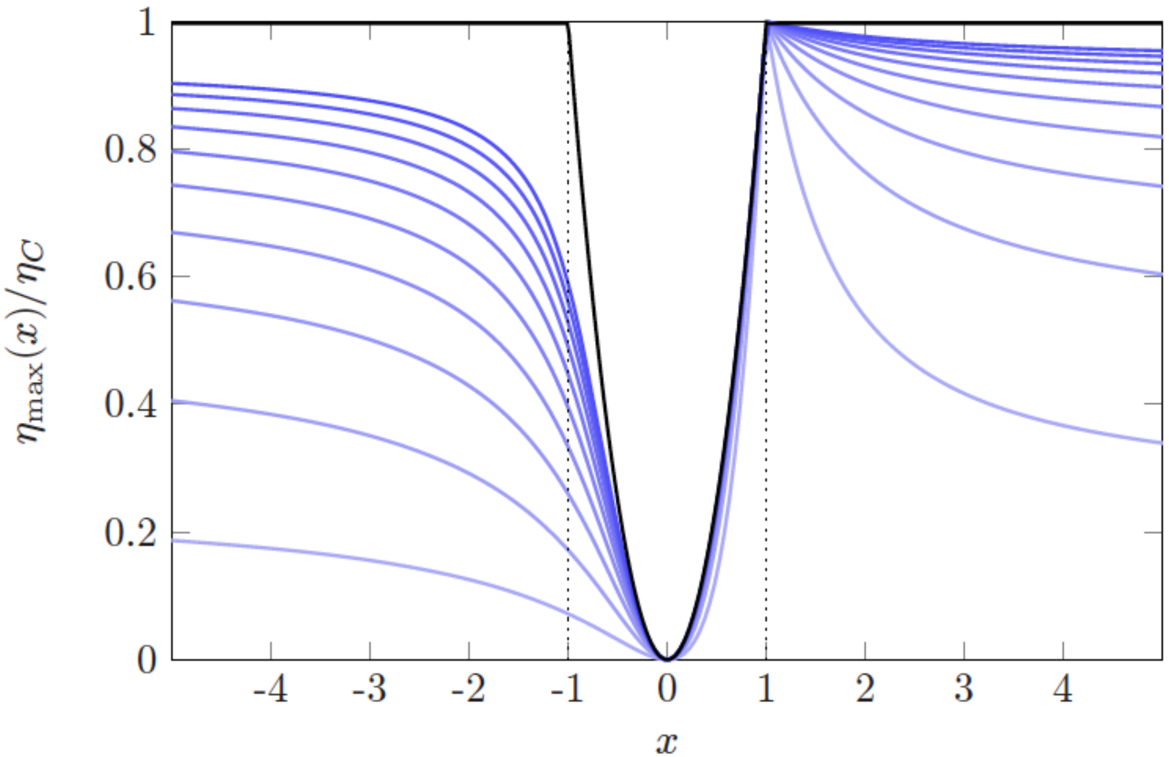
[V.. Balachandran, G. B., G. Casati, PRB **87**, 165419 (2013)]

Bound obtained from the unitarity of the S-matrix

[K.. Brandner, K. Saito, U. Seifert, PRL **110**, 070603 (2013)]

