Exact relations in Non-Equilibrium Statistical Mechanics

Adrian Baule

June 2012

Equilibrium vs non-equilibrium

Equilibrium

- Thermodynamics: minimum of free energy
- Statistical mechanics
  $\longrightarrow$ Ensembletheory
  $\longrightarrow$ Fluctuations

Equilibrium vs non-equilibrium

Equilibrium

- Thermodynamics: minimum of free energy
- Statistical mechanics
  $\longrightarrow$ Ensembletheory
  $\longrightarrow$ Fluctuations

Non-equilibrium

- Transient or steady state
- Athermal systems
- Depends on driving/dissipation mechanisms

Universal statistical mechanical approach?

Exact relations in non-equilibrium statistical mechanics

- *Fluctuation theorems* for heat, work, currents ("X-Y"-FTs)
  - Transient: Jarzynski, Crooks, Evans-Searles
  - Steady state: Gallavotti-Cohen
  - Generalizations
  - Quantum FTs

$$\lim_{\tau\to\infty} \frac{1}{c\tau} \ln \frac{\Pi_\tau(p)}{\Pi_\tau(-p)} = p$$

- *Fluctuation-dissipation relations* for steady states
- *Additivity principle*
- *Ensembletheories*
  - Ensemble of phase space trajectories → *non-equilibrium counterpart to detailed balance*
  - Edward's statistical mechanics for granular matter: energy → volume

How universal? How useful?

Fluctuations in non-equilibrium steady states

- Next simplest generalization of equilibrium is a *nonequilibrium steady state* (NESS)
- Physically a NESS is maintained by a balance between

Driving forces	$\longleftrightarrow$	Dissipative forces
▸ Temperature gradient ▸ Shear		▸ Friction ▸ Viscosity

- Characteristics of a NESS depend on the particular driving/dissipation (thermostatting) mechanisms
- Use *large deviation formalism*

$$p = \int_0^\tau A(x(t))\mathrm{d}t, \qquad \lim_{\tau\to\infty} \frac{1}{\tau} \ln \Pi_\tau(p) = I(p)$$

- Rate function characterizes fluctuations in the NESS

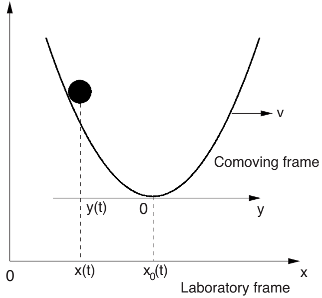
A nonequilibrium particle model

- Particle in a moving harmonic potential

$$m\ddot{x}(t) + \alpha\dot{x}(t) = -\kappa(x(t) - vt) + \xi(t)$$

- Mechanical work done on the particle

$$W_\tau = -\kappa v \int_0^\tau (x(t) - vt)\mathrm{d}t$$



- Stationary process in the comoving frame $y = x - vt$:

$$m\ddot{y}(t) + \alpha\dot{y}(t) = -\kappa y(t) - \alpha v + \xi(t) \quad , \quad W_\tau = -\kappa v \int_0^\tau y(t)\mathrm{d}t$$

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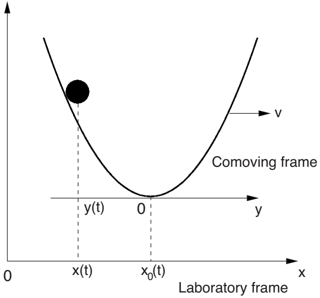

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External noise

- Noise and friction originate from physically *independent* mechanisms
- Investigate role of *time scales* and *singularities* in the context of FTs

A general type of noise

Poissonian shot noise (PSN)

$$z(t) = \sum_{k=1}^{n_t} \Gamma_k \delta(t - t_k)$$

- n_t Poisson distributed with mean λ
- Γ_k exponentially distributed with mean Γ_0
- White noise

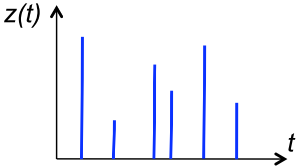
- Characteristic functional

$$G_{z(t)}[g(t)] = \exp\left\{\lambda \int_0^\infty \left(\frac{1}{1 - i\Gamma_0 g(t)} - 1\right) \mathrm{d}t\right\}$$

- Consider *zero mean noise*:

$$\xi(t) = z(t) - \lambda\Gamma_0$$

- Gaussian noise in the limits
  $\lambda \to \infty, \quad \Gamma_0 \to 0, \quad \lambda\Gamma_0^2 = const.$



