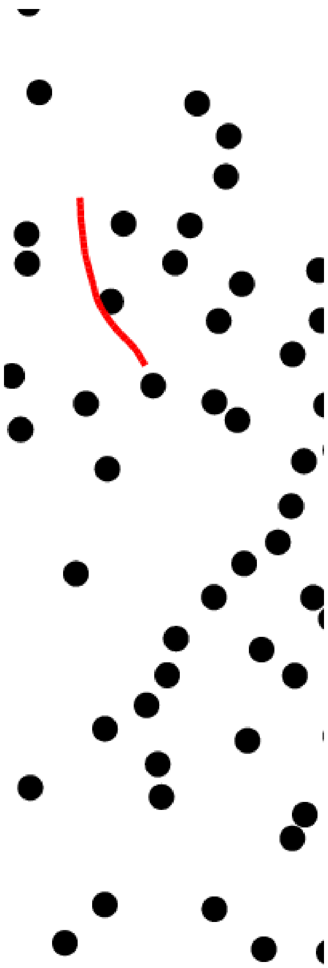
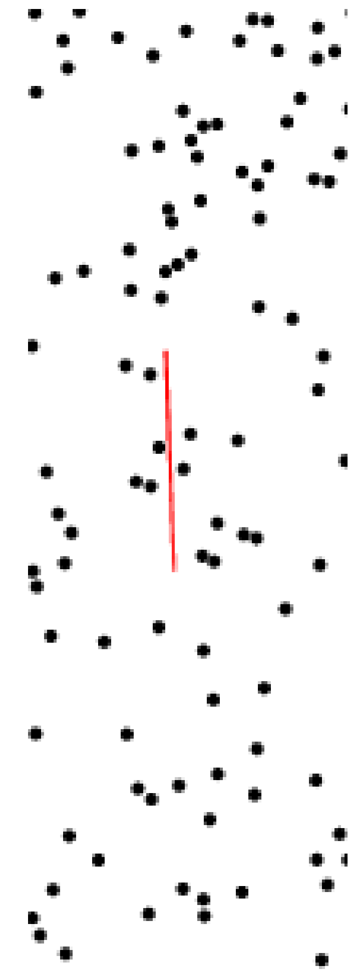


Nonmonotonic size dependence of the electrophoretic mobility of stiff and slightly flexible rods in random arrays of obstacles



Mykyta V. Chubynsky

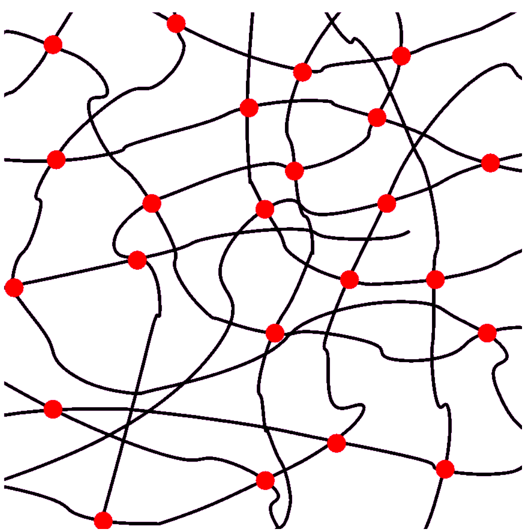
Gary W. Slater

Department of Physics, University of Ottawa, Canada

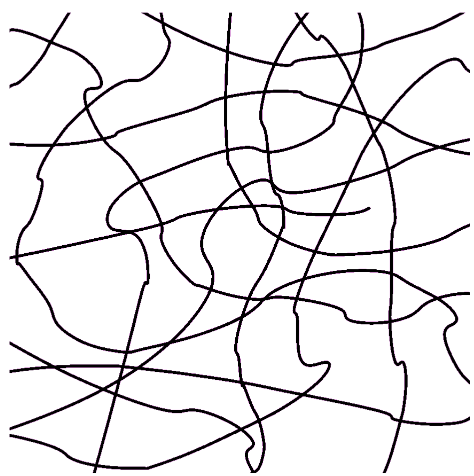
Electrophoresis is motion of charged particles in a fluid in electric field.

Electrophoresis is used to separate particles and molecules (i.e., DNA separation by length). However, for elongated objects with a constant linear charge density (e.g., polyelectrolytes like DNA), mobility is independent of length *N*.

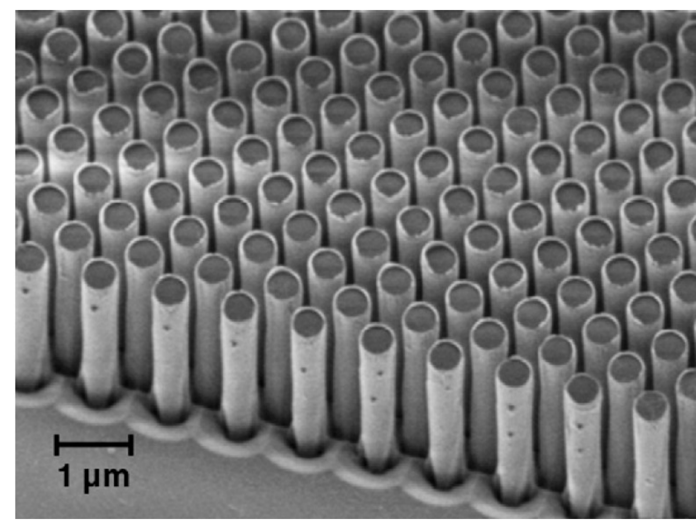
DNA cannot be separated in free solution; need a nanostructured medium, e.g.:



