KU LEUVEN

Third law for nonequilibrium processes

Work together with Faezeh Khodabandehlou, Karel Netocny and Christian Maes

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1 Outline

1. Subject and main result
2. Definitions and Notations
3. Quasistatic limit
4. Excess heat and heat capacity
5. Proof

1 Subject and main result

Give conditions for the excess heat to vanish at zero temperature for Markov jump processes.

In particular: Heat capacity tends to zero with temperature for quite general (but finite state space) interacting particle systems.

1 Subject and main result

Explain the setup, define heat, excess heat and heat capacity.

Nonequilibrium particle system, driven but in contact with heat bath at T.
It constantly dissipates in the stationary distribution.

Ask for the excess heat when changing the temperature.

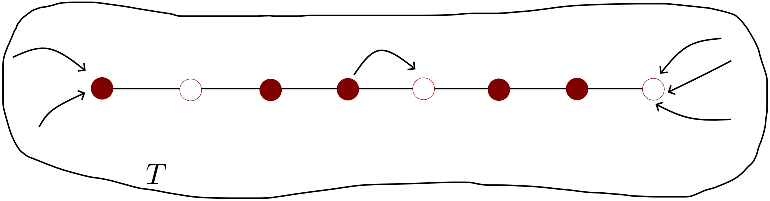

Figure: Boundery driven exclusion process

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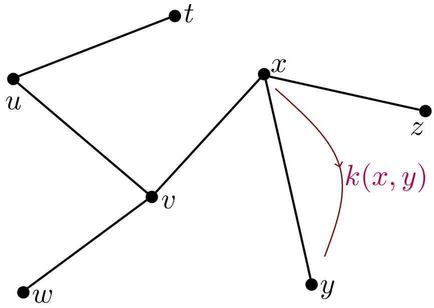
2 Markov jump process

Connected and finite graph $G = (\mathcal{V}, \mathcal{E})$

- Position of random walker at time t is $X_t \in \mathcal{V}$.
- Transition rate $k(x, y) > 0$ for the jump from state x to y $\Leftrightarrow \{x, y\} \in \mathcal{E}$.



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Corresponding backward generator L is matrix

$$\begin{cases} L_{x,y} & = k(x,y) \qquad \text{if} \quad y \neq x \\ L_{x,x} & = -\sum_y k(x,y) \end{cases}$$

Master equation: $\frac{d}{dt}\rho_t = L^\dagger \rho_t$.

2 Stationary distribution and dependence on parameters

- Assume irreducibility of the graph:
  There is a unique Stationary probability distribution $\rho^s > 0$, solution of $L^\dagger \rho = 0$.

Notations:

$$\langle f \rangle^s = \sum_x f(x)\rho^s(x)$$

$$\langle f(X_t) \,|X_0 = x\rangle = e^{tL} f(x)$$

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- Parameters $\lambda = (\beta, \alpha)$ with $\alpha = (\alpha_1, \alpha_2, \dots, \alpha_n) \in \mathcal{A} \subset \mathbb{R}^n$.
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  For every λ, stationary distribution ρ^s_λ.

2 Nonequilibrium dynamics

For every vertex x, energy $E(x, \alpha)$

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Equilibrium dynamics - Detailed balance:

$$\log \frac{k_\lambda(x,y)}{k_\lambda(y,x)} = \frac{1}{k_B T}\, q_\alpha(x,y), \text{ with } q_\alpha(x,y) = E(x,\alpha) - E(y,\alpha)$$

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Nonequilibrium dynamics - Local detailed balance:

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- $q_\alpha(x,y)$ is **the heat to the environment** when $x \to y$
  $W(x,y) = -W(y,x)$ is the irreversible work done by the environment in the transition $x \to y$

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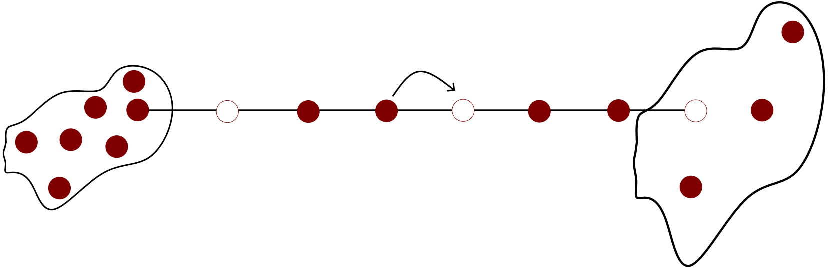

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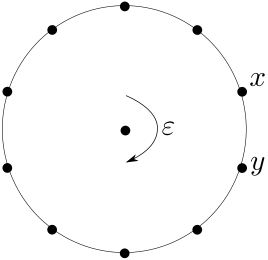

