A justification and test for the statistical mechanics of trajectories

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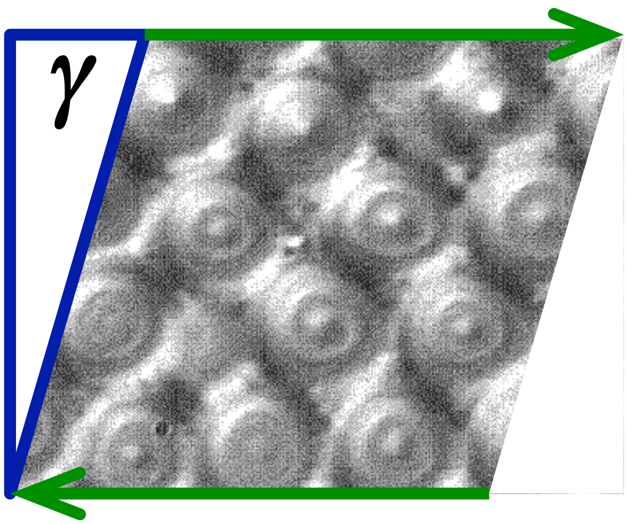
e.g. Onion phase



*A system in continuous shear has the **same equations of motion** as at equilibrium; only boundaries differ.*

Form an ensemble of such systems...

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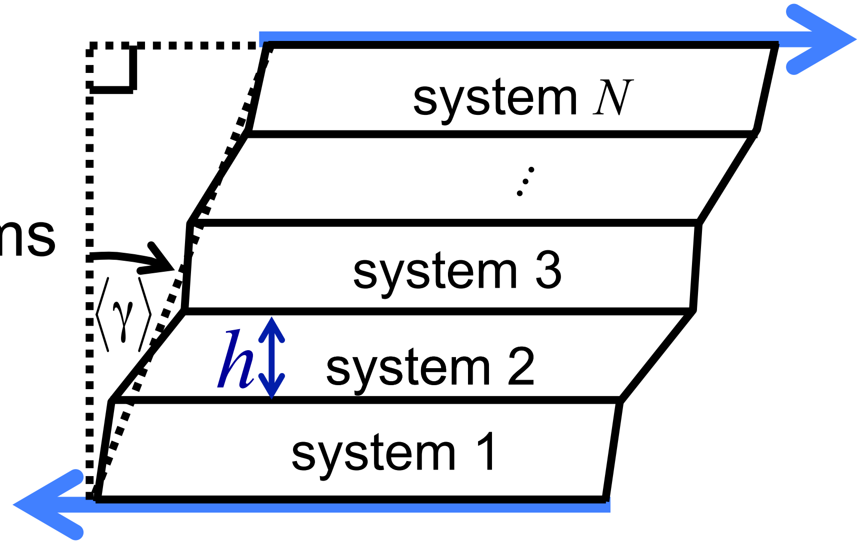
Take thermodynamic limit, so

$h >>$ largest correlation length.

Weakly-coupled uncorrelated systems



Noise from neighbours determines which path a system follows through its microstate-space.

What is the probability p_π that a system takes a particular path π?

p_π = fraction of systems that take path π.

Most likely distribution p_π of uncorrelated objects π is the one with maximum statistical weight,

$$\Omega_N = \frac{N!}{\prod_{\text{paths } \pi} N_\pi !}$$

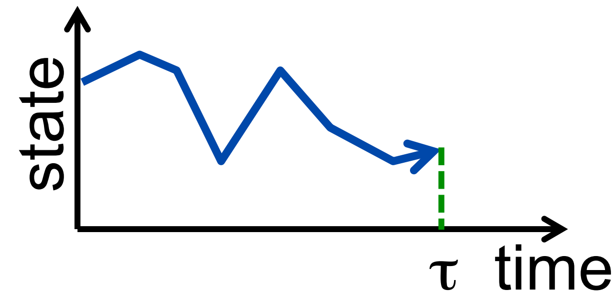
or, equivalently,

$$H = -\sum_{\text{paths } \pi} p_\pi \ln p_\pi$$

for *equilibrium* paths π subject to flux constraint $\sum_\pi p_\pi \gamma_\pi = \langle \gamma \rangle$.

Result

$$p_\pi^{\text{driven}} \propto p_\pi^{\text{equilib}}\, e^{\nu\gamma_\pi}$$



As in equilibrium stat. mech., sum the unnormalized probabilities (statistical weight) to define a "free energy" $r(\nu)$:

$$e^{-\tau r(\nu)} \equiv \sum_\pi p_\pi^{\text{equilib.}} e^{\nu\gamma_\pi} \qquad = \int_{-\infty}^{\infty} p^{\text{eq.}}(\gamma)\, e^{\nu\gamma_\pi}\, \mathrm{d}\gamma$$

and a "flux-dependent free energy" $r(\gamma_0,\nu)$: [A rate funct$^{\underline{n}}$ in LDT]

$$e^{-\tau r(\nu,\gamma_0)} \equiv \sum_\pi \delta(\gamma_\pi - \gamma_0)\, p_\pi^{\text{equilib.}} e^{\nu\gamma_\pi} \quad = p^{\text{eq.}}(\gamma)\, e^{\nu\gamma_\pi}$$

Then $-\dfrac{\partial r}{\partial \nu} = \langle\gamma\rangle$ (like $-\partial F/\partial H = M$ for equilib. magnetism.)

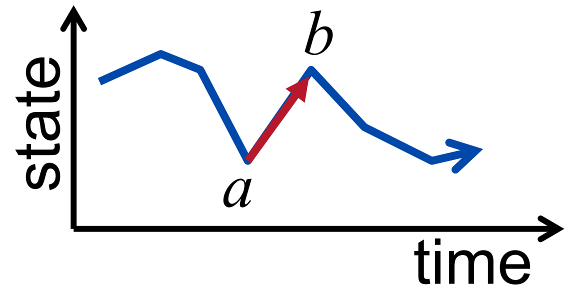
and $-\dfrac{\partial \tilde{r}(\gamma_0,\nu)}{\partial \gamma_0} = 0$ at $\gamma_0 = \langle\gamma\rangle$ i.e. Minimize $\tilde{r}$ w.r.t. flux (a **variational principle**).

Recall

Prob. of a path π: $p_\pi^{\text{driven}} \propto p_\pi^{\text{equilib}}\, e^{\nu\gamma_\pi}$

Find prob. of a transition $\Pr\left(a \to b \,\middle|\, a\right) \equiv \omega_{ab}\,\Delta t$

by counting all paths that contain the transition.



$$\omega_{ab}^{\text{dr}} = \omega_{ab}^{\text{eq}} \exp\left[\nu\,\gamma_{ab} + q_b - q_a - Q(\nu)\,\Delta t\right]$$

where $$Q(\nu) = \lim_{\tau\to\infty}\left\{\frac{1}{\tau}\ln\int_{-\infty}^{\infty} p_\tau^{\text{eq}}(\gamma)\,e^{\nu\gamma}\,\mathrm{d}\gamma\right\}$$

& $$q_a(\nu) = \lim_{\tau\to\infty}\left\{\tau Q(\nu) + \ln\int_{-\infty}^{\infty} p_\tau^{\text{eq}}(\gamma\,|\,a)\,e^{\nu\gamma}\,\mathrm{d}\gamma\right.$$

