Spatio-temporal patterns in ultra-thin polymeric films

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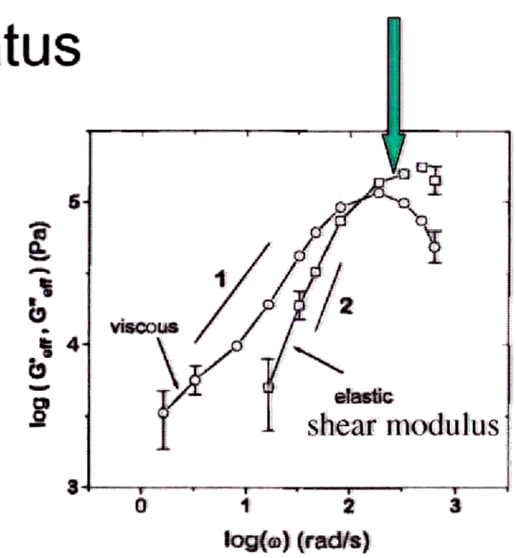
Patterns in simulations of approx. 1.5 nanometer thin polymer films under oscillatory shear with shear amplitude of about 1.5 nm.

Experimental

Surface Forces Apparatus

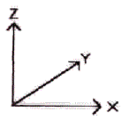
- flexible elastic state of matter (solidlike)
- slow kinetics (training)
- memory of previous deformations (minutes)

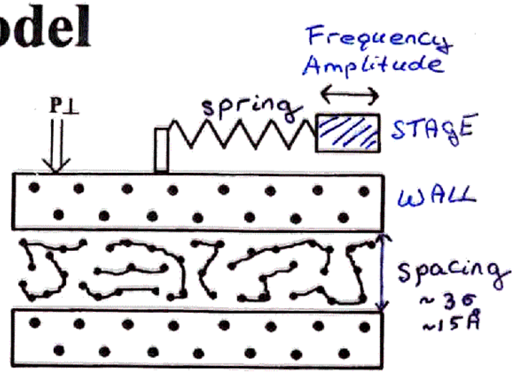
- “transition” to this state
-decrease thickness
-increase frequency



Dhinojwala/ Granick (1996)

Model





periodic BC's
in x-y plane

Bead-Spring Model (n = 6)

Fluid:

- Lennard Jones: $4\epsilon\left((\sigma/r)^{12} - (\sigma/r)^{6}\right)$ $r < r_c = 2.2\ \sigma$

  $\sigma \sim 0.5$ nm $\epsilon \sim 30$meV $\tau \equiv \sqrt{(m\sigma^2/\epsilon)} \sim 5$ ns
- Strong attractive FENE potential between connected beads

Fluid-wall: Lennard Jones: $\sigma^{wf} = 0.9\sigma$

$\epsilon^{wf} = 3\epsilon$

Wall: fcc(1,1,1) lattice

Temperature control (NPT)

