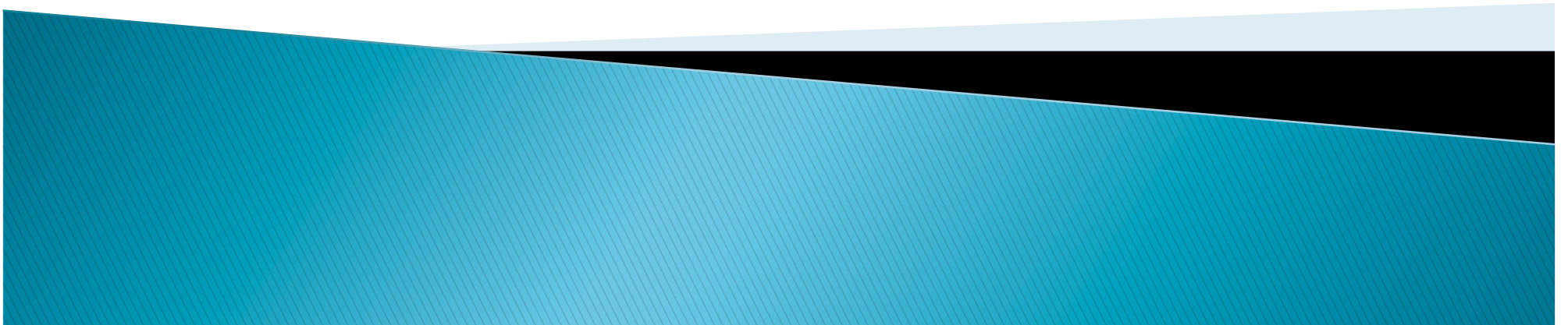


A Igualdade de Jarzysnki e suas aplicações a sistemas pequenos e/ou biológicos

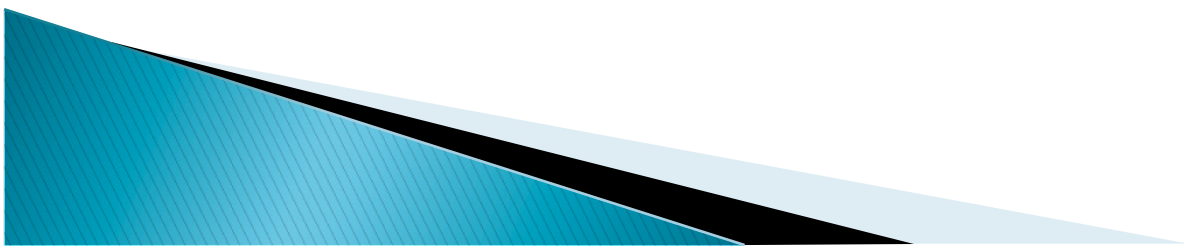
Welles A. M. Morgado – PUC–Rio

INCT – SC

04/03/2010

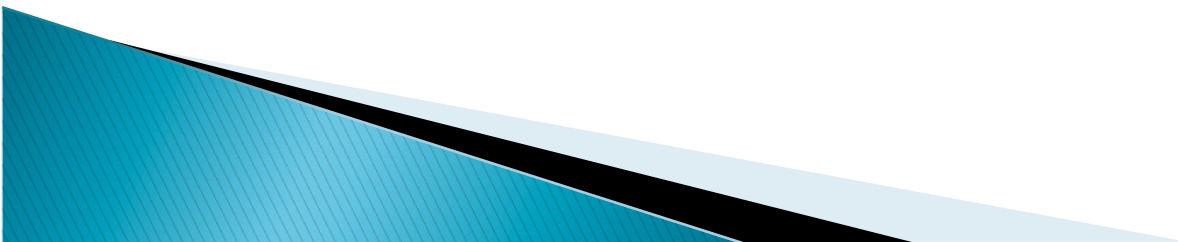


Resumo



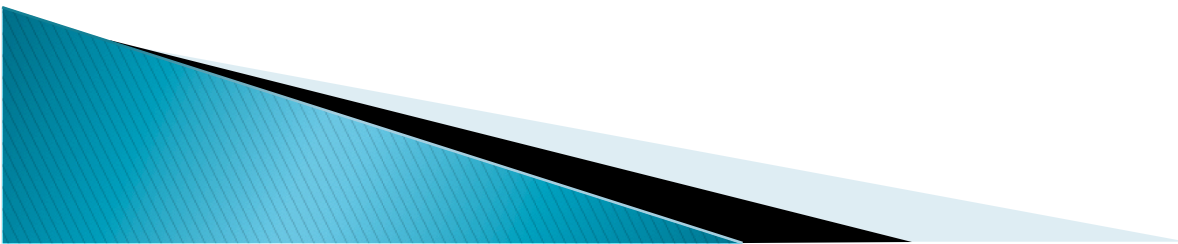
Resumo

- ▶ Introdução a teoremas de flutuação



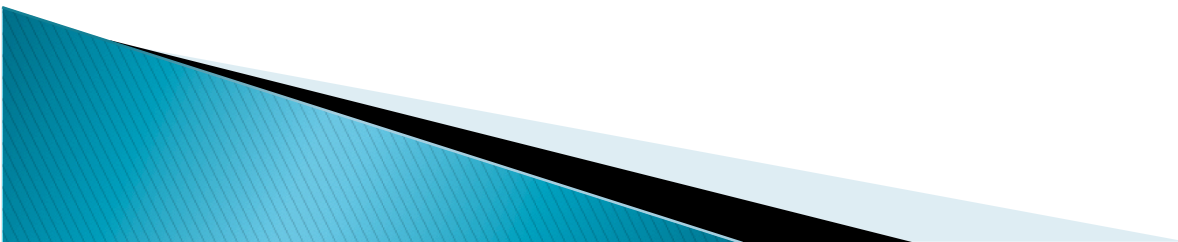
Resumo

- ▶ Introdução a teoremas de flutuação
- ▶ Igualdade de Jarzynski (JE)



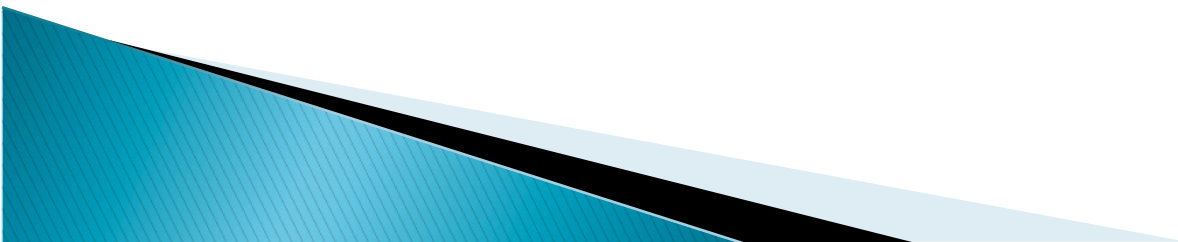
Resumo

- ▶ Introdução a teoremas de flutuação
- ▶ Igualdade de Jarzynski (JE)
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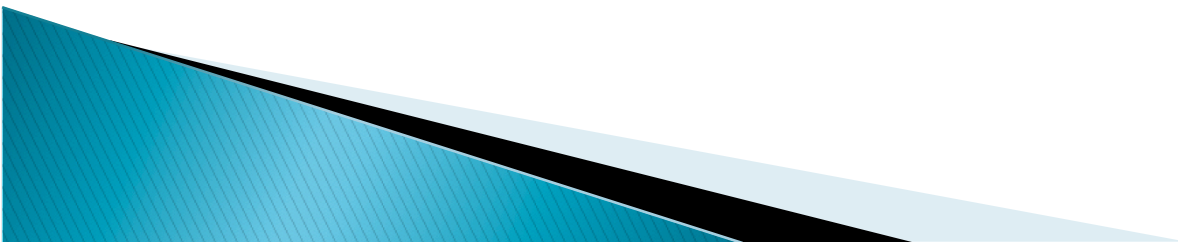
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- ▶ Introdução a teoremas de flutuação
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- ▶ Pequeno modelo mecânico



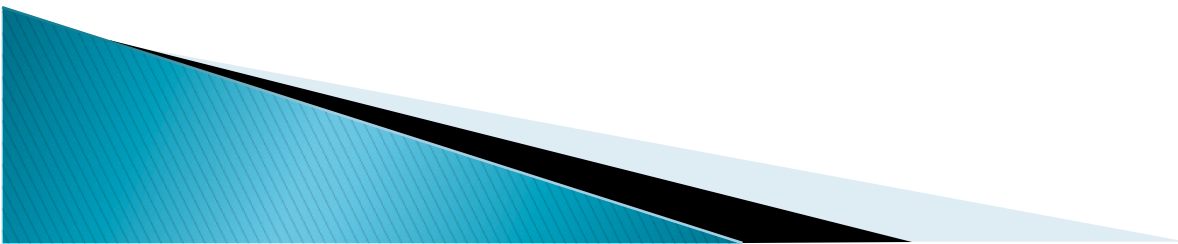
Resumo

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- ▶ Igualdade de Jarzynski (JE)
- ▶ Aplicações a sistemas biológicos
- ▶ Pequeno modelo mecânico
- ▶ Verificando a JE



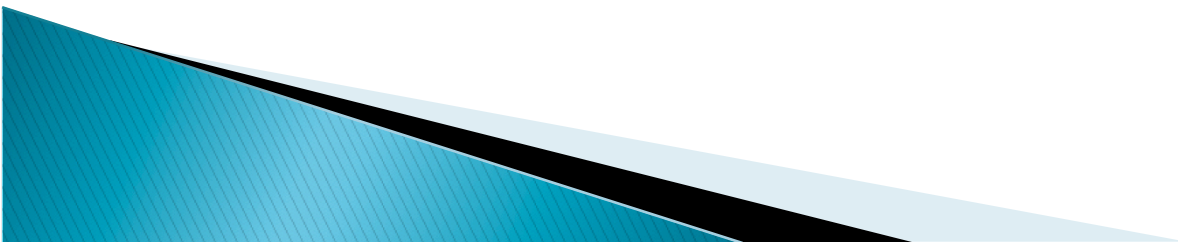
Motivação

- ▶ Conexão exata entre equilíbrio e não-equilíbrio



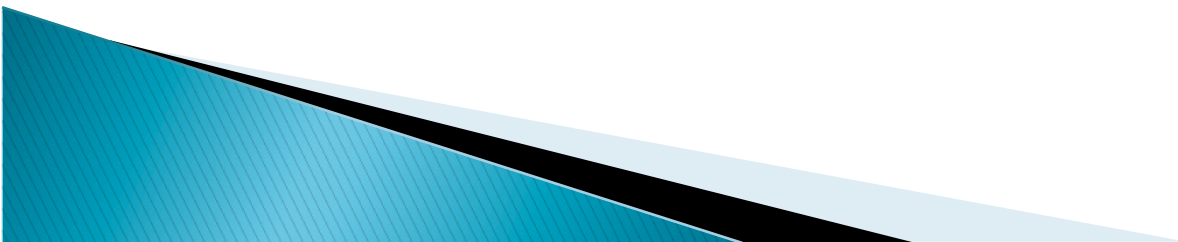
Motivação

- ▶ Conexão exata entre equilíbrio e não-equilíbrio
- ▶ Acesso a informações termodinâmicas para sistemas moleculares