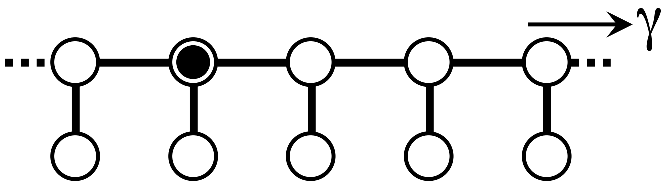
T Welsh: Leeds University Thesis 2012

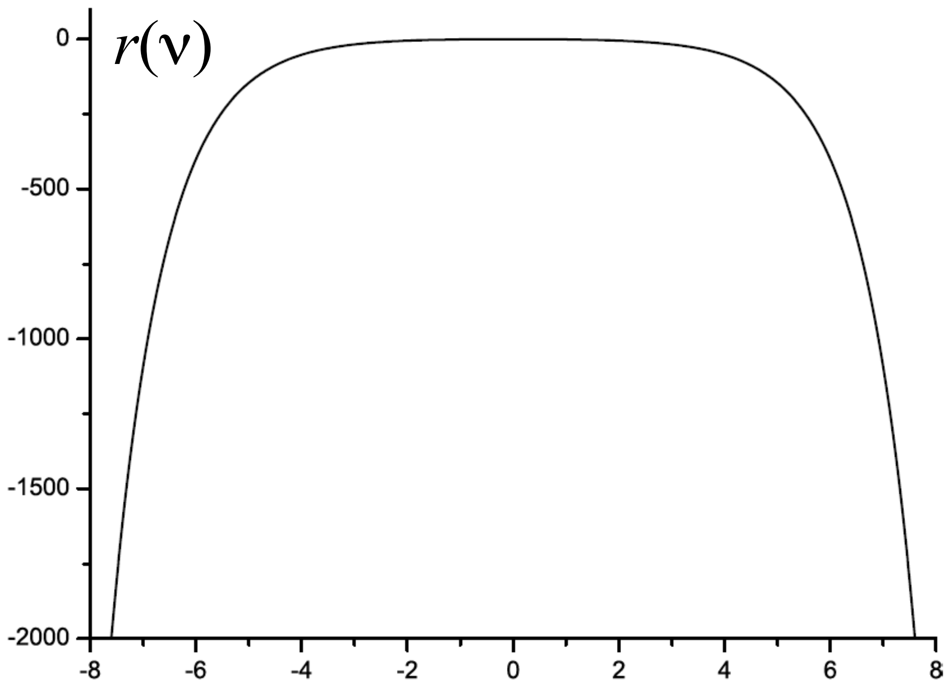
By a derivation too long to present here,

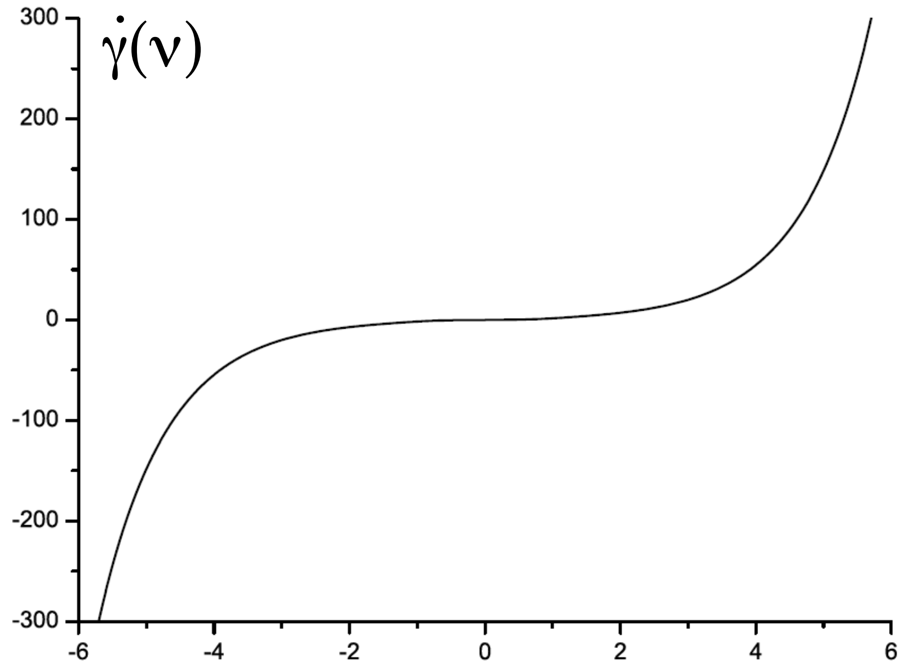
$r(\nu)$ = Most positive eigenvalue of the matrix

$$M_{ij} = \begin{cases} \omega_{ji}^{\text{eq}} \, e^{\nu \gamma_{ji}} & \text{if} \quad i \neq j \\ -\sum_j \omega_{ij}^{\text{eq}} & \text{if} \quad i = j \end{cases}$$

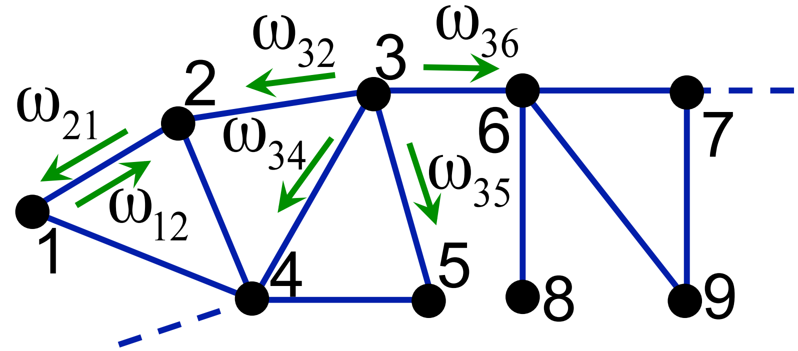
e.g. For **comb model**,







Obtain exact relationships for any state space:



(i) $$\omega_{ab}^{\mathrm{dr}}\omega_{ba}^{\mathrm{dr}} = \omega_{ab}^{\mathrm{eq}}\omega_{ba}^{\mathrm{eq}} \quad \forall\, a,b$$

