To what extent are the mechanical features of a small system relevant to its thermostatistical behaviour?

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Plan

- Model and analytic approach

- Business (almost) as usual: the Gaussian case

- Introducing Poissonian reservoirs

- Conclusion

Plan

- **Model and analytic approach**

- **Business (almost) as usual: the Gaussian case**

- **Introducing Poissonian reservoirs**

- **Conclusion**

IS THE LAW OF HEAT CONDUCTION INDEPENDENT OF THE NATURE OF THE RESERVOIRS?

Mesdames et Messieurs, faites vos jeux…

The model

Classical 1-D massive particles the dynamics of which is ruled by,

$$m\frac{dv_i(t)}{dt} = -kx_i(t) - \gamma v_i(t) - \sum_{l=1}^{2} k_{2l-1}[x_i(t) - x_j(t)]^{2l-1} + \eta_i(t)$$

Reservoir

Dissipation

Confining potential
(permits stationary solutions)

Coupling between particles

In statistical mechanics one aims at making predictions by computing probabilities and cumulants, often in the steady state.

How can we do it in this problem?

I – Hammering away at the Kramers-like equation and get the PDFs (which can be a pain in the bottom of the back).

II – Considering a time averaging approach (which easily turns into a pain in the neck)

Redundant with the Kramers equation approach for Brownian reservoirs

BUT

Outperforms the Kramers equation for non-Brownian reservoirs as Fokker-Planck methods are generally poor approximations to the actual solution.

Other 'pain prone' methods can be chosen as well, *e.g.*, Cáceres & Budini (1997) and Kanazawa, Sagawa & Hayakawa (2012).

Steady state analysis

$$p_{ss}(x,v) = \lim_{z\to 0} z \int_0^{\infty} dt\, e^{-zt} < \delta(x - x(t))\delta(v - v(t)) > .$$

Or

$$\begin{aligned} p_{ss}(x,v) &= \sum_{n,m=0}^{\infty} \int_{-\infty}^{+\infty} \frac{\mathrm{d}Q}{2\pi}\frac{\mathrm{d}P}{2\pi}\, \mathrm{e}^{\mathrm{i}(Qx+Pv)} \frac{(-\mathrm{i}Q)^n}{n!}\frac{(-\mathrm{i}P)^m}{m!} \overline{\langle x^n v^m \rangle} \\ &= \int_{-\infty}^{+\infty} \frac{\mathrm{d}Q}{2\pi}\frac{\mathrm{d}P}{2\pi}\, \mathrm{e}^{\mathrm{i}(Qx+Pv)} \exp\left\{ \sum_{n,m=0:(m+n>0)}^{\infty} \frac{(-\mathrm{i}Q)^n}{n!}\frac{(-\mathrm{i}P)^m}{m!} \overline{\langle x^n v^m \rangle_c} \right\}. \end{aligned}$$

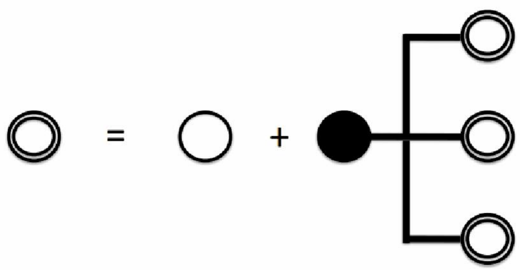
In the time averaging approach one Laplace transforms the dynamical equations,
[Morgado, DQ (2014)]

$$\begin{cases} \tilde{x}(s) = \frac{\tilde{\eta}(s)}{R(s)} - \frac{k_3}{R(s)} \lim_{\epsilon\to 0^+} \int_{-\infty}^{+\infty} \frac{dq_1}{2\pi} \int_{-\infty}^{+\infty} \frac{dq_2}{2\pi} \int_{-\infty}^{+\infty} \frac{dq_3}{2\pi} \frac{\tilde{x}(\mathrm{i}\,q_1+\epsilon)\,\tilde{x}(\mathrm{i}\,q_2+\epsilon)\,\tilde{x}(\mathrm{i}\,q_3+\epsilon)}{s-(\mathrm{i}\,q_1+\mathrm{i}\,q_2+\mathrm{i}\,q_3+3\epsilon)}, \\ \\ \tilde{v}(s) = s\,\tilde{x}(s), \end{cases}$$

$$R(s) \equiv m\,s^2 + \gamma s + k_1 = m\,(s-\zeta_+)(s-\zeta_-).$$

$$< \tilde{\eta}(s_1)\tilde{\eta}(s_2) >_c = \frac{2\,\gamma\,T}{s_1+s_2},$$

Diagrammatically,



Energy and power

$$\begin{aligned}\mathcal{E}(\Theta) &\equiv \mathcal{J}_I(\Theta) + \mathcal{J}_D(\Theta) \\ &= \int_0^{\Theta} \eta(t)\; v(t)\, dt - \gamma \int_0^{\Theta} v(t)^2\; dt.\end{aligned}$$

$$p(j_I) = \frac{2\,c}{\pi\, f\,\sigma\,\omega} \exp\left[\frac{c}{f^2\omega^2} j_I\right] K_0 \left[\frac{\sqrt{(c\,\sigma)^2 + f^2\omega^2}}{f^2\omega^2\,\sigma}\,|j_I|\right], \qquad p(|j_D|) = \sqrt{\frac{m}{2\pi\,\gamma\,T\;|j_D|}} \exp\left[-\frac{m}{2\gamma T}\,|j_D|\right],$$

Energy and power

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Because the system attains an equilibrium steady state we must verify,

$$\lim_{\Theta \gg \theta} \langle \mathcal{J}_I(\Theta) + \mathcal{J}_D(\Theta) \rangle = \langle \mathcal{E} \rangle = \overline{\mathcal{E}},$$