Motivação

- ▶ Conexão exata entre equilíbrio e não-equilíbrio
- ▶ Acesso a informações termodinâmicas para sistemas moleculares
- ▶ Calibragem de simulações de sistemas Hamiltonianos



Métodos experimentais utilizados

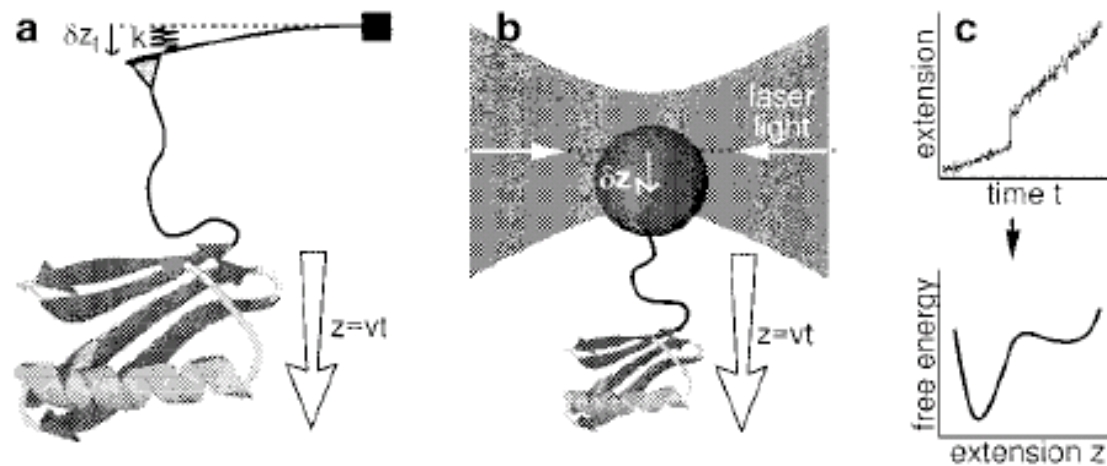


Fig. 1. Single-molecule force measuring experiments by using AFM (a) and laser tweezers (b). In the AFM experiment (a), the sample is moved at a constant speed v relative to the cantilever with spring constant k . The position $z_t = vt + \delta z_t$ of the cantilever tip with respect to the sample is recorded, where δz_t is the displacement of the cantilever tip. From repeated measurements of z_t , the free energy profile $G_0(z)$ of the unperturbed system can be determined exactly (c).

Gerhard Hummer* and Attila Szabo

PNAS | March 27, 2001 | vol. 98 | no. 7

Caracterizando sistemas termodinâmicos

Carlos Bustamante, Jan Liphardt, and Felix Ritort
July 2005 Physics Today 43

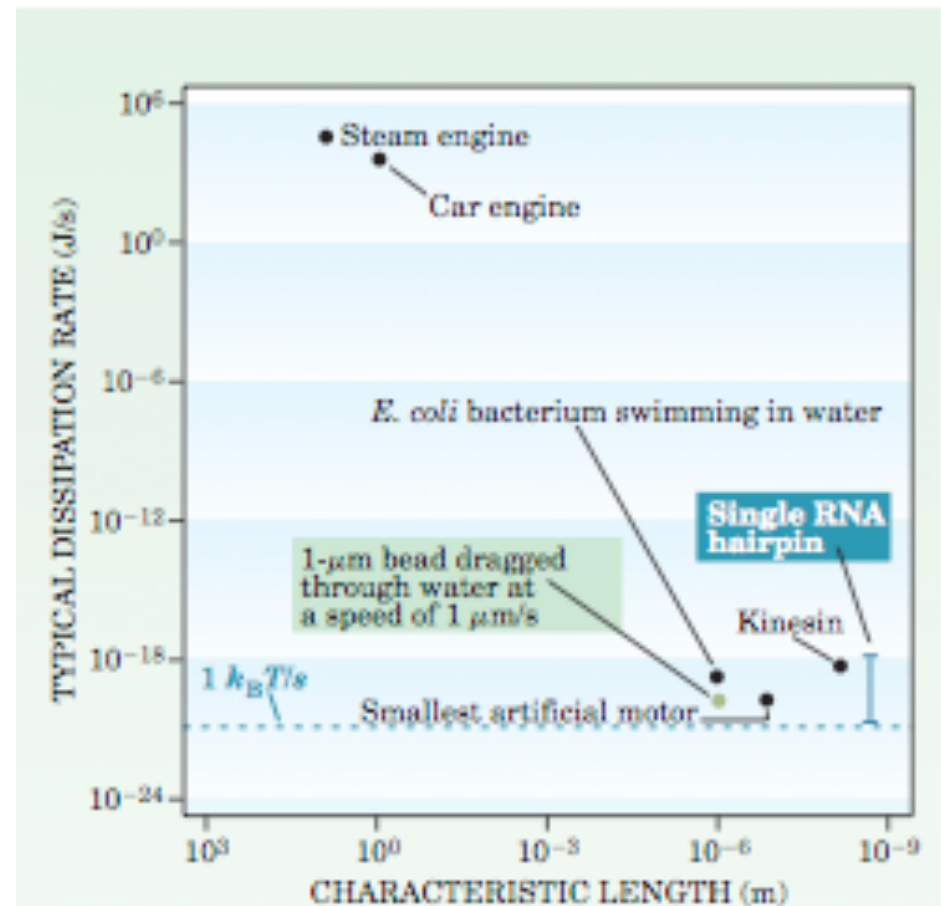
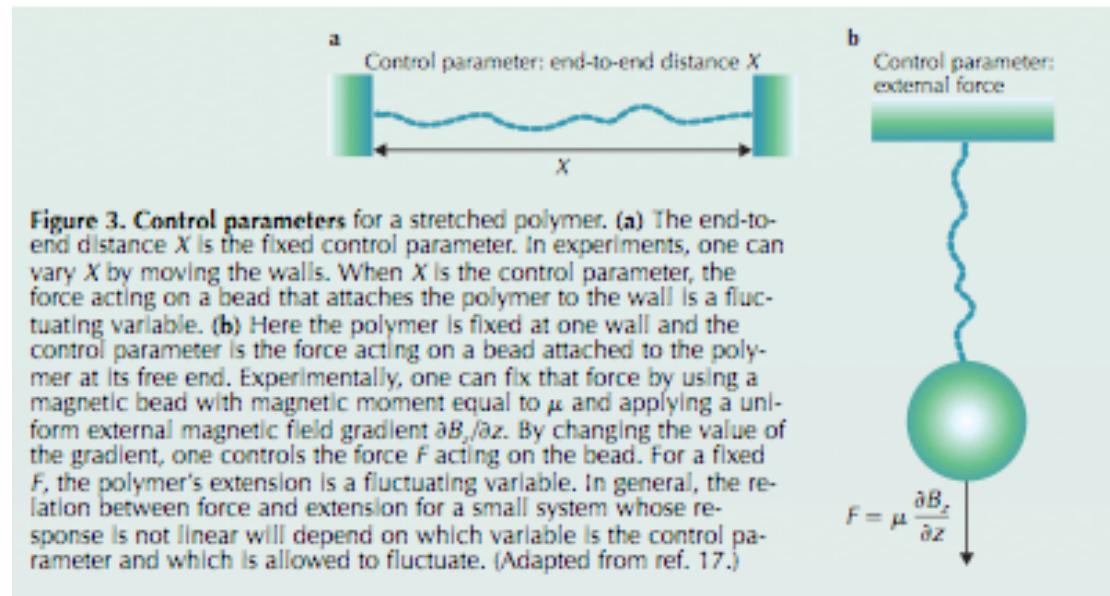


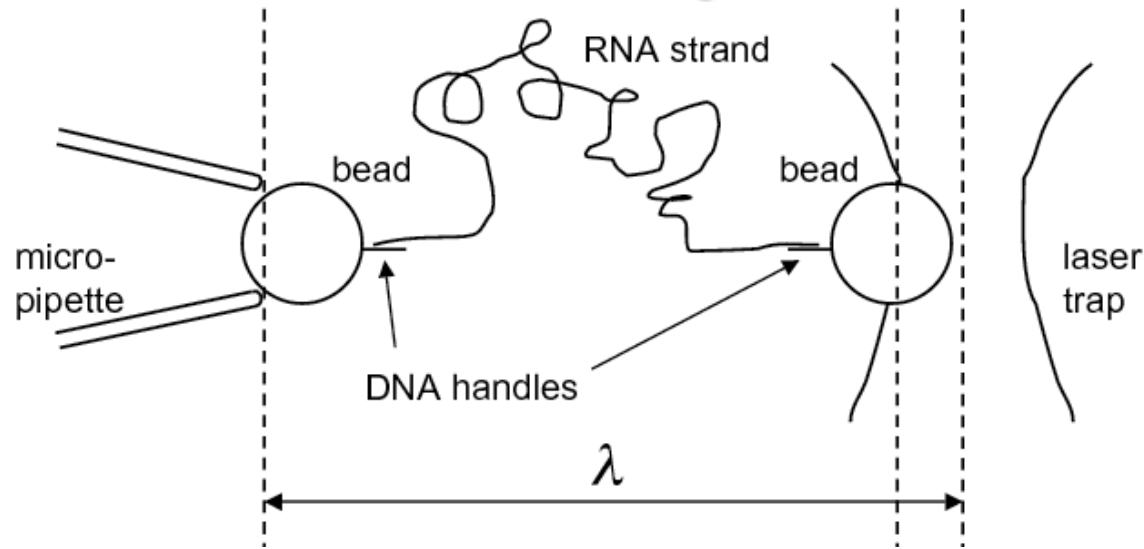
Figure 2. Thermodynamic systems characterized according to their typical length scales and energy dissipation rates. The two systems set off by boxes have been used to test fluctuation theorems and the Jarzynski equality as described in the text.

