Jarzynski equality for ideal gases

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Collaboration

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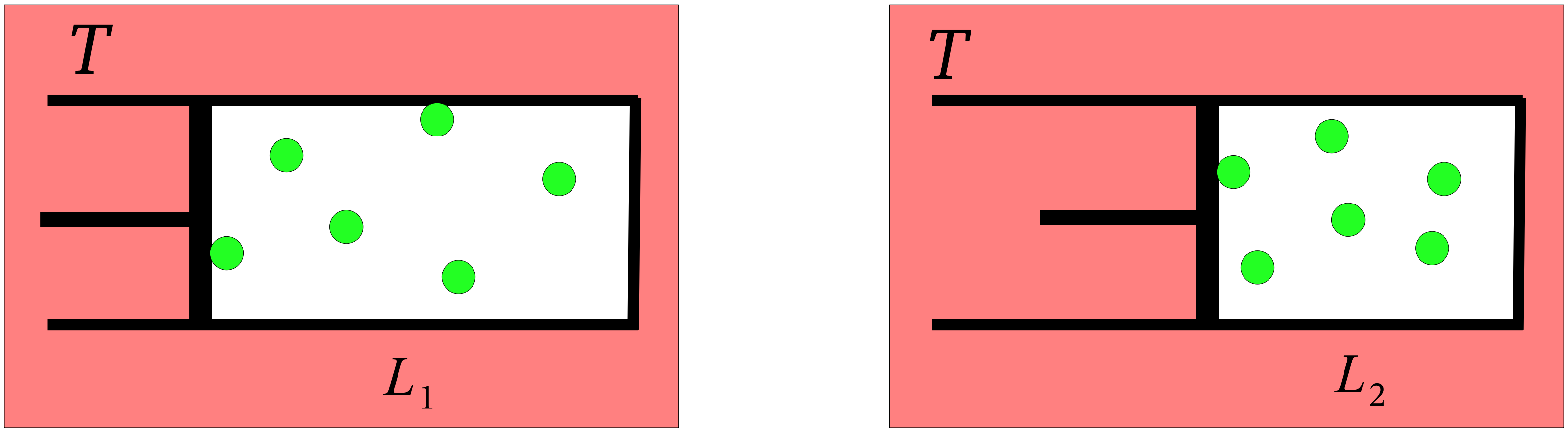
A simple piston and cylinder filled with an ideal gas

Reversible case (infinitely slow)



$$W_{rev} = -\int_{L_1}^{L_2} AP\,dx = NkT \log\left(L_1 / L_2\right)$$

$$\Delta Q = T\,\Delta S = -NkT \log\left(L_1 / L_2\right)$$

$$\Delta E = W_{rev} + \Delta Q = 0$$

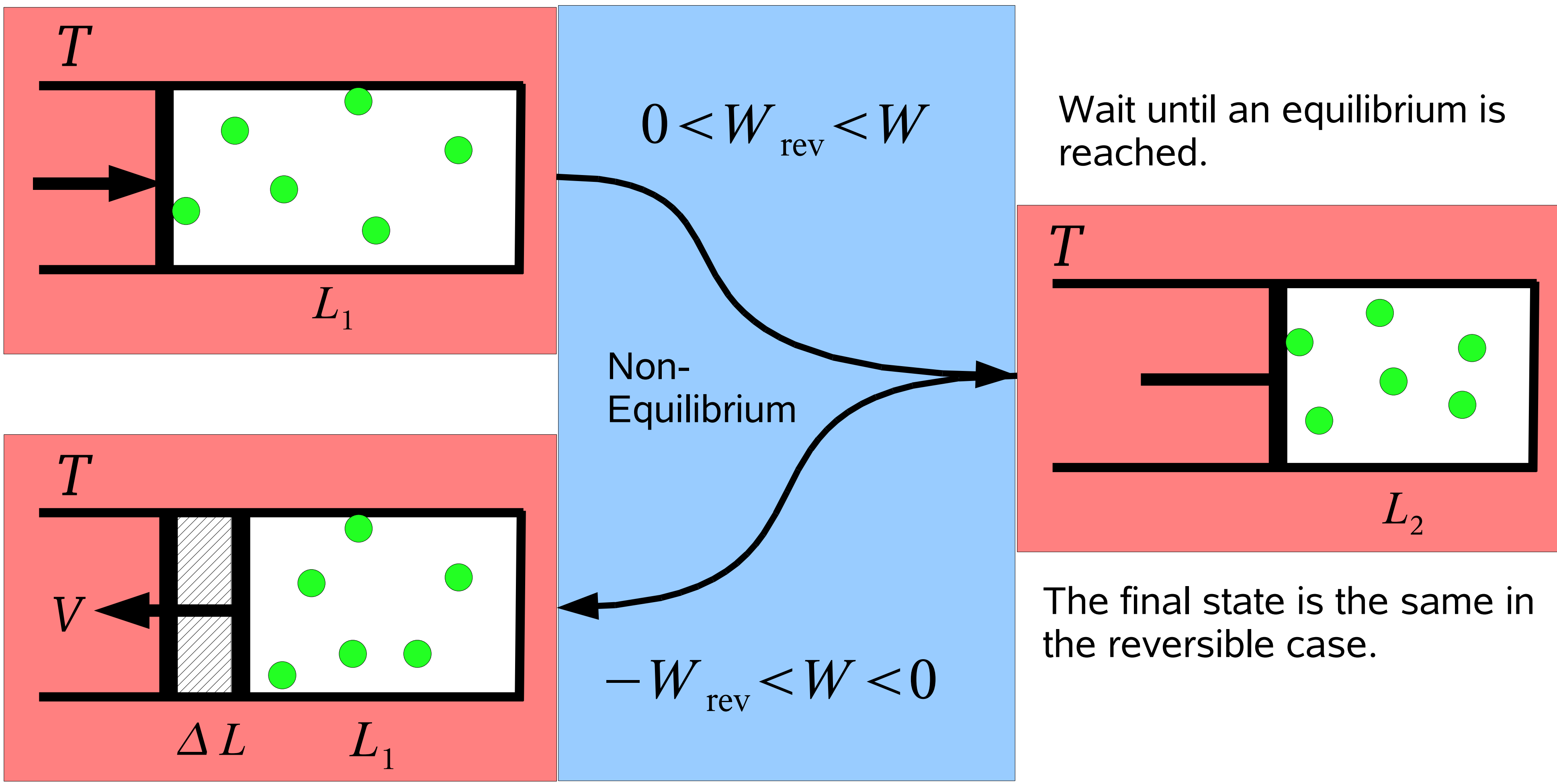
$$\Delta F = \Delta E - T\,\Delta S = W_{rev}$$

A simple piston and cylinder filled with an ideal gas

Irreversible case (finite time)

Initially the system is in an equilibrium.

Wait until an equilibrium is reached.



The final state is the same in the reversible case.

