Fluctuation-dissipation relations
&
fluctuation theorems

18.S995 - L11

1.7 Fluctuation-dissipation relation

$$
\begin{aligned}
dx_i &= \frac{\partial H}{\partial p_i} dt \\
dp_i &= -\frac{\partial H}{\partial x_i} dt - \gamma p_i dt + \sqrt{2\mathfrak{D}}\, dB_i(t).
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If the Hamiltonian has the standard form

$$
H = \sum_i \frac{p_i^2}{2m} + U(x_1, \ldots, x_N), \tag{1.133}
$$

corresponding to momentum coordinates $p_i = m\dot{x}_i$, then the overdamped SDE is formally recovered by assuming $dp_i \simeq 0$ in Eq. (1.132b) and dividing by $m\gamma$, yielding

$$
dx_i = -\frac{1}{m\gamma} \frac{\partial U}{\partial x_i}\, dt + \sqrt{\frac{2\mathfrak{D}}{m^2\gamma^2}}\, dB_i(t). \tag{1.134}
$$

We see that the spatial diffusion constant D and the momentum diffusion constant $\mathfrak{D}$ are related by

$$
D = \frac{\mathfrak{D}}{m^2\gamma^2}. \tag{1.135}
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The Fokker-Planck equation (FPE) governing the phase space PDF $f(t, x_1, \ldots, x_N, p_1, \ldots, p_N)$ of the stochastic process (1.132) reads

$$
\partial_t f + \sum_i \left(\frac{\partial H}{\partial p_i} \frac{\partial f}{\partial x_i} - \frac{\partial H}{\partial x_i} \frac{\partial f}{\partial p_i} \right) = \sum_i \frac{\partial}{\partial p_i} \left(\gamma p_i f + \mathfrak{D} \frac{\partial f}{\partial p_i} \right) \tag{1.136}
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The lhs. vanishes if f is a function of the Hamiltonian H. The rhs. vanishes for the particular ansatz

$$f = \frac{1}{Z} \exp\left(-\frac{H}{k_B T} \right). \tag{1.137}$$

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where T is the temperature of the surrounding heat bath. To see this, note that

$$\frac{\partial f}{\partial p_i} = -\frac{1}{k_B T} \frac{\partial H}{\partial p_i} \frac{1}{Z} \exp\left(-\frac{H}{k_B T} \right) = -\frac{1}{k_B T} \frac{p_i}{m} f \tag{1.138}$$

so that the components of the dissipative momentum current,

$$J_i = -\left(\gamma p_i f + \mathcal{D} \frac{\partial f}{\partial p_i} \right) = -\left(\gamma p_i f - \frac{\mathcal{D}}{k_B T} \frac{p_i}{m} f \right) = -\left(\gamma - \frac{\mathcal{D}}{m k_B T} \right) p_i f \tag{1.139}$$