Analysis of the average injected power

$$\langle \mathcal{J}_{I,0}(\Theta) \rangle = \lim_{\Theta \gg \theta} \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} \frac{dq_1}{2\pi} \int_{-\infty}^{\infty} \frac{dq_2}{2\pi} \frac{\exp[(\mathrm{i}\, q_1 + \mathrm{i}\, q_2 + 2\epsilon)\,\Theta]}{(\mathrm{i}\, q_1 + \mathrm{i}\, q_2 + 2\epsilon)} \times$$

$$\times\, (\mathrm{i}\, q_1 + \epsilon) \frac{1}{R(\mathrm{i}\, q_1 + \epsilon)} \langle \tilde{\eta}(\mathrm{i}\, q_1 + \epsilon)\, \tilde{\eta}(\mathrm{i}\, q_2 + \epsilon) \rangle,$$

$$= \frac{\gamma}{m} T\, \Theta$$

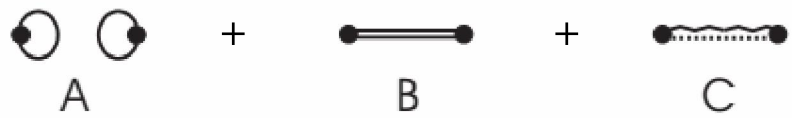
← The same for dissipation

The non-linearity does not affect the long term behaviour of the injected (nor dissipated) power. Its effect only appears in the constant (transient) terms of the dissipation which equal the average energy.

Construction the large deviation of the injected/dissipated power

$$\langle \mathcal{J}_I^2(\Theta) \rangle = \lim_{\Theta \gg \theta} \lim_{\epsilon \to 0} \int_0^\Theta dt \int_0^\Theta dt' \int_{-\infty}^{\infty} \frac{dq_1}{2\pi} \dots \int_{-\infty}^{\infty} \frac{dq_4}{2\pi} \exp\left[(\mathrm{i}\, q_1 + \mathrm{i}\, q_2 + 2\epsilon)\, t + (\mathrm{i}\, q_3 + \mathrm{i}\, q_4 + 2\epsilon)\, t'\right] \times$$
$$\times \frac{(\mathrm{i}\, q_2 + \epsilon)\,(\mathrm{i}\, q_4 + \epsilon)}{\prod_{l=1}^{2} R(\mathrm{i}\, q_{2l} + \epsilon)} \langle \tilde{\eta}(\mathrm{i}\, q_1 + \epsilon)\, \tilde{\eta}(\mathrm{i}\, q_2 + \epsilon)\, \tilde{\eta}(\mathrm{i}\, q_3 + \epsilon)\, \tilde{\eta}(\mathrm{i}\, q_4 + \epsilon) \rangle\,, \tag{26}$$

=



Construction the large deviation of the injected/dissipated power

$$
\left\langle \mathcal{J}_I^2\left(\Theta\right)\right\rangle = \lim_{\Theta \gg \theta} \lim_{\epsilon \to 0} \int_0^{\Theta} dt \int_0^{\Theta} dt' \int_{-\infty}^{\infty} \frac{dq_1}{2\pi} \dots \int_{-\infty}^{\infty} \frac{dq_4}{2\pi} \exp\left[\left(\mathrm{i}\, q_1 + \mathrm{i}\, q_2 + 2\epsilon\right) t + \left(\mathrm{i}\, q_3 + \mathrm{i}\, q_4 + 2\epsilon\right) t'\right] \times \\
\times \frac{\left(\mathrm{i}\, q_2 + \epsilon\right)\left(\mathrm{i}\, q_4 + \epsilon\right)}{\prod_{l=1}^{2} R(\mathrm{i}\, q_{2\,l} + \epsilon)} \left\langle \tilde{\eta}(\mathrm{i}\, q_1 + \epsilon)\, \tilde{\eta}(\mathrm{i}\, q_2 + \epsilon)\, \tilde{\eta}(\mathrm{i}\, q_3 + \epsilon)\, \tilde{\eta}(\mathrm{i}\, q_4 + \epsilon)\right\rangle , \qquad (26)
$$

=  +  + 

A   B   C

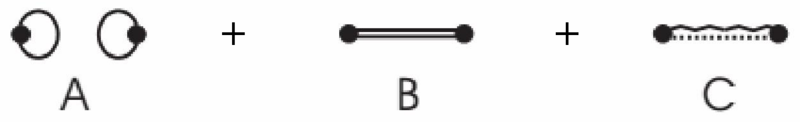
$= \left\langle \mathcal{J}_I\left(\Theta\right)\right\rangle^2$ $= 0$

Second-order cumulant

Construction of the large deviation of the injected/dissipated power

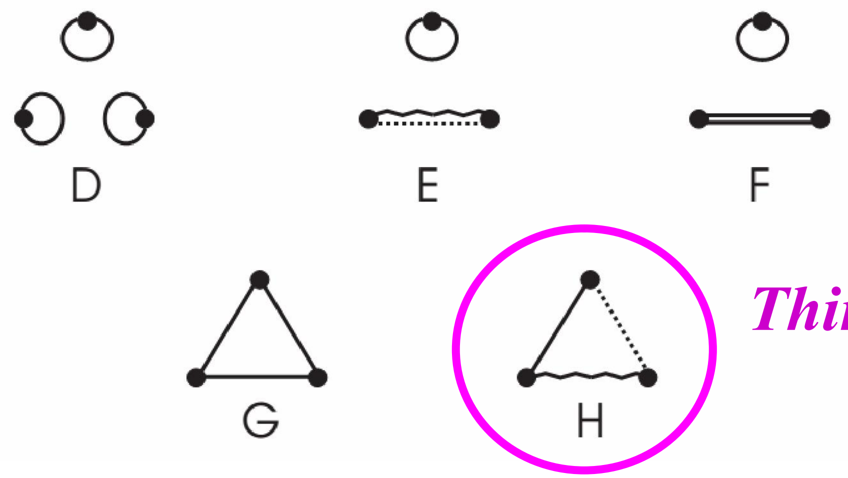
$$\left\langle \mathcal{J}_I^2\left(\Theta\right)\right\rangle = \lim_{\Theta \gg \theta}\lim_{\epsilon \to 0}\int_0^\Theta dt \int_0^\Theta dt' \int_{-\infty}^{\infty}\frac{dq_1}{2\pi}\dots\int_{-\infty}^{\infty}\frac{dq_4}{2\pi}\exp\left[\left(\mathrm{i}\,q_1+\mathrm{i}\,q_2+2\epsilon\right)t+\left(\mathrm{i}\,q_3+\mathrm{i}\,q_4+2\epsilon\right)t'\right]\times \\ \times\frac{\left(\mathrm{i}\,q_2+\epsilon\right)\left(\mathrm{i}\,q_4+\epsilon\right)}{\prod_{l=1}^{2}R\left(\mathrm{i}\,q_{2\,l}+\epsilon\right)}\left\langle \tilde{\eta}(\mathrm{i}\,q_1+\epsilon)\,\tilde{\eta}(\mathrm{i}\,q_2+\epsilon)\,\tilde{\eta}(\mathrm{i}\,q_3+\epsilon)\,\tilde{\eta}(\mathrm{i}\,q_4+\epsilon)\right\rangle, \qquad (26)$$