Time scales

- Time scales of the harmonic oscillator

Inertial time

$$\tau_m = \frac{m}{\alpha}$$

Relaxation time

$$\tau_r = \frac{\alpha}{\kappa}$$

- Additional time scales due to PSN

Mean waiting time between pulses

$$\tau_\lambda = \frac{1}{\lambda}$$

'Poisson' time

$$\tau_p = \frac{\Gamma_0}{\alpha|v|}$$

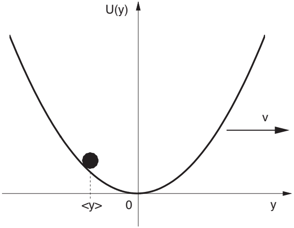
- Qualitative transition behavior due to interplay of these time scales

Symmetries and singularities

Zero mean noise

$$\xi(t) = z(t) - \lambda\Gamma_0$$

- Mean position in NESS: $\langle y \rangle = -v\tau_r$
- Mean work in NESS: $\langle W_\tau \rangle = \alpha v^2 \tau$



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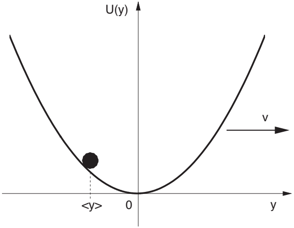
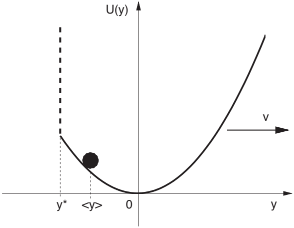
1. Distinguish $v > 0$ and $v < 0$
2. *Singular features* due to noise:
   - Effective velocity: $v_e \equiv v + \lambda\Gamma_0/\alpha$
   - Force balance: $v_e = -\frac{1}{\tau_r} y^*$





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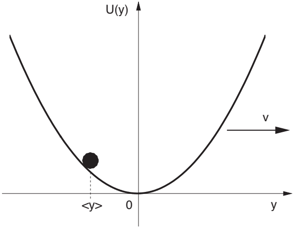

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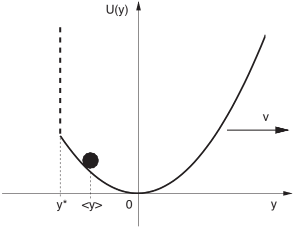


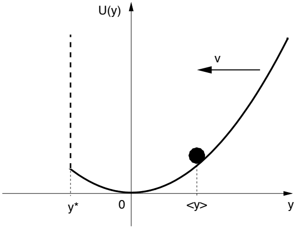
Effective nonlinearity

- Position cut-off $y^* = -v_e\tau_r$
- Infinite barrier in harmonic potential

Symmetries and singularities

- Negative v

$\tau_p > \tau_\lambda$



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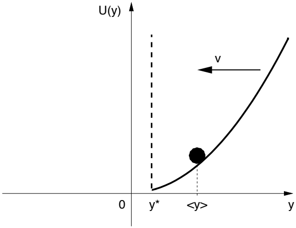

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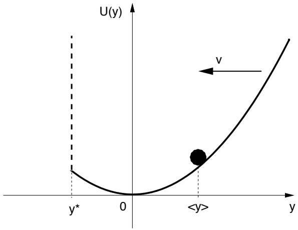

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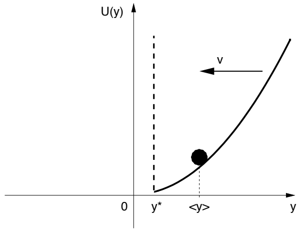


- Work given by: $W_\tau = -\kappa v \int_0^\tau y(t)\mathrm{d}t$

Work cut-off

$$W_\tau^* = -\kappa v y^* \tau$$

- $v > 0$: W_τ^* maximal work in time τ
- $v < 0$: W_τ^* minimal work in time τ

- If $v < 0$ and $\tau_p < \tau_\lambda$: minimal work $W_\tau^* > 0$ and no negative work fluctuations can occur.

Generalized Ornstein-Uhlenbeck process

- Overdamped regime $\tau_m \ll \tau_r$

$$\dot{y}(t) = -\frac{1}{\tau_r} y(t) - v_e + z(t)$$

- Obtain characteristic functional:

$$G_{y(t)}[h(t)] = e^{ik_0 y_0 - iv_e \int_0^\infty k(t)\mathrm{d}t} G_{z(t)}[k(t)],$$

where $k(t) = \int_t^\infty e^{(t-s)/\tau_r} h(s)\mathrm{d}s$.