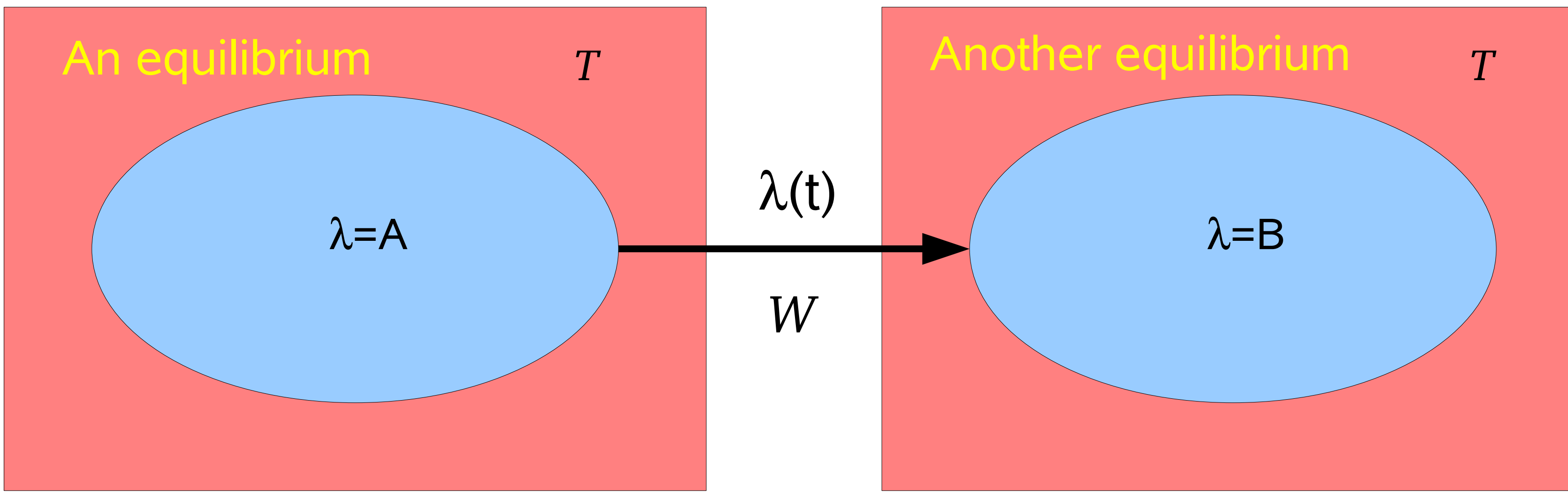
Wait until an equilibrium is reached.

Jarzynski Equality

C. Jarzynski

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F)$$

Phys. Rev. Lett. 78 (1997), 2690



W: Work done on the system by a perturbation

<...>   Average over an ensemble of work measurements

$\Delta F = F(\mathrm{B}) - F(\mathrm{A})$: Helmholtz free energy

Dissipated Work

$$W_{dis} = W - W_{rev} = T\Delta S - \Delta Q$$

The Second Law of Thermodynamics

$$W_{dis} \geq 0 \qquad W \geq W_{rev} = \Delta F$$

$$\langle W_{dis} \rangle \geq 0 \qquad \langle W \rangle \geq W_{rev} = \Delta F$$

Jarzynski Equality, W_{dis}, and 2nd Law

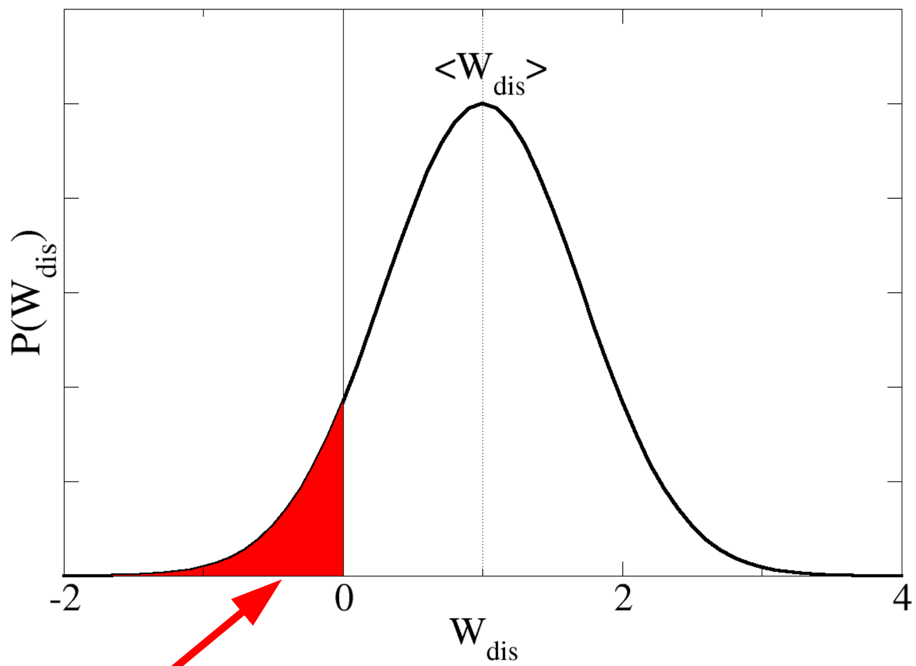
$$\langle \exp[-\beta(W-\Delta F)]\rangle = \langle \exp(-\beta W_{dis})\rangle = 1$$

$$\Rightarrow \langle W_{dis}\rangle \geq 0$$

Using the Jensen's equality

$$\langle \exp(x)\rangle \geq \exp(\langle x\rangle)$$

- The average dissipated work is positive. (the 2nd law)
- But ***negative*** dissipated work is necessary to satisfy the Jarzynski equality.



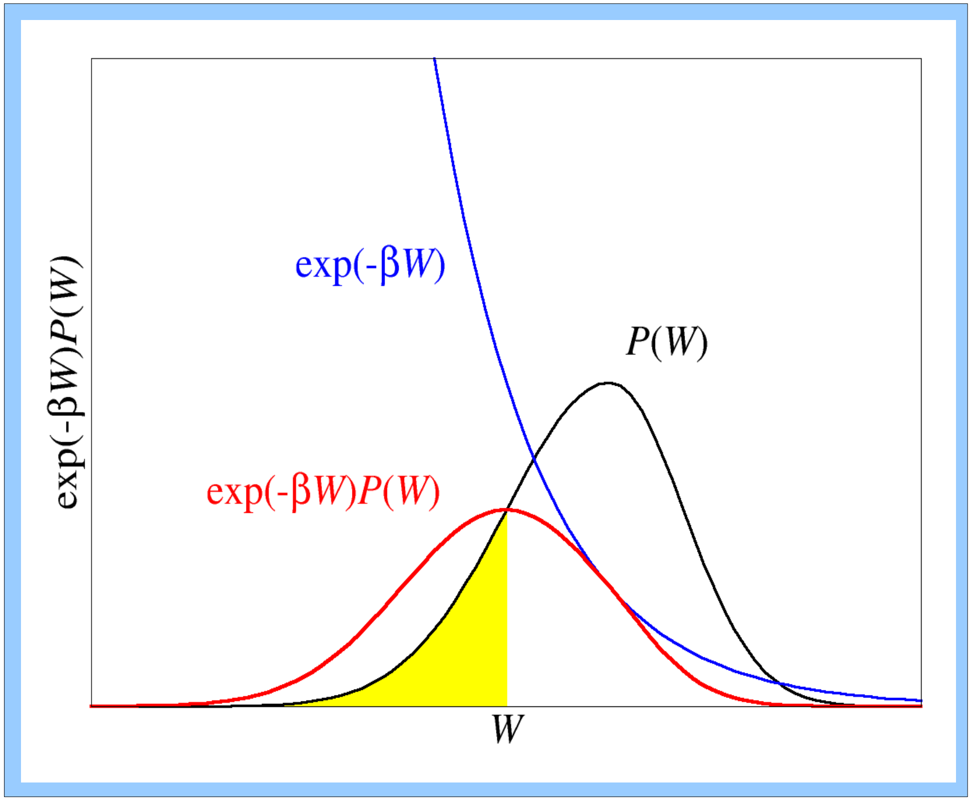
Transient violation of the 2nd law

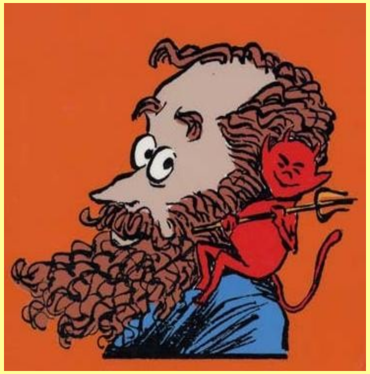
Work Distribution $P(W)$

$$\exp(-\beta \Delta F) = \langle \exp(-\beta W) \rangle = \int_{-\infty}^{+\infty} \exp(-\beta W) P(W) dW$$

Due to the exponential weight, *negative* dissipated work plays a key role in the Jarzynski equality.