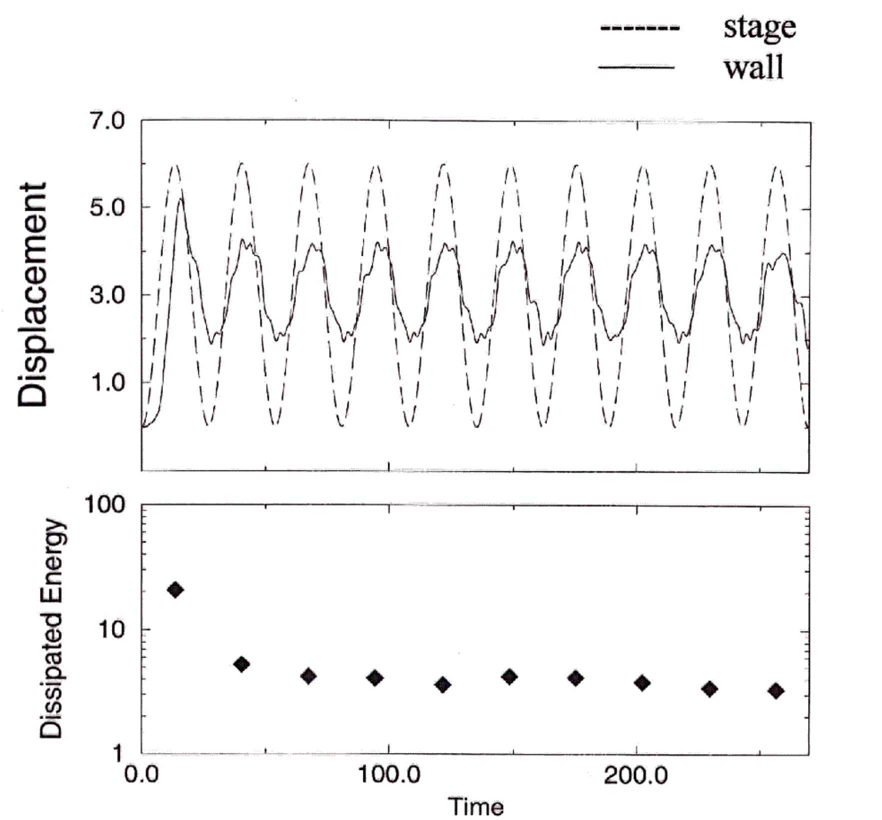
Frequency = 0.037 $1/\tau$

Temperature = 1.1 ϵ/k_B

$P_\perp = 6\ \epsilon/\sigma^3$

molecular
dynamics

Dynamics of Flexible Elastic State

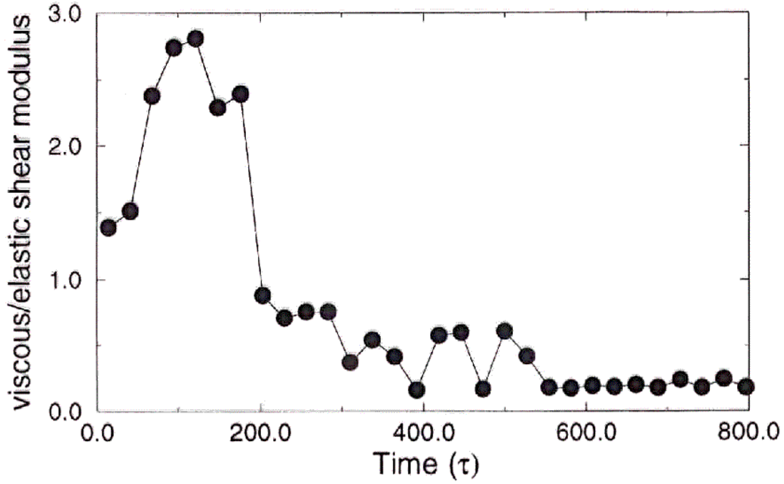


- fast relaxation ➡ slow relaxation
- decrease in energy dissipated in each cycle
- compaction
- viscous/elastic shear modulus approx. 1/3