1. Characteristic function of particle position: $h(t) = h_1 \delta(t - t_1)$
2. Characteristic function of the work: $h(t) = -qv\kappa\Theta(\tau - t)$

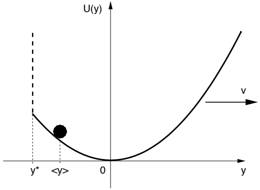
$$G_{y(t)}[h(t)] = \left\langle e^{-iqv\kappa \int_0^\tau y(t)\mathrm{d}t} \right\rangle = \left\langle e^{iqW_\tau} \right\rangle$$

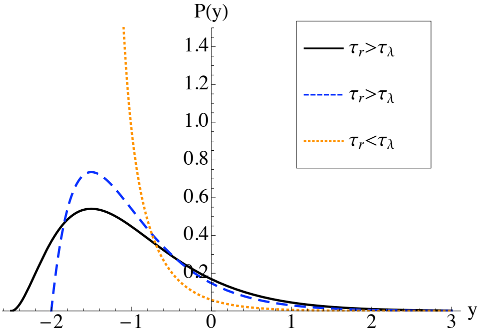
Stationary distribution

- Particle position in the NESS:

$$P(y) \propto \left(\frac{\alpha}{\Gamma_0}(y - y^*)\right)^{\tau_r/\tau_\lambda - 1} e^{-(y-y^*)\alpha/\Gamma_0}$$

- Transition behavior for $\tau_r < \tau_\lambda$





Work distribution

- Distribution of rescaled work $p \equiv W_\tau / \langle W_\tau \rangle$ for large τ

$$\Pi_\tau(p) \propto \left(\sqrt{\frac{p^*-p}{p^*-1}}\right)^{-\frac{\tau_r}{\tau_\lambda}\left(\sqrt{\frac{p^*-p}{p^*-1}}-1\right)-\frac{3}{2}} \exp\left\{-\frac{\tau}{\tau_\lambda}\left(\sqrt{\frac{p^*-p}{p^*-1}}-1\right)^2\right\}$$

- Rescaled work cut-off: $p^* = 1 + \sigma(v)\frac{\tau_p}{\tau_\lambda}$
- Rate function: $I(p) = \frac{1}{\tau_\lambda}\left(\sqrt{\frac{p^*-p}{p^*-1}}-1\right)^2$

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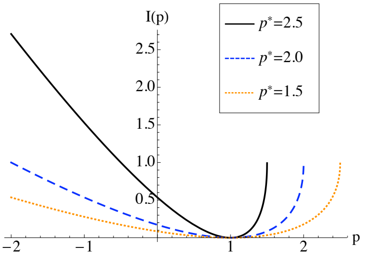
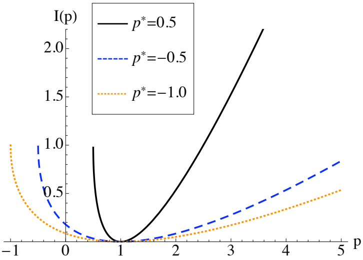
$v > 0$



$v < 0$



Fluctuation theorem

- Define dimensionless fluctuation function using $a \equiv \frac{\alpha}{\lambda\Gamma_0^2}$

$$f_\tau(p) = \frac{1}{a\langle W_\tau\rangle} \ln \frac{\Pi_\tau(p)}{\Pi_\tau(-p)}$$

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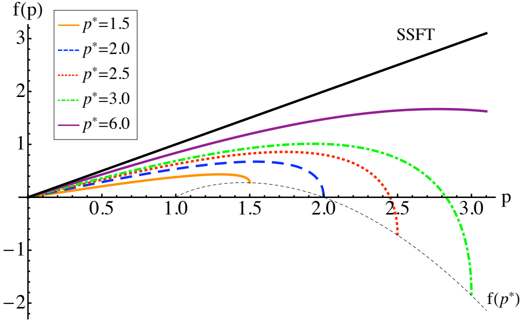
- In the asymptotic regime $\tau \to \infty$, $v > 0$:



- $f(p)$ defined on $[-p^*, p^*]$ and only depends on p, p^*
- SSFT for $p^* \to \infty$ (Gaussian limit)
- Vertical slope for $p \to p^*$
- Negative fluctuation function for $p^* > 2$ (i.e. $\tau_p > \tau_r$)