(ii) Define total exit rate of state a: $\Sigma_a \equiv \sum_b \omega_{ab}$

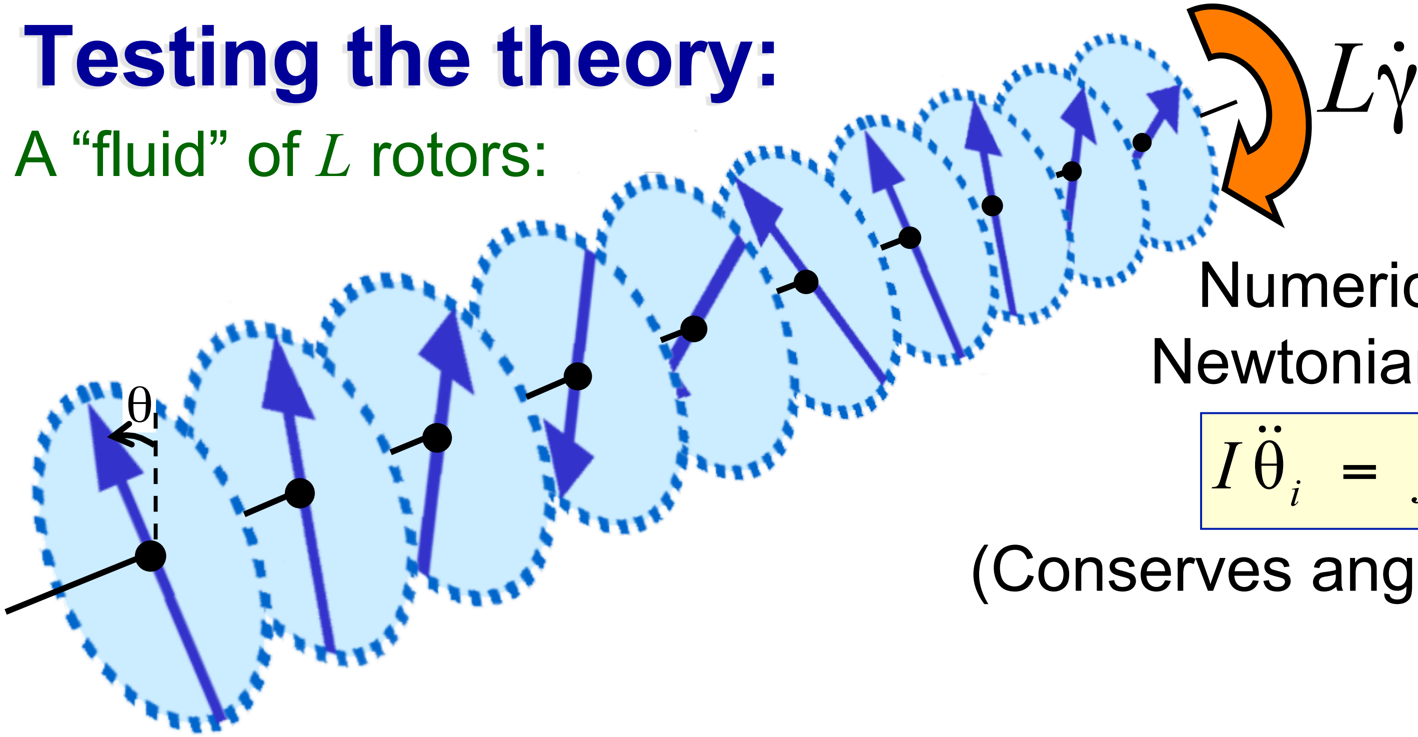
then

$$\Sigma_a^{\mathrm{dr}} - \Sigma_a^{\mathrm{eq}} = Q(\nu) \quad \forall\, a$$

Constant, independent of microstate a.

Testing the theory:

A "fluid" of L rotors:

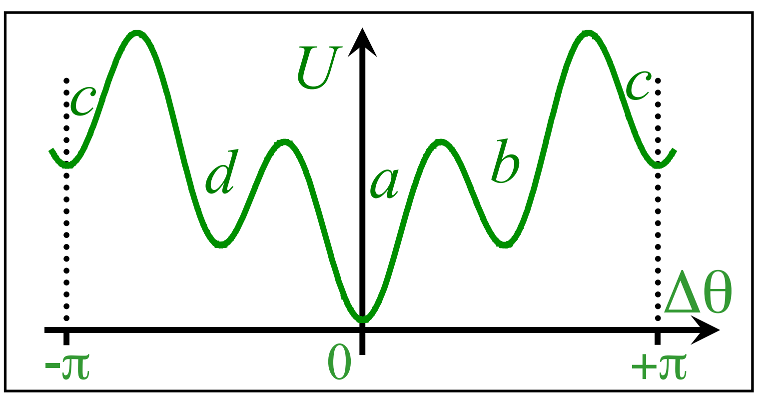


← Twist

Numerically time-step Newtonian eq^s^. of motion:

$$I\ddot{\theta}_i = f_{i+1,i} - f_{i,i-1}$$

(Conserves angular momentum)

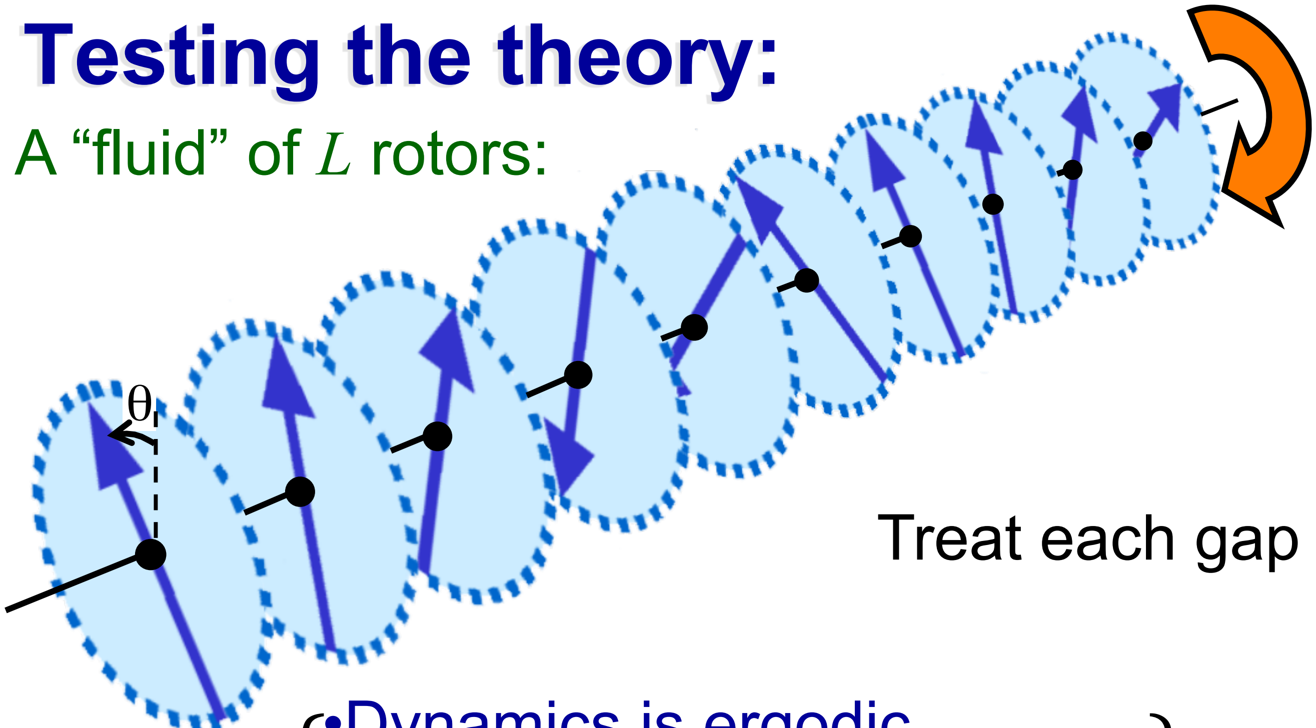


$$f_{ij} = U'(\theta_i - \theta_j)$$

$$U(x) = -\cos x - \cos 4x$$

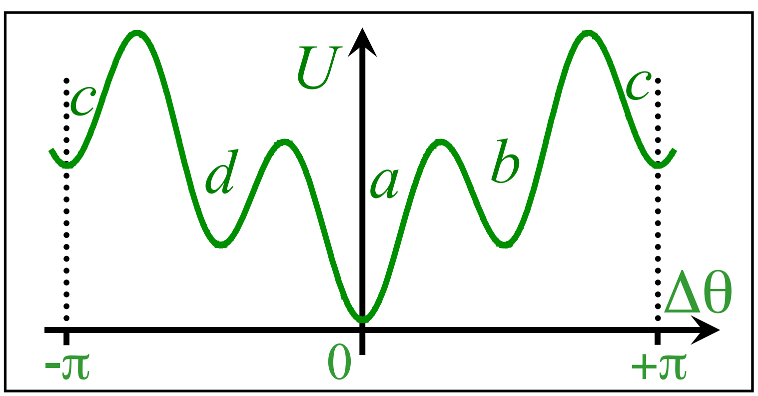
Testing the theory:

A “fluid” of L rotors:



Treat each gap ($\Delta\theta$) as “system”!

If : { •Dynamics is ergodic
•Potential wells = microstates
•Correlations are small
(not generally required) } ***then*** the theorem applies here.