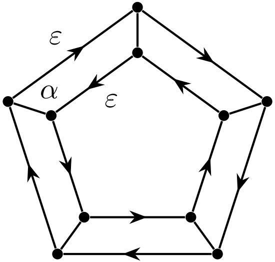

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$$\mathcal{P}_\lambda(x) := \sum_y k_\lambda(x,y) q_\alpha(x,y).$$

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- Expected heat flux when in state x:

$$\mathcal{P}_\lambda(x) := \sum_y k_\lambda(x,y) q_\alpha(x,y).$$

- Expected heat flux: $\langle \mathcal{P}_\lambda \rangle_\lambda^s \geq 0.$

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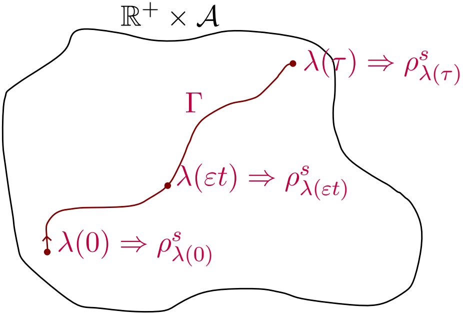
3 Time-dependent parameters

Smooth time dependence $\lambda(t)$, $t \in [0, \tau]$ with image Γ in $\mathbb{R}^+ \times \mathcal{A}$

Define $\lambda^\varepsilon(t) := \lambda(\varepsilon t)$, $t \in [0, \varepsilon^{-1}\tau]$.

Let $\varepsilon \downarrow 0 \Rightarrow$ quasistatic process.



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4 Excess heat

At every time t the time-dependent Master equation

$$\frac{\partial}{\partial t}\rho_t^\varepsilon = L^\dagger_{\lambda(\varepsilon t)}\rho_t^\varepsilon\,.$$

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At every time t the time-dependent Master equation

$$\frac{\partial}{\partial t}\rho_t^\varepsilon = L_{\lambda(\varepsilon t)}^\dagger \rho_t^\varepsilon \,.$$

Remember

$$\left\langle \mathcal{P}_{\lambda(\varepsilon t)}(X_t) \right\rangle^\varepsilon = \sum_x \mathcal{P}_{\lambda(\varepsilon t)}(x)\rho_t^\varepsilon(x)$$

$$\left\langle \mathcal{P}_{\lambda(\varepsilon t)} \right\rangle_{\lambda(\varepsilon t)}^s = \sum_x \mathcal{P}_{\lambda(\varepsilon t)}(x)\rho_{\lambda(\varepsilon t)}^s(x)$$

$$\langle \mathcal{P}_\lambda(X_t) \,|\, X_0 = x \rangle_\lambda = e^{tL_\lambda}\mathcal{P}_\lambda(x)$$

4 Excess heat

$$\left\langle \mathcal{P}_{\lambda(\varepsilon t)}(X_t) \right\rangle^{\varepsilon} = \sum_x \mathcal{P}_{\lambda(\varepsilon t)}(x)\rho_t^{\varepsilon}(x)$$

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$$\langle \mathcal{P}_\lambda(X_t) \,|\, X_0 = x \rangle_\lambda = e^{tL_\lambda}\mathcal{P}_\lambda(x)$$

For given λ^ε, define the excess heat Q_ε towards thermal bath at β and the quasipotential V_λ

$$Q_\varepsilon := \int_0^{\tau/\varepsilon} dt \left(\left\langle \mathcal{P}_{\lambda(\varepsilon t)}(X_t) \right\rangle^{\varepsilon} - \left\langle \mathcal{P}_{\lambda(\varepsilon t)} \right\rangle^{s}_{\lambda(\varepsilon t)} \right)$$

$$V_\lambda(x) := \int_0^{+\infty} dt \left(\langle \mathcal{P}_\lambda(X_t) \,|\, X_0 = x \rangle_\lambda - \langle \mathcal{P}_\lambda \rangle^s_\lambda \right)$$

4 Result

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Proposition

$$\lim_{\varepsilon \downarrow 0} Q_\varepsilon = Q(\Gamma) = \int d\lambda \cdot \langle \nabla_\lambda V_\lambda \rangle_\lambda$$

This is independent of parametrization of the curve.