Baule and Cohen, PRE (2009)

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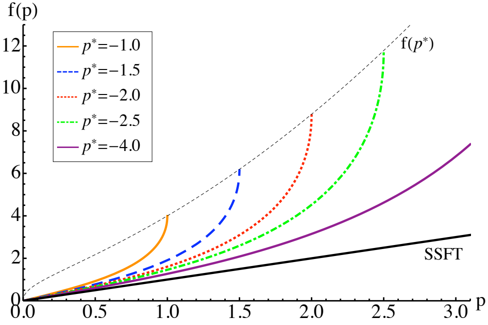
$$f_\tau(p) = \frac{1}{a \langle W_\tau \rangle} \ln \frac{\Pi_\tau(p)}{\Pi_\tau(-p)}$$

- In the asymptotic regime $\tau \to \infty$, $v < 0$ and $\tau_p > \tau_\lambda$:



  - $f(p)$ always > 0 for $p > 0$
  - SSFT for $p^* \to \infty$ (Gaussian limit)
  - Vertical slope for $p \to p^*$

Baule and Cohen, PRE (2009)

Additional thermal Gaussian noise

- Add Gaussian noise $\eta(t)$ with $\langle \eta(t) \rangle = 0$, $\langle \eta(t)\eta(t') \rangle = 2\frac{\alpha}{\beta}\delta(t-t')$

$$m\ddot{x}(t) + \alpha\dot{x}(t) = -\kappa(x(t) - vt) + \xi(t) + \eta(t)$$

- Product of characteristic functionals

$$G_{y(t)}[h(t)] = e^{ik_0 y_0 - iv_e \int_0^\infty k(t)\mathrm{d}t} G_{z(t)}[k(t)] G_{\eta(t)}[k(t)]$$

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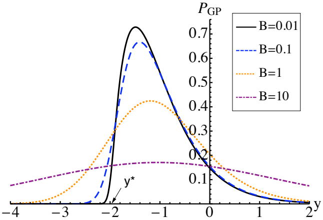
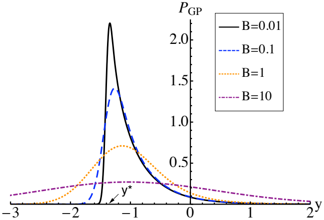
- Stationary distribution given by convolution of $P(y)$ and $P_G(y)$

$\tau_r > \tau_\lambda$



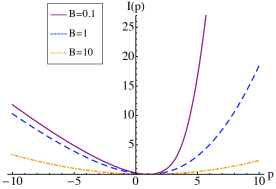
$\tau_r < \tau_\lambda$

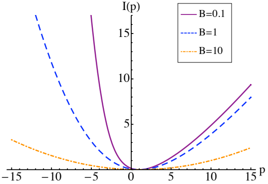


- B = ratio of noise powers Gauss/PSN

Work fluctuations

- Rate function

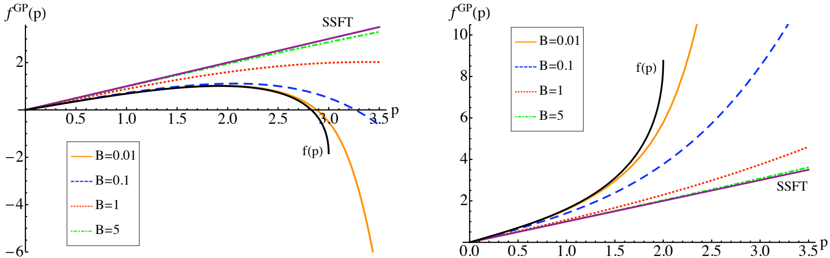




Work fluctuations

- Rate function

- Fluctuation function



Equilibrium ensembles

Equilibrium

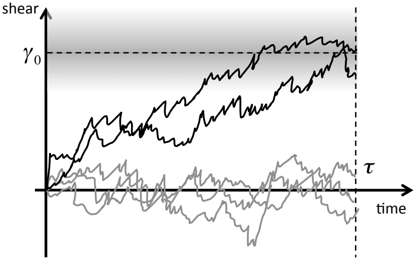
- Thermodynamics: minimum of free energy
- Statistical mechanics
  $\longrightarrow$ Ensembletheory
  $\longrightarrow$ Fluctuations