Multi-terminal non-interacting bound



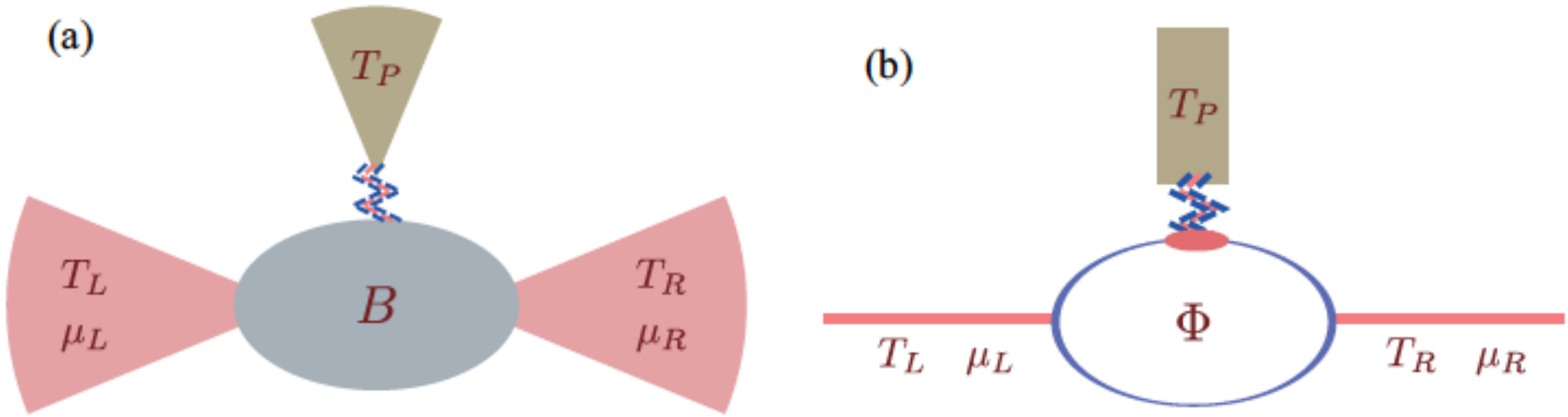


$n = 3, \ldots, 12$ terminals

Numerical evidence that the power vanishes when the Carnot efficiency is approached

[Brandner and Seifert, NJP **15**, 105003 (2013); PRE **91**, 012121 (2015)]

Bounds with electron-phonon scattering



Efficiency bounded by the non-negativity of the entropy production of the original three-terminal junction.

[Yamamoto, Entin-Wohlman, Aharony, Hatano; PRB **94**, 121402(R) (2015)]

Power-efficiency trade-off

For heat engines described as Markov processes:

$$P \leq A(\eta_C - \eta)$$

[N. Shiraishi, K. Saito, H. Tasaki, PRL **117**, 190601 (2016)]

The prefactor A may be arbitrarily large, for instance diverge close to a phase transition

Moreover, the problem remains open for a generic purely Hamiltonian two-terminal system with interactions

Onsager relations with broken time-reversal symmetry

Onsager relations under an applied magnetic field remain valid:

1) for noninteracting systems

2) if the magnetic field is constant

[Bonella, Ciccotti, Rondoni, EPL **108**, 60004 (2014)]

What about for a generic, spatially dependent magnetic field?

Symmetry without magnetic field inversion

$$H = \sum_{i}^{N} \frac{[\boldsymbol{p}_i - q_i \boldsymbol{A}(\boldsymbol{r}_i)]^2}{2m_i} + \frac{1}{2}\sum_{i \neq j} V(r_{ij})$$