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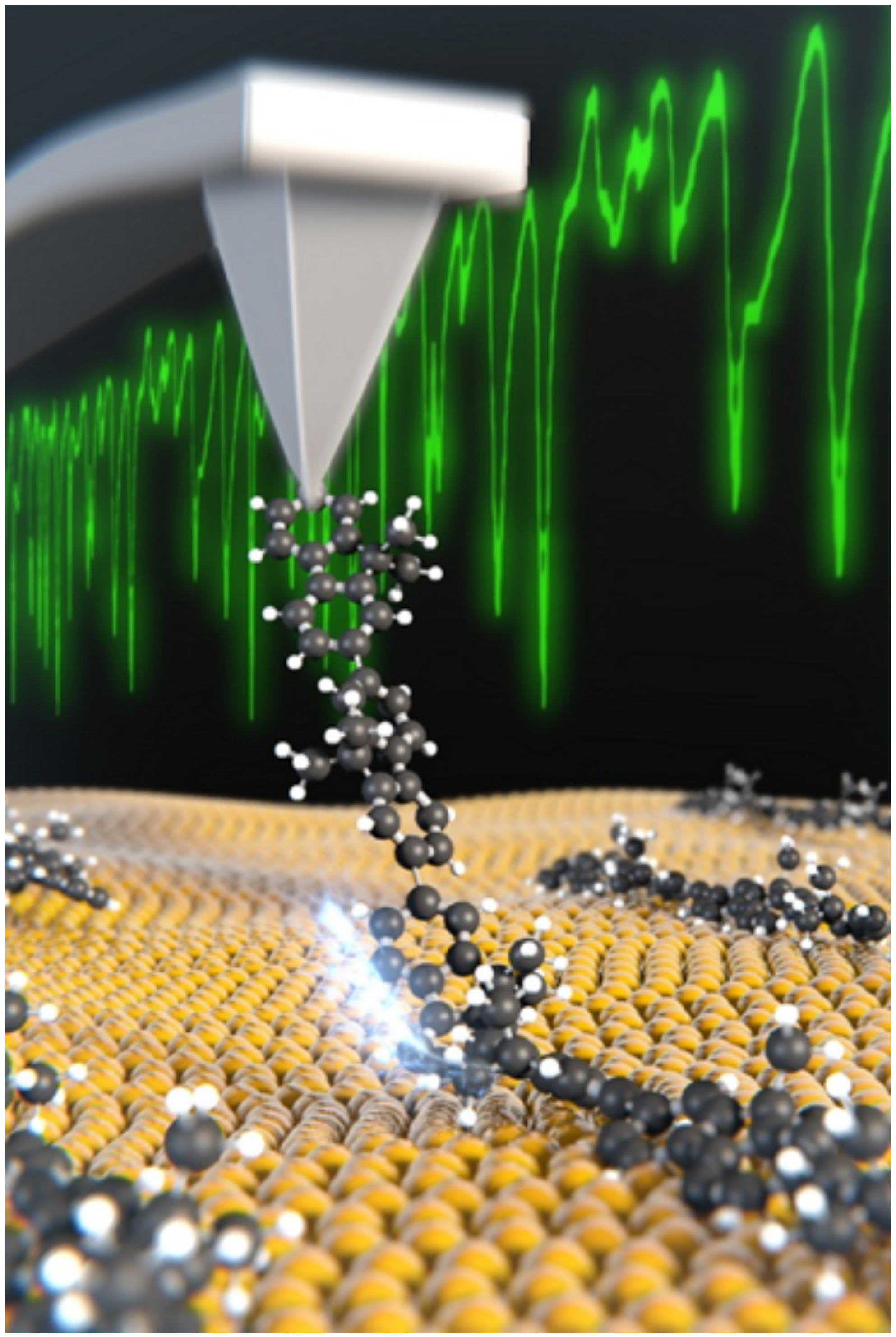
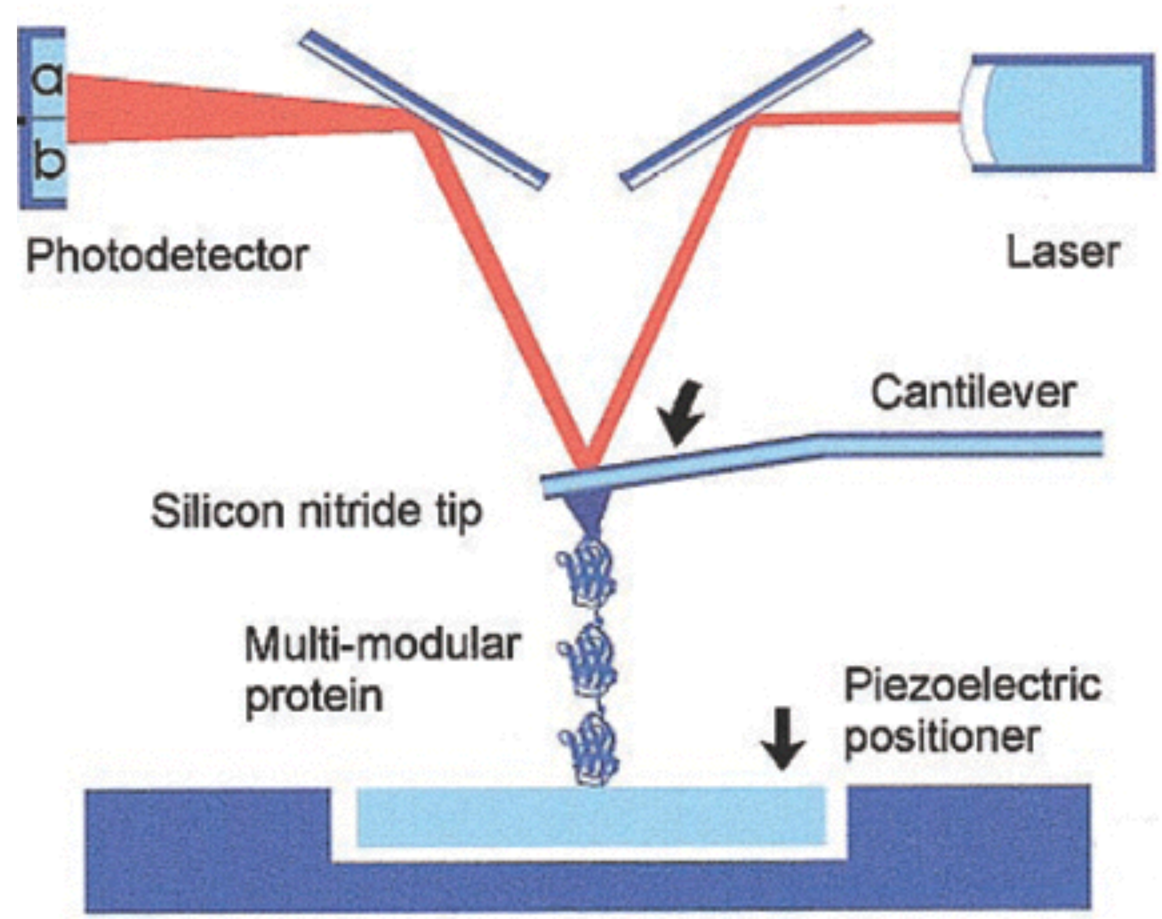
vanishes if

$$\boxed{\mathcal{D} = \gamma m k_B T \qquad \Leftrightarrow \qquad D = \frac{k_B T}{\gamma m}.} \tag{1.140}$$