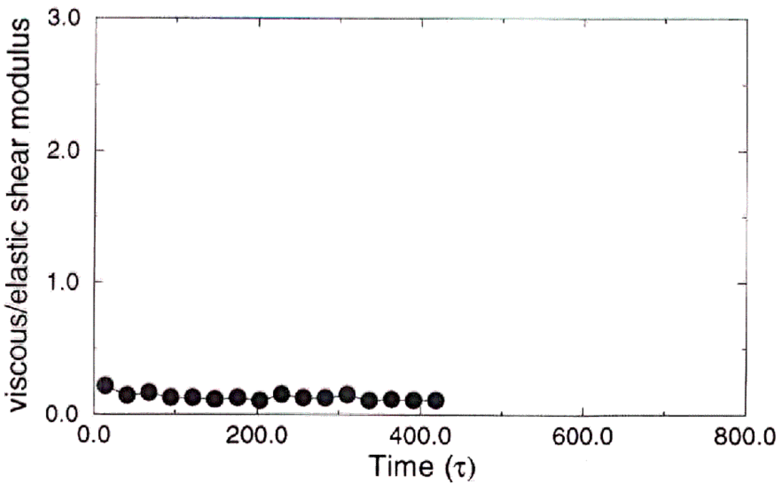
History Dependence

wall spacing = 2.8 σ
amplitude = 1 σ

strain = 0.357

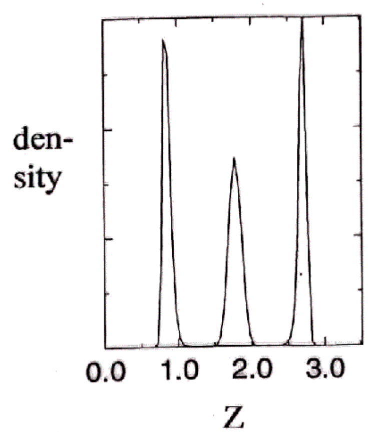