- *Ergodicity*: system samples entire phase space over time
  $\longrightarrow$ equivalence of time averages and ensemble averages over stationary probability distributions $p(x)$
- *Microcanonical ensemble*: $p(x)$ is uniform at constant energy E
- *Entropy*: $S = -k_B \ln \Omega(E)$
- *Canonical ensemble*: energy exchange with heat bath $p(x) \propto e^{-\beta H(x)}$
  $\longrightarrow$ thermal equilibrium fluctuations
- Rules for transition rates: *detailed balance*

Biased ensemble of trajectories

- Consider time-integrated observable of *equilibrium* dynamics $x(t)$

$$\gamma_\Gamma = \int_0^\tau A(x(t))\mathrm{d}t$$



- Construct *biased ensemble*:
  - *Microcanonical*
  - *Canonical*: $\langle\gamma_\Gamma\rangle = \gamma_0$
- Distribution of uncorrelated objects Γ is given by maximizing

$$S = -\sum_\Gamma p_\Gamma \ln p_\Gamma$$

for equilibrium paths Γ subject to **constraint** $\sum_\Gamma p_\Gamma\gamma_\Gamma = \gamma_0$

Result:

$$p_\Gamma^{dr} \propto p_\Gamma^{eq} e^{\nu\gamma_\Gamma}$$

Biased ensemble of trajectories

Probability of non-equilibrium trajectories

$$p_\Gamma^{dr} \propto p_\Gamma^{eq} e^{\nu \gamma_\Gamma}$$

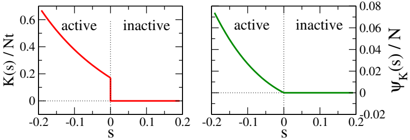
- Shear flows of complex fluids (R.M.L. Evans): *shear*
- Models for glass formers (Garrahan et al): *activity*

- Calculate *dynamical partition function*

$$Z(\nu, t) = \langle e^{\nu \gamma_\Gamma} \rangle$$

- Consider *dynamical free energy*:

$$\psi(\nu) = - \lim_{t \to \infty} \frac{1}{t} \log Z(\nu, t)$$



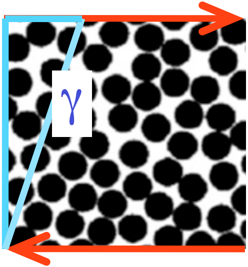
Garrahan et al, PRL (2007)

Fluid in shear flow

A sheared NESS has much in common with equilibrium:

Sheared NESS

- same Hamiltonian, only boundaries differ
- ergodic
- reproducible phase behavior
- spatial and temporal fluctuations
- ubiquitous

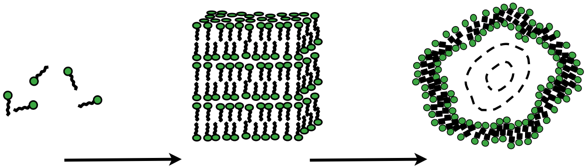


...yet not solved by equilibrium statistical mechanics!

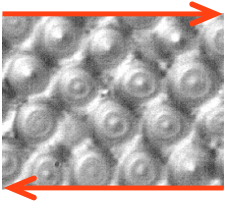
In general, $\dot{\gamma}$ influential, if relaxation times τ_r are long: $\dot{\gamma}\tau_r \gg 1$

Phenomena in shear flows of complex fluids

- Amphiphiles:



equilibrium continuous shear



Micrograph courtesy of Mark Buchanan

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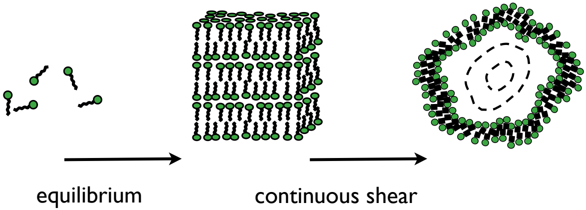
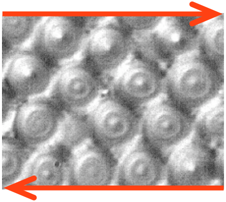
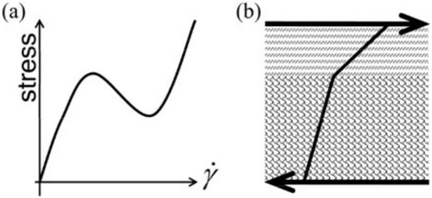




Micrograph courtesy of Mark Buchanan

- Shear banding:

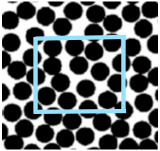


Phase transition

controlled by **shear rate** in addition to temperature, concentration, etc.