1.8 Fluctuation theorems

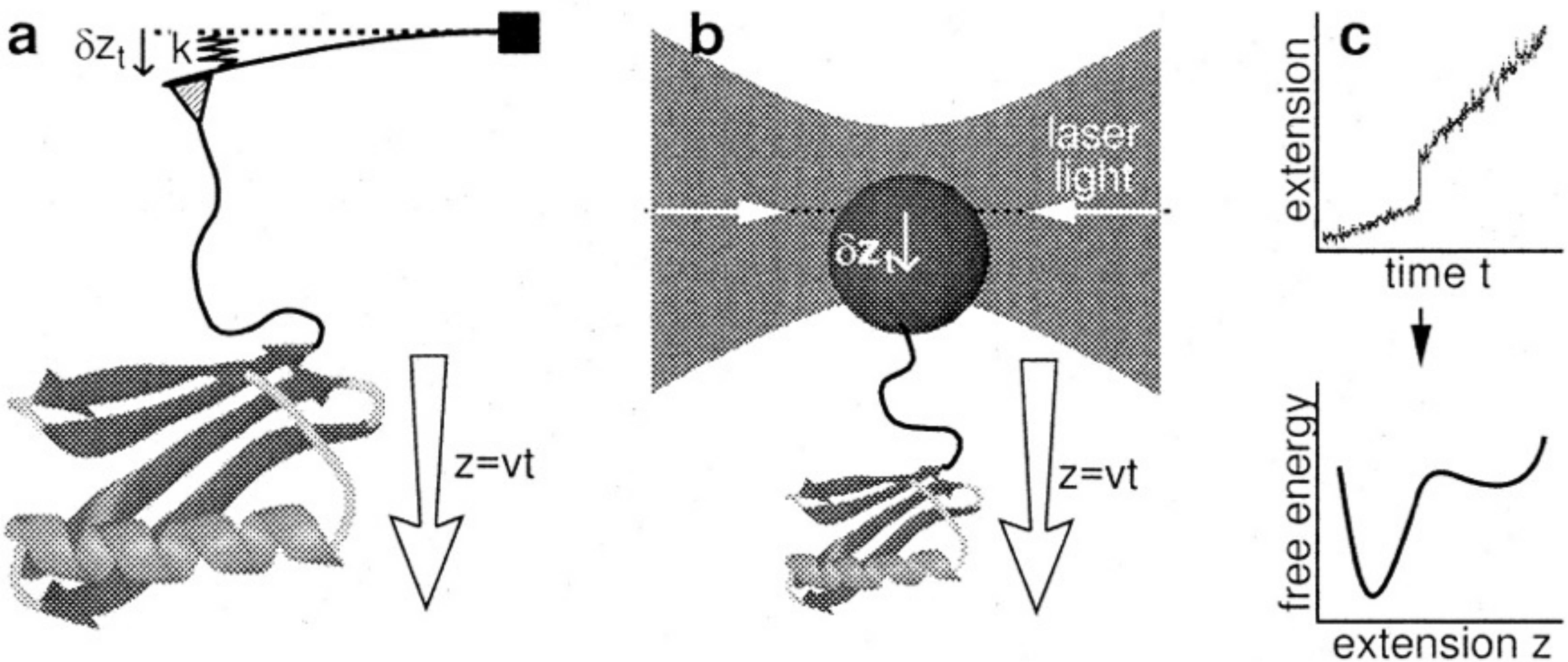


http://www.microscopy-analysis.com



http://hansmalab.physics.ucsb.edu/forcespec.html

Single-molecule force measuring experiments by using AFM (a) and laser tweezers (b).