For far-from-equilibrium processes, the *tail* part of $P(W)$ becomes significantly important.

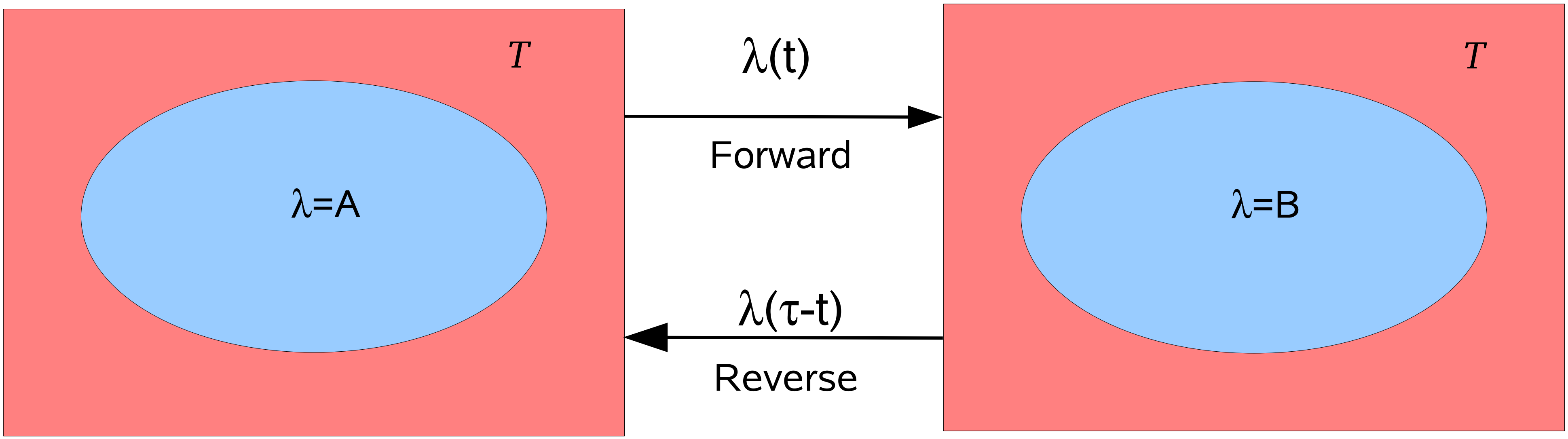




Is Jarzynski a friend of Maxwell's demon?

Crooks Relation

$$\frac{P_F(W)}{P_R(-W)} = \exp\left(\beta(W - \Delta F)\right) = \exp\left(\beta W_{dis}\right)$$



G. E. Crooks: Phys. Rev. E61 (2000), 2361

Computing ΔF

Slow growth method: $\Delta F = W_{rev} \sim W$

Infinitely Slow switching. A single long simulation.

Linear response regime: $\Delta F \sim \langle W \rangle - \frac{\beta}{2} \sigma^2$

Slow switching. Sampling over many trajectories.

Jarzynski equality: $\Delta F = \frac{-1}{\beta} \log(\langle \exp(-\beta W) \rangle)$

Fast switching. Sampling over lots of trajectories.

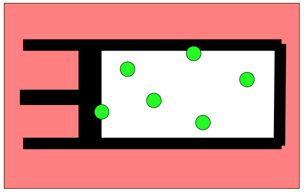
Zwanzig's perturbation: $\Delta F = \frac{-1}{\beta} \log[\int d\xi \, P(\xi) \exp(-\beta \Delta E)]$

Instantaneous switching. No trajectory calculation.

Objectives

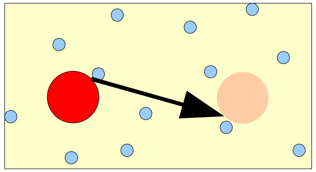
Try to understand the Jarzynski equality
using two exactly solvable models:

1. Compression and expansion of ideal gases.



Bena, Van den Broeck, Kawai
Europhys. Lett. (2005)
DOI: 10/1209/epl/i2005-10177-0

2. An object moving in ideal gases

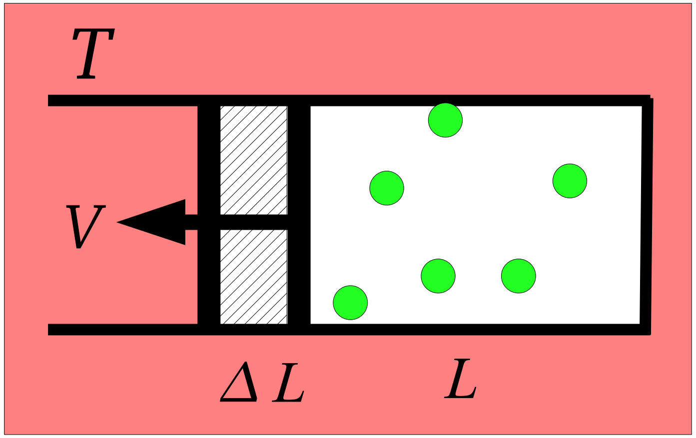


An Exactly Solvable Model

- Gas molecules are noninteracting point particles with velocities randomly chosen from the Maxwellian distribution (ideal gas)
- The volume of the cylinder is very large so that the same particle does not collide with the piston twice. ($L >> \Delta L$)
- The piston has an infinite mass and moves with a constant velocity.

Work due to collision with *j*-th particle at time t

$$W_j = 2mV(u_j - V)\theta(x_j + u_j t - Vt)$$



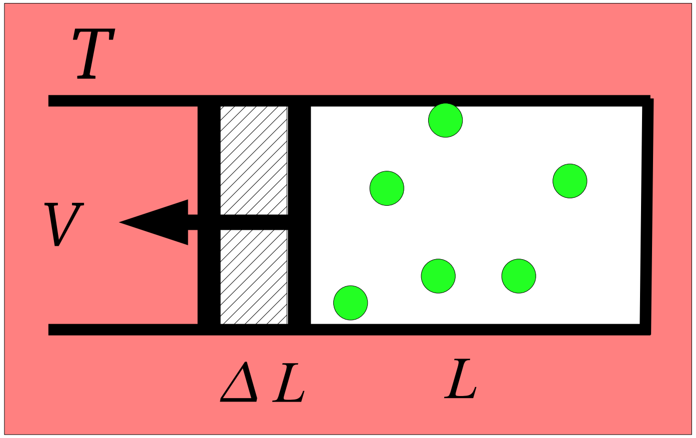
x_j and u_j are the x components of initial position and velocity of the particle, respectively.

Exact Results

$$P(W) = \langle \delta(W - \sum_{j=0}^{N} W_j) \rangle$$
$$= \int_{-\infty}^{+\infty} \frac{dk}{2\pi} \exp\left\{ ikW - nt \int_{V}^{\infty} du(u-V)\phi(u)\{1-\exp[-2ikmV(u-V)]\} \right\}¿$$

n: one-dimensional "projected" density
m: mass of a gas particle
$\phi(u)$: one-dimensional Maxwellian velocity distribution

V: velocity of the piston ($V<0$ for expansion and $V>0$ for compression)
t: duration of the expansion or compression. $\Delta L = |Vt|$



$$v = \sqrt{\frac{m\beta}{2}}\,V$$

piston velocity relative to thermal velocity of the gas particles

$$\tau = \frac{nt}{\sqrt{2m\beta}}$$

average number of collisions during the time interval t

$$\omega = \beta W\,; \qquad v\tau = nVt$$

$$P(\omega) = \int_{-\infty}^{+\infty} \frac{dq}{2\pi} \exp\left[-iq\omega - \tau C(q)\right]$$

$$C(q) = v(1+2iq)\,\mathrm{erfc}\left[v(1+2iq)\right]\exp\left[v^2(1+2iq)^2 - v^2\right] - v\,\mathrm{erfc}(v)$$