=



$= \left\langle \mathcal{J}_I\left(\Theta\right)\right\rangle^2$ $\quad = 0$

For the third-order moment,



Third-order cumulant

Computing further moments (and with the help of the `on-line encyclopaedia of integers and series`) we are able to find the moment generating function,

$$\begin{aligned}\mathcal{M}_{\mathcal{J}_I(\Theta)}(\lambda) &\equiv \langle \exp\left[\lambda\,\mathcal{J}_I(\Theta)\right]\rangle \\ &= \exp\left[\frac{\gamma\,\Theta}{2\,m}\left(1-\sqrt{1+4\,T\,\lambda}\right)\right]\end{aligned}$$

Heeding that the injected energy corresponds to the integral of the injected power with respect to time, we can use large deviation theory and obtain the distribution of the total injected energy imposing the Gartner-Ellis theorem which yields,

$$L(\mathcal{J}_I) \sim \exp\left[-\frac{\left(\mathcal{J}_I-\gamma\,T\,\Theta/m\right)^2}{4\,T\,\mathcal{J}_I}\right] H(\mathcal{J}_I)$$

matching Farago's solution who does the computation for a harmonic system.

For 2-particle systems and T_1 different to T_2 one has a steady state instead. A relevant thermal quantity is the heat flux between particles,

$$J_{1\to 2} = \frac{dW_{1\to 2} - dW_{2\to 1}}{2\,dt} = \frac{F_{1\to 2}v_2 - F_{2\to 1}v_1}{2}$$

whence we highlight its average value,

$$J_Q = \langle J_{1\to 2}\rangle \equiv \kappa_T\,(T_2 - T_1)$$

Heat conductance

which for the linear version of the model gives,

$$\kappa_T = \frac{1}{2}\frac{k_1^2\gamma}{m\,k_1^2 + \gamma^2\left(k + k_1\right)}$$

Using the same time averaging approach we can obtain the distribution of the heat flux, namely its cumulant generating function,

$$\mathcal{G}_{J_{1\to 2}}(\lambda) \equiv \sum_{n=1}^{\infty} \kappa_n \frac{\lambda^n}{n!} = \ln \frac{1}{\sqrt{\left[1-\left(A+\sqrt{B}\right)\lambda\right]\left[1-\left(A-\sqrt{B}\right)\lambda\right]}}$$

$$A = -\frac{1}{2}\frac{\gamma\, k_1^2}{k_1^2 m + (k+k_1)\,\gamma^2}\,(T_1 - T_2)\,,$$

$$B = \frac{1}{4}\frac{k_1^2}{m\,\gamma\,(k+2k_1)}\,(T_1 + T_2)^2\,,$$

$\sigma^2_{J_{1\to 2}}$ $\qquad$ $\overline{J_{1\to 2}}$

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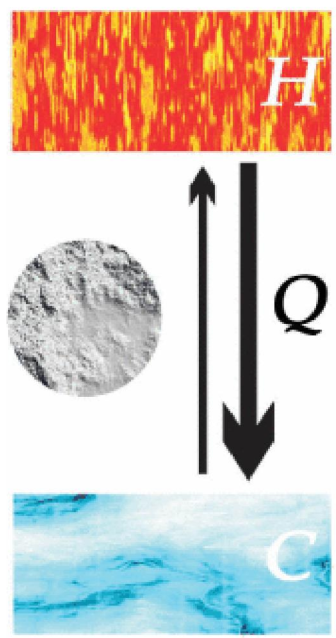
$$= \ln \frac{1}{\sqrt{\left[1-\left(A+\underbrace{\sqrt{B}}_{\sigma^2_{J_{1\to 2}}}\right)\lambda\right]\left[1-\left(\underbrace{A}_{\overline{J_{1\to 2}}}-\sqrt{B}\right)\lambda\right]}}$$

$$A = -\frac{1}{2}\frac{\gamma\, k_1^2}{k_1^2 m + (k+k_1)\,\gamma^2}\,(T_1 - T_2)\,,$$

$$B = \frac{1}{4}\frac{k_1^2}{m\,\gamma\,(k+2k_1)}\,(T_1+T_2)^2\,,$$

Whence the fluctuation relation can be obtained,

$$\lim_{|J_{1\to 2}|\to\infty} \frac{p\left(|J_{1\to 2}|\right)}{p\left(-|J_{1\to 2}|\right)} = \exp\left[2\frac{\overline{J_{1\to 2}}}{\sigma^2_{J_{1\to 2}}}\,|J_{1\to 2}|\right]$$



Introducing Poissonian reservoirs

$$\eta(t) = \sum\nolimits_\ell \Phi(t)\delta(t - t_\ell), \quad \lambda(t) = \lambda_0[1 + A\cos(\omega t)], \qquad (0 \le A < 1).$$

in what follows $A = 0$ (homogeneous process) and

$$\langle \eta(t_1) \ldots \eta(t_n) \rangle_c = \lambda(t_1)\, \overline{\Phi^n}\, \delta(t_1 - t_2) \ldots \delta(t_{n-1} - t_n).$$

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$$\langle \eta(t_1)\ldots\eta(t_n)\rangle_c = \lambda(t_1)\,\overline{\Phi^n}\,\delta(t_1 - t_2)\ldots\delta(t_{n-1} - t_n).$$

Why is this relevant?