Test 1: Total exit rate relation

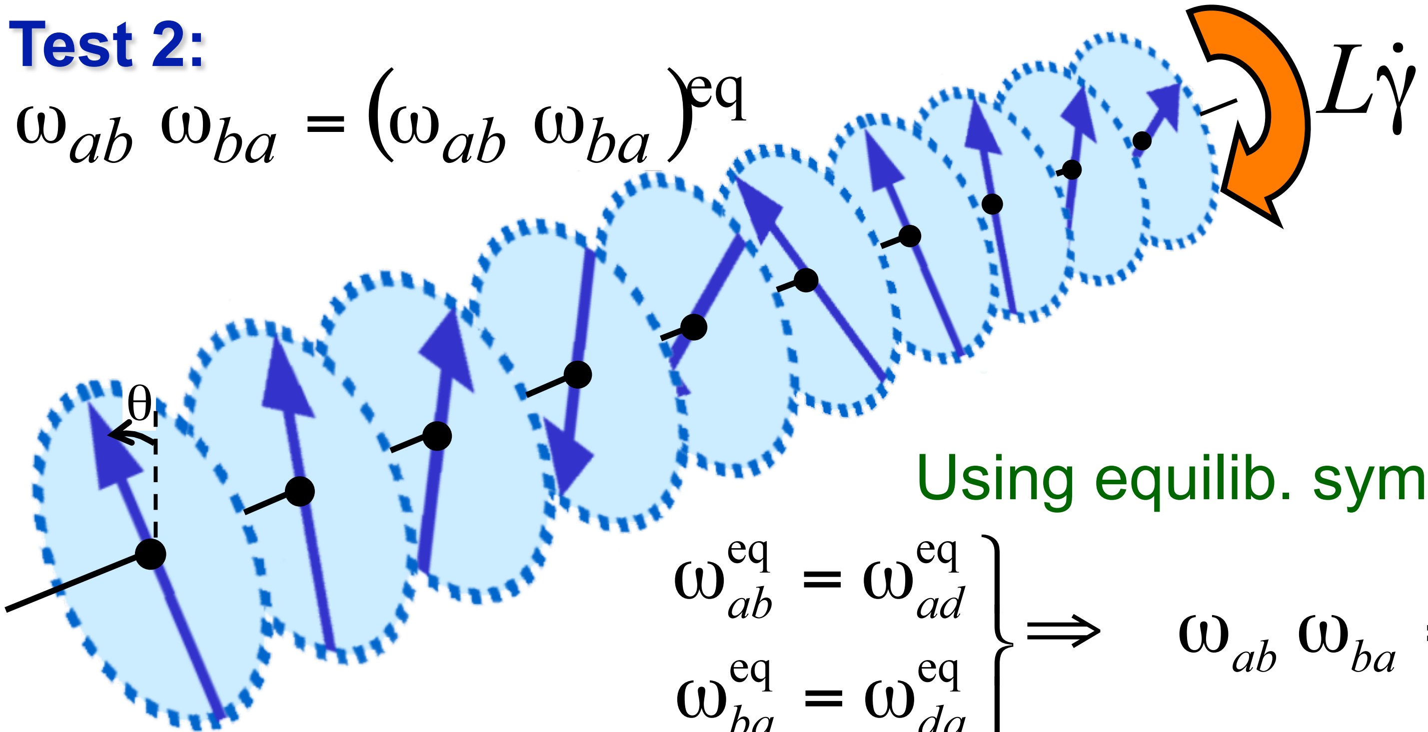
$$\Sigma_b^{\mathrm{dr}} - \Sigma_b^{\mathrm{eq}} = \Sigma_d^{\mathrm{dr}} - \Sigma_d^{\mathrm{eq}}$$

Equilib. symmetry: $\Sigma_b^{\mathrm{eq}} = \Sigma_d^{\mathrm{eq}}$

$$\Rightarrow \quad \omega_{ba} + \omega_{bc} = \omega_{da} + \omega_{dc}$$

Test 2:

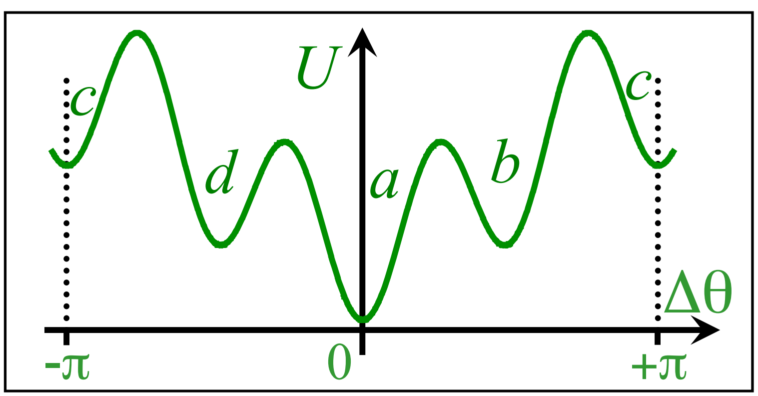
$$\omega_{ab}\,\omega_{ba} = \left(\omega_{ab}\,\omega_{ba}\right)^{eq}$$

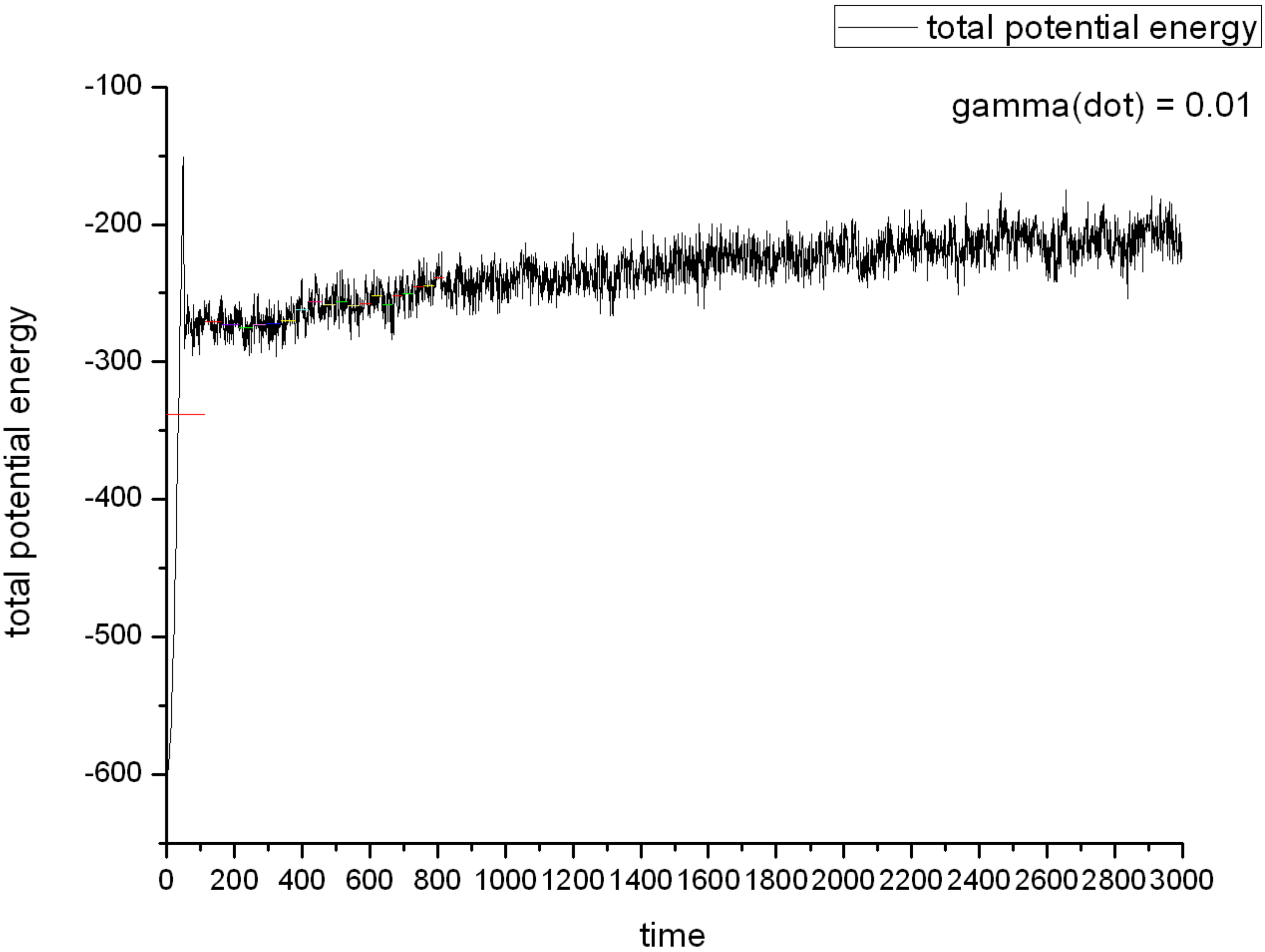


Using equilib. symmetries:

$$\left.\begin{array}{l}\omega_{ab}^{eq} = \omega_{ad}^{eq} \\ \omega_{ba}^{eq} = \omega_{da}^{eq}\end{array}\right\} \Rightarrow \quad \omega_{ab}\,\omega_{ba} = \omega_{ad}\,\omega_{da} \quad \forall\,\dot{\gamma}$$

& similarly for *cb* & *cd*.