Parâmetros de controle

- ▶ Comprimento x da molécula
- ▶ Força F sobre a esfera na extremidade

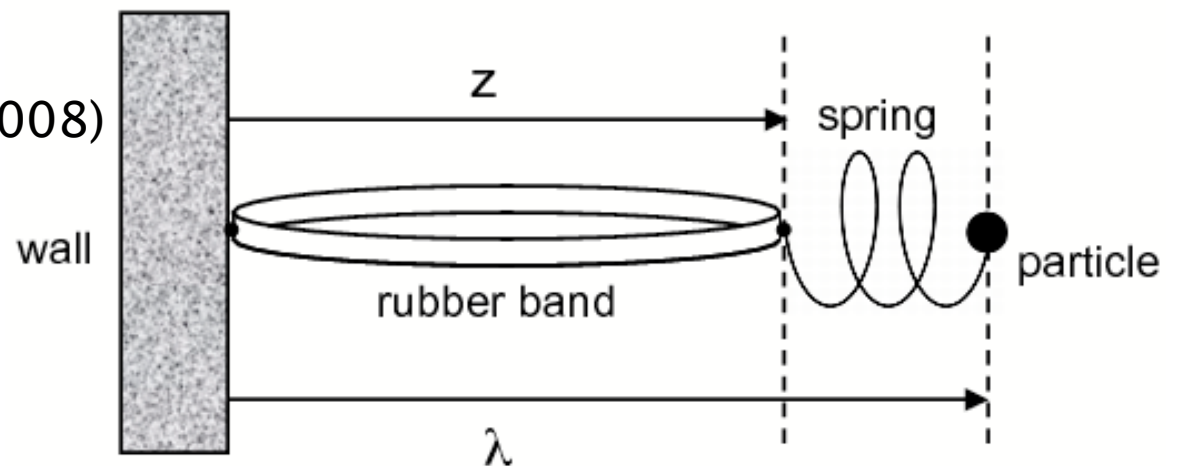


Manipulando moléculas de modo controlado: esquemática



C. Jarzynski

Eur. Phys. J. B 64, 331-340 (2008)

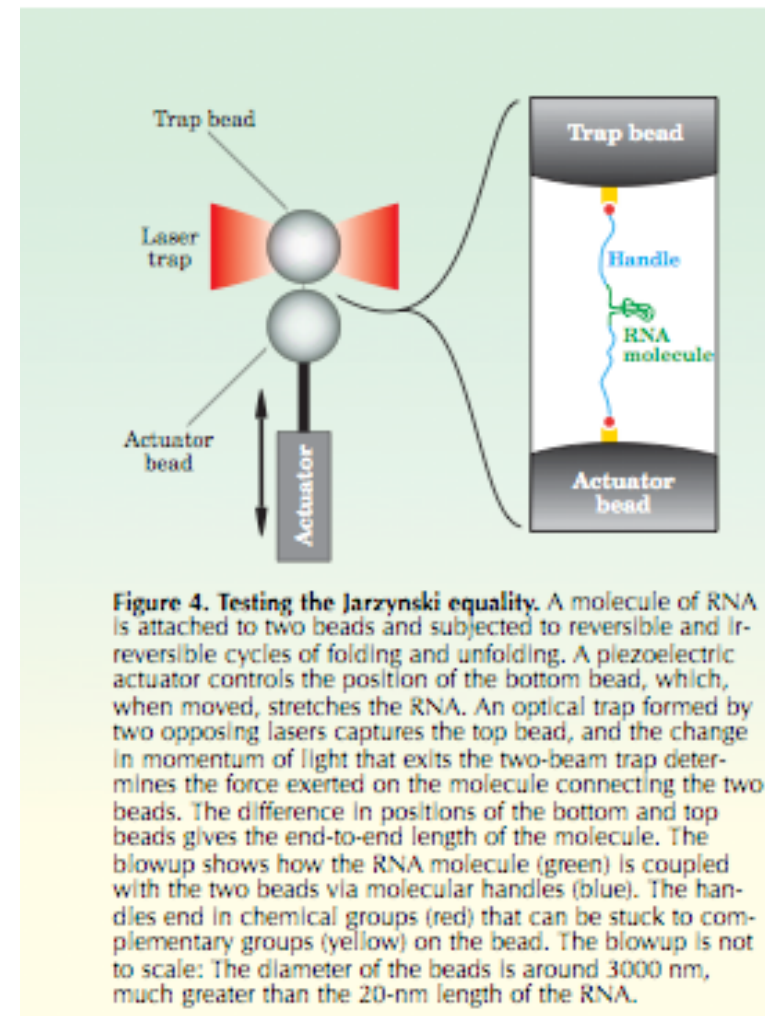


Na realidade...

- ▶ As dimensões são bem menores

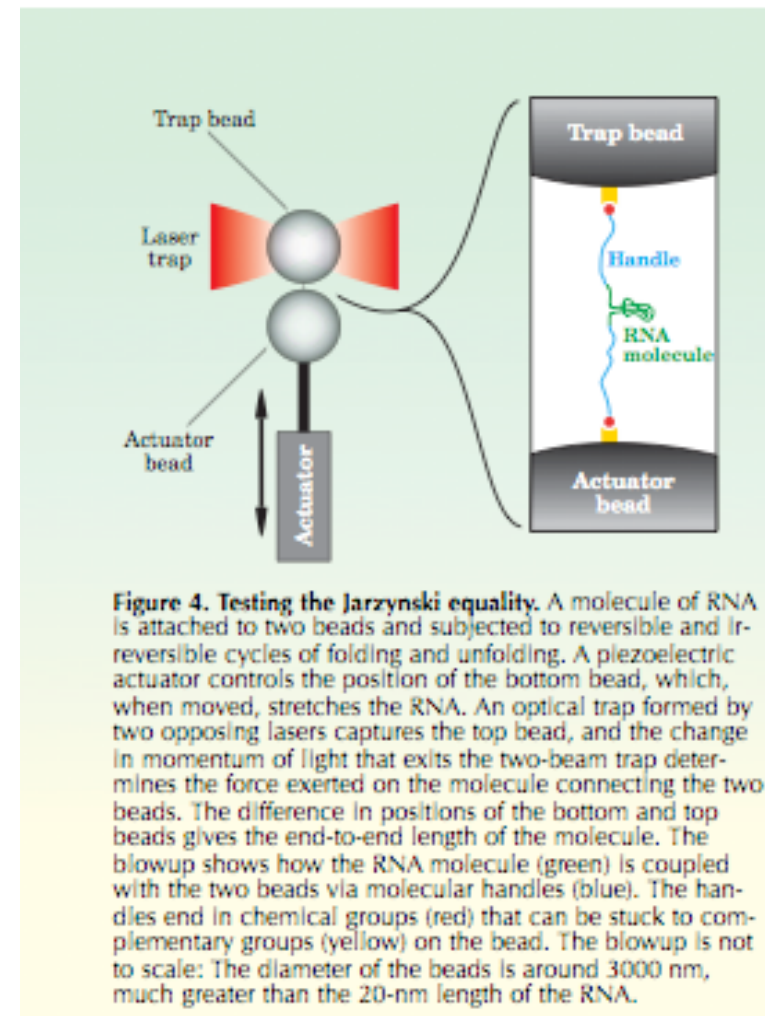
Na realidade...

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Na realidade...

- ▶ As dimensões são bem menores



Maquinas moleculares em outros contextos

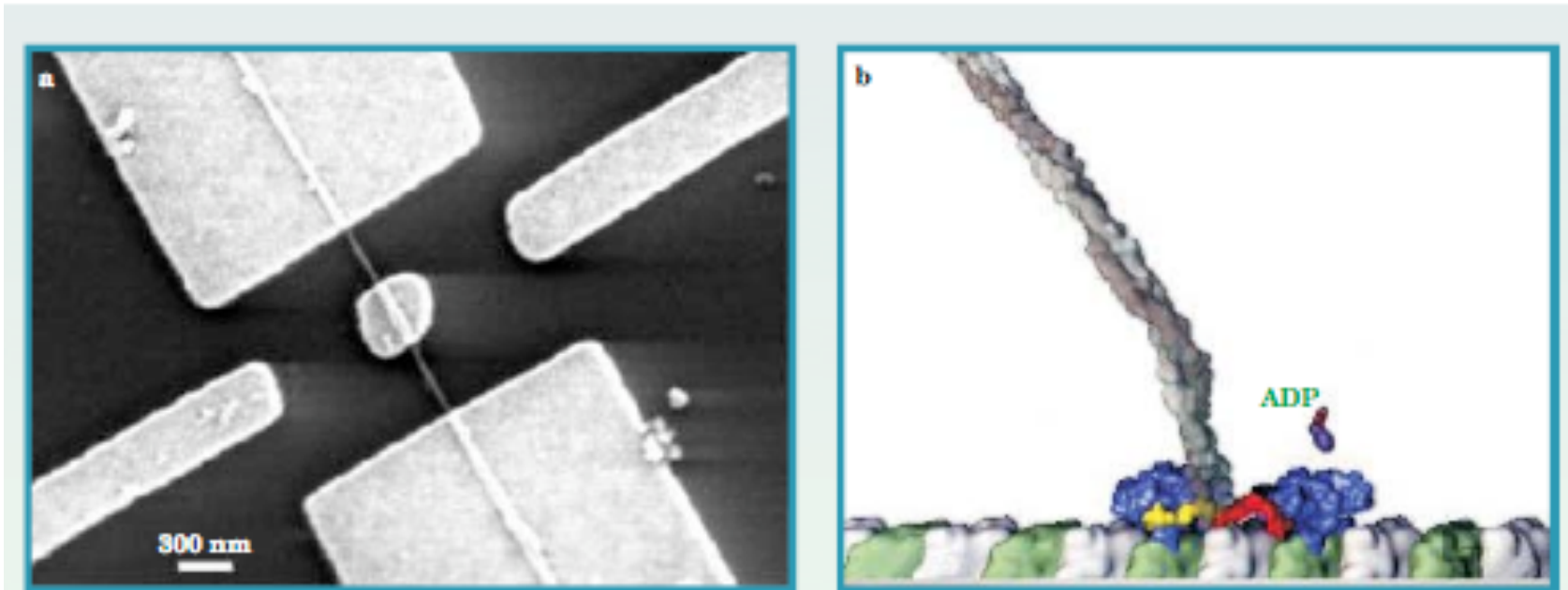


Figure 1. Nonequilibrium small systems. (a) In this scanning electron microscope image of an integrated synthetic actuator, the central metal-plate rotor is attached to a multiwalled carbon nanotube (MWNT) that acts as a support shaft. Electrical contact to the rotor plate is made via the MWNT and its anchor pads. A synchronized electrostatic force can induce rotary motion about the axis of the MWNT. (Adapted from ref. 16.) (b) This artist's rendition, based on crystallographic studies, shows a kinesin motor walking along a microtubule in a hand-over-hand (blue regions) fashion to carry organelles and other cargo from one part of the cell to another. Every step of the motor involves the hydrolytic conversion of chemical energy from adenosinetriphosphate into mechanical work. The reaction cycle is completed with the release of the hydrolysis product, adenosinediphosphate (ADP). Each of the motor's hands is about 5 nm long.

Medindo a força

- ▶ Área azul representa o trabalho realizado sobre a máquina no processo: estendido → dobrado

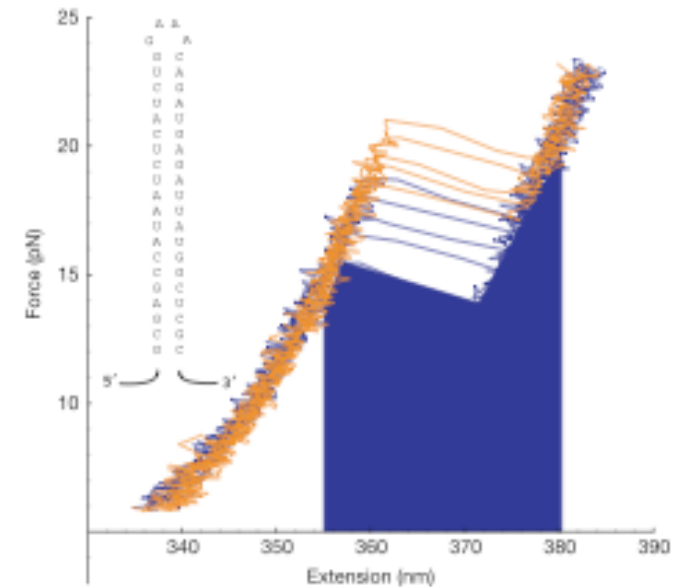


Figure 1 | Force–extension curves. The stochasticity of the unfolding and refolding process is characterized by a distribution of unfolding or refolding work trajectories. Five unfolding (orange) and refolding (blue) force–extension curves for the RNA hairpin are shown (loading rate of 7.5 pN s^{-1}). The blue area under the curve represents the work returned to the machine as the molecule switches from the unfolded to the folded state. The RNA sequence is shown as an inset.