I – Theoretical relevance

Poisson noise is the quintessential stochastic process with singular measure.
The *Lévy-Itô theorem* states that every white noise is represented by a superposition of Brownian and Poisson noises.

II – Factual relevance

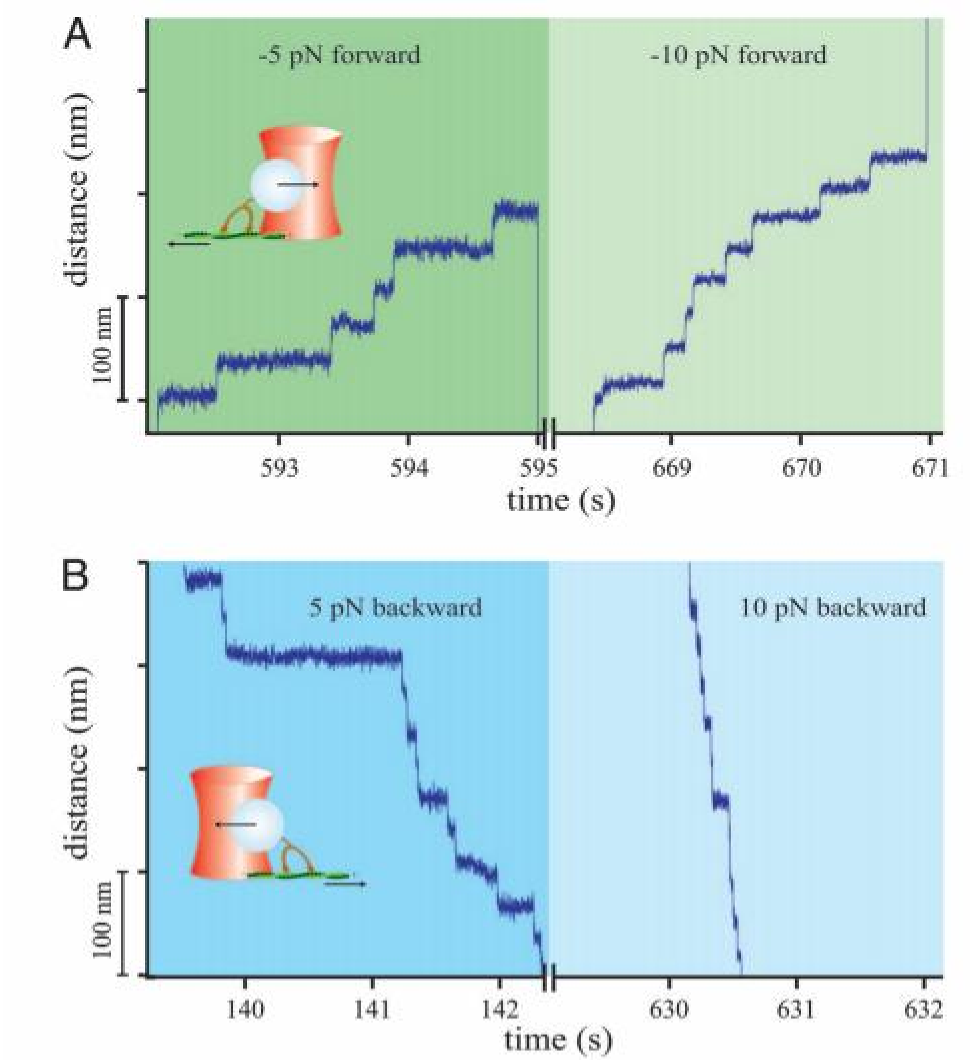
Physical-Chemical problems using Anderson thermostats;

Landsberg types engine systems

RLC circuits

Surface diffusion of interacting adsorvates

Molecular motors (*e.g.*, Myosin-V)



J Christof *et al*, PNAS **103**, 8680 (2006)

1-Particle steady state probabilistcs

[Morgado, DQ, Soares-Pinto, JSTAT P06010 (2011)]

After a raft of tedious calculations,

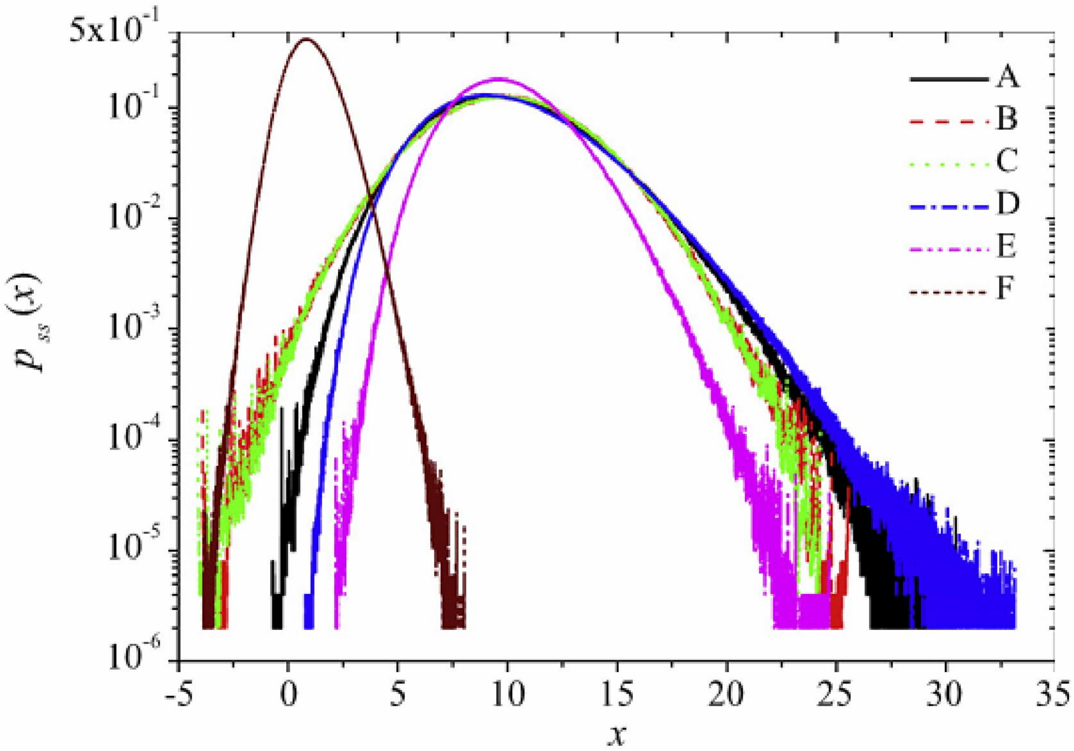
$$p_{ss}(x,v) = \mathcal{F}_{x,v}\left[\exp\left\{\sum_{n,m=0:(m+n>0)}^{\infty} \lambda_0 (n+m)!\frac{Q^n}{n!}\frac{P^m}{m!}(\mathrm{i}\bar{\Phi})^{n+m} \times \left(\Psi_{1x}\,\delta_{m,0} + \Psi_{1v}\,\delta_{n,0} + \Psi_2\,\delta_{m,1} + \sum_{m=2}^{n+m-1}\Psi_3\,(m)\right)\right\}\right]$$