Key:

$$\lim_{\varepsilon \downarrow 0} \frac{1}{\varepsilon} \left| \rho_t^\varepsilon(x) - \rho^s_{\lambda(\varepsilon t)}(x) \right| = (L_\lambda^\dagger)^{-1} \nabla_\lambda \rho^s_\lambda(x)$$

4 Heat capacity

The **heat capacity**

$$C(\beta) := \beta^2 \left\langle \frac{\partial V_\lambda}{\partial \beta} \right\rangle_\lambda$$

In equilibrium: $C(T) = \frac{d\langle E_\alpha \rangle_\lambda^s}{dT}$

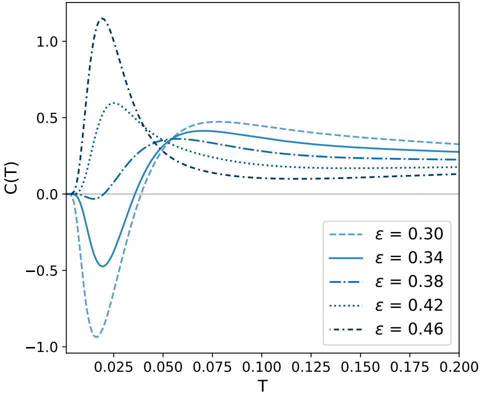
Theorem

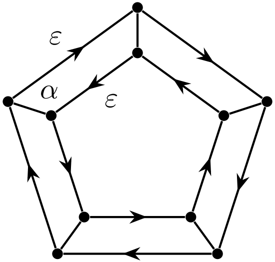
Under *some conditions*

$$\lim_{\beta \uparrow \infty} C(\beta) = 0$$

Extension of Nernst heat postulate.

4 Example - Active particle





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4 Some conditions

- "Avoid degeneracy":
  $\exists\,\delta > 0$ uniform in α and x such that as $\beta \uparrow \infty$

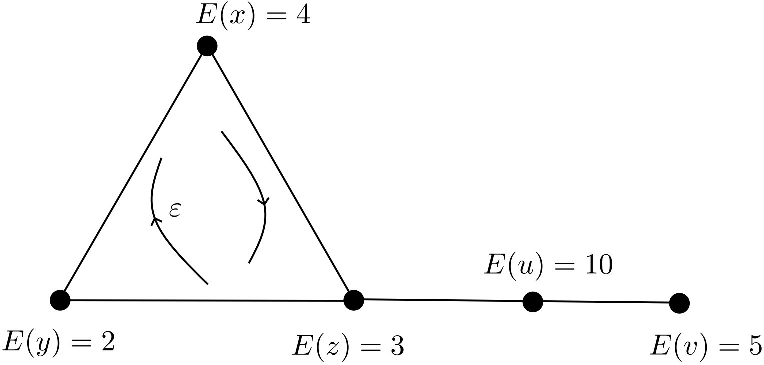
$$|\rho^s_\lambda(x) - \delta_{x,x^*}(x)| \leq e^{-\delta\beta}$$

- "No delay condition"

$$\Rightarrow V_\lambda(x) < \infty \text{ uniformly in } \beta \uparrow \infty$$

4 Counterexample

$$k(x,y) = \frac{1}{1+e^{-\beta(q(x,y))}}, \quad q(x,y) = E(x) - E(y) + W(x,y)$$



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5 Key in proof of theorem

$$V_\lambda(x) := \int_0^{+\infty} dt \left(\langle \mathcal{P}_\lambda(X_t) \,|\, X_0 = x\rangle_\lambda - \langle \mathcal{P}_\lambda\rangle_\lambda^s\right)$$

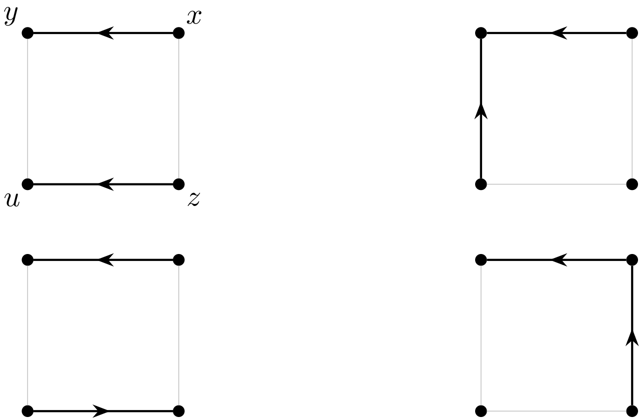
can be obtained as solution of equations

$$\sum_{x'} k(x,x') \left(V_\lambda(x') - V_\lambda(x) + q_\alpha(x,x')\right) = \langle \mathcal{P}_\lambda\rangle_\lambda^s$$

together with $\langle V\rangle = 0$.
Use this to show that there is a **graphical representation for** V_λ in terms of trees and forests in the graph:

$$V_\lambda(x) = \frac{1}{W}\sum_y w\left(\mathcal{F}^{x\to y}\right)\left(-\mathcal{P}_\lambda(y) + \langle \mathcal{P}_\lambda\rangle_\lambda^s\right).$$

5 Spanning forests



6 References

[1] F. Khodabandehlou and I. Maes, *Drazin-Inverse and heat capacity for driven random walks on the ring*. arXiv:2204.04974 (2022).

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Thank you!