Analytical result for $\boldsymbol{B} = B(x)\,\boldsymbol{k}$

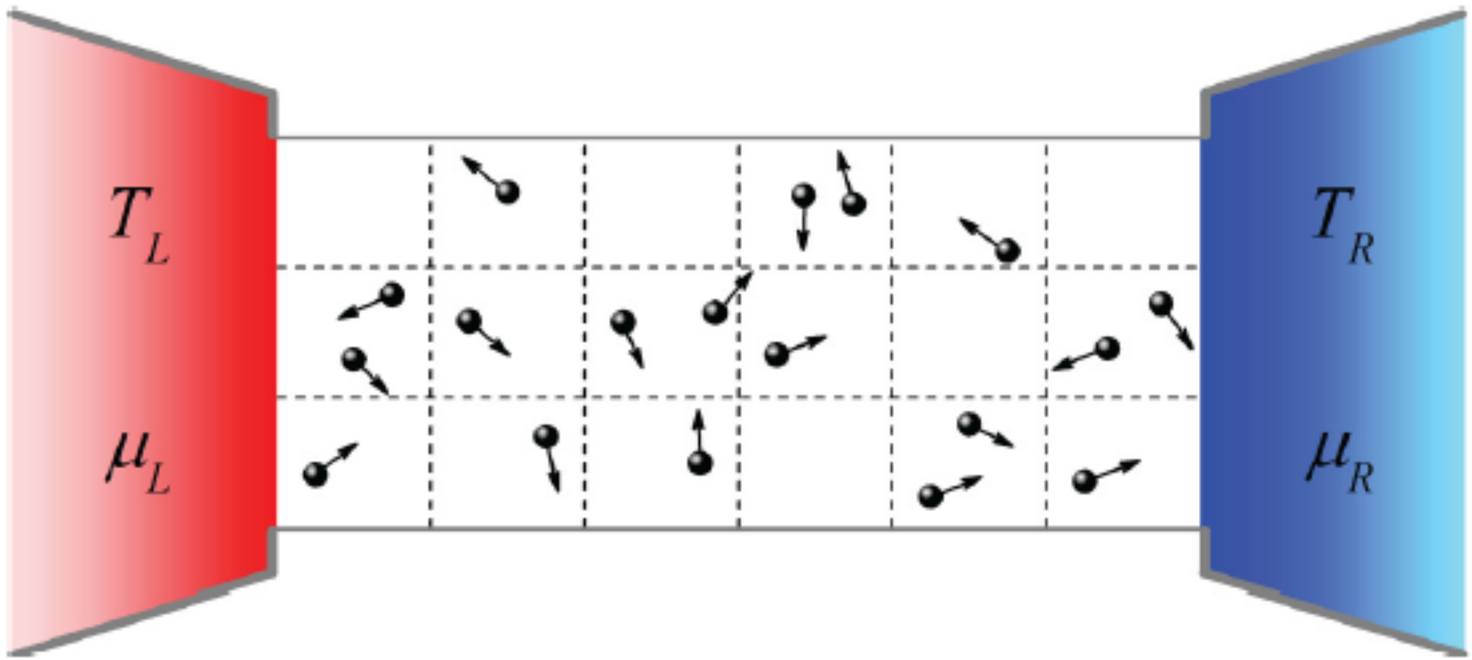
Landau gauge: $A(x)\,\boldsymbol{j}$

$$\begin{cases} \dot{x}_i = \frac{p_i^x}{m_i}, \\ \dot{y}_i = \frac{1}{m_i}\,[p_i^y - q_i A(x_i)], \\ \dot{z}_i = \frac{p_i^z}{m_i}, \\ \dot{p}_i^x = F_i^x + \frac{q_i}{m_i}\,[p_i^y - q_i A(x_i)]\,B(x_i), \\ \dot{p}_i^y = F_i^y, \\ \dot{p}_i^z = F_i^z, \end{cases} \qquad F_i^\alpha = -\frac{\partial \sum_{j \neq i} V(r_{ij})}{\partial \alpha}$$

Equations of motion invariant under:

$$\mathcal{M}(x, y, z, p^x, p^y, p^z, t, \boldsymbol{B}) \equiv (x, -y, z, -p^x, p^y, -p^z, -t, \boldsymbol{B})$$

Numerics for a generic magnetic field



Use a stochastic model for the reservoirs

Dynamics described by the multi-particle collision method (Kapral method)

Multiparticle collision dynamics (Kapral model)

Streaming step: free propagation during a time τ

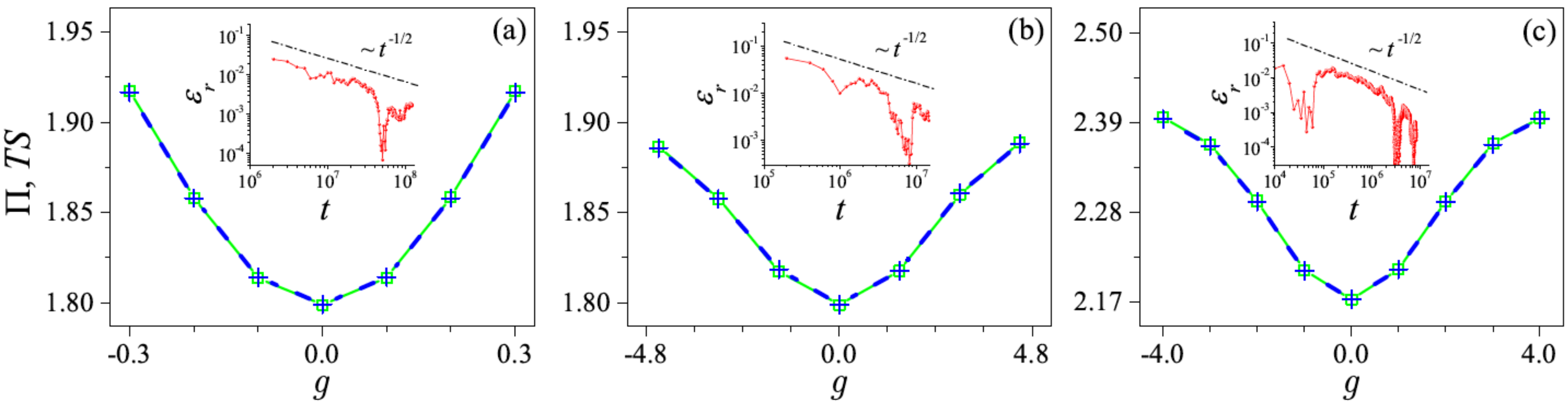
$$\vec{r}_i \longrightarrow \vec{r}_i + \vec{v}_i \tau$$