yielding the marginal steady state distributions …

$$p_{ss}(x) = \mathcal{F}_x\left[\exp\left\{\sum_{n>0}^{\infty}\lambda_0 Q^n\,\bar{\Phi}^n\,\Psi_{1x}\right\}\right], \qquad \kappa_n \equiv \overline{\langle x^n\rangle_c} = n!\lambda_0\,(\mathrm{i}\bar{\Phi})^n\,\Psi_{1x}.$$

and thus,

$$\kappa_n^{(x)} = \lambda_0\left(\frac{\bar{\Phi}}{M}\right)^n(-1)^{n-1}\frac{(n!)^2}{D_n} \qquad (n \geq 1).$$



$$\overline{\langle x \rangle} = \bar{\Phi}\,\frac{\lambda_0}{k_0},$$

$$\overline{\langle x^2 \rangle} - \overline{\langle x \rangle}^2 = \bar{\Phi}^2 \frac{\lambda_0}{\gamma\, k_0}.$$

Figure 1. Numerically obtained probability density function $p_{ss}(x)$ versus position x for various cases with $\lambda_0 = 10$, $\bar{\Phi} = 1$ and the noise defined by equation (4) with $\omega = \pi$. Following the legend in the figure we have the respective cases, A: $M = 1, k_0 = 1, \gamma = 1, A = 0$, B: $M = 10, k_0 = 1, \gamma = 1, A = 0$, C: $M = 10, k_0 = 1, \gamma = 1, A = 1/2$, D: $M = 0.1, k_0 = 1, \gamma = 1, A = 0$, E: $M = 1, k_0 = 1, \gamma = 2, A = 0$ and F: $M = 1, k_0 = 10, \gamma = 1, A = 0$.

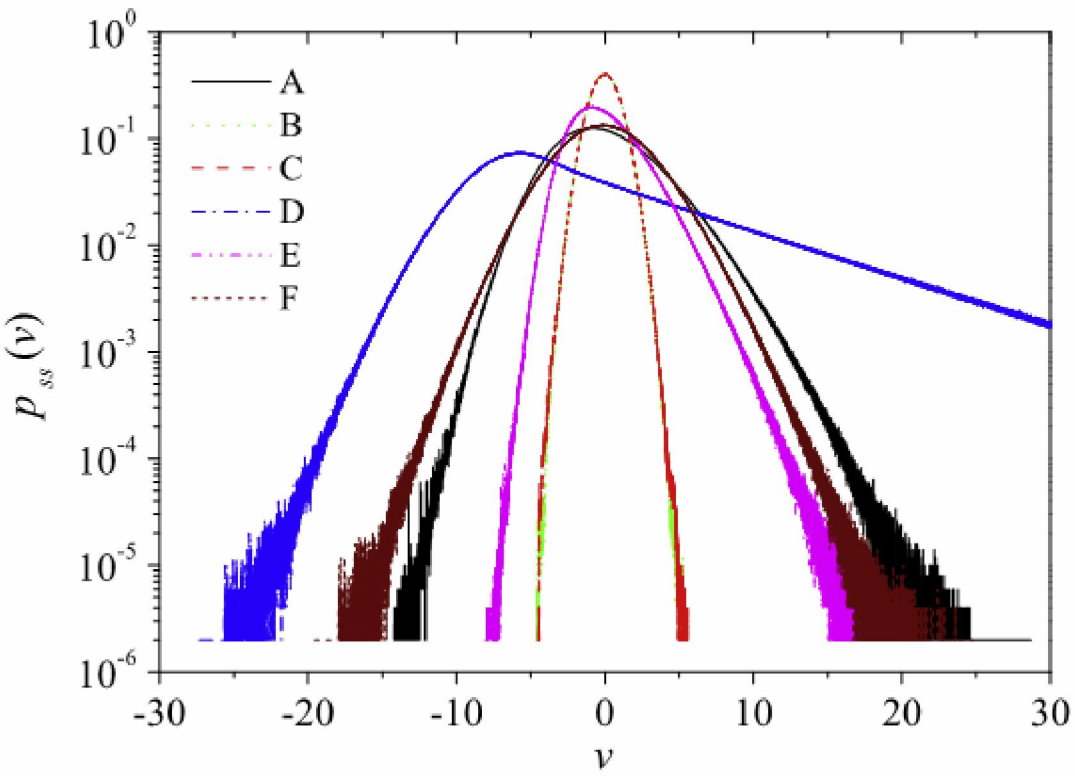


Figure 2. Numerically obtained probability density function $p_{ss}(v)$ versus scalar velocity v for the same parameter sets of figure 1.

$$\kappa_1^v \equiv \overline{\langle v \rangle} = 0,$$

$$\kappa_2^v \equiv \overline{\langle v^2 \rangle} = \frac{\lambda_0\,\bar{\Phi}^2}{M\,\gamma}.$$

Neither $p_{ss}(x)$ nor $p_{ss}(v)$ are Gaussians.