Hummer G , and Szabo A PNAS 2001;98:3658-3661

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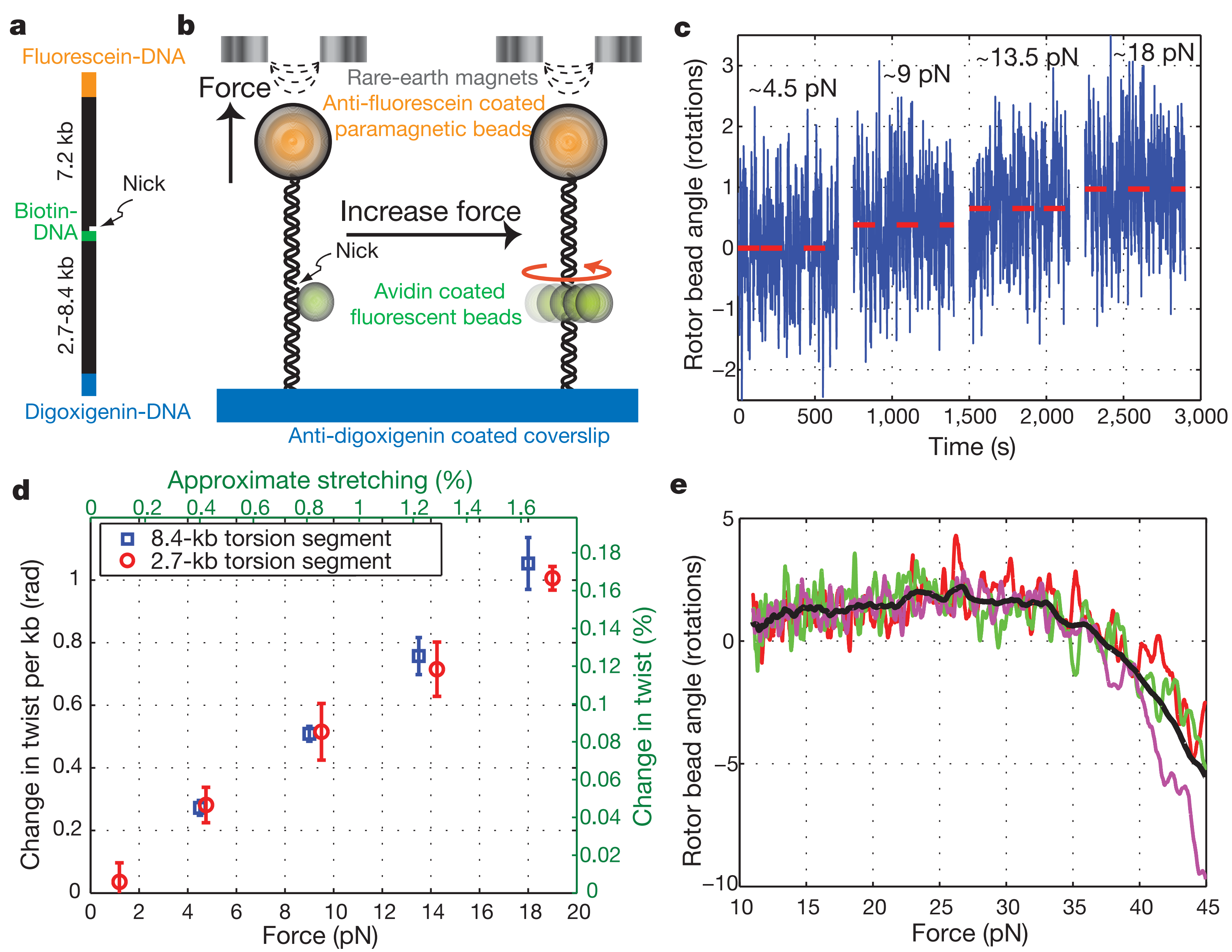
LETTERS

DNA overwinds when stretched

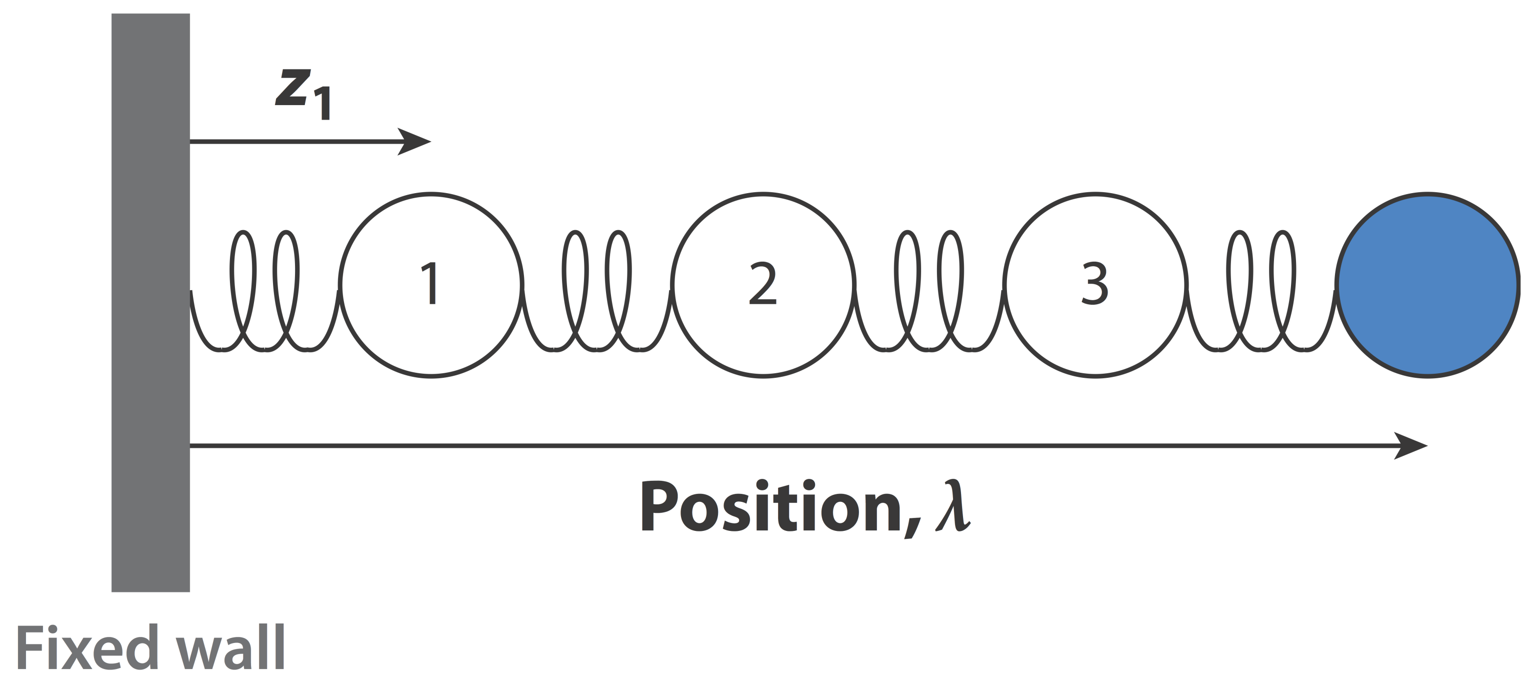
Jeff Gore[1]†, Zev Bryant[2,4]†, Marcelo Nöllmann[2], Mai U. Le[2], Nicholas R. Cozzarelli[2]‡ & Carlos Bustamante[1–4]