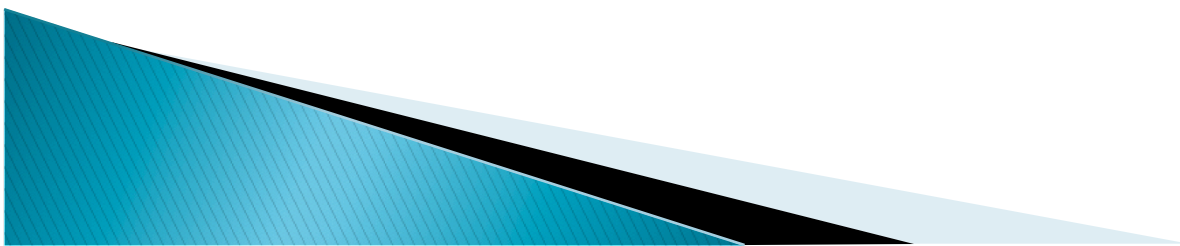
Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies

D. Collin^{1*}, F. Ritort^{2*}, C. Jarzynski³, S. B. Smith⁴, I. Tinoco Jr⁵ & C. Bustamante^{1,6}

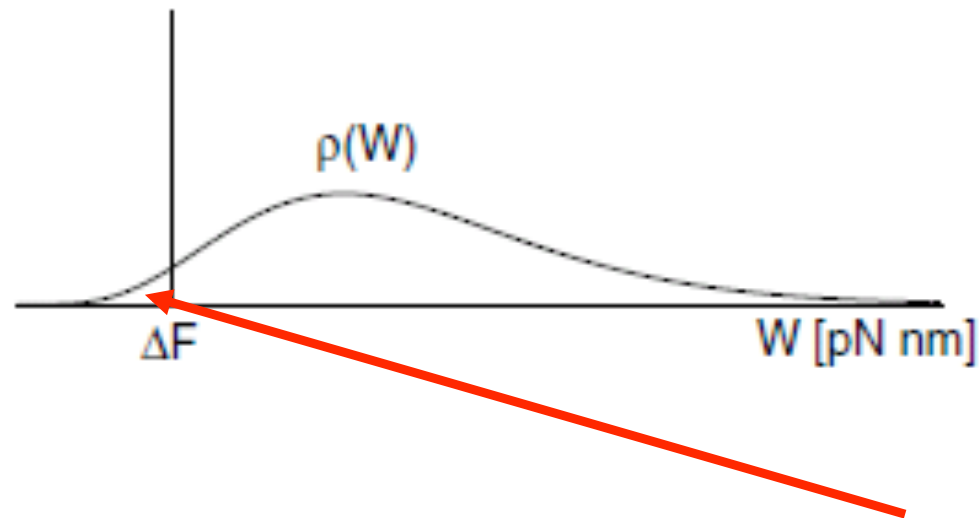
Vol 437/8 September 2005 | doi:10.1038/nature04061

Derivando o trabalho microscópico

- ▶ Trabalho é obtido por integração dos valores medidos da força
- ▶ Valores do trabalho podem então ser usados para obtermos ΔF via CFT ou JE



Valores do trabalho medidos



W segue distribuição de probabilidades e pode “violiar” a segunda Lei da Termodinâmica

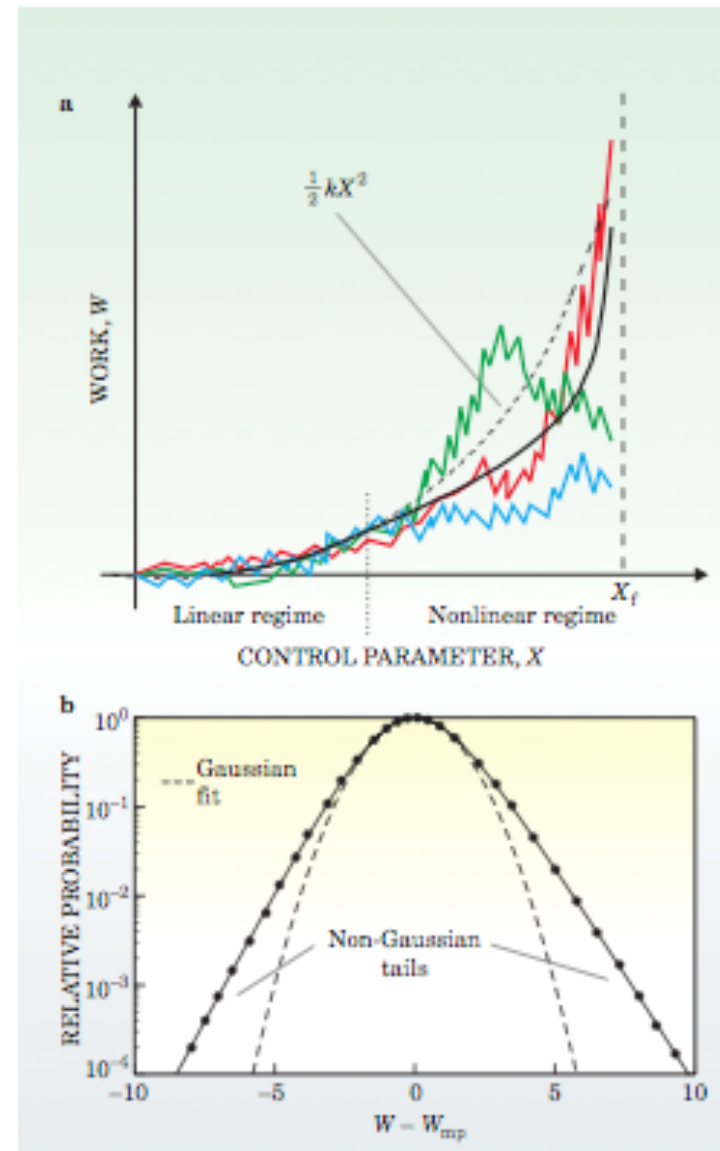
C. Jarzynski

Eur. Phys. J. B 64, 331–340 (2008)

Simulações não-lineares

Carlos Bustamante, Jan Liphardt, and Felix Ritort

July 2005 Physics Today 43



Teste para caso de W não-gaussiano

Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies

D. Collin^{1*}, F. Ritort^{2*}, C. Jarzynski³, S. B. Smith¹, L. Tinoco Jr³ & C. Bustamante^{1,4}

Vol 437/8 September 2005 | doi:10.1038/nature04061

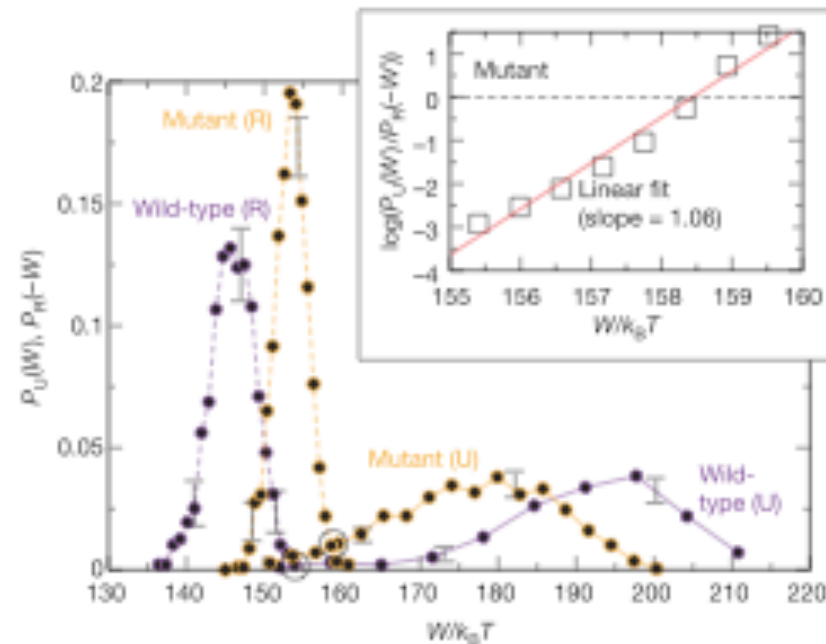


Figure 3 | Free-energy recovery and test of the CFT for non-gaussian work distributions. Experiments were carried out on the wild-type and mutant S15 three-helix junction without Mg^{2+} . Unfolding (continuous lines) and refolding (dashed lines) work distributions. Statistics: 900 pulls and two molecules (wild type, purple); 1,200 pulls and five molecules (mutant type, orange). Crossings between distributions are indicated by black circles. Work histograms were found to be reproducible among different molecules (error bars indicating the range of variability). Inset, test of the CFT for the mutant. Data have been linearly interpolated between contiguous bins of the unfolding and refolding work distributions.

ΔF via CFT

Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies

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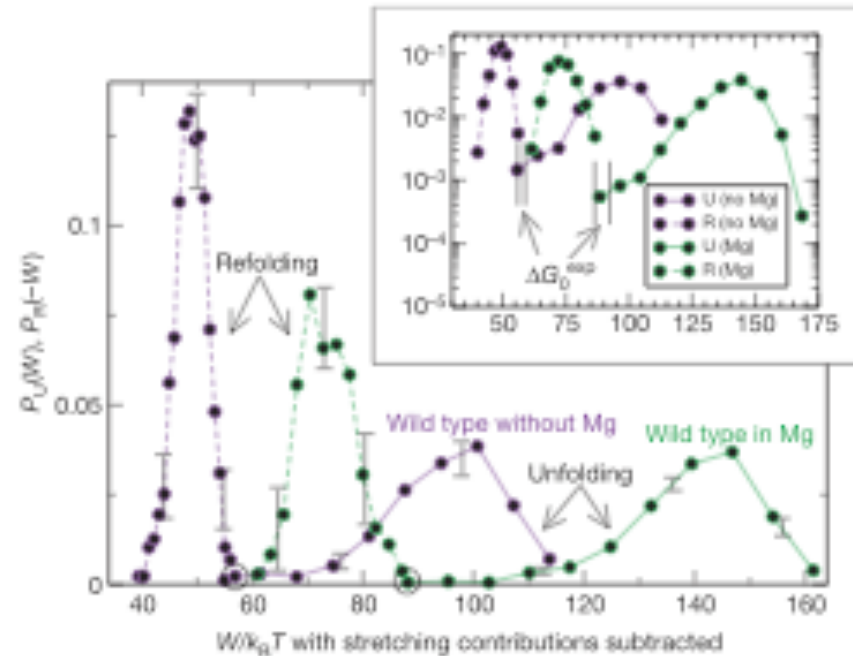
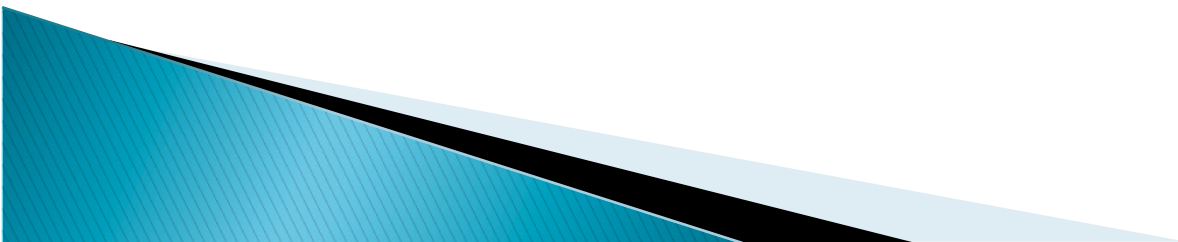


Figure 4 | Use of CFT to extract the stabilizing contribution of Mg^{2+} to the free energy of the 515 three-helix junction (wild type). Unfolding (continuous lines) and refolding (dashed lines) work distributions. Green curves, 450 pulls and two molecules in Mg^{2+} ; purple curves, 900 pulls and two molecules without Mg^{2+} . Crossings between distributions are indicated by black circles. Work histograms are reproducible between the molecules (error bars indicating the range of variability). Inset, the same histograms in logarithmic scale (axes labels as for the main panel) showing (vertical black bars) the regions of work values where unfolding and refolding distributions are expected to cross each other by Bennett's acceptance ratio method (Supplementary Information).