Nonequilibrium statistical mechanics of shear flow

- A model fluid



is defined by a set of n rates $\{\omega_{ab}\}$
for jumping between microstates a, b

Can the transition rates be chosen arbitrarily ?

Balance equation for the probability distribution p_a:

$$\dot{p}_a = \sum_b [\omega_{ba} p_b - \omega_{ab} p_a] = 0$$

Satisfied by (equilibrium condition): $\omega_{ba} p_b - \omega_{ab} p_a = 0$

$\rightarrow$ Equilibrium heat bath:

$$\omega_{ab}/\omega_{ba} = e^{-(E_b - E_a)/k_B T}$$

Condition of *detailed balance*

Nonequilibrium statistical mechanics of shear flow

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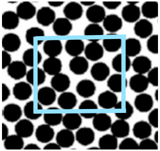

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→ *Do similar constraints apply in a sheared NESS ?*

Nonequilibrium statistical mechanics of shear flow

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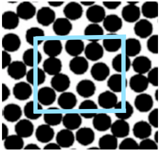
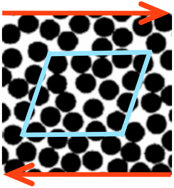


$\rightarrow$ *Do similar constraints apply in a sheared NESS ?*

- A fluid volume in the bulk feels shear only intermediated through surrounding fluid



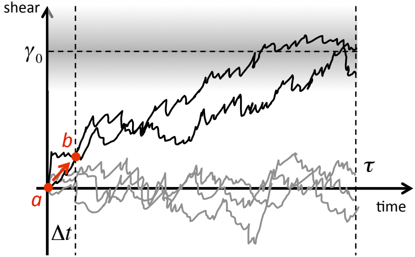
Postulate: statistics of sheared NESS obtained from a biased ensemble of equilibrium trajectories

Nonequilibrium counterpart to detailed balance

→ Unnormalized probability of a path: $p_\Gamma^{dr} \propto p_\Gamma^{eq} e^{\nu\gamma_\Gamma}$

→ Want: probability of a transition

$$\omega_{ab} = Pr(a \to b|a)/\Delta t$$



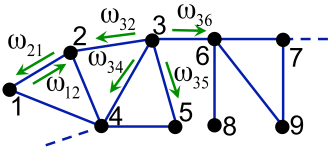
By counting all trajectories that contain transition $a \to b$ obtain **exact** relations for the transition rates:

$$\omega_{ab}^{dr} = \omega_{ab}^{eq} e^{\nu\Delta\gamma_{ba} + \Delta q_{ba}}$$

- *Local* contribution: $\Delta\gamma_{ba}$ is the immediate shear contribution of the transition $a \to b$
- *Global* contribution: Δq_{ba} measures the propensity for future shear given $a \to b$

Predictions

- *Invariant quantities* in the sheared NESS



Product constraint

$$\omega_{ab}^{dr}\omega_{ba}^{dr} = \omega_{ab}^{eq}\omega_{ba}^{eq} \qquad \forall a, b$$

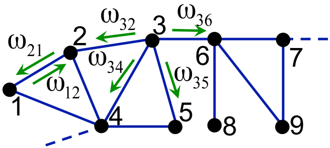
Total exit rate constraint

$$\sum_a^{dr} - \sum_b^{dr} = \sum_a^{eq} - \sum_b^{eq} \qquad \forall a, b$$

$$\sum_a \equiv \sum_j \omega_{aj}$$

Predictions

- *Invariant quantities* in the sheared NESS



Product constraint

$$\omega^{dr}_{ab}\omega^{dr}_{ba} = \omega^{eq}_{ab}\omega^{eq}_{ba} \qquad \forall a, b$$

Total exit rate constraint

$$\Sigma^{dr}_{a} - \Sigma^{dr}_{b} = \Sigma^{eq}_{a} - \Sigma^{eq}_{b} \qquad \forall a, b$$

$$\Sigma_a \equiv \sum_j \omega_{aj}$$

- Introduce shear current (rate) $J = \gamma/\tau$ of a trajectory

Current fluctuations

$$\frac{p_\tau(J)}{p_\tau(-J)} \cong e^{\nu J \tau} \qquad \tau \to \infty$$

→ *Fluctuation theorem*

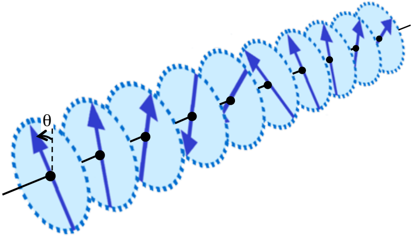
Baule and Evans, PRL (2008); JSTAT (2010)