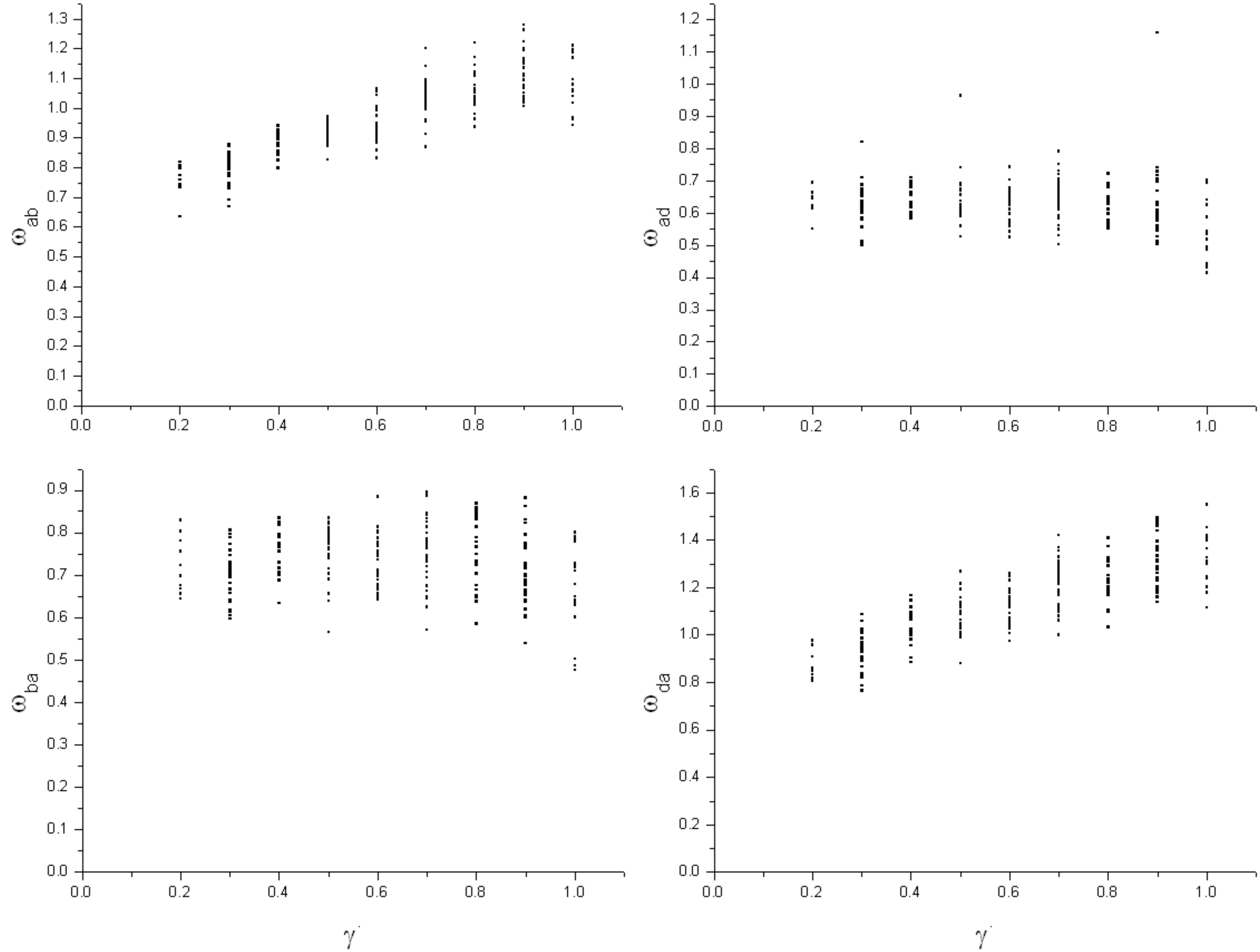




total potential energy
gamma(dot) = 0.01
-100
-200
-300
-400
-500
-600
total potential energy
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
time

Transition rates between 4 potential wells a,b,c,d.

Mean potential energy per rotor during measurement lies in the interval (-0.120,-0.117).