1.8 Fluctuation theorems

The total Hamiltonian comprising the system of interest, e.g. a DNA molecule described by coordinates $\boldsymbol{x}(t)$), its environment $\boldsymbol{y}$ and mutual interactions reads

$$H(\boldsymbol{x}, \boldsymbol{y}; \lambda(t)) = H(\boldsymbol{x}; \lambda(t)) + H_{\mathrm{env}}(\boldsymbol{y}) + H_{\mathrm{int}}(\boldsymbol{x}, \boldsymbol{y}) \tag{1.141}$$



$$H(\boldsymbol{x}; \lambda(t)) = \sum_{i=1}^{3} \frac{p_i^2}{2m} + \sum_{k=0}^{2} u(z_{k+1} - z_k) + u(\lambda - z_3)$$

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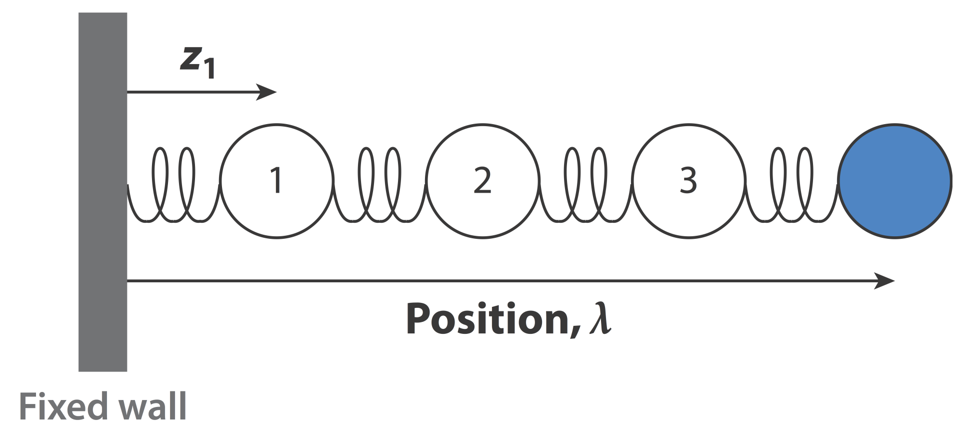

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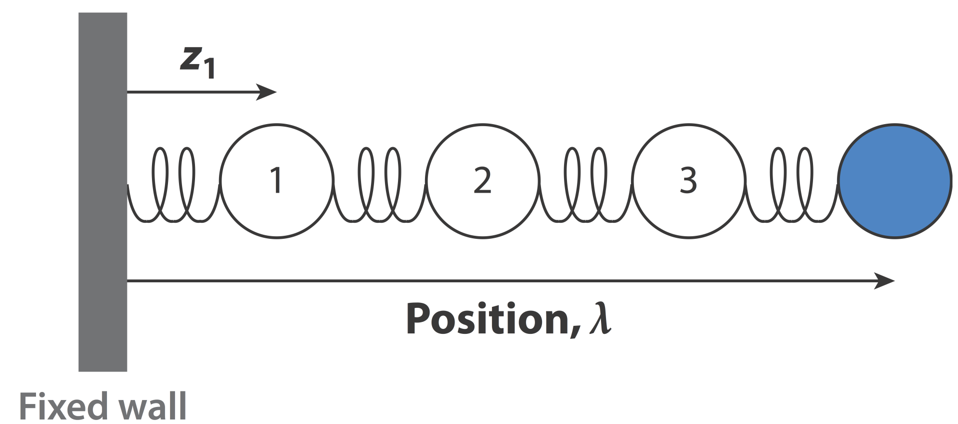
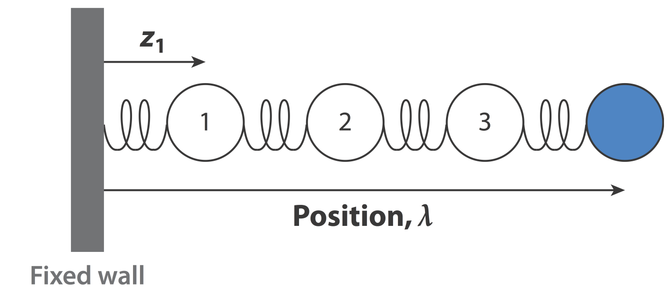


$$\delta W := d\lambda \, \frac{\partial H}{\partial \lambda}(\boldsymbol{x}; \lambda)$$

$$W = \int \delta W = \int_0^\tau dt \, \dot{\lambda}(t) \, \frac{\partial H}{\partial \lambda}(\boldsymbol{x}(t); \lambda(t))$$