Teoremas de Flutuação

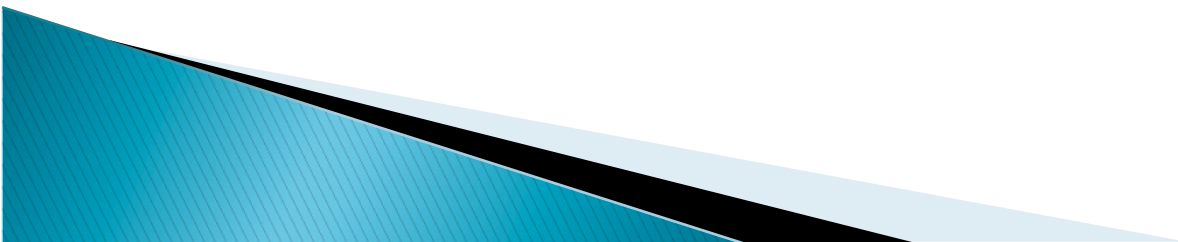
- ▶ Crooks Fluctuation Theorem \rightarrow CFT
- ▶ CFT conecta as probabilidades de trajetórias diretas (estado inicial de Eq. A temperatura T) e suas “reversas” no espaço de fases de sistemas isolados ou em contato com termostato (T)



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$$\frac{P_F[\gamma^F]}{P_R[\gamma^R]} = e^{\beta(W - \Delta F)}.$$

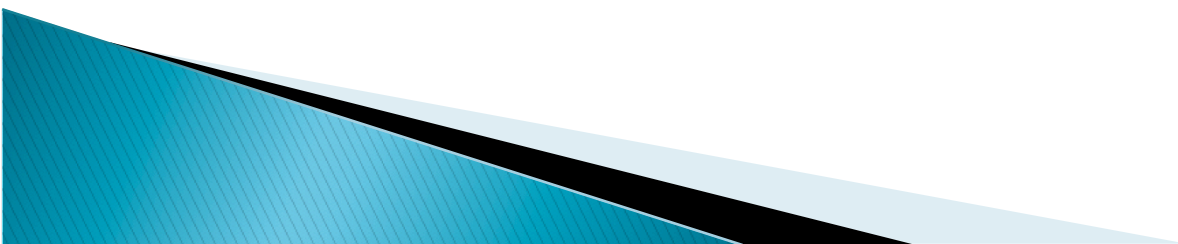


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- ▶ Jarzynski Equality → JE
- ▶ Obtida do CFT fazendo uma integração direta



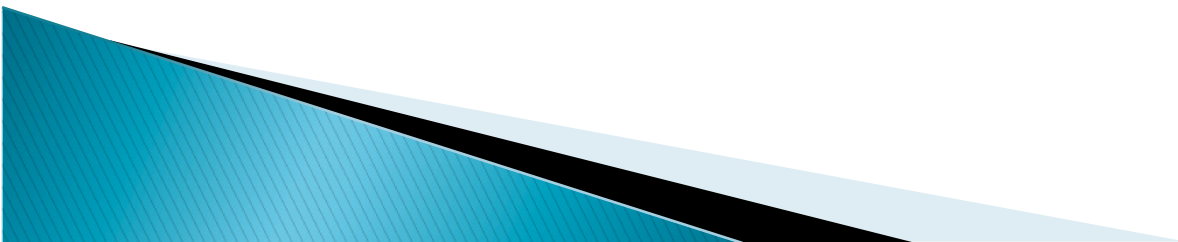
Teoremas de Flutuação

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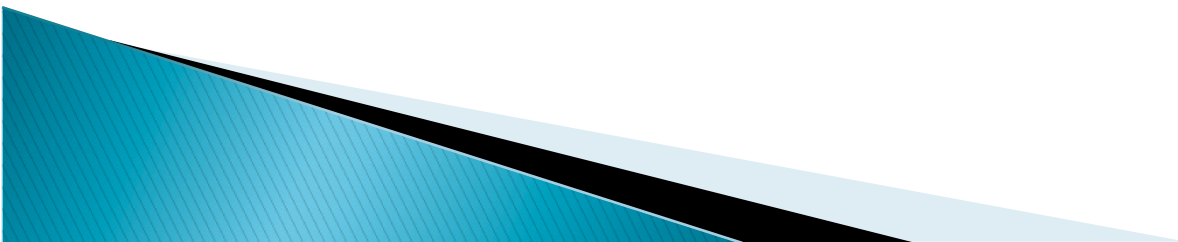
$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}.$$



Trabalho mais usual de força de vínculo

- ▶ Neste caso escrevemos

$$\bar{W} = \int_0^T \dot{\lambda} \frac{\partial H}{\partial \lambda} dt + \int_0^T X \dot{\alpha} dt,$$

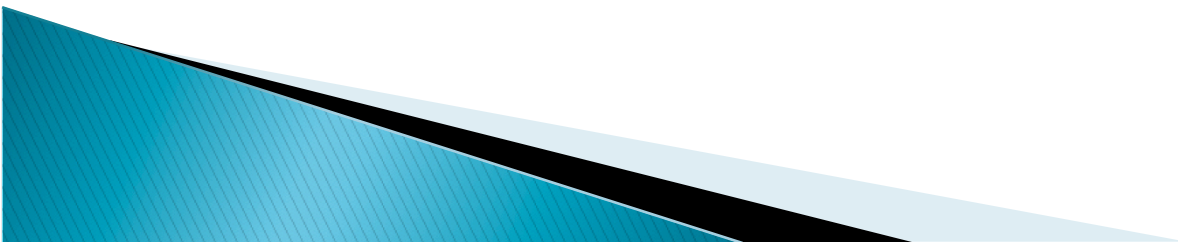


Trabalho mais usual de força de vínculo

- ▶ Neste caso escrevemos

$$\bar{W} = \int_0^T \dot{\lambda} \frac{\partial H}{\partial \lambda} dt + \int_0^T X \dot{\alpha} dt,$$

- ▶ O 1º termo é da forma **F dx** usual
- ▶ Mesma demonstração que o anterior



Demonstrando CFT

► Sistema é reversível temporalmente

Consider a classical system with N degrees of freedom, described by coordinates $\mathbf{q} = (q_1, \dots, q_N)$ and conjugate momenta $\mathbf{p} = (p_1, \dots, p_N)$, and let $z = (\mathbf{q}, \mathbf{p})$ denote a point in its phase space. We will be interested in the evolution of this system, in the presence of an externally controlled, time-dependent force X_t . In this section we model this evolution using Hamilton's equations, assuming a time-dependent Hamiltonian of the form

$$H(z; X_t) = H_0(z) - X_t \alpha(z). \quad (3)$$

Here α is the coordinate conjugate to the external force X , and the 'bare' Hamiltonian H_0 denotes the energy of the system in the absence of this force. For simplicity, we further assume that H is time-reversal-invariant for any fixed value of the external force, that is,

$$H(z^*; X) = H(z; X), \quad (4)$$

where the asterisk denotes a reversal of momenta, $\mathbf{p} \rightarrow -\mathbf{p}$.

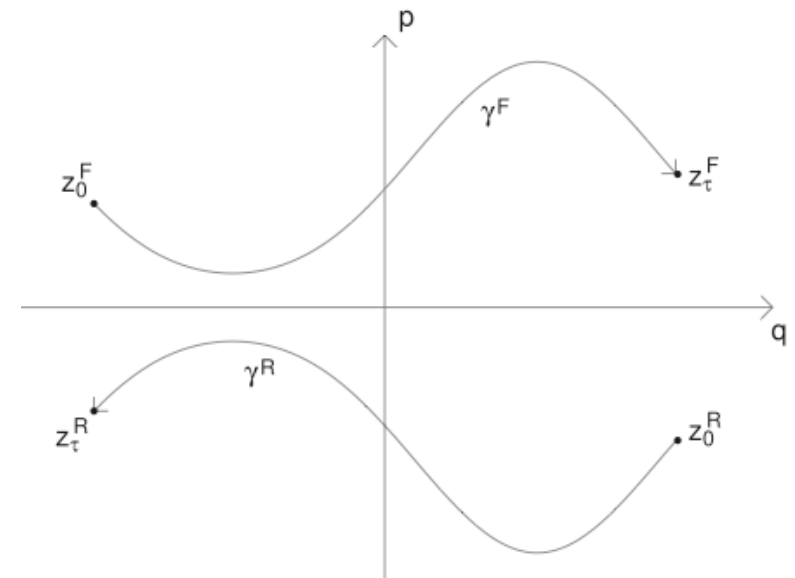


Figure 1. Schematic depiction of a forward trajectory γ^F and its conjugate twin γ^R . The two are related by a reversal of momenta and the direction of time, i.e. $z_t^R = z_{\tau-t}^F$ for $0 \leq t \leq \tau$.