Thermostatistically, although $p^{P}_{ss}(x,v)$ is quite different from $p^{G}_{ss}(x,v)$, one has the same 1-particle thermal properties as if Brownian (equilibrium) were considered instead.

$$\int_0^{\Theta} [\eta(t)\, v(t) - \gamma v(t)^2]\, \mathrm{d}t = \tfrac{1}{2} M v(t)^2 \big|_{t=0}^{t=\Theta} + \tfrac{1}{2} k_0 x(t)^2 \big|_{t=0}^{t=\Theta}.$$

$$E_M^c = \tfrac{1}{2} M \overline{\langle v(t)^2 \rangle_{asy}} + \tfrac{1}{2} k_0 \overline{\langle x(t)^2 \rangle_{asy}} = \lambda_0 \frac{\bar{\Phi}^2}{\gamma} \cdot$$

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$$E^c_M = \tfrac{1}{2} M \overline{\langle v(t)^2 \rangle_{asy}} + \tfrac{1}{2} k_0 \overline{\langle x(t)^2 \rangle_{asy}} = \lambda_0 \frac{\bar{\Phi}^2}{\gamma} \equiv T$$

Both long-term asymptotic injected and dissipated heat terms equal to

$$\lim_{\Theta\to\infty} \left| \left\langle J_{inj,dis}(\Theta) \right\rangle \right| = \lambda_0 \frac{\bar{\Phi}^2}{M} \Theta \to \gamma \frac{T}{M} \Theta$$

2-particle steady state heat transport

[Morgado, DQ, PRE **86**, 041108 (2012)]

$$J_Q = \langle J_{1\to 2} \rangle \equiv \kappa_T \left(T_2 - T_1 \right)$$

Using the Laplace transform time averaging, the calculations boil down to evaluating,

$$\begin{aligned} \overline{\mathcal{J}_{rs}} &= \lim_{z\to 0} \lim_{\varepsilon\to 0} \int \frac{dq_1}{2\pi} \frac{dq_2}{2\pi} \frac{z}{z - \mathrm{i} \left(q_1 + q_2 + 2\varepsilon \right)} \\ &\quad \times \left\langle \tilde{x}_r \left(\mathrm{i}\; q_1 + \varepsilon \right) \tilde{v}_s \left(\mathrm{i}\; q_2 + \varepsilon \right) \right\rangle . \end{aligned}$$

Assuming (once again) the temperature of a Poissonian particle as,

$$T_i = \lambda_0 \frac{\overline{\Phi_i}^2}{\gamma}$$

the integration renders up in the linear case,

2-particle steady state heat transport

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Assuming (once again) the temperature of a Poissonian particle as,

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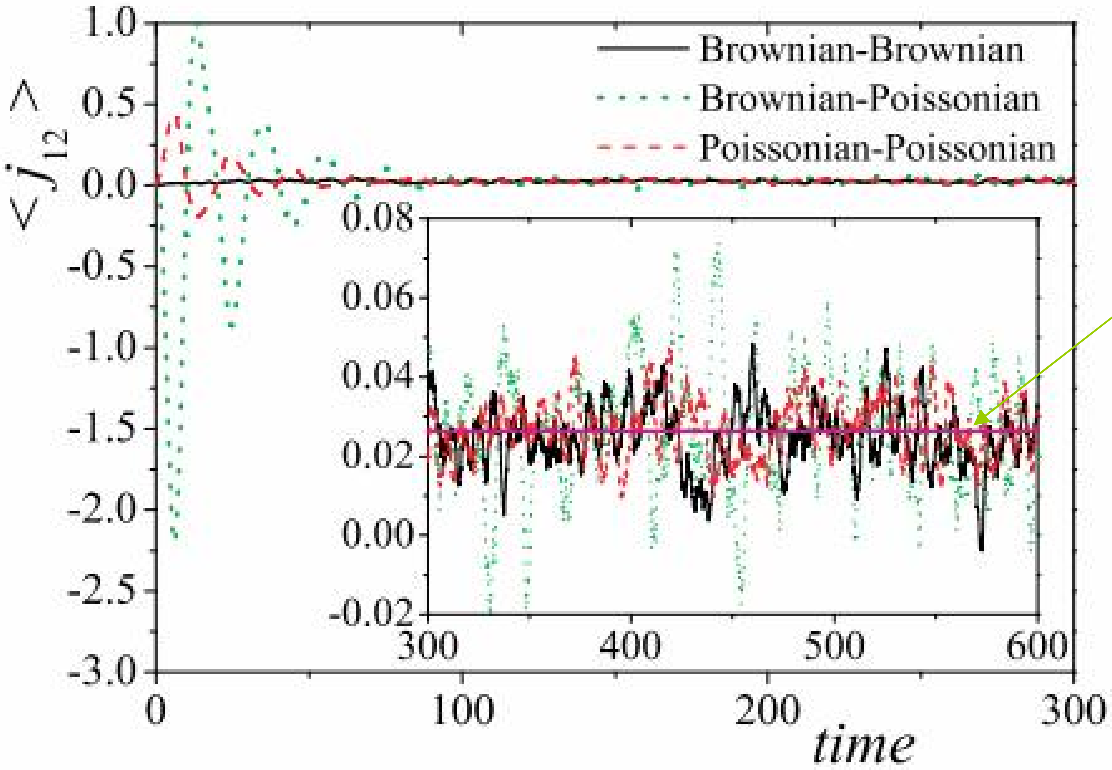
the integration renders up in the linear case,

$$\kappa = \frac{1}{2}\frac{k_c^2 \gamma}{m\, k_c^2 + \gamma^2\left(k + k_c\right)}$$

The exact same result obtained in the Gaussian case.

Even mixing different kinds of reservoirs the behaviour does not change



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RASH CONCLUSION:

THE SINGULAR NATURE OF THE MEASURE OF A POISSONIAN PARTICLE IS IRRELEVANT FOR THERMAL PURPOSES.