1.8 Fluctuation theorems



Repeat process and measure

$$W = \int \delta W = \int_0^\tau dt\ \dot{\lambda}(t)\ \frac{\partial H}{\partial \lambda}(\boldsymbol{x}(t); \lambda(t))$$

we will observe different values of work $\{W_1, W_2, \ldots, \}$

$$\langle G(W) \rangle := \int dW\ \rho(W)\ G(W), \tag{1.145}$$

FTs = exact (in)equalities for certain *G(W)*

Reminder: Canonical free energy

$$\mathcal{H}(\boldsymbol{x}, \boldsymbol{y}; \lambda(t)) = H(\boldsymbol{x}; \lambda(t)) + H_{\mathrm{env}}(\boldsymbol{y}) + H_{\mathrm{int}}(\boldsymbol{x}, \boldsymbol{y})$$

0

(weak coupling)

To simplify the subsequent discussion, let us assume that we are able to decouple the system from the environment[21] at time $t = 0$, and assume that at time $t = 0$ the PDF of the system state is given by a canonical distribution

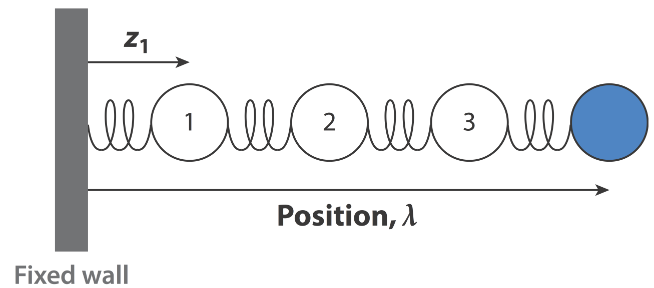
$$f(\boldsymbol{x}_0; \lambda_0, T) = \frac{1}{Z(\lambda_0, T)} \exp\left[-\frac{H(\boldsymbol{x}_0; \lambda_0)}{k_B T}\right], \tag{1.146a}$$

where T is the *initial* equilibrium temperature of system and environment at $t = 0$, and

$$Z(\lambda_0, T) = \int d\boldsymbol{x}_0 \exp\left[-\frac{H(\boldsymbol{x}_0; \lambda_0)}{k_B T}\right] \tag{1.146b}$$

the classical partition function. In this case, the *initial* free energy of the system is given by

$$F_0 = -k_B T \ln Z(\lambda_0, T). \tag{1.147}$$



Moreover, since the dynamics for $t > 0$ is completely Hamiltonian, we have

$$
\begin{aligned}
\frac{dH}{dt} &= \sum_i \left(\frac{\partial H}{\partial p_i} \dot{p}_i + \frac{\partial H}{\partial z_i} \dot{z}_i \right) + \frac{\partial H}{\partial t} \\
&= \sum_i \left[\frac{\partial H}{\partial p_i} \left(- \frac{\partial H}{\partial z_i} \right) + \frac{\partial H}{\partial z_i} \left(\frac{\partial H}{\partial p_i} \right) \right] + \frac{\partial H}{\partial \lambda} \dot{\lambda} \\
&= \frac{\partial H}{\partial \lambda} \dot{\lambda}
\end{aligned}
\tag{1.148}
$$

and, therefore,

$$
W = \int_0^\tau dt \, \dot{\lambda} \, \frac{\partial H}{\partial \lambda} = \int_0^\tau dH = H(\boldsymbol{x}_\tau; \lambda_\tau) - H(\boldsymbol{x}_0; \lambda_0) \tag{1.149}
$$

where $\boldsymbol{x}(\tau) = \boldsymbol{x}_\tau$

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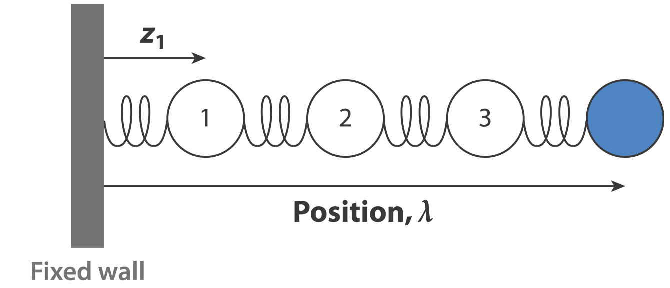
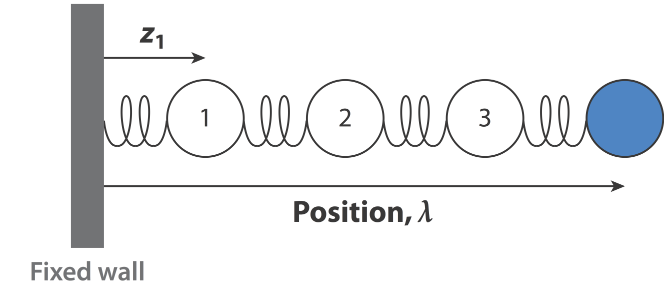


$$\langle G(W) \rangle := \int dW\ \rho(W)\ G(W),$$

$$G(W) = e^{-W/(k_B T)}$$



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$$\langle G(W)\rangle := \int dW\ \rho(W)\ G(W), \qquad\qquad G(W) = e^{-W/(k_BT)}$$