Confirmation of Jarzynski equality

$$\langle \exp(-\beta W) \rangle = \langle \exp(-\omega) \rangle = \int_{-\infty}^{+\infty} \exp(-\omega) P(\omega) d\omega$$
$$= \int_{-\infty}^{+\infty} \frac{dq}{2\pi} \exp[-\tau C(q)] \int_{-\infty}^{+\infty} \omega \exp(-iq\omega - \omega) = \exp(\nu\tau)$$

$$\beta \Delta F = N \log\left(\frac{L - \Delta L}{L}\right) \approx -N \frac{\Delta L}{L} = -nVt = -\nu\tau$$

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F)$$

Moments and Cumulants

$$\langle \omega \rangle = 2 v \tau [(1+2 v^2) \operatorname{erfc}(v) - \frac{2}{\sqrt{\pi}} \exp(-v^2)]$$

$$\sigma^2 = \langle (\omega - \langle \omega \rangle)^2 \rangle = 8 v^2 \tau \left[\frac{2}{\sqrt{\pi}} (1+v^2) \exp(-v^2) - v (3+2 v^2) \operatorname{erfc}(v) \right]$$

$$\mu_3 = \langle (\omega - \langle \omega \rangle)^3 \rangle = -16 v^3 \tau \left[\frac{2}{\sqrt{\pi}} v (5+2 v^2) \exp(-v^2) - (3+12 v^2 + 4 v^4) \operatorname{erfc}(v) \right]$$

$$\mu_4 = \langle (\omega - \langle \omega \rangle)^4 \rangle = 3 \sigma^4 + 64 v^4 \tau \left[\frac{2}{\sqrt{\pi}} (4+9 v^2 + 2 v^4) \exp(-v^2) - v (15+20 v^2 + 4 v^4) \operatorname{erfc}(v) \right]$$

skewness $\gamma_3 = \frac{\mu_3}{\sigma^3} \sim o(\tau^{-1/2})$ kurtosis $\gamma_4 = \frac{\mu_4}{\sigma^4} - 3 \sim o(\tau^{-1})$

$$P(\omega) \sim \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{-(\omega - \langle\omega\rangle)^2}{2\sigma^2}\right] \quad \text{for} \quad \tau \gg 1 \quad \text{or} \quad |v| \ll 1$$

$$\langle\omega\rangle = \omega_{rev} + \frac{\sigma^2}{2} \quad , \quad \sigma^2 = \frac{16}{\sqrt{\pi}} v^2 \tau$$

$$\to \delta(\omega - \omega_{rev})$$

This does not mean that the Gaussian approximation is useful for the application of the Jarzynski equality. For any finite τ, even for a very large τ, the non-Gaussian tails may make a significant contribution to the exponentially weighted average.

$$P(\omega) \sim (1 - \tau C_0)\,\delta(\omega) + \frac{\tau|\omega|}{8\sqrt{\pi}v^2} \exp\left[-\left(\frac{\omega}{4v} + v\right)^2\right] \theta(\omega v) \quad \text{for} \quad \tau \ll 1$$

$$C_0 = \frac{1}{\sqrt{\pi}} \exp(-v^2) - v\,\mathrm{erfc}(v)$$

Lua and Grosberg, J. Phys. Chem. B109 (2005), 6805

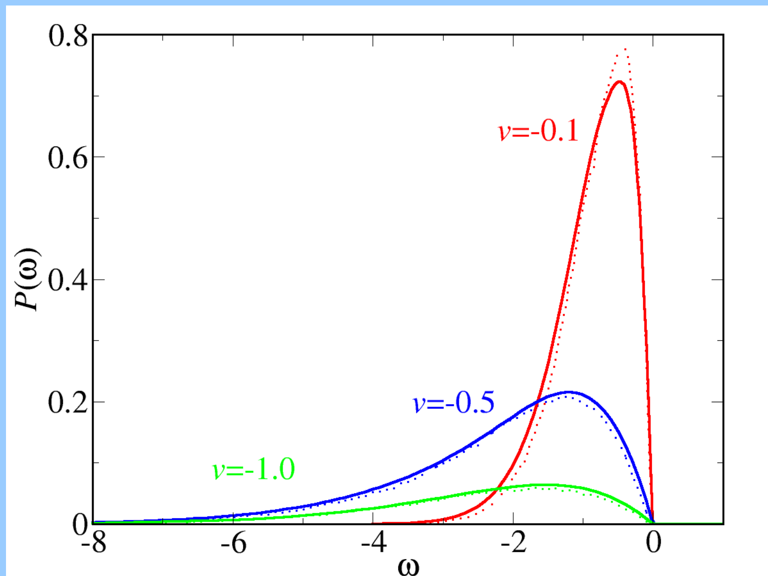
Comparison with Molecular Dynamics Simulation

2D hard disk molecular dynamics simulation

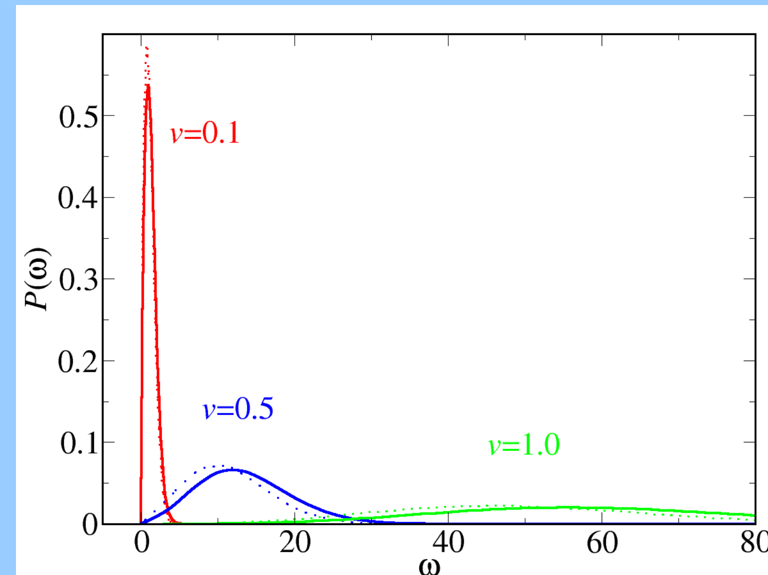
- N=2000
- L=10000
- $\rho=0.002$
- Microcanonical ensemble: 400,000 trajectories

Fixed Time (τ = 5)

(Expansion)

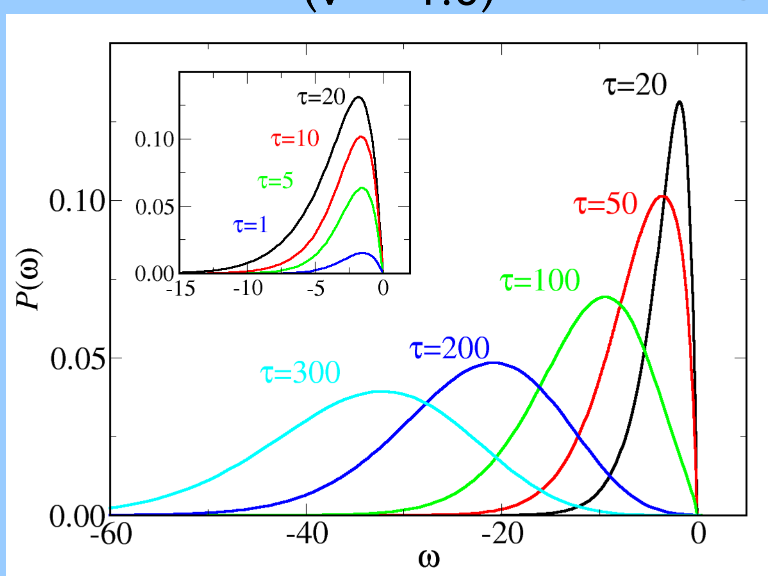


(Compression)