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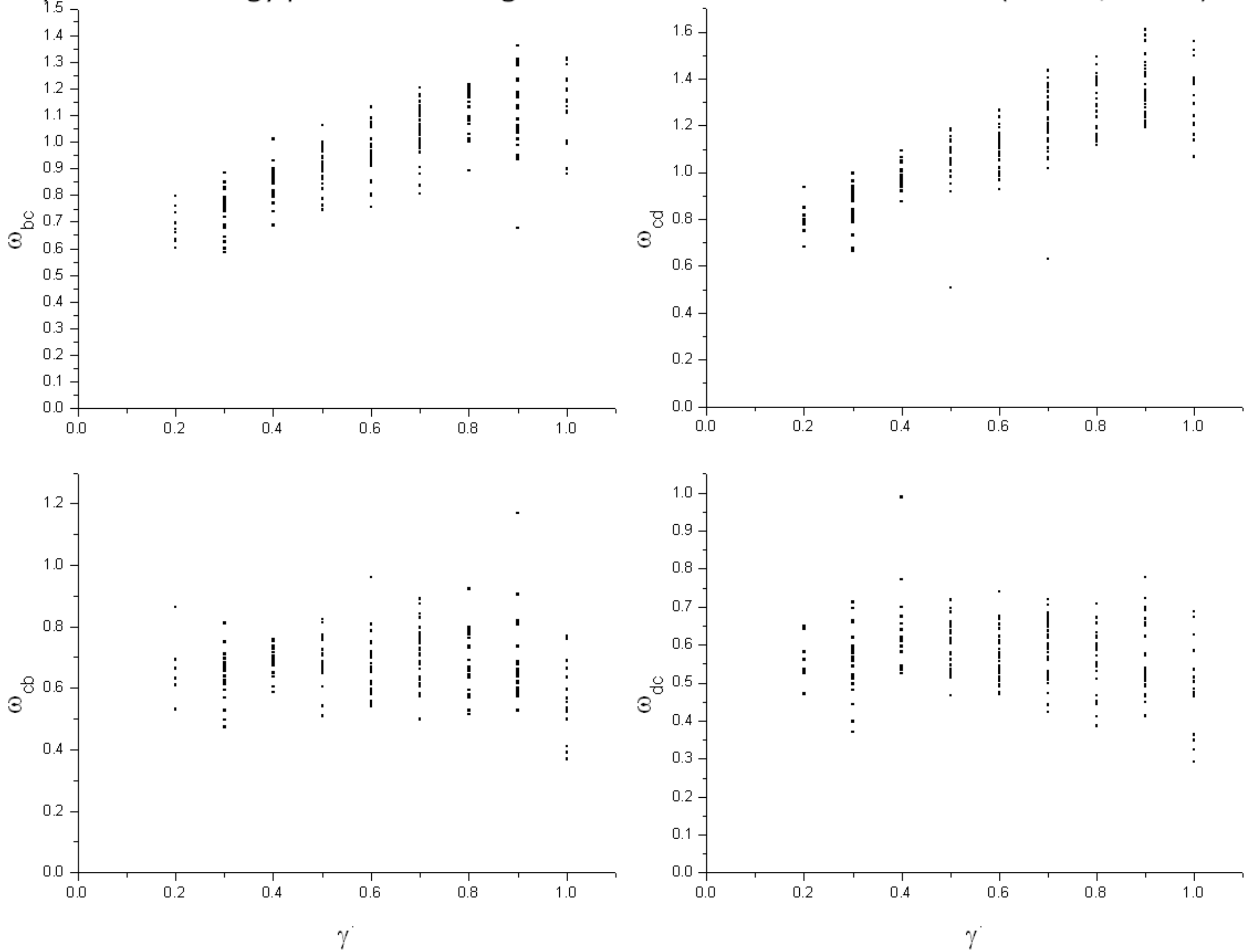
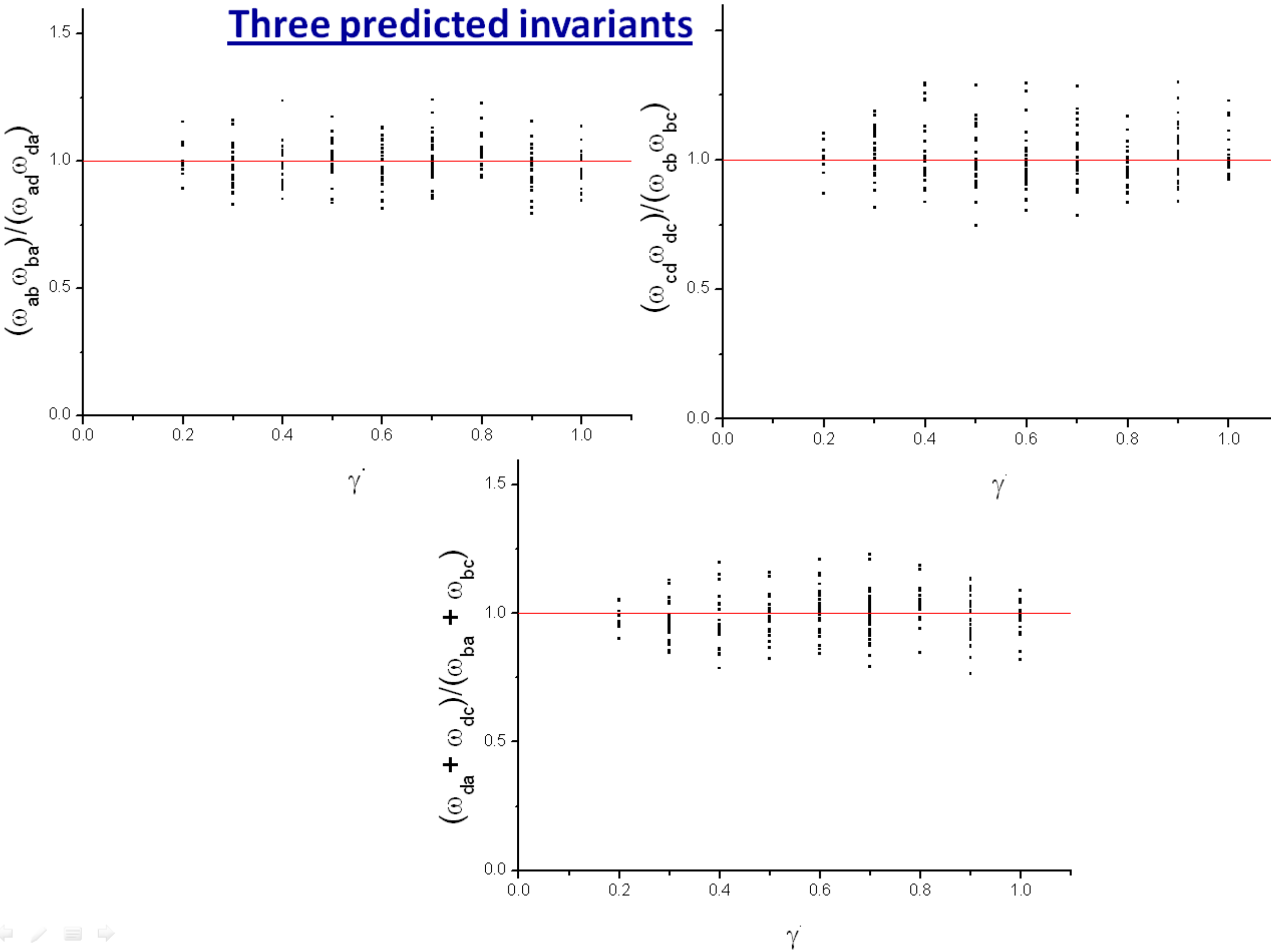


Three predicted invariants



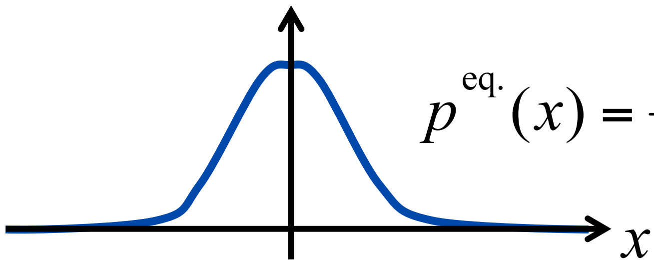
Conclusions

- Non-equilibrium ensemble of trajectories is justified for shear flux.
- Data on quasi-steady state of frictionless rotor model are consistent with predicted non-equilibrium invariants.

References

- Statistical mechanics of boundary driven systems
  T Welsh thesis, University of Leeds 2012.
- Invariant quantities in shear flow
  A Baule & R M L Evans, Phys. Rev. Lett. 101, 240601 (2008).
- Statistical mechanics far from equilibrium
  R M L Evans, R A Simha, A Baule, P D Olmsted,
  Phys. Rev. E 81, 051109 (2010).
- Properties of a nonequilibrium heat bath
  A Simha, R M L Evans, A Baule, Phys. Rev. E 77, 031117 (2008).

Test case: 1-dimensional random walk



$$p^{\text{eq.}}(x) = \frac{1}{\sqrt{4\pi D\tau}} \exp\left(\frac{-x^2}{4D\tau} \right)$$ & define $J \equiv x/\tau$.