CFT

- ▶ Estados iniciais de equilíbrio direto/reverso

$$p_A^{\text{eq}}(z_0^{\text{F}}) = \frac{1}{Z(A)} \exp[-\beta H(z_0^{\text{F}}; A)] \quad \Bigg| \quad p_B^{\text{eq}}(z_0^{\text{R}}) = \frac{1}{Z(B)} \exp[-\beta H(z_0^{\text{R}}; B)]$$

CFT

- ▶ Estados iniciais de equilíbrio direto/reverso

$$p_A^{\text{eq}}(z_0^{\text{F}}) = \frac{1}{Z(A)} \exp[-\beta H(z_0^{\text{F}}; A)] \quad \Bigg| \quad p_B^{\text{eq}}(z_0^{\text{R}}) = \frac{1}{Z(B)} \exp[-\beta H(z_0^{\text{R}}; B)]$$

- ▶ Trabalho externo

$$W \equiv \int_0^\tau \dot{X} \frac{\partial H}{\partial X} dt = - \int_0^\tau \dot{X} \alpha dt = H(z_\tau; X_\tau) - H(z_0; X_0)$$

CFT

- ▶ Estados iniciais de equilíbrio direto/reverso

$$p_A^{\text{eq}}(z_0^{\text{F}}) = \frac{1}{Z(A)} \exp[-\beta H(z_0^{\text{F}}; A)] \quad \Bigg| \quad p_B^{\text{eq}}(z_0^{\text{R}}) = \frac{1}{Z(B)} \exp[-\beta H(z_0^{\text{R}}; B)]$$

- ▶ Trabalho externo

$$W \equiv \int_0^\tau \dot{X} \frac{\partial H}{\partial X} dt = - \int_0^\tau \dot{X} \alpha dt = H(z_\tau; X_\tau) - H(z_0; X_0)$$

- ▶ “Ponto de fases” $z = (\mathbf{q}, \mathbf{p}) \quad \gamma^{\text{F}} = \{z_t^{\text{F}}\}$

CFT

- ▶ Criamos um protocolo para o trabalho externo feito sobre o sistema X_t
- ▶ “Força generalizada”

$$X_0^F = A \text{ to } X_\tau^F = B$$

$$X_t^R = X_{\tau-t}^F$$

- ▶ “Ponto de fases”

$$z_t^R = z_{\tau-t}^{F*} \text{ for } 0 \leq t \leq \tau$$

$$H(z^*; X) = H(z; X),$$

where the asterisk denotes a reversal of momenta, $\mathbf{p} \rightarrow -\mathbf{p}$

Medidas nos espaços de trajetórias

- ▶ Medida de probabilidade para cada trajetória é definida pelo ensemble de pontos no espaço de fases

$$d\gamma^F = dz_0^F = d^N q_0 d^N p_0$$

- ▶ O mesmo para as trajetórias reversas

$$d\gamma^R = dz_0^R$$

Probabilidades das trajetórias

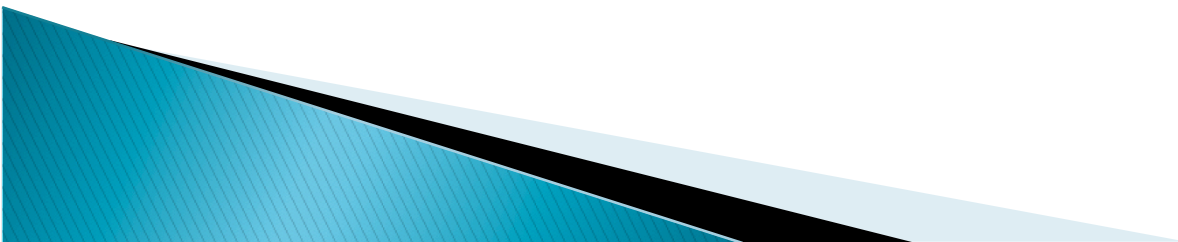
- ▶ Portanto:

$$P_F[\gamma^F] = p_A^{\text{eq}}(z_0^F) = \frac{1}{Z(A)} \exp[-\beta H(z_0^F; A)]$$

$$P_R[\gamma^R] = p_B^{\text{eq}}(z_0^R) = \frac{1}{Z(B)} \exp[-\beta H(z_0^R; B)]$$

- ▶ Onde

$$Z(X) = \int dz e^{-\beta H(z; X)}$$



Probabilidades das trajetórias

▶ Portanto:

$$P_F[\gamma^F] = p_A^{\text{eq}}(z_0^F) = \frac{1}{Z(A)} \exp[-\beta H(z_0^F; A)]$$

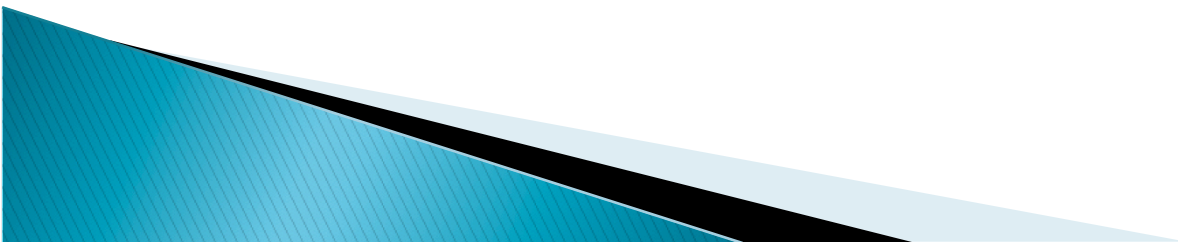
$$P_R[\gamma^R] = p_B^{\text{eq}}(z_0^R) = \frac{1}{Z(B)} \exp[-\beta H(z_0^R; B)]$$

▶ Onde

$$Z(X) = \int dz e^{-\beta H(z; X)}$$

▶ Assim:

$$\frac{P_F[\gamma^F]}{P_R[\gamma^R]} = e^{-\beta \Delta F} e^{\beta [H(z_0^R; B) - H(z_0^F; A)]}$$



Probabilidades das trajetórias

▶ Portanto:

$$P_F[\gamma^F] = p_A^{\text{eq}}(z_0^F) = \frac{1}{Z(A)} \exp[-\beta H(z_0^F; A)]$$

$$P_R[\gamma^R] = p_B^{\text{eq}}(z_0^R) = \frac{1}{Z(B)} \exp[-\beta H(z_0^R; B)]$$

▶ Onde

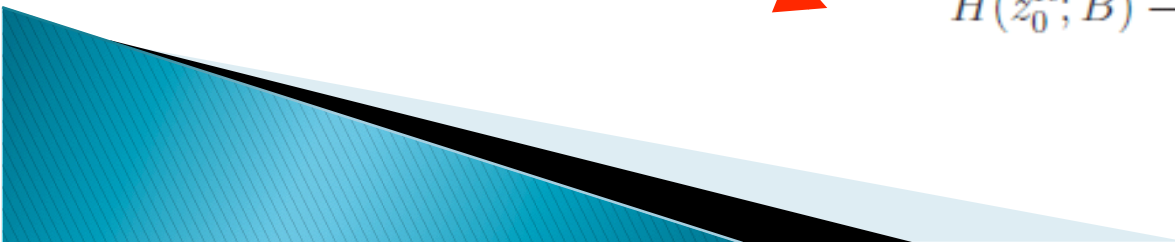
$$Z(X) = \int dz e^{-\beta H(z; X)}$$

▶ Assim:

$$\frac{P_F[\gamma^F]}{P_R[\gamma^R]} = e^{-\beta \Delta F} e^{\beta [H(z_0^R; B) - H(z_0^F; A)]}$$



$$\begin{aligned} H(z_0^R; B) - H(z_0^F; A) &= H(z_\tau^{F*}; B) - H(z_0^F; A) \\ &= H(z_\tau^F; B) - H(z_0^F; A) \\ &= W, \end{aligned}$$



E finalmente...

- ▶ CFT

$$\frac{P_F[\gamma^F]}{P_R[\gamma^R]} = e^{\beta(W - \Delta F)}$$

$$\frac{\rho_F(W)}{\rho_R(-W)} = e^{\beta(W - \Delta F)}$$

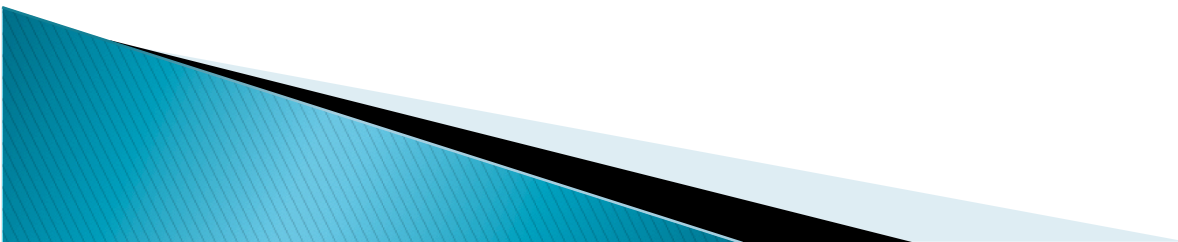
- ▶ Integrando em γ_R ,
temos JE

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}.$$

$$W_d = W - \Delta F$$



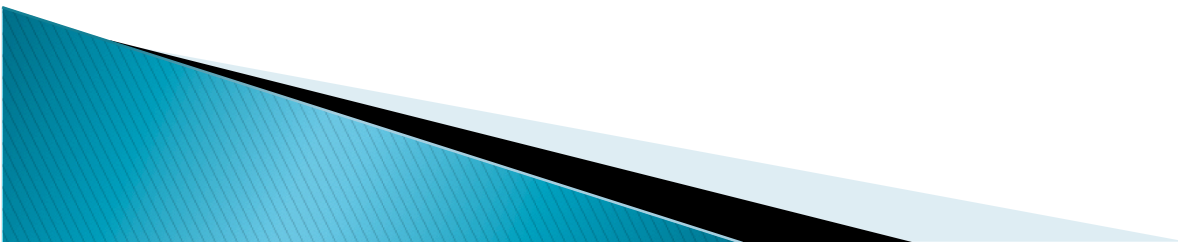
Trabalho dissipativo



Ligação com 2^a Lei da termodinâmica

- ▶ Processo quase estático a temperatura T :

$$dF = dW \rightarrow W = \Delta F$$



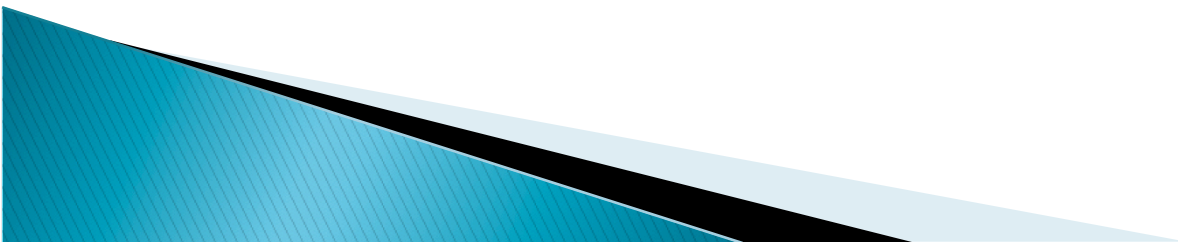
Ligação com 2ª Lei da termodinâmica

- ▶ Processo quase estático a temperatura T :

$$dF = dW \rightarrow W = \Delta F$$

- ▶ Processo irreversível \rightarrow trabalho dissipado:

$$\langle W \rangle > \Delta F$$



Ligação com 2^a Lei da termodinâmica

- ▶ Processo quase estático a temperatura T :