wait 2000 t



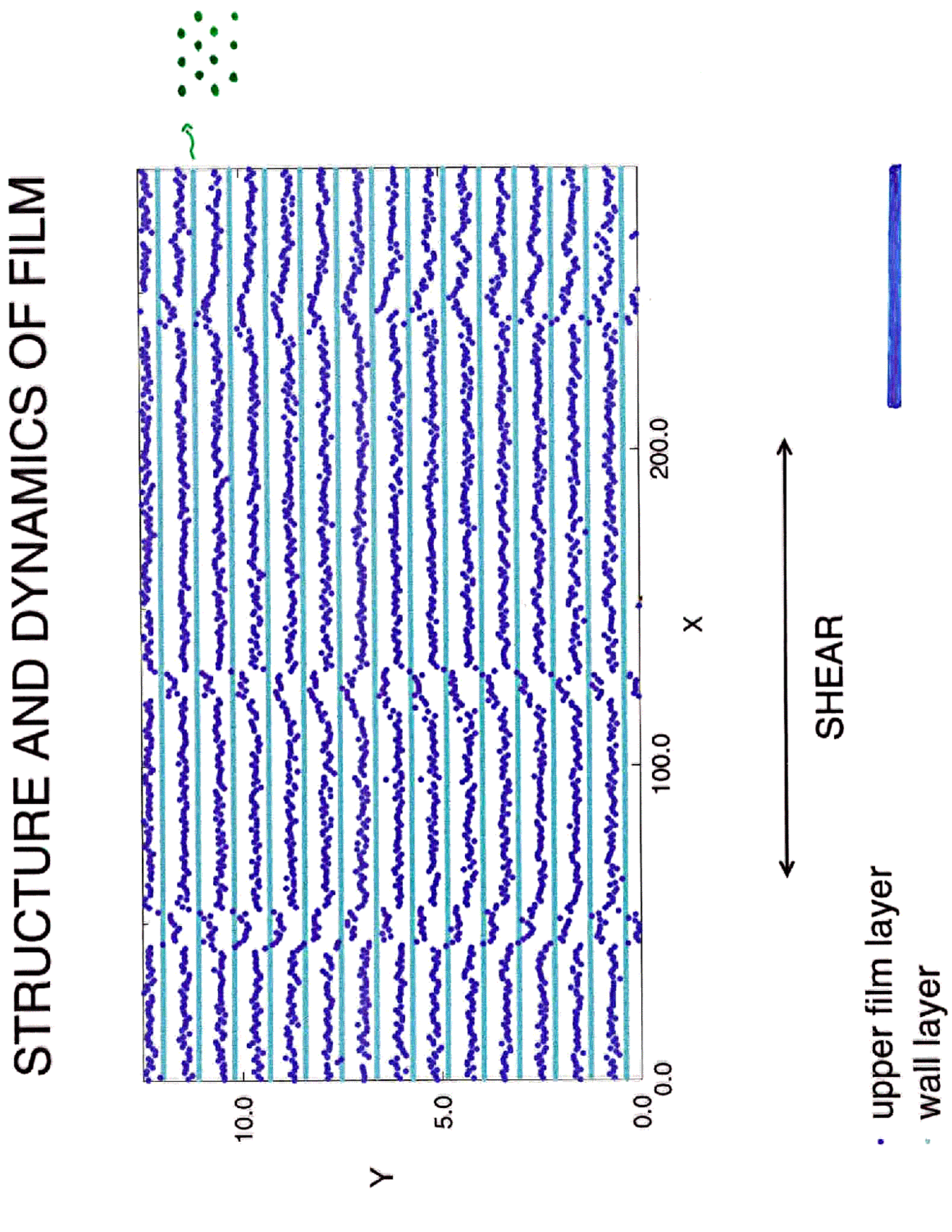
Spatio-temporal Dynamics
Patterns

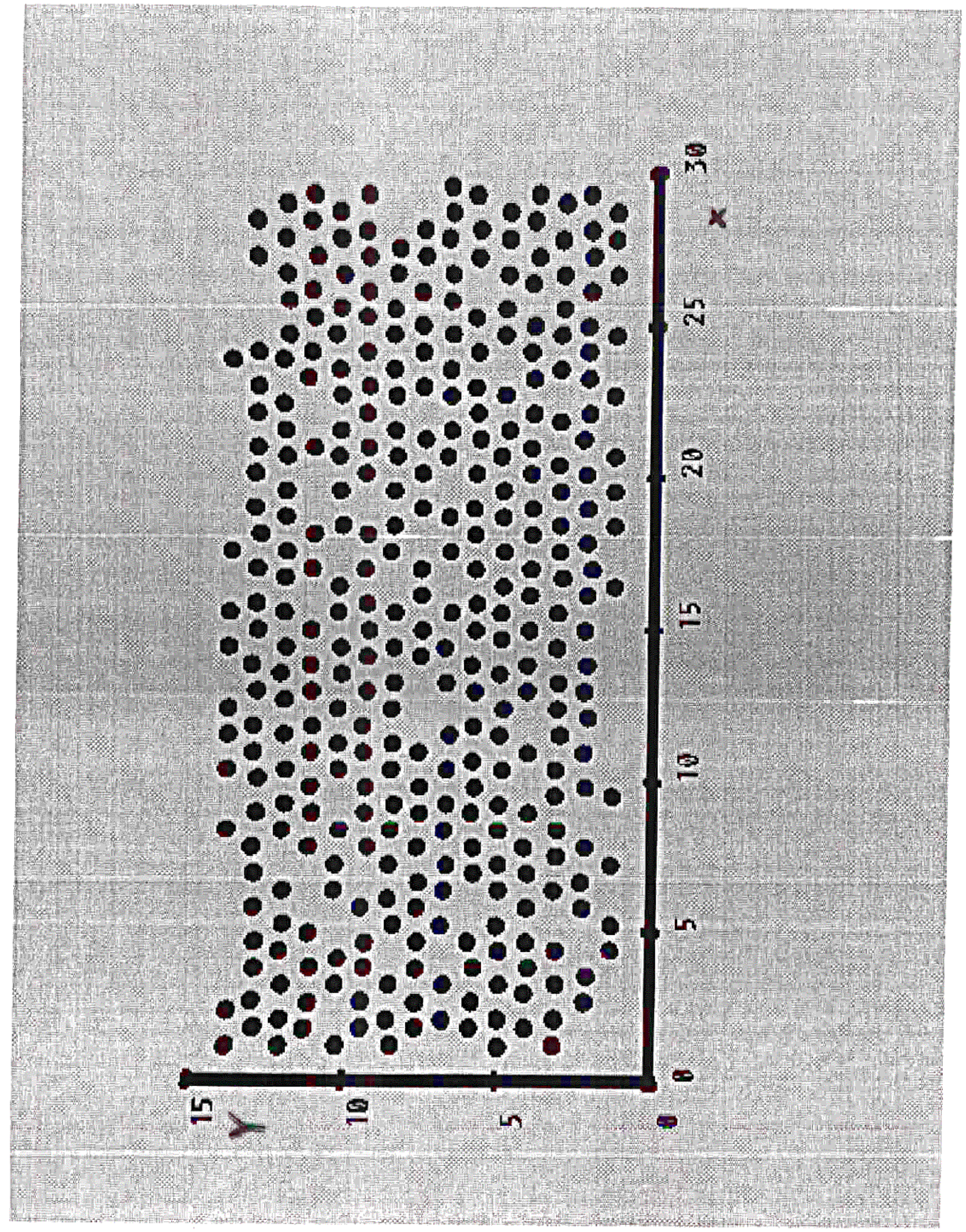
"movie"