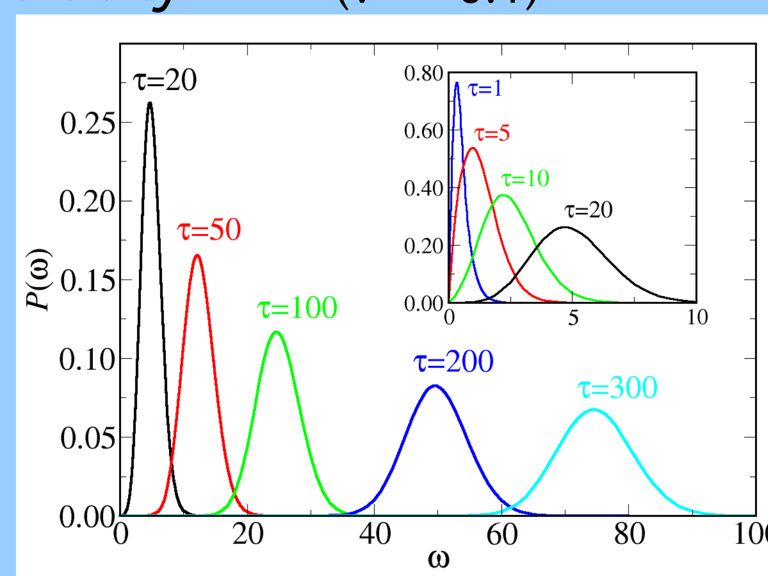


Fixed Velocity

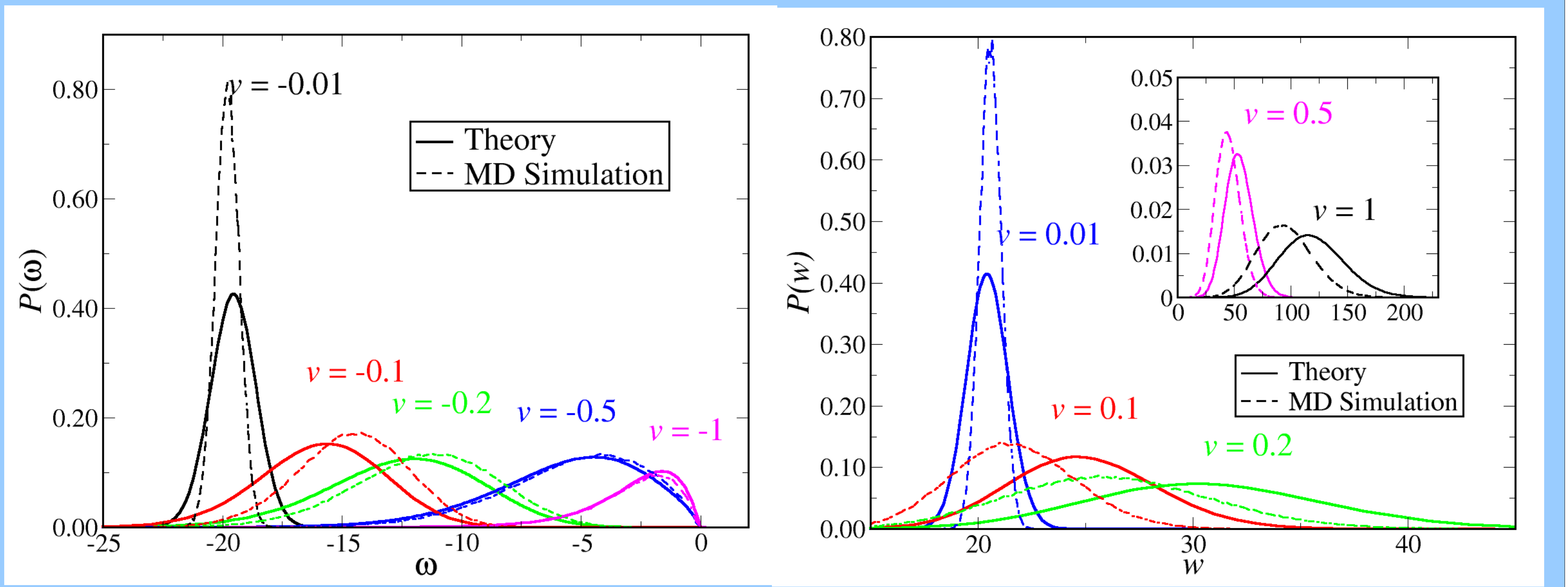
(v = -1.0)



(v = +0.1)

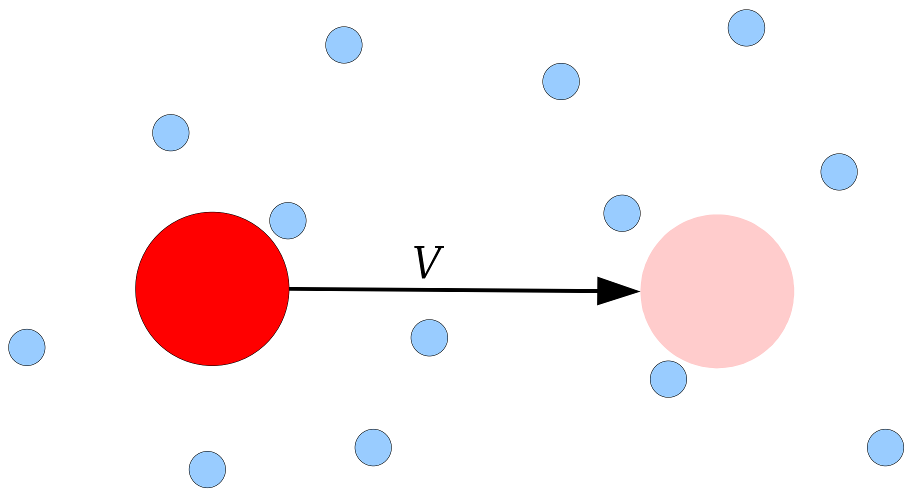


Fixed Distance (vτ=10)



Another Exactly Solvable Model

An object moving through an ideal gas with a constant velocity



$$\Delta F = W_{rev} = 0$$

- Collision at the front side: W>0,   at the backside: W<0
- Final equilibrium state = Initial equilibrium state

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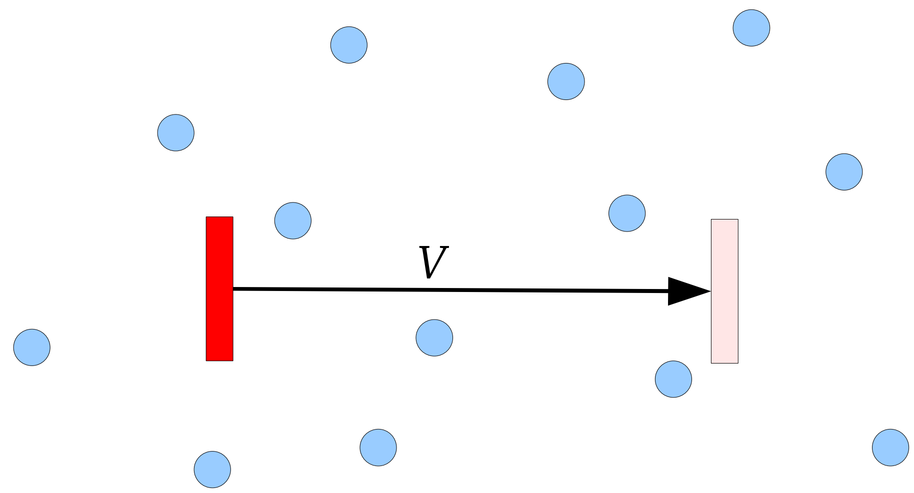