THENCE

IN ANALYTICALLY TREATING THE THERMOSTATISTICS OF SUCH PARTICLES ONE CAN HEDGE ALL THOSE NASTY CALCULATIONS BY USING BROWNIAN PROXIES!

Ultimately, Poissonian particles are thermally a '*damp squib*'.

A brand new day: non-linear systems [Morgado, DQ, PRE **86**, 041108 (2012)]

$$m\frac{dv_i(t)}{dt} = -k\,x_i(t) - \gamma\,v_i(t) - \sum_{l=1}^{2} k_{2l-1}\left[x_i(t) - x_j(t)\right]^{2l-1} + \eta_i(t)$$

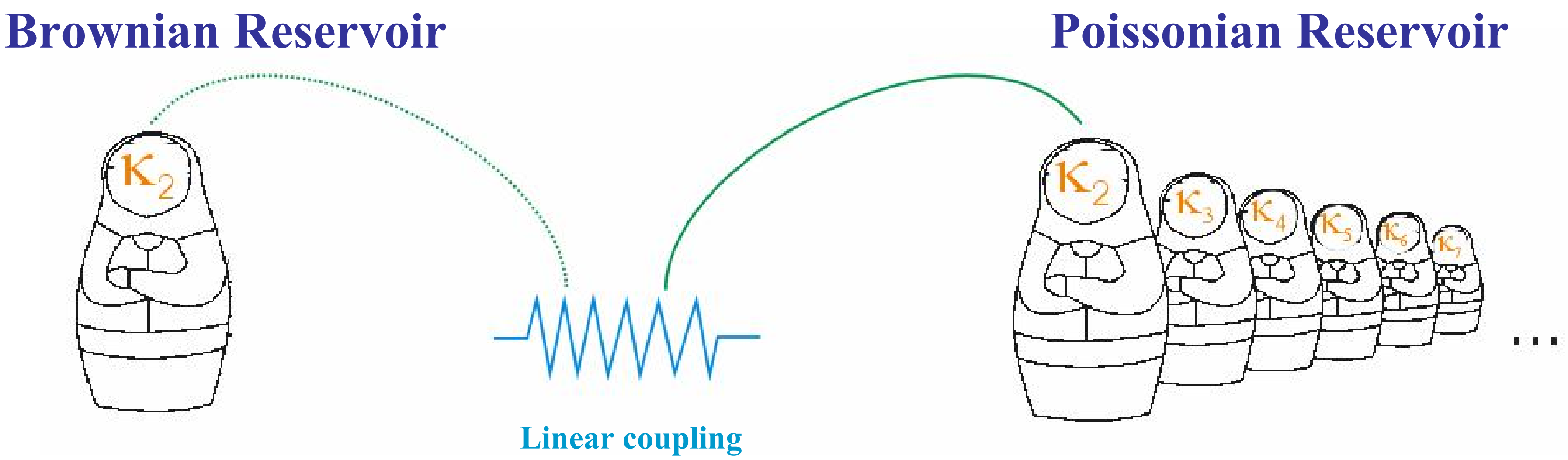
$$\overline{\langle j_{12}\rangle} = \overline{\left\langle j_{12}^{(0)}\right\rangle} + \overline{\left\langle j_{12}^{(1)}\right\rangle} + \overline{\left\langle j_{12}^{(s)}\right\rangle} + \mathcal{O}\left(k_3^2\right)$$

$$\begin{cases} \overline{\left\langle j_{12}^{(0)}\right\rangle} = -\frac{k_1^2}{4}\frac{\left[\mathcal{A}_1(2)-\mathcal{A}_2(2)\right]}{m\,k_1^2+\gamma^2(k+k_1)} \\ \overline{\left\langle j_{12}^{(1)}\right\rangle} = -\frac{3}{8}\gamma\,k_1\,k_3\frac{(2\,k+k_1)\left[\mathcal{A}_1(2)^2-\mathcal{A}_2(2)^2\right]}{(k+2\,k_1)\left[\gamma^2(k+k_1)+m\,k_1^2\right]^2} \end{cases}$$

$$\overline{\left\langle j_{12}^{(s)}\right\rangle} = -\frac{27}{2}\gamma^2\frac{k_1\,k_3}{\lambda}\frac{\mathcal{N}}{\mathcal{D}}\left(\left[\mathcal{A}_1(2)^2 - \mathcal{A}_2(2)^2\right]\right)$$

THERMOSTATISTICS DOES CARE ABOUT THE NATURE OF THE RESERVOIRS

Pictorial *conclusions* (this time for real)