motion of upper layer of film

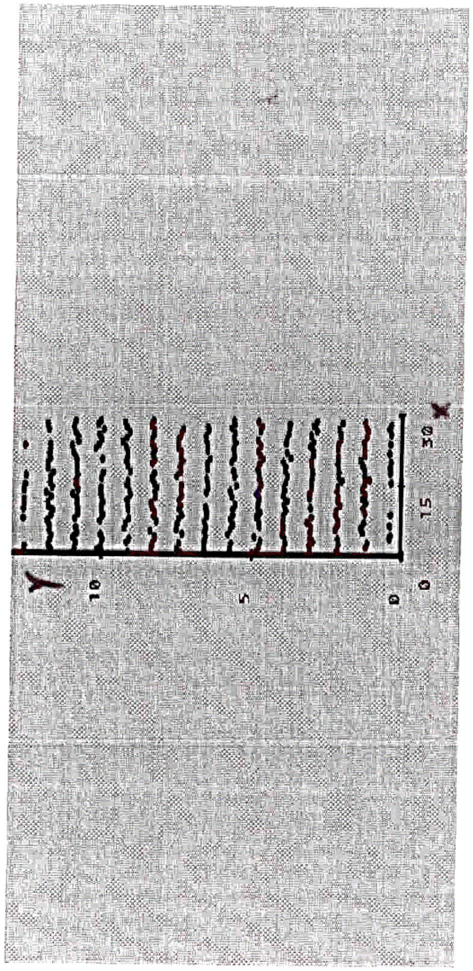


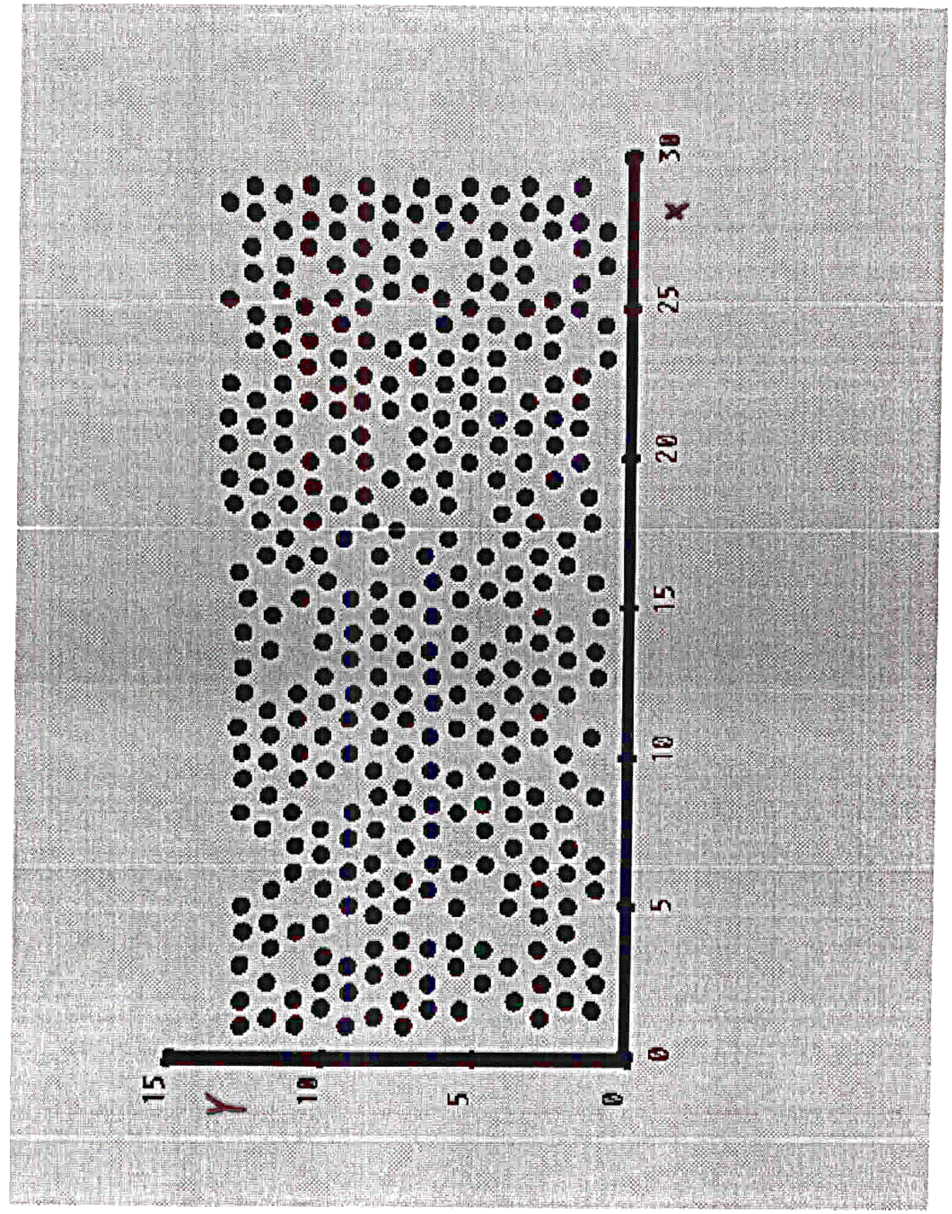
density profile

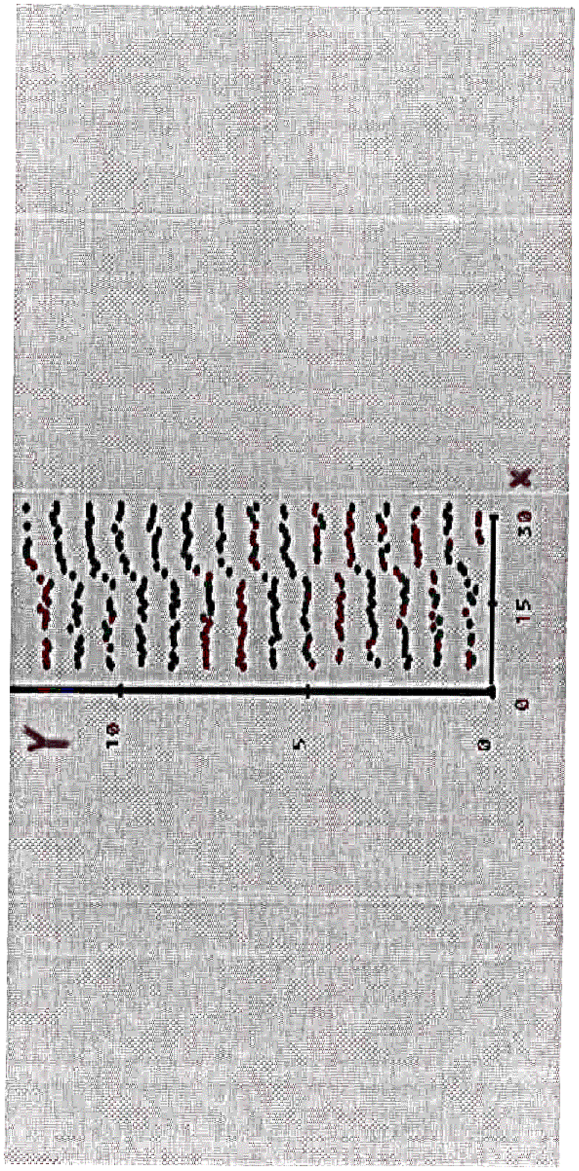
only the monomers are shown
not the bonds


STRUCTURE AND DYNAMICS OF FILM
Y
X
10.0
5.0
0.0
100.0
200.0
SHEAR
upper film layer
wall layer