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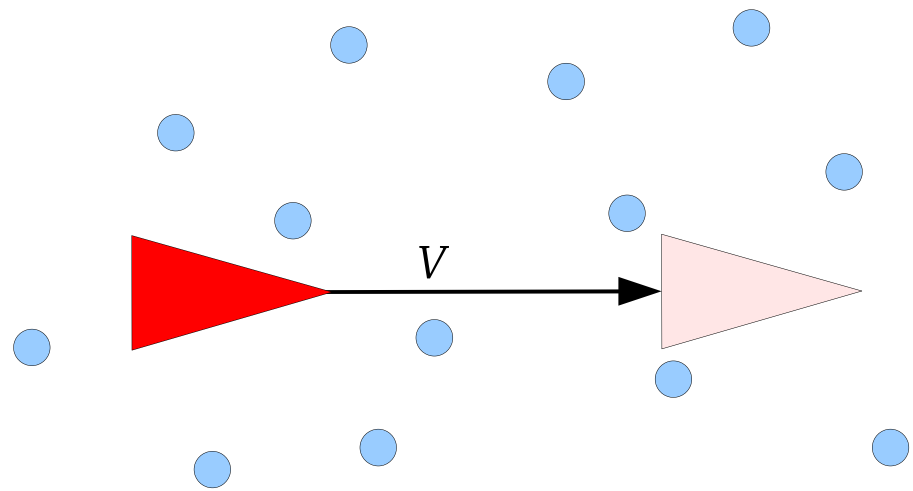

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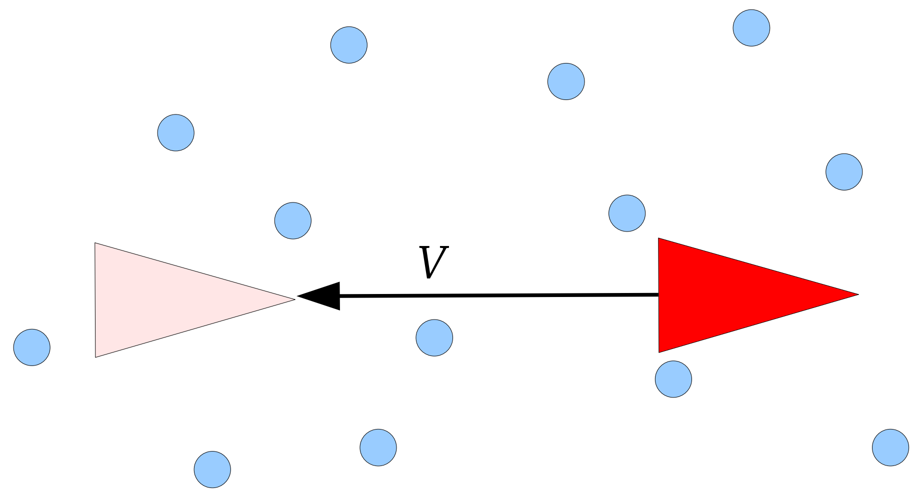

$$\Delta F = W_{rev} = 0$$

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- Final equilibrium state = Initial equilibrium state

Jarzynski Equality: $\langle \exp(-\beta W) \rangle = 1$

Crooks Relation: $\dfrac{P_F(W)}{P_R(-W)} = \exp(\beta W)$

These relations do not depend on the velocity, traveling time nor traveling distance of the object.

Master Equation for the Work Distribution

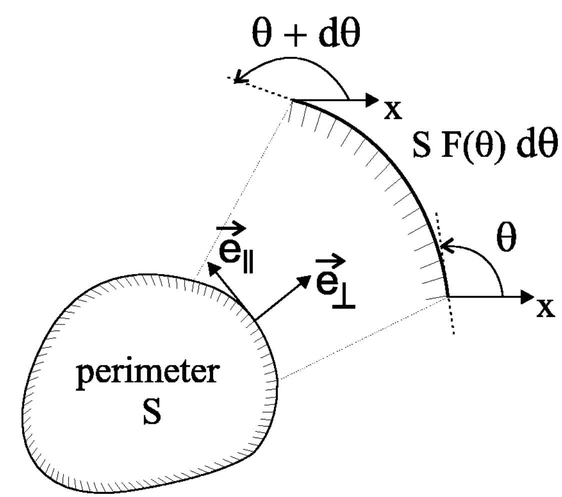
$$\partial_\tau P(\omega,\tau)=\int_{-\infty}^{+\infty}\Gamma(\omega)\left[\exp\left(-\omega\frac{\partial}{\partial\omega}\right)-1\right]P(\omega,\tau)\,d\omega$$

where the transition probability is given by

$$\Gamma(\omega)=\int_0^{2\pi}\frac{F(\theta)}{8\sqrt{\pi}}\frac{\omega}{v^2\sin^2\theta}H\left(\frac{\omega}{v\sin\theta}\right)\exp\left[-\left(v\sin\theta-\frac{\omega}{4v\sin\theta}\right)^2\right]d\omega$$

Friction coefficient

$$\gamma=4S\rho\sqrt{\frac{m}{2\pi\beta}}\int_0^{2\pi}F(\theta)\sin^2\theta\,d\theta$$



Moments

$$\langle\omega\rangle = -\tau \int_0^{+2\pi} d\theta\, F(\theta) \left\{ \frac{4v^2 \sin^2\theta\, e^{-v^2\sin^2\theta}}{\sqrt{\pi}} + 2v\sin\theta [1 + 2v^2\sin^2\theta][1 + \mathrm{erfc}(v\sin\theta\right.$$

$$\sigma^2 = 8\tau \int_0^{2\pi} d\theta\, F(\theta)\, v^2 \sin^2\theta$$

$$\times \left[\frac{2(1+v^2\sin^2\theta)\, e^{-v^2\sin^2\theta}}{\sqrt{\pi}} + v\sin\theta [3 + 2v^2\sin^2\theta][1 + \mathrm{erf}(v\sin\theta)] \right]$$

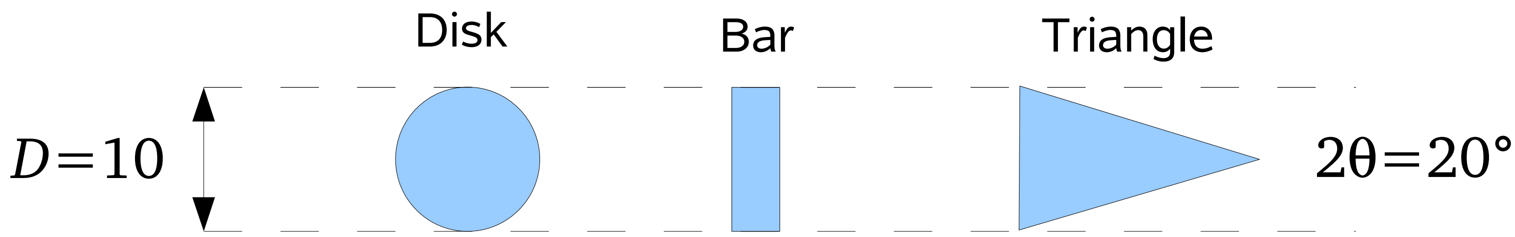
$$\mu_3 = -16\tau \int_0^{2\pi} d\theta\, F(\theta)\, v^3 \sin^3\theta$$

$$\times \left[\frac{2v\sin\theta(5 + 2v^2\sin^2\theta)\, e^{-v^2\sin^2\theta}}{\sqrt{\pi}} + [3 + 12v^2\sin^2\theta + 4v^4\sin^4\theta][1 + \mathrm{erf}(v\sin\theta)] \right]$$

$$\mu_4 = 3\sigma^4 + 64\tau \int_0^{2\pi} d\theta\, F(\theta)\, v^4 \sin^4\theta$$

$$\times \left[\frac{2(4 + 9v^2\sin^2\theta + 2v^4\sin^4\theta)\, e^{-v^2\sin^2\theta}}{\sqrt{\pi}} + v\sin\theta [15 + 20v^2\sin^2\theta + 4v^4\sin^4\theta][1 + \mathrm{erf}(v\sin\theta)] \right]$$