Testing the theory: a fluid of rotors

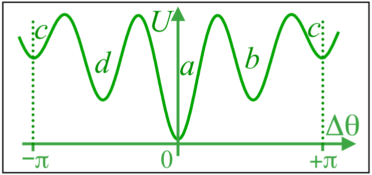
Numerically time-stepping
Newtonian eqs of motion

$$I\ddot{\Theta} = F_{i+1,i} - F_{i,i-1}$$

Conserves angular momentum



Inter-neighbour torque: $F_{ij} = F_{ij}^{conserv} + F_{ij}^{dissip} + F_{ij}^{random}$



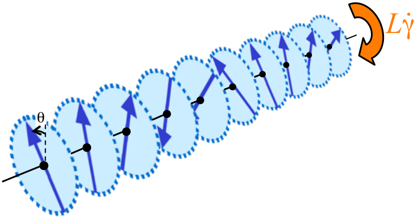
$$\begin{aligned} F_{ij}^{dissip} &\propto \dot{\Theta}_i - \dot{\Theta}_j \\ F_{ij}^{conserv} &= -U'(\Theta_i - \Theta_j) \\ F_{ij}^{random} &= -F_{ji}^{random} \end{aligned}$$

Testing the theory: a fluid of rotors

At equilibrium

- Boltzmann statistics in $U(\Delta\Theta)$
- Transitions between wells satisfy detailed balance

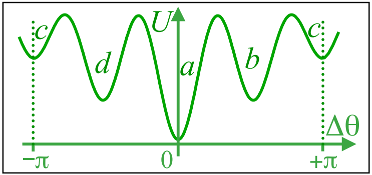
Impose shear at the boundaries...



If

- Dynamics is ergodic
- Correlations are small
- Potential wells=microstates

then the theory applies here !



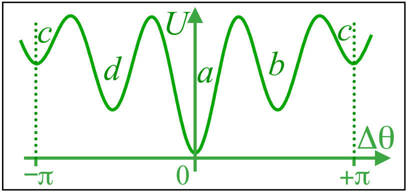
In order to expedite data collection

- Take overdamped (low mass) limit
- Treat each gap ($\Delta\Theta$) as "system"

Testing the product constraint

Use equilibrium symmetries

$$\omega^{eq}_{ab} = \omega^{eq}_{ad}$$
$$\omega^{eq}_{ba} = \omega^{eq}_{da}$$
$$\vdots$$



Product constraint

$$\omega_{ab}\omega_{ba} = \omega^{eq}_{ab}\omega^{eq}_{ba} \qquad \forall a, b$$

$$\rightarrow \qquad \omega_{ab}\omega_{ba} = \omega_{da}\omega_{ad}$$

and similarly for transitions $c \rightarrow b$ and $c \rightarrow d$

Evans, Simha, Baule, Olmsted, PRE 2010

Testing the product constraint

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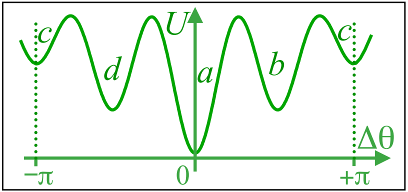

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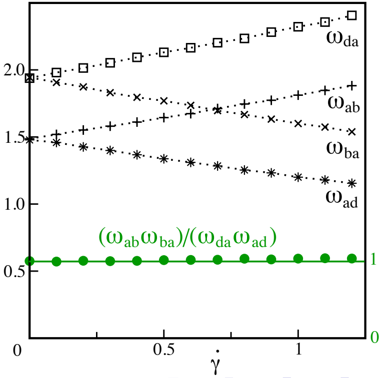

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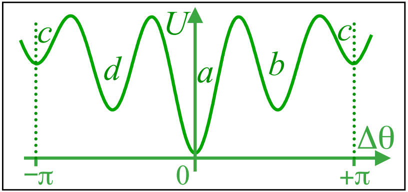