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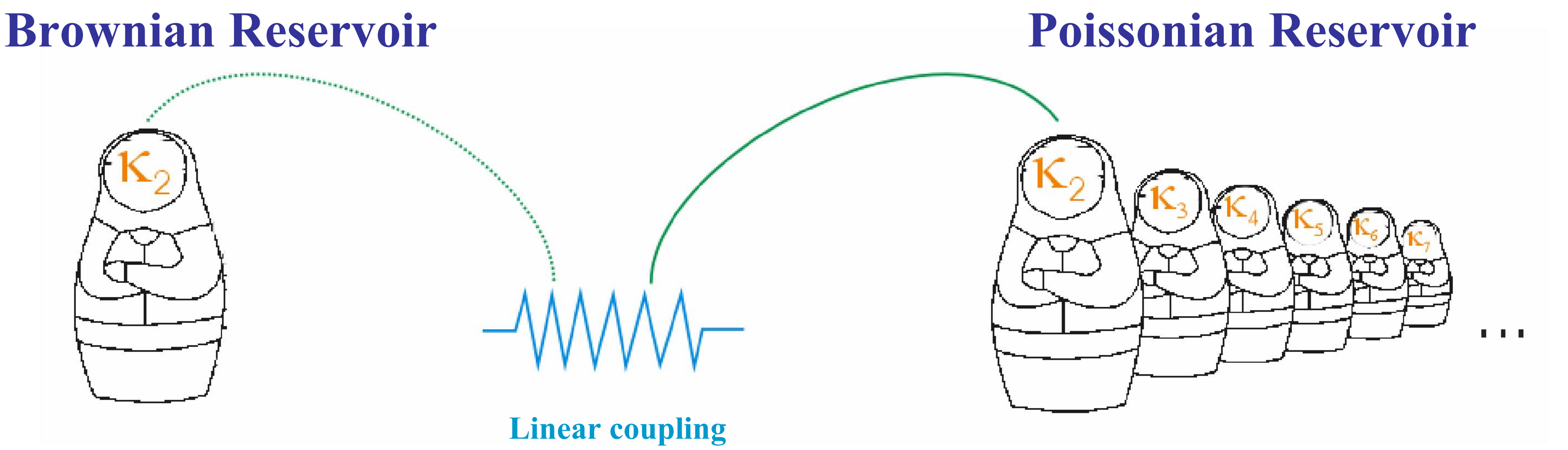
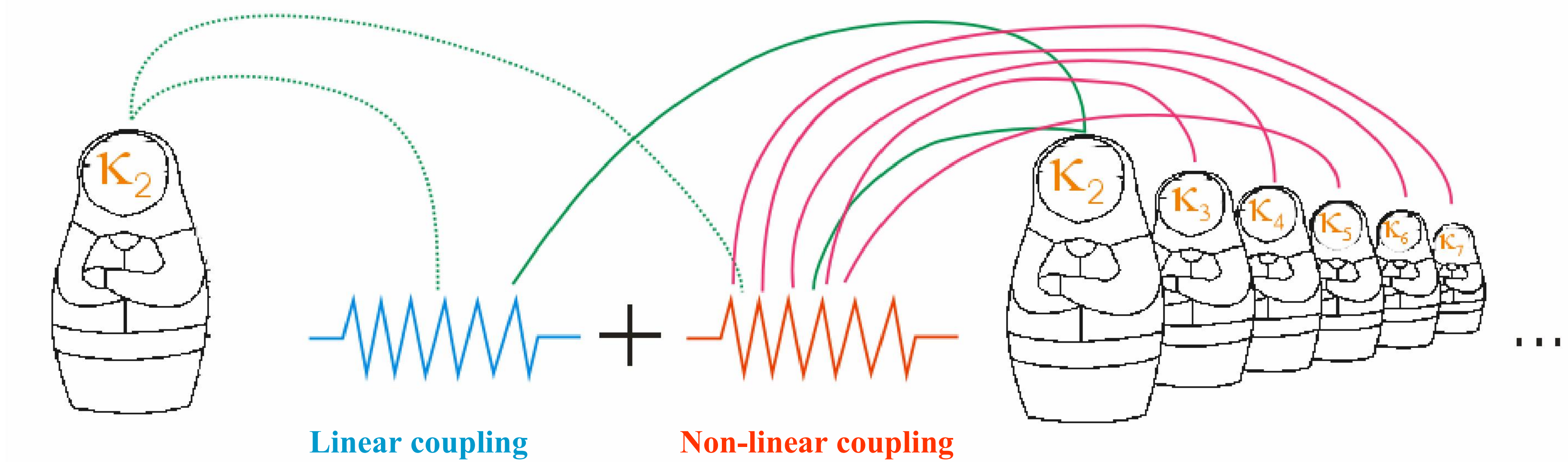
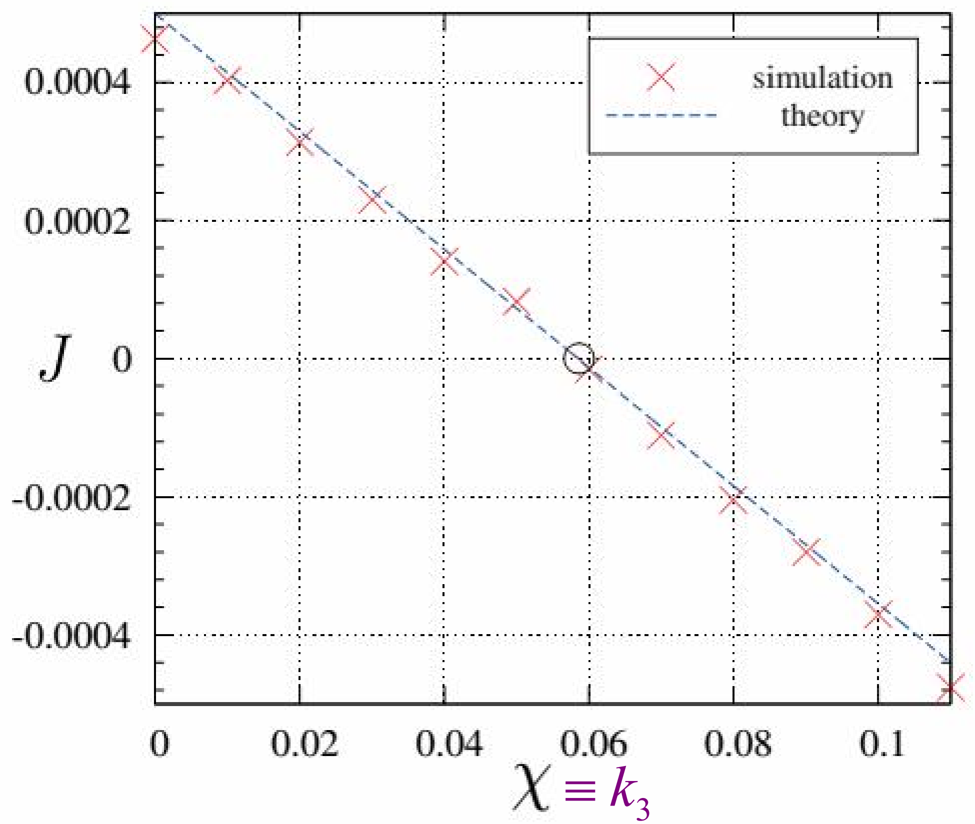




Numerical verification [Kanazawa, Sagawa, Hayakawa (2013) PRE]



Average heat flux through a non-linear system between a Gaussian and symmetric Poissonian reservoir at different temperatures.

Consequence

For non-Gaussian heat reservoirs the zeroth law of thermodynamics is not universal as it depends on the mechanical features of the system.