Collision step: random rotations of the velocities of the particles in cells of linear size *a* with respect to the center of mass velocity:

$$\vec{v}_i \longrightarrow \vec{V}_{\mathrm{CM}} + \hat{\mathcal{R}}^{\pm\alpha}\left(\vec{v}_i - \vec{V}_{\mathrm{CM}}\right)$$

Total energy and total momentum are conserved

Numerical results



$B(x) = gx$

generic 2D case:

$$B(x,y) = g\sin[\pi x/(2L)]\sin[\pi y/(2W)]$$

Theoretical argument:
divide the system into small volumes dV_α

Time-reversal trajectories without reversing the field for $dV_\alpha \to 0$

generic 3D case:

$$\boldsymbol{B} = g(B_x, B_y, B_z),$$
$$B_x = f_y f_z,\ B_y = f_z f_x,\ B_z = f_x f_y,$$
$$f_x = \sin[\pi x/(2L)],\ f_y = \sin[\pi y/(2W)],$$
$$f_z = \sin[\pi z/(2H)]$$

Final remarks

No-go theorem for finite power at the Carnot efficiency on purely thermodynamic grounds?

Onsager reciprocal relations much more general than expected so far.

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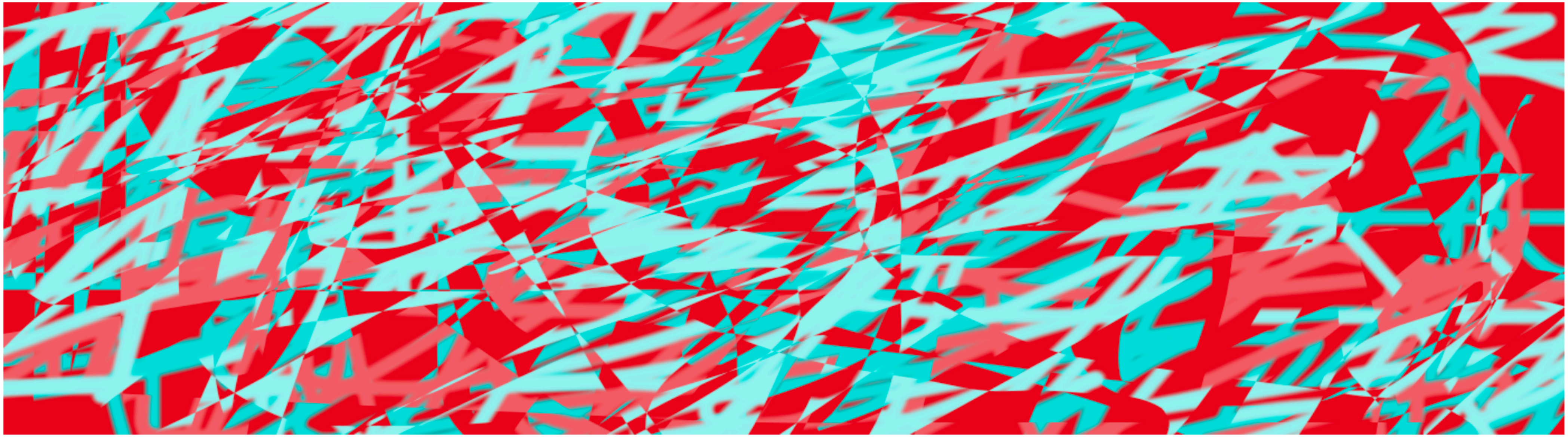

A network of scientists dedicated to understanding the thermodynamics of quantum systems and quantum transport.

Quantum computation and information is a rapidly developing interdisciplinary field. It is not easy to understand its fundamental concepts and central results without facing numerous technical details. This book provides the reader with a useful guide. In particular, the initial chapters offer a simple and self-contained introduction; no previous knowledge of quantum mechanics or classical computation is required.

Various important aspects of quantum computation and information are covered in depth, starting from the foundations (the basic concepts of computational complexity, energy, entropy, and information, quantum superposition and entanglement, elementary quantum gates, the main quantum algorithms, quantum teleportation, and quantum cryptography) up to advanced topics (like entanglement measures, quantum discord, quantum noise, quantum channels, quantum error correction, quantum simulators, and tensor networks).

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Principles of Quantum Computation and Information
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