Results and Comparison with MD Simulation



2D Hard Disk Molecular Dynamics Simulation

- gas atom: mass=1, diameter=1
- N=2000, Average over 400000 Trajectories
- ρ=0.002 and 0.02

Quantities $\langle \omega \rangle$, σ^{2}, $\gamma_3(\text{skewness}) = \frac{\mu_3}{\sigma^3}$, $\gamma_4(\text{kurtosis}) = \frac{\mu_4}{\sigma^4} - 3$

Fluctuation-Dissipation Ratio: $R = \frac{\sigma^2}{2\langle \omega \rangle}$

Jarzynski Equality: $\langle \exp(-\omega) \rangle = 1$

Crooks Relation: $\frac{P_F(\omega)}{P_R(-\omega)} = e^{\omega}$

BAR (L=10, ρ=0.002, $v\tau$=10)

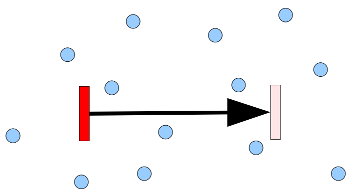
v	$\langle\omega\rangle$		σ^2		γ_3		γ_4		R		$\langle\exp(-\omega)\rangle$
	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation
0.01	0.277	0.451	0.569	0.903	0.002	0.002	0.001	0.004	1.026	1.001	1.01
0.10	4.370	4.529	8.961	9.298	0.048	0.051	0.030	0.035	1.025	1.026	0.96
0.20	8.834	9.147	19.288	20.235	0.115	0.132	0.050	0.068	1.092	1.106	0.99
0.50	23.478	24.403	73.245	80.374	0.295	0.315	0.139	0.135	1.560	1.647	6.51E-02
1.00	55.658	58.864	344.104	403.498	0.344	0.373	0.118	0.154	3.091	3.427	3.53E-03
2.00	163.864	179.985	2701.935	3520.070	0.306	0.352	0.088	0.131	8.244	9.779	3.26E-05

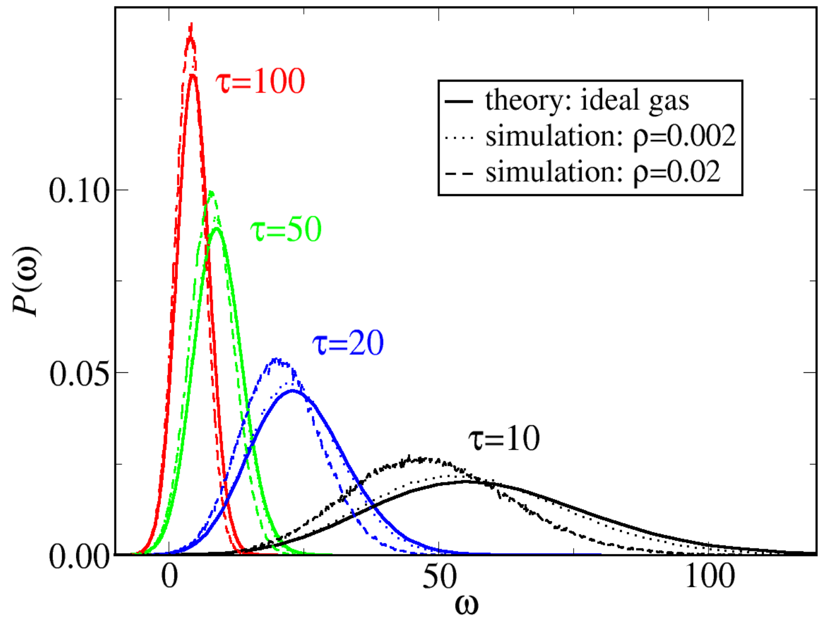
DISK (L=10, ρ=0.002, $v\tau$=10)

v	$\langle\omega\rangle$		σ^2		γ_3		γ_4		R		$\langle\exp(-\omega)\rangle$
	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation
0.01	0.190	0.226	0.394	0.451	0.004	0.002	-0.009	0.005	1.039	0.998	1.01
0.10	2.458	2.262	5.040	4.615	0.051	0.055	0.042	0.053	1.025	1.020	0.99
0.20	4.953	4.559	10.661	9.844	0.136	0.145	0.087	0.105	1.076	1.080	1.03
0.50	13.001	11.975	38.348	35.696	0.353	0.385	0.191	0.229	1.475	1.490	0.31
1.00	30.123	27.792	168.581	160.043	0.466	0.509	0.234	0.300	2.798	2.879	3.35E-02
2.00	86.311	80.205	1306.647	1277.540	0.458	0.507	0.225	0.282	7.569	7.964	4.27E-03

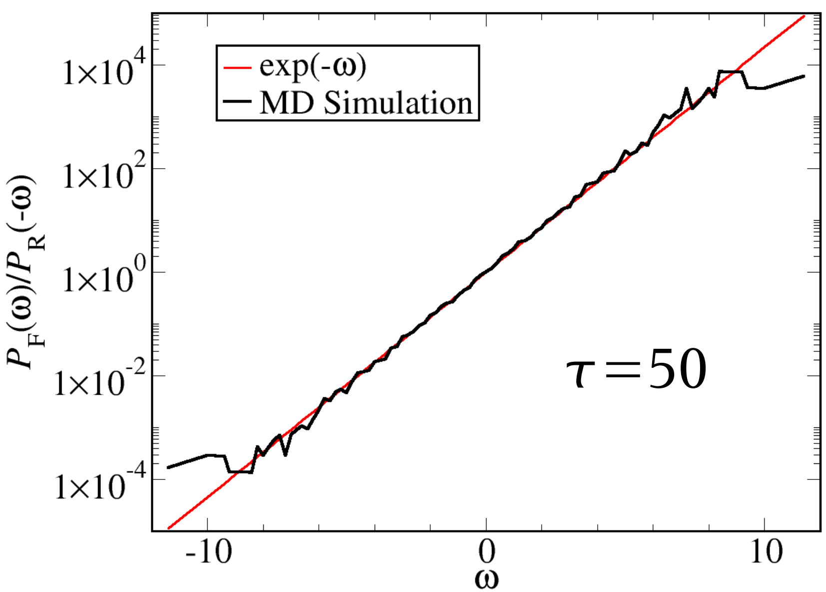
TRIANGLE (L=10, θ_0=10°, ρ=0.002, $v\tau$=10)

v	$\langle\omega\rangle$		σ^2		γ_3		γ_4		R		$\langle\exp(-\omega)\rangle$
	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation	Theory	Simulation
0.01	0.078	0.078	0.156	0.153	-0.076	-0.111	0.012	0.018	1.004	0.981	1.00
-0.01	0.079	0.078	0.159	0.160	0.002	0.111	0.024	0.017	1.006	1.026	1.00
0.10	0.776	0.729	1.388	1.261	-0.253	-0.353	0.137	0.193	0.894	0.865	1.00
-0.10	0.877	0.843	1.980	1.955	0.281	0.342	0.126	0.156	1.129	1.160	1.00
0.20	1.449	1.356	2.338	2.044	-0.327	-0.489	0.312	0.417	0.807	0.754	1.00
-0.20	1.836	1.815	4.791	4.875	0.419	0.465	0.246	0.275	1.305	1.343	1.01
0.50	2.947	2.757	3.700	2.990	-0.217	-0.530	0.801	1.031	0.628	0.542	0.77
-0.50	5.542	5.627	21.609	23.166	0.592	0.629	0.407	0.464	1.950	2.058	0.99
1.00	4.324	4.141	5.046	4.140	0.395	0.189	0.965	0.737	0.583	0.500	0.53
-1.00	14.934	15.620	106.886	120.320	0.633	0.679	0.417	0.511	3.579	3.851	0.97
2.00	6.082	6.095	11.062	10.988	0.641	0.627	0.504	0.446	0.909	0.901	0.07
-2.00	52.000	48.370	855.128	1043.340	0.569	0.646	0.288	0.443	8.222	10.785	0.87