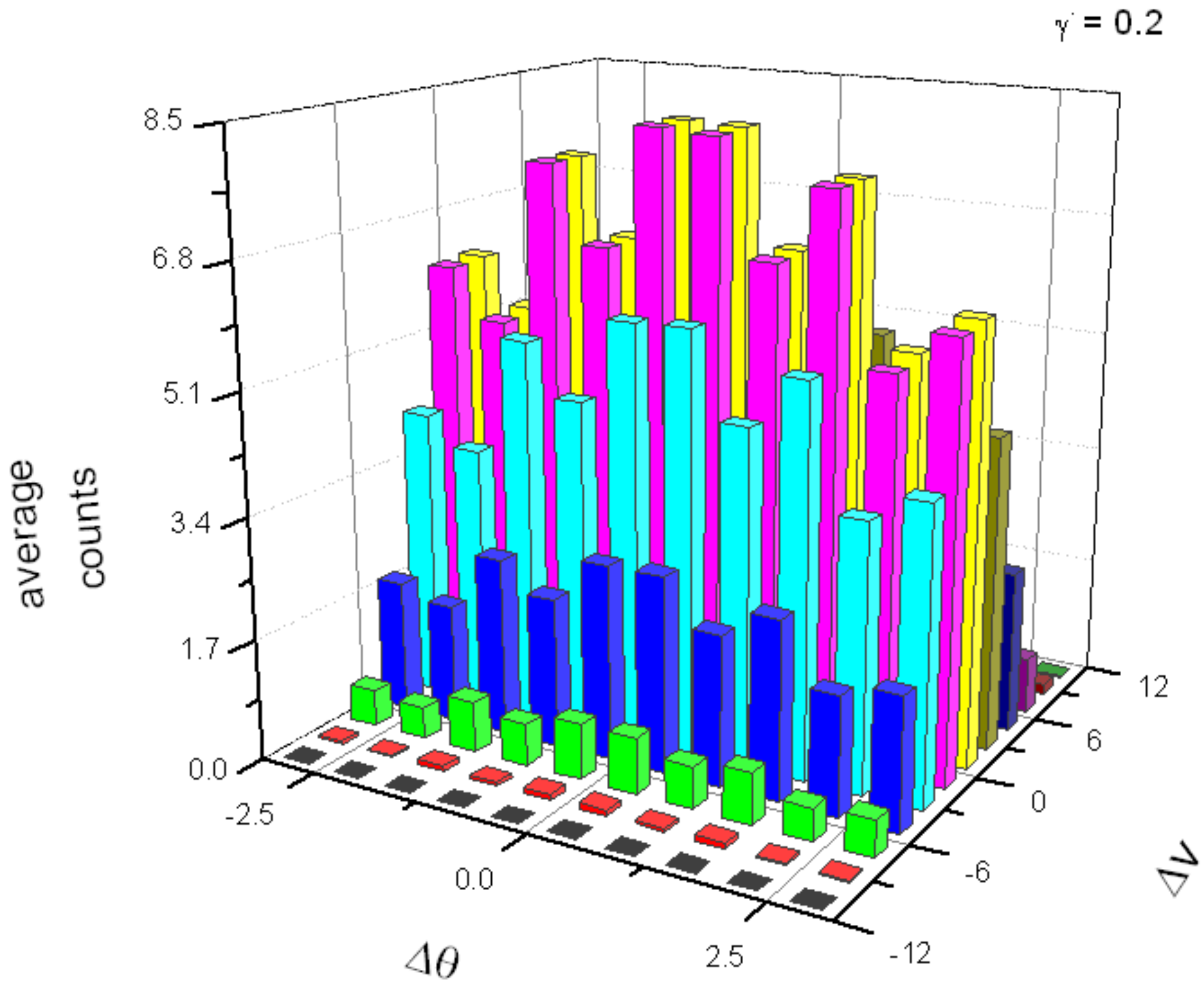
Can evaluate the “free energy” functions in this case:

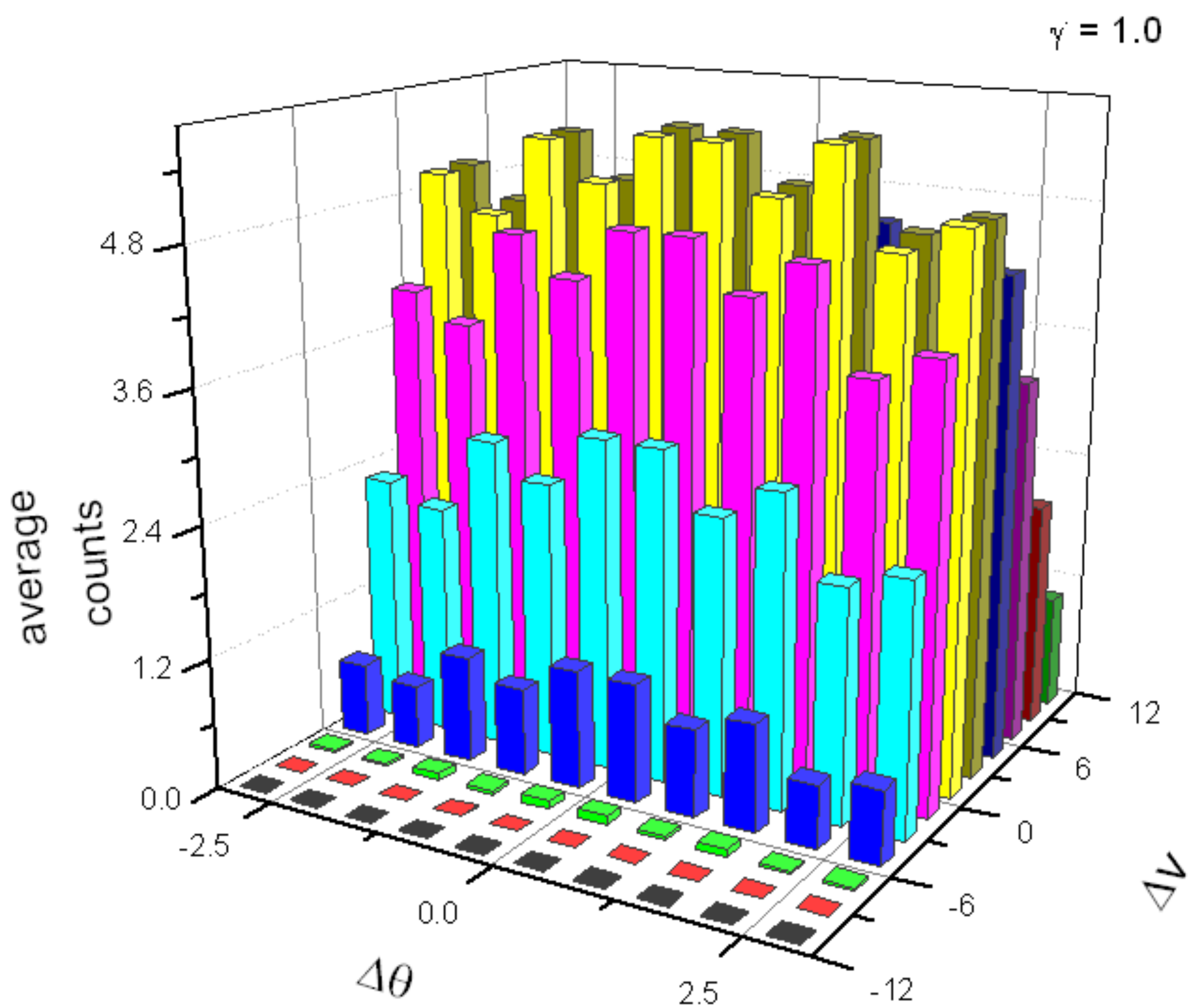
(i) $r(\nu) = -D\nu^2$ giving mean flux $\langle J \rangle = -\dfrac{\partial r}{\partial \nu} = 2D\nu.$