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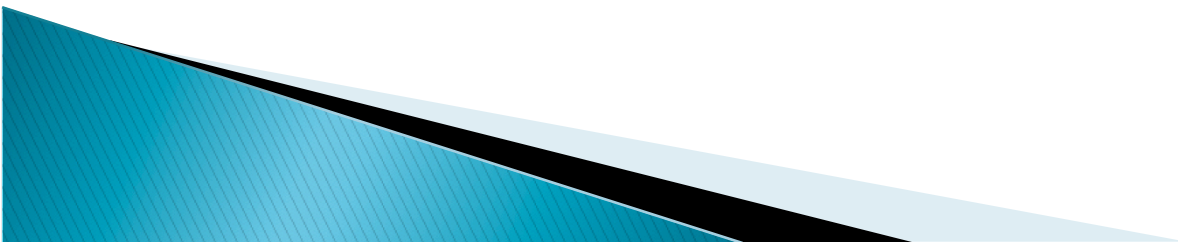
- ▶ Processo irreversível \rightarrow trabalho dissipado:

$$\langle W \rangle > \Delta F$$

- ▶ Igualdade de Jarzynski

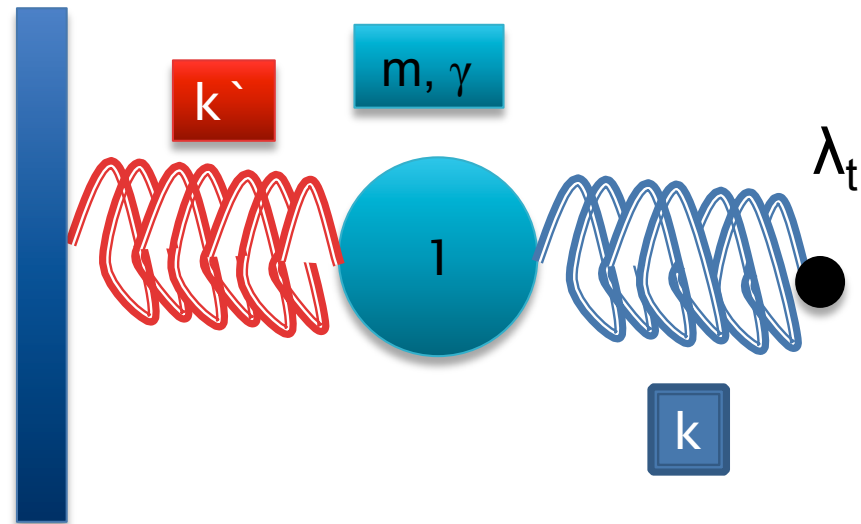
$$\Delta F = \langle W \rangle - \frac{1}{2} \beta \langle (W^2 - \langle W \rangle^2) \rangle + \dots$$

- ▶ Equivale a forma acima da 2^a Lei



Modelo mecânico estocástico

- ▶ Partícula submetida a temperatura T , ligada à origem e a outra mola puxada seguindo um protocolo temporal λ_t
- ▶ Trabalho externo é realizado pela força de vínculo



Termodinâmica do modelo

- ▶ Energia-livre F e função de partição Z podem ser calculadas diretamente

A few thermodynamic properties for our system can be obtained directly from the equilibrium partition function $Z = \int_{-\infty}^{\infty} \frac{dp dx}{h} e^{-\beta \mathcal{H}(x,p)}$, where $\beta \mathcal{H}(x,p) = \frac{1}{2T} \left(\frac{p^2}{m} + kx^2 + k'(x-L)^2 \right)$. We find $F = \left(\frac{kk'}{k+k'} \right) \frac{L^2}{2} - T \ln \left(\frac{2\pi T}{h} \sqrt{\frac{m}{k+k'}} \right)$, $S = \ln \left(\frac{2\pi T}{h} \sqrt{\frac{m}{k+k'}} \right) + 1$, and $E = T + \left(\frac{kk'}{k+k'} \right) \frac{L^2}{2}$, where T corresponds to the kinetic and elastic energy contributions around equilibrium (via equipartition theorem $2 \times T/2$). The second term on the RHS is the rest-energy of two springs, k and k' , of zero length, connected serially with total extension L .



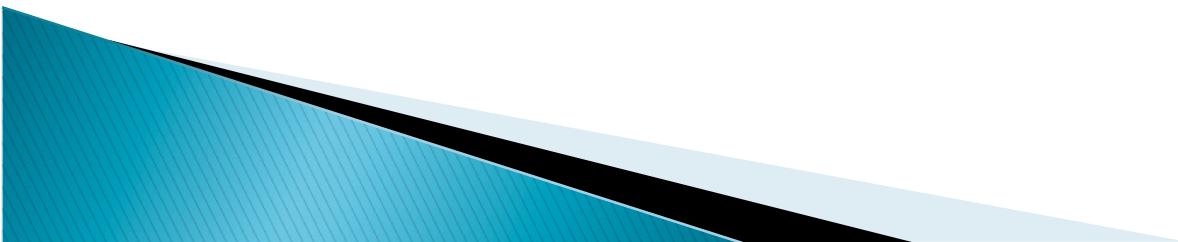
Sistema estocástico & protocolo

- ▶ Equação de Langevin com ruído branco

$$\begin{aligned}m\dot{v} &= -\gamma v - kx - k'(x - L) + \eta, \\ \dot{x} &= v, \\ L &= L_0 \left(1 - e^{-t/\lambda}\right).\end{aligned}$$

- ▶ Protocolo $L(t)$
- ▶ Ruído transformado por Laplace

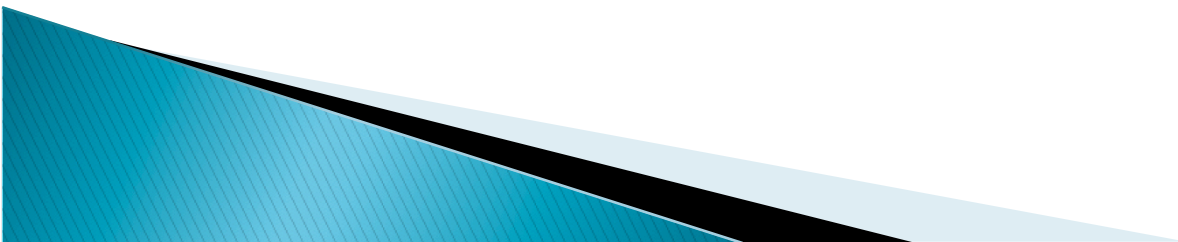
$$\langle \tilde{\eta}(z_1) \tilde{\eta}(z_2) \rangle = \frac{2\gamma T}{z_1 + z_2}.$$



Função Geratriz para Trabalho (FGT)

- ▶ Expressão para o trabalho

$$\begin{aligned}W_{\tau} &= \int_0^{\tau} F_{\text{ext}} dL = -k' \int_0^{\tau} dt \frac{dL}{dt} (x(t) - L(t)) \\ &= \Delta U - k' \int_0^{\tau} dt \frac{dL(t)}{dt} x(t),\end{aligned}$$



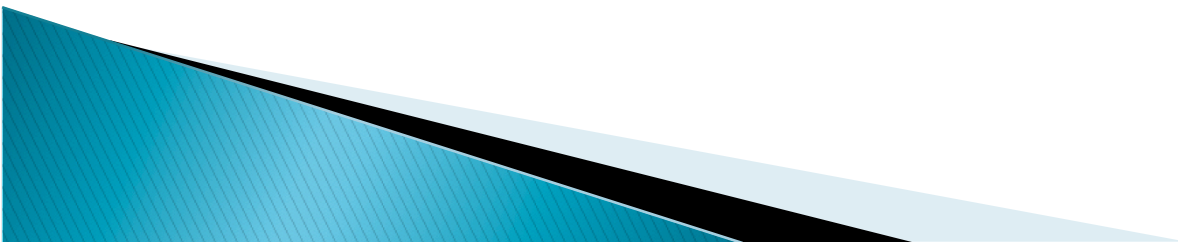
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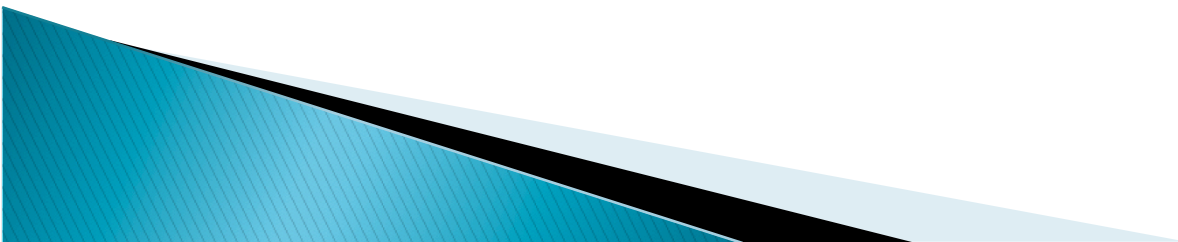
- ▶ Definindo a FGT

$$F(u) \equiv \exp \{-i u W_{\tau}\} = \sum_{n=0}^{\infty} \frac{(-i u)^n}{n!} W_{\tau}^n,$$



Tomando tempos infinitos

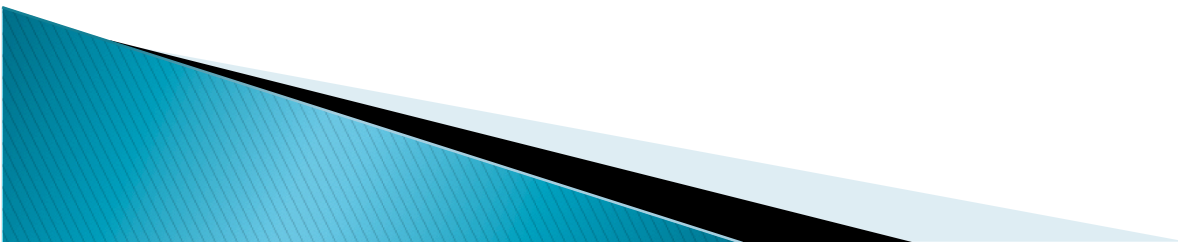
- ▶ Faremos o limite $t \rightarrow \infty$
- ▶ Usando o método de funções de Green podemos obter as contribuições a tempo infinito para o trabalho



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$$\begin{aligned}\mathcal{F}(u) &= \langle \overline{F(u)} \rangle \\ &= \sum_{n=0}^{\infty} \frac{(-iu)^n}{n!} \langle (\Delta U + \Delta W_p + \Delta W_h + \Delta W_\eta)^n \rangle, \\ &= e^{-iu(\Delta U + \Delta W_p)} \times \\ &\times \sum_{k=0}^{\infty} \frac{(-iu)^k}{k!} \overline{(\Delta W_h)^k} \sum_{l=0}^{\infty} \frac{(-iu)^l}{l!} \langle (\Delta W_\eta)^l \rangle,\end{aligned}$$



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$$\begin{aligned} \Delta W_h^\infty &= \frac{k' L (v_0 + x_0 [\theta + \frac{1}{\lambda}])}{\lambda (\frac{1}{\lambda^2} + \frac{\theta}{\lambda} + \omega^2)}, \\ \Delta W_p^\infty &= -\frac{1}{2m} \frac{L^2 k'^2}{(\frac{1}{\lambda^2} + \frac{\theta}{\lambda} + \omega^2)}. \end{aligned}$$

$$\begin{aligned} \langle \Delta W_\eta^{2n+1} \rangle &= 0, \\ \langle \Delta W_\eta^{2n} \rangle &= \left(\frac{k^2 L_0^2 \theta \lambda T}{2m\lambda^2 (\frac{1}{\lambda^2} + \frac{\theta}{\lambda} + \omega^2)^2} \right)^n \frac{(2n)!}{n!}, \\ \langle \Delta W_h^{2n+1} \rangle &= 0, \\ \langle \Delta W_h^{2n} \rangle &= \left(\frac{k^2 L_0^2 T \{ [\theta + \frac{1}{\lambda}]^2 + \omega^2 \}}{2m\lambda^2 \omega^2 (\frac{1}{\lambda^2} + \frac{\theta}{\lambda} + \omega^2)^2} \right)^n \frac{(2n)!}{n!}. \end{aligned}$$