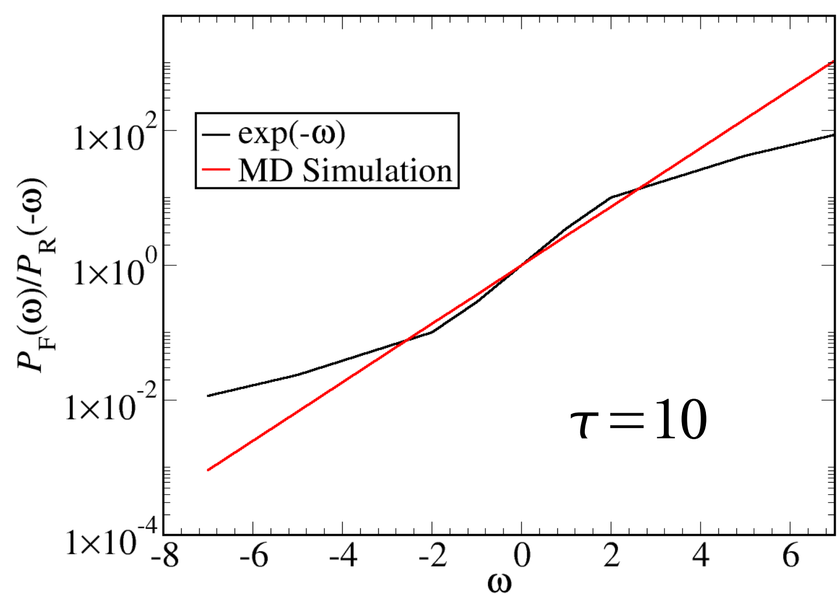




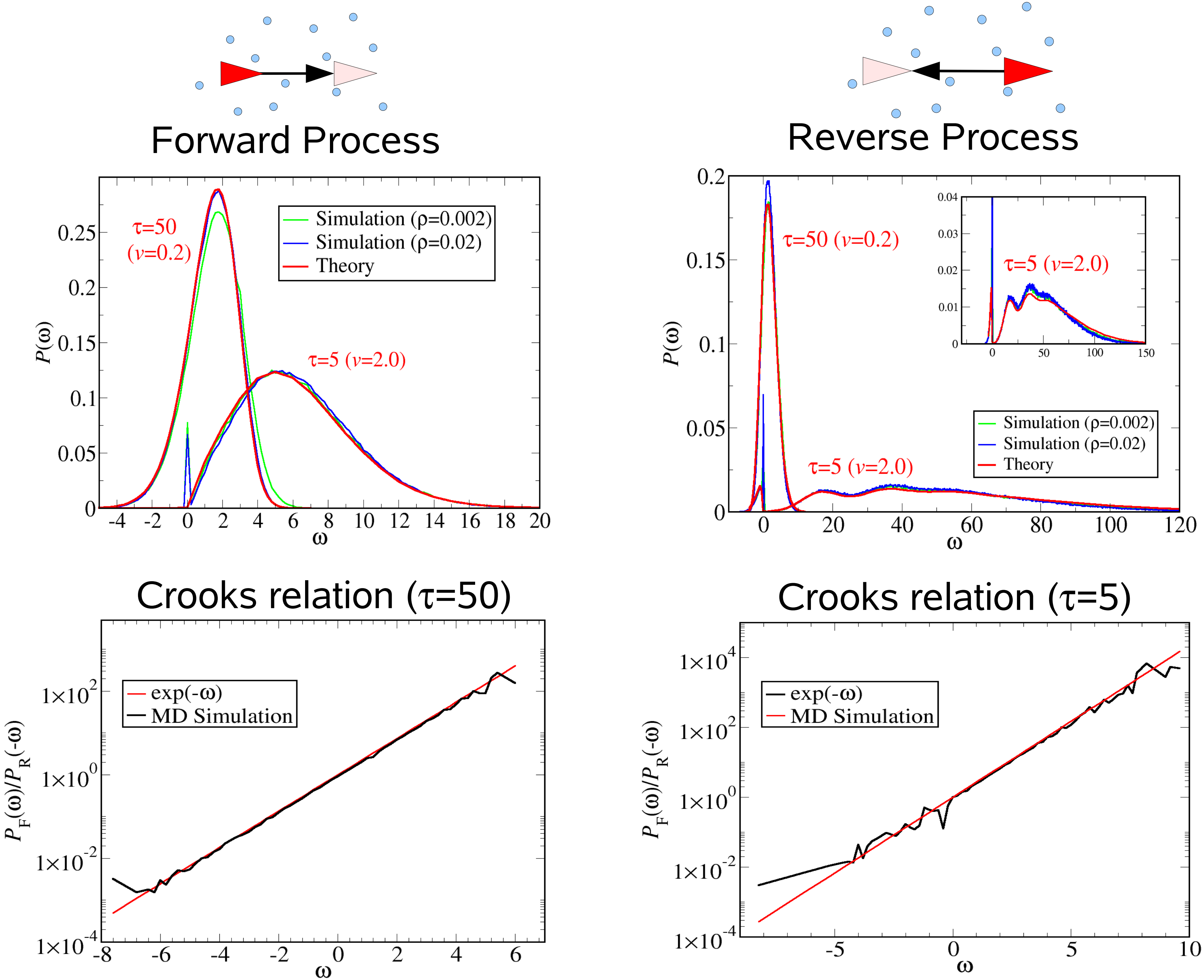
τ=100
τ=50
τ=20
τ=10
theory: ideal gas
simulation: ρ=0.002
simulation: ρ=0.02
P(ω)
0.10
0.05
0.00
0
50
100
ω



exp(-ω)
MD Simulation
τ=50
P_F(ω)/P_R(-ω)
1x10^4
1x10^2
1x10^0
1x10^-2
1x10^-4
-10
0
10
ω



exp(-ω)
MD Simulation
τ=10
P_F(ω)/P_R(-ω)
1x10^2
1x10^0
1x10^-2
1x10^-4
-8
-6
-4
-2
0
2
4
6
ω


Forward Process
Reverse Process
τ=50
(v=0.2)
τ=5 (v=2.0)
Simulation (ρ=0.002)
Simulation (ρ=0.02)
Theory
P(ω)
ω
τ=50 (v=0.2)
τ=5 (v=2.0)
Simulation (ρ=0.002)
Simulation (ρ=0.02)
Theory
P(ω)
ω
Crooks relation (τ=50)
exp(-ω)
MD Simulation
P_F(ω)/P_R(-ω)
ω
Crooks relation (τ=5)
exp(-ω)
MD Simulation
P_F(ω)/P_R(-ω)
ω

Conclusions

- Two exactly solvable models are used to investigate the Jarzynski equality.

- The Jarzynski equality is confirmed in these models.

- Closed form expressions of mean, variance, and higher moments are obtained. For fast switching, all moments contribute to the Jarzynski equality. (Molecular dynamics simulation fails due to finite sampling and finite size.)

- The exact expressions of P(W) are obtained and compared with molecular dynamics simulation. In naked eyes, they agree but the simulations lack the necessary accuracy in the tail of P(W).

Conclusions (Continued)

- The Crooks relation is confirmed.

- For slow switching, a Gaussian form of $P(W)$ is obtained as expected.

- In most cases, MD simulations agree with the Jarzynski equality and the Crooks relation only when the system is in the linear response regime (R=1).

- An exception is the case where the number of collisions contributing to $W_{\mathrm{dis}}<0$ is larger than that to $W_{\mathrm{dis}}>0$.