$$\begin{aligned}
\left\langle e^{-W/(k_BT)}\right\rangle &= \int d\boldsymbol{x}_0\ f(\boldsymbol{x}_0;\lambda_0,T)\ e^{-W/(k_BT)} \\
&= \int d\boldsymbol{x}_0\ f(\boldsymbol{x}_0;\lambda_0,T)\ e^{-[H(\boldsymbol{x}_\tau;\lambda_\tau)-H(\boldsymbol{x}_0;\lambda_0)]/(k_BT)} \\
&= \frac{1}{Z(\lambda_0,T)}\int d\boldsymbol{x}_0\ \exp\left[-\frac{H(\boldsymbol{x}_0;\lambda_0)}{k_BT}\right]\ e^{-[H(\boldsymbol{x}_\tau;\lambda_\tau)-H(\boldsymbol{x}_0;\lambda_0)]/(k_BT)} \\
&= \frac{1}{Z(\lambda_0,T)}\int d\boldsymbol{x}_0\ e^{-H(\boldsymbol{x}_\tau;\lambda_\tau)/(k_BT)} \qquad (1.150)
\end{aligned}$$

$$\boxed{\left\langle e^{-W/(k_B T)} \right\rangle \quad = \quad \frac{1}{Z(\lambda_0, T)} \int d\boldsymbol{x}_0 \; e^{-H(\boldsymbol{x}_\tau;\lambda_\tau)/(k_B T)}}$$

Changing the integration variable from $\boldsymbol{x}_0 \mapsto \boldsymbol{x}_\tau$, we can write this as

$$\begin{aligned} \left\langle e^{-W/(k_B T)} \right\rangle &= \frac{1}{Z(\lambda_0, T)} \int d\boldsymbol{x}_\tau \left| \frac{\partial \boldsymbol{x}_\tau}{\partial \boldsymbol{x}_0} \right|^{-1} e^{-H(\boldsymbol{x}_\tau;\lambda_\tau)/(k_B T)} \\ &= \frac{1}{Z(\lambda_0, T)} \int d\boldsymbol{x}_\tau \; e^{-H(\boldsymbol{x}_\tau;\lambda_\tau)/(k_B T)} \\ &= \frac{Z(\lambda_\tau, T)}{Z(\lambda_0, T)} \end{aligned} \tag{1.151}$$

Here, we have used Liouville's theorem, which states that the phase volume is conserved under a purely Hamiltonian evolution $\boldsymbol{x}_0 \mapsto \boldsymbol{x}(\tau)$,

$$\left| \frac{\partial \boldsymbol{x}_\tau}{\partial \boldsymbol{x}_0} \right| = 1 \tag{1.152}$$

$$\boxed{\left\langle e^{-W/(k_B T)} \right\rangle = \frac{Z(\lambda_\tau, T)}{Z(\lambda_0, T)}}$$

Rewriting further

$$\begin{aligned}
\left\langle e^{-W/(k_B T)} \right\rangle &= \exp\left\{ \frac{k_B T}{k_B T} \ln \left[\frac{Z(\lambda_\tau, T)}{Z(\lambda_0, T)} \right] \right\} \\
&= \exp\left\{ -\frac{1}{k_B T} \left[-k_B T \ln Z(\lambda_\tau, T) - (-k_B T) \ln Z(\lambda_0, T) \right] \right\}
\end{aligned}$$

one thus finds the FT

$$\left\langle e^{-W/(k_B T)} \right\rangle = e^{-\Delta F/(k_B T)} \qquad (1.153a)$$