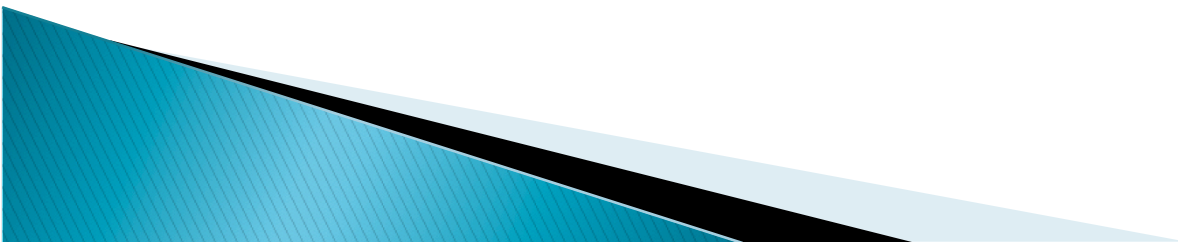
where $\theta = \gamma/m$, and $\omega^2 = (k + k')/m$.

FGT – expressão

$$\mathcal{F}(u) = \langle F_W(u) \rangle = \exp \{ -i u \mathcal{R}_1 - u^2 \mathcal{R}_2 \}$$

where

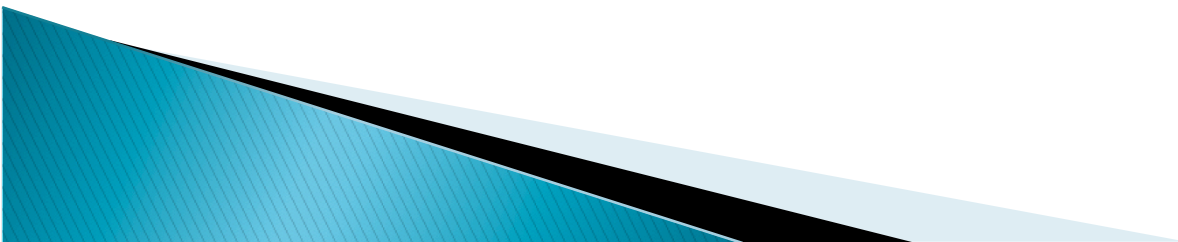
$$\mathcal{R}_1 = \frac{k' L_0^2}{2} - \frac{k'^2 L_0^2}{2m \left(\omega^2 + \frac{1}{\lambda^2} + \frac{\theta}{\lambda} \right)},$$
$$\mathcal{R}_2 = \frac{k'^2 L_0^2 \left\{ \frac{1}{\lambda^2} + \frac{\theta}{\lambda} \right\}}{2m\omega^2 \left(\frac{1}{\lambda^2} + \frac{\theta}{\lambda} + \omega^2 \right)} T.$$



JE via FGT

- ▶ Para isso devemos tomar o limite $u \rightarrow -i/T$

$$\begin{aligned}\mathcal{F}(u) &= \exp\left(-\frac{(\Delta U)}{T} + \frac{1}{2m\omega^2 T} \frac{L_0^2 k'^2 \omega^2}{\left(\frac{1}{\lambda^2} + \frac{\theta}{\lambda} + \omega^2\right)}\right. \\ &\quad \left.+ \frac{k'^2 L_0^2 \left\{\frac{1}{\lambda^2} + \frac{\theta}{\lambda}\right\}}{2m\omega^2 T \left(\frac{1}{\lambda^2} + \frac{\theta}{\lambda} + \omega^2\right)}\right) \\ &= \exp\left(-\frac{k' L_0^2}{2T} + \frac{k'^2 L_0^2}{2(k+k')T}\right) = \exp\left(-\frac{\Delta F}{T}\right).\end{aligned}$$



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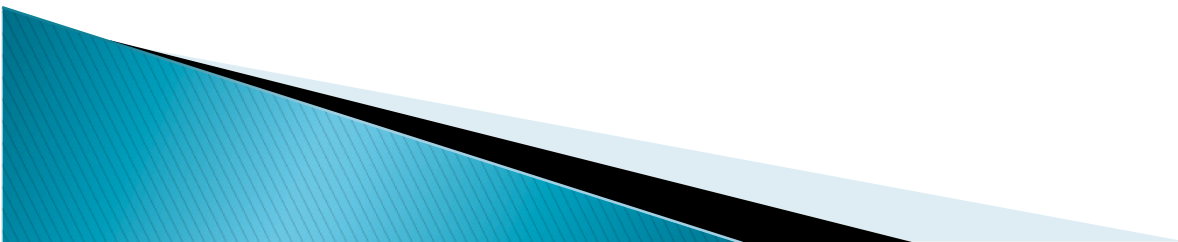
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Verificando a JE



Distribuição de probabilidades para o trabalho

$$p(W) = \int_{-\infty}^{\infty} \frac{du}{2\pi} \mathcal{F}(u) e^{iuW}.$$

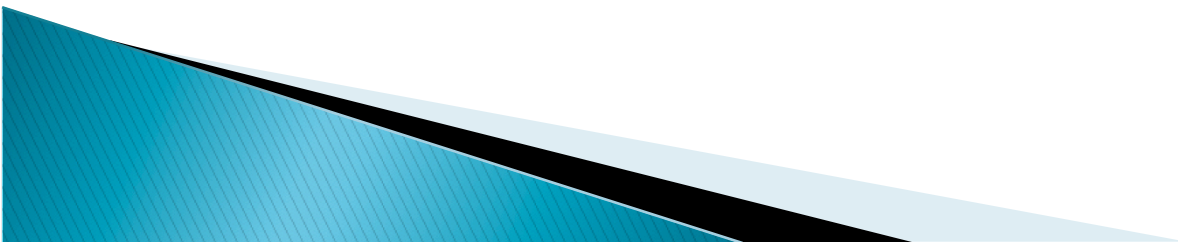


Distribuição de probabilidades para o trabalho

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$$p(W) = \sqrt{\frac{\pi}{\mathcal{R}_2}} \exp \left\{ -\frac{(W - \mathcal{R}_1)^2}{4 \mathcal{R}_2} \right\}.$$

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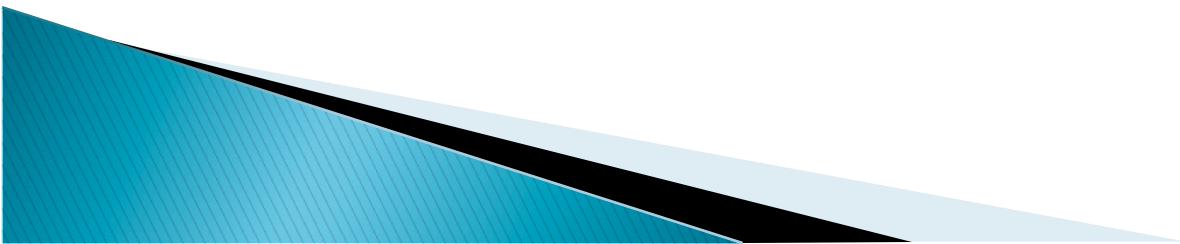
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$$\frac{p(W)}{p(-W)} = \exp \left\{ \frac{W}{\mathcal{R}_2} \left(\frac{k'L_0^2}{2} - \frac{k'^2 L_0^2}{2m \left(\omega^2 + \frac{1}{\lambda^2} + \frac{\theta}{\lambda} \right)} \right) \right\}.$$

Permite violação da 2ª Lei se $k'L_0 \ll T$

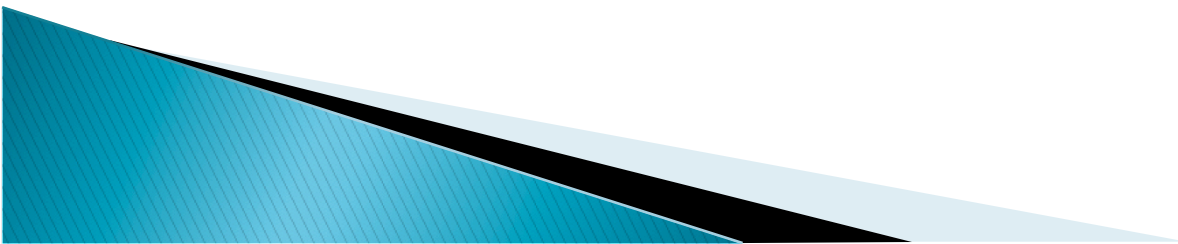
Conclusões

- ▶ Modelo não trivial, apesar de linear



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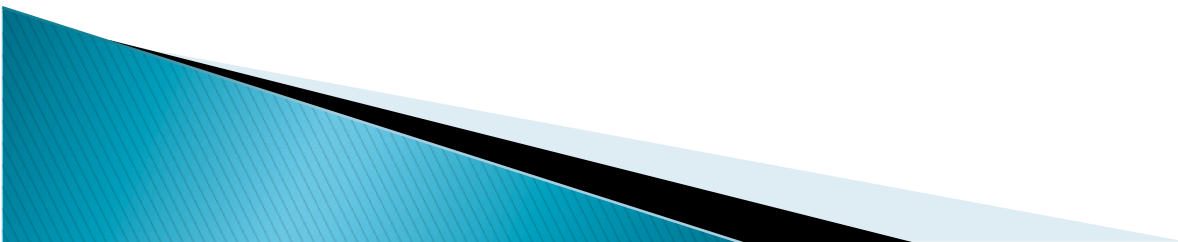
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- ▶ Resultados exatos



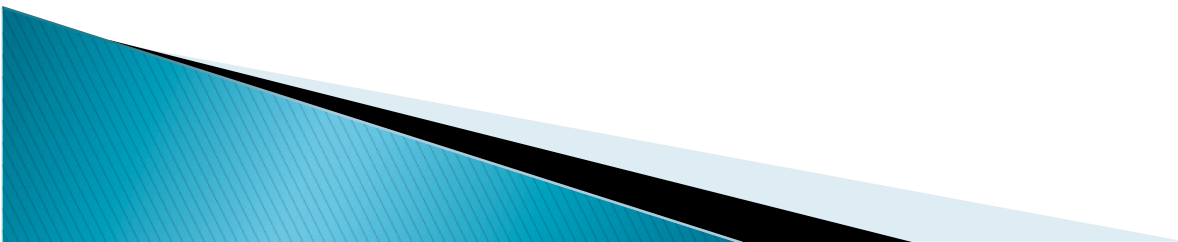
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- ▶ Resultados exatos
- ▶ Estendendo para tempos finitos
- ▶ Modelos não lineares: FGT?



Obrigado!



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