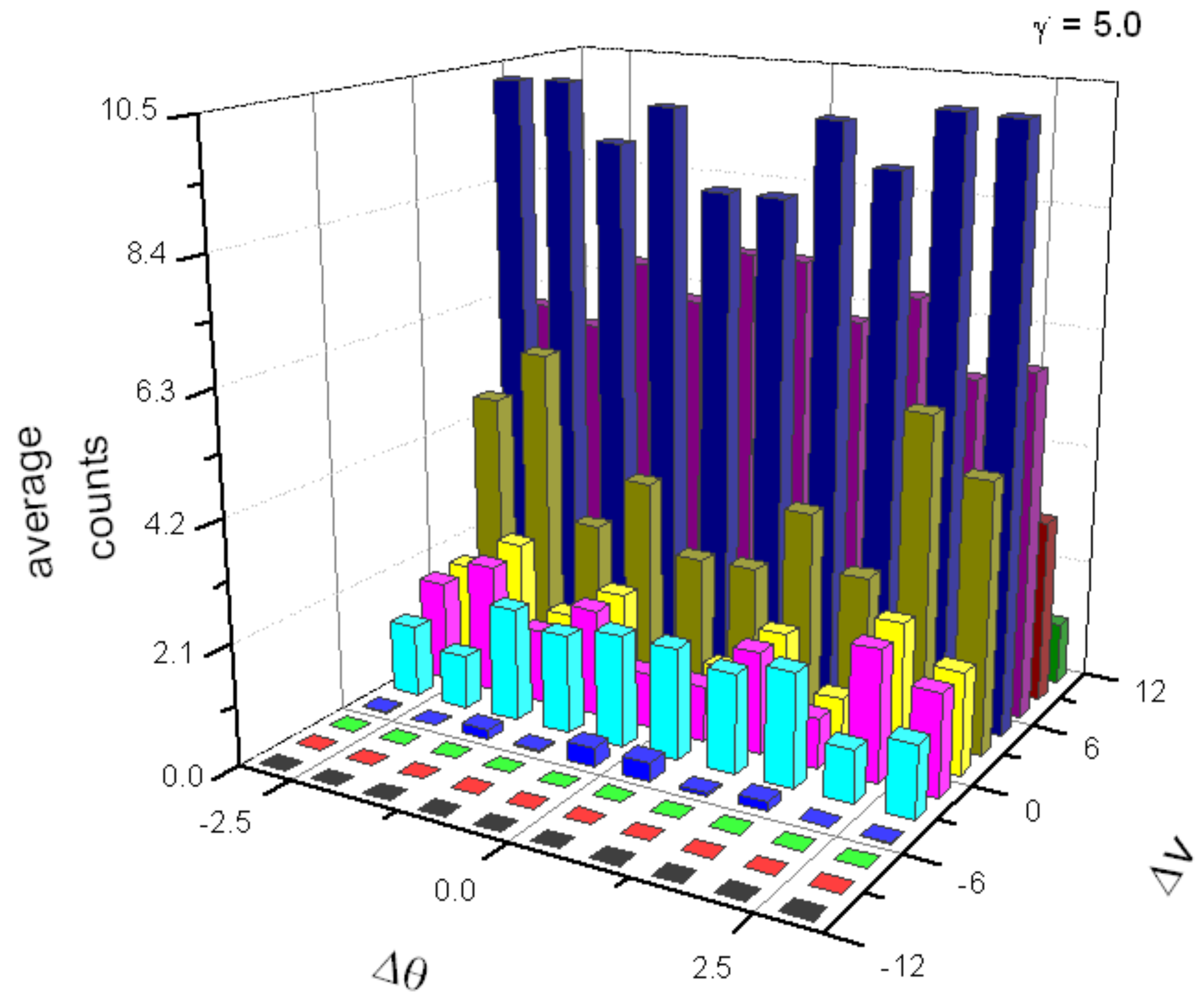
(We expect $\langle J \rangle = \dfrac{\text{Force}}{2k_B T} \times D$ $\Rightarrow$ Interpret $\boxed{\nu = \dfrac{\text{Driving Force}}{2k_B T}}$)

(ii) $\tilde{r}(J_0, \nu) = \dfrac{J_0^2}{4D} - \nu J_0$ (A “rate function” of Large Deviation Theory)

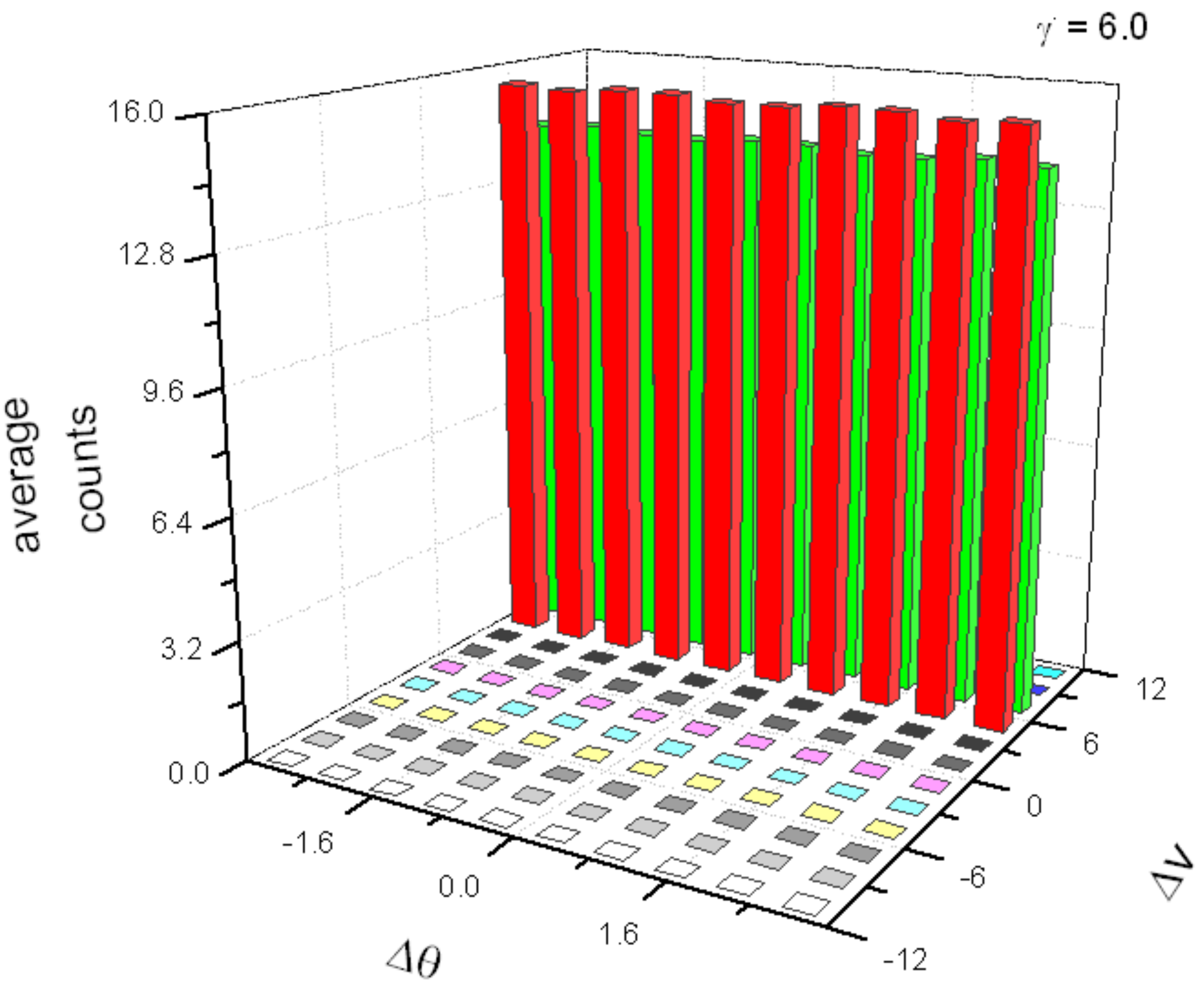
Test variational principle: minimizing w.r.t. flux $\Rightarrow$ $J_0 = 2D\nu$ ✓


γ' = 0.2
8.5
6.8
5.1
3.4
1.7
0.0
average counts
-2.5
0.0
2.5
Δθ
12
6
0
-6
-12
Δν


γ = 1.0
average
counts
4.8
3.6
2.4
1.2
0.0
-2.5
0.0
2.5
Δθ
12
6
0
-6
-12
Δν



γ = 5.0
average counts
10.5
8.4
6.3
4.2
2.1
0.0
-2.5
0.0
2.5
Δθ
12
6
0
-6
-12
Δν


γ = 6.0
16.0
12.8
9.6
6.4
3.2
0.0
average counts
-1.6
0.0
1.6
Δθ
12
6
0
-6
-12
Δv