where

$$\Delta F = F(\lambda_\tau, T) - F(\lambda_0, T) \qquad (1.153b)$$

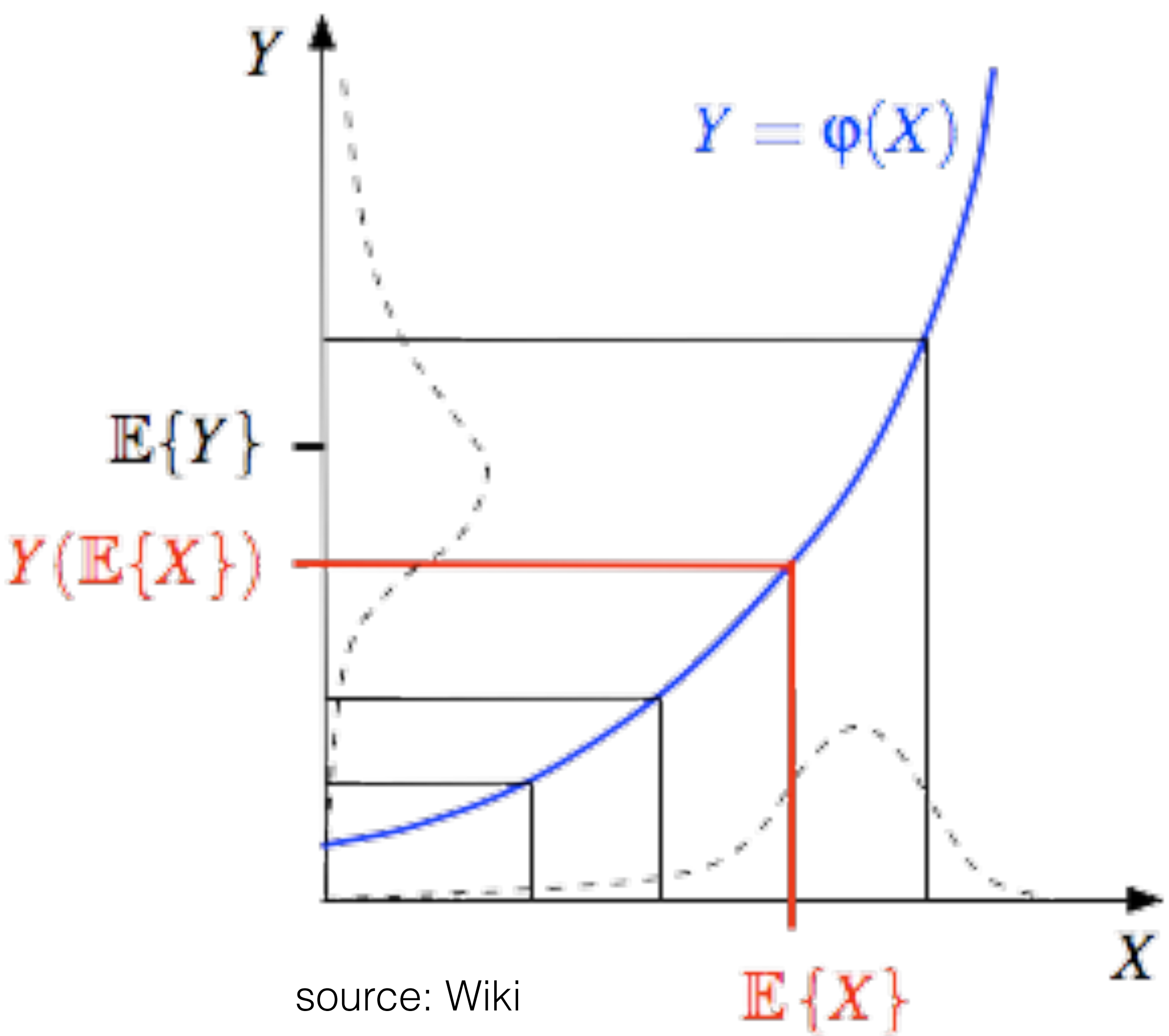
Jensen's inequality

[22]Jensens's inequality states that, if $\phi(x)$ is convex then

$$\mathbb{E}[\phi(X)] \geq \phi(\mathbb{E}[X])$$

Proof: Let $L(x) = a + bx$ be a line, tangent to $\phi(x)$ at the point $x_* = \mathbb{E}[X]$. Since ϕ is convex, we have $\phi(x) \geq L(x)$. Hence

$$\mathbb{E}[\phi(X)] \geq \mathbb{E}[L(X)] = a + b\mathbb{E}[X] = L(\mathbb{E}[X]) = \phi(\mathbb{E}[X])$$



source: Wiki

$$\langle e^x \rangle \geq e^{\langle x \rangle}$$

$$\left\langle e^{-W/(k_B T)} \right\rangle \;=\; e^{-\Delta F/(k_B T)} \tag{1.153a}$$

where

$$\Delta F = F(\lambda_\tau, T) - F(\lambda_0, T) \tag{1.153b}$$

Furthermore, using Jensen's inequality

$$\langle e^x \rangle \geq e^{\langle x \rangle} \tag{1.154}$$

we find

$$e^{-\Delta F/(k_B T)} = \left\langle e^{-W/(k_B T)} \right\rangle \geq e^{\langle -W/(k_B T) \rangle}$$

which is equivalent to the *Clausius inequality*

$$\Delta F \leq \langle W \rangle, \tag{1.155}$$

i.e., the average work provides an upper bound for the free energy difference.

Finally, we still note that

$$\begin{aligned}
\mathbb{P}[W < \Delta F - \epsilon] &:= \int_{-\infty}^{\Delta F-\epsilon} dW\ \rho(W) \\
&\leq \int_{-\infty}^{\Delta F-\epsilon} dW\ \rho(W)\ e^{(\Delta F-\epsilon-W)/(k_B T)} \\
&\leq e^{(\Delta F-\epsilon)/(k_B T)} \int_{-\infty}^{\infty} dW\ \rho(W)\ e^{-W/(k_B T)} \\
&= e^{(\Delta F-\epsilon)/(k_B T)} \left\langle e^{-W/(k_B T)} \right\rangle \\
&= e^{-\epsilon/(k_B T)} \qquad (1.156)
\end{aligned}$$

That is, the probability that a certain realization W violates the Clausius relation by an amount ϵ is exponentially small.

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&\leq \;\; \int_{-\infty}^{\Delta F - \epsilon} dW \; \rho(W) \; e^{(\Delta F - \epsilon - W)/(k_B T)} \\
&\leq \;\; e^{(\Delta F - \epsilon)/(k_B T)} \int_{-\infty}^{\infty} dW \; \rho(W) \; e^{-W/(k_B T)} \\
&= \;\; e^{(\Delta F - \epsilon)/(k_B T)} \left\langle e^{-W/(k_B T)} \right\rangle \\
&= \;\; e^{-\epsilon/(k_B T)} \qquad (1.156)
\end{aligned}
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