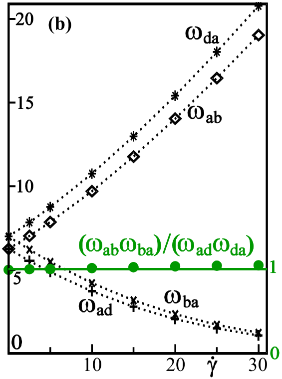

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Evans, Simha, Baule, Olmsted, PRE 2010

Testing the total exit rate constraint

Use equilibrium symmetries

$$\omega^{eq}_{ab} = \omega^{eq}_{ad}$$
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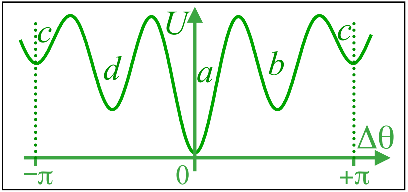
$$\vdots$$



Total exit rate constraint

$$\sum_a^{dr} - \sum_b^{dr} = \sum_a^{eq} - \sum_b^{eq} \qquad \forall a, b$$

$$\rightarrow \qquad \omega_{ba} + \omega_{bc} = \omega_{da} + \omega_{dc}$$

Evans, Simha, Baule, Olmsted, PRE (2010)

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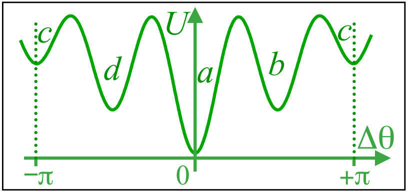

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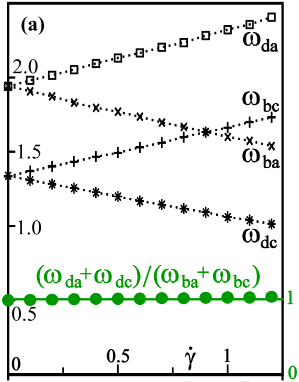

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Evans, Simha, Baule, Olmsted, PRE (2010)

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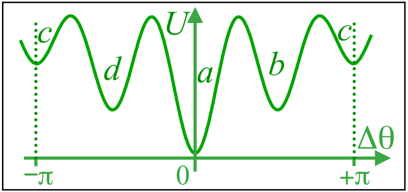

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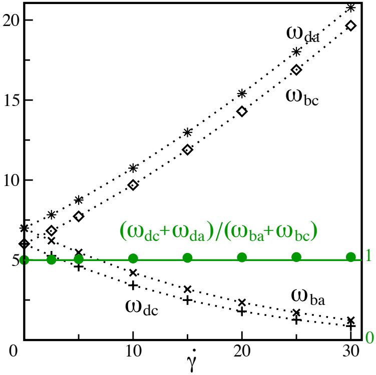
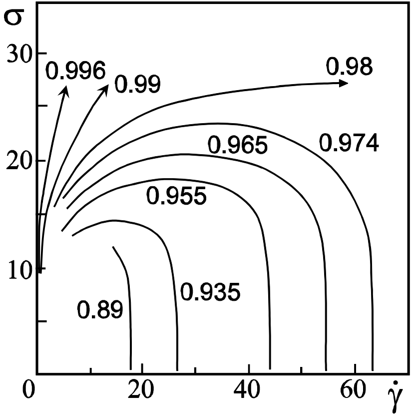


$$\rightarrow \qquad \omega_{ba} + \omega_{bc} = \omega_{da} + \omega_{dc}$$

Evans, Simha, Baule, Olmsted, PRE (2010)

Testing the total exit rate constraint

- Measured ratio close to unity for all parameter values
- Discrepancies in lower left corner
- In low noise regime ergodicity might break down
- Discrepancies do not increase with $\dot{\gamma}$
  $\rightarrow$ *theory is not a near-equilibrium approximation*



Outlook

- Deviations from SSFT for non-Gaussian fluctuations
  - Paradigmatic non-equilibrium particle model
  - PSN as generalization of Gaussion noise (mechanical random force)
- Statistical mechanics of some non-equilibrium systems might be treated using ensemble approaches as in equilibrium
- Connect non-equilibrium trajectory ensemble with thermodynamics of phase transitions under shear
  - Shear thickening in Brownian and non-Brownian colloidal suspensions
  - Needs suitable lattice model where shear can be identified

- *Acknowledgements*
  - E. G. D. Cohen (New York)
  - R. Aditi Simha (Madras)
  - R. M. L. Evans (Leeds)
  - P. D. Olmsted (Leeds)