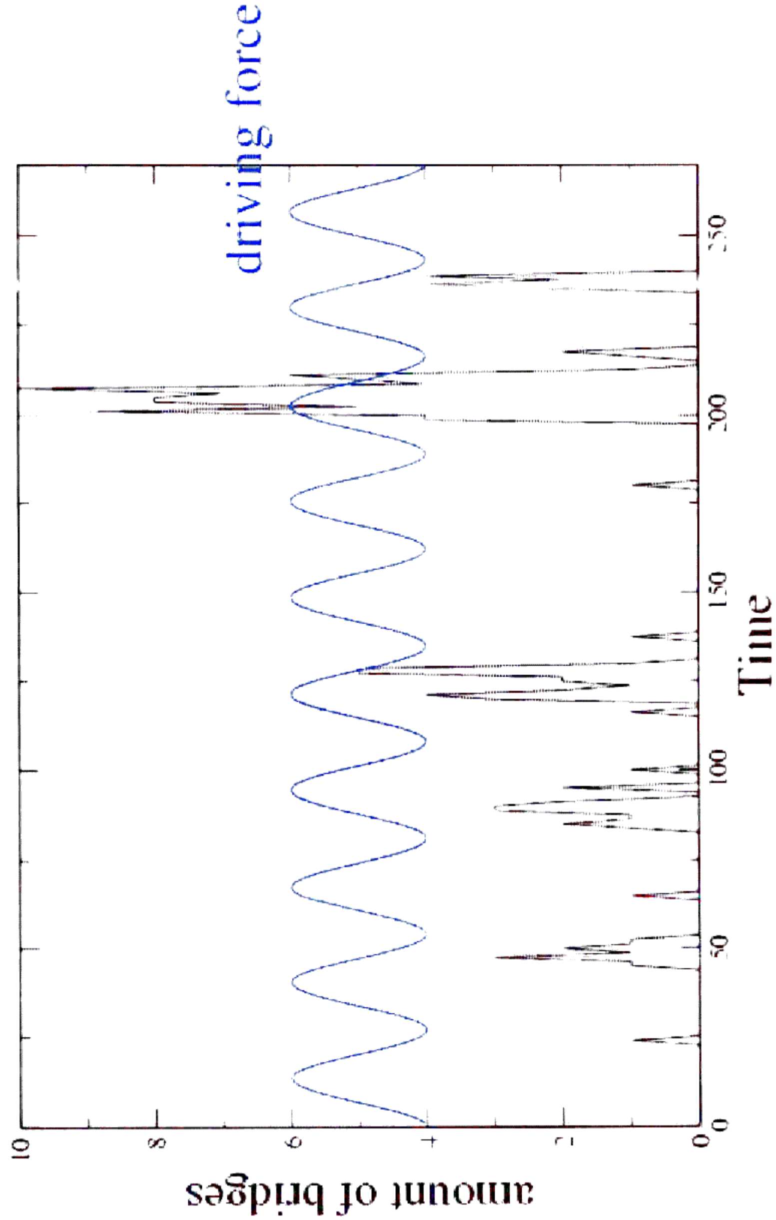

Y
X
0
5
10
15
20
25
30


Y
10
5
0
15
30
X


15
Y
10
5
0
0
5
10
15
20
25
30
X


Y
X
10
5
0
0
15
30

Rhythm?


driving force
amount of bridges
Time
0
50
100
150
200
250
10
8
6
4
2
0

Conclusions

- Simulated films under oscillatory shear ($T = 27\ \tau$, $A = 3\ \sigma$).
- Flexible elastic state
  - slow kinetics
  - memory
  - spatio-temporal pattern
- Structure at the mesoscopic length scale involving several molecules
- Crystalline domains form and move elastically
- Dissipation occurs at their boundaries
- The size of these crystalline domains grows over time (slow kinetics)
- Crystalline domains stay when shear stops (memory)
- Pattern at the boundary fluctuates (spatio-temporal pattern) periodicity close to 38 τ

Solidlike thin films → Biological hydrogels