Gels



Entangled polymer solutions



R. Ogawa *et al.*, Thin Solid Films 515 (2007) 5167

Microfabricated 2D arrays

Theories of electrophoresis in nanoporous media

Rigid particles in weak field (close to equilibrium): Ogston theory. Also applicable to flexible polymers with R_g ~ (pore size), since the coil remains undeformed (Ogston, 1958; Rodbard & Chrambach, 1970)

Flexible and semiflexible polymers in weak and moderate fields (equilibrium at least on the scale of a single pore): reptation theory (Lumpkin, Déjardin, Zimm, 1985; Slater, Noolandi, 1985; Semenov, Duke, Viovy, 1995).

Flexible polymers in a strong field: "geometration" (Deutsch, 1988; Patel & Shaqfeh, 2003; Mohan & Doyle, 2007; ...)

The case of rigid particles in a strong field has not been studied as much.

Subject of this work: electrophoresis of rigid and slightly flexible rods in a nanoporous medium modeled as a sparse array of obstacles. Use both simulations and theory.

Some previous simulations of electrophoresis of rods, but either specifically limited to weak fields (Allison *et al.*, 2002), or concentrating on dependence on the shape of the particles, rather than the size (Wheeler and Chrambach, 1995).

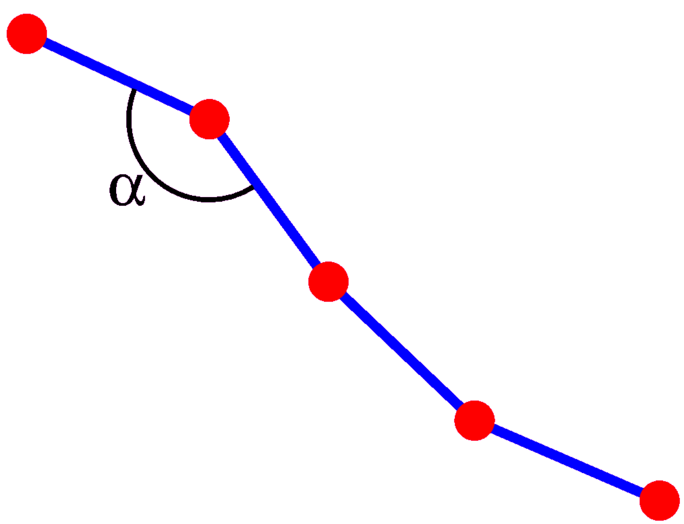
Model

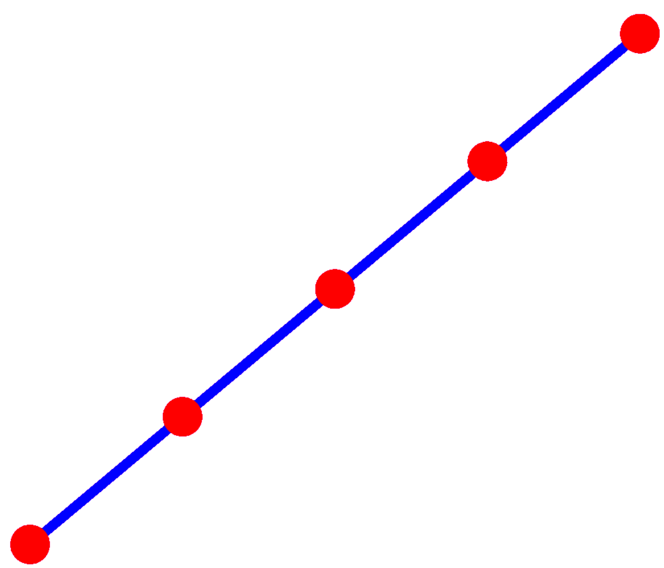
Brownian Dynamics simulations of a perfectly stiff rod or a semiflexible polymer in an array of obstacles.

Details:

1. 2D. Dimensionality less important than for flexible polymers; microfabricated arrays are 2D.

2. The polymer is a bead-stick chain. Consists of N beads, distances between neighbouring beads are strictly fixed. Two variants: with angular forces (semiflexible rods) and with angles strictly fixed at 180° (perfectly stiff rods).





$$U = A\cos\alpha$$

Details of the model (cont'd):

3. No non-bonded bead-bead interactions (excluded volume, electrostatic, etc.)

Makes sense for nearly stiff or perfectly stiff rods.

4. Bead-obstacle interaction is repulsive Lennard-Jones:

$$U = U_0 \left[\left(\frac{d}{r} \right)^{12} - 2 \left(\frac{d}{r} \right)^{6} + 1 \right], r < d \, ; 0 \, \text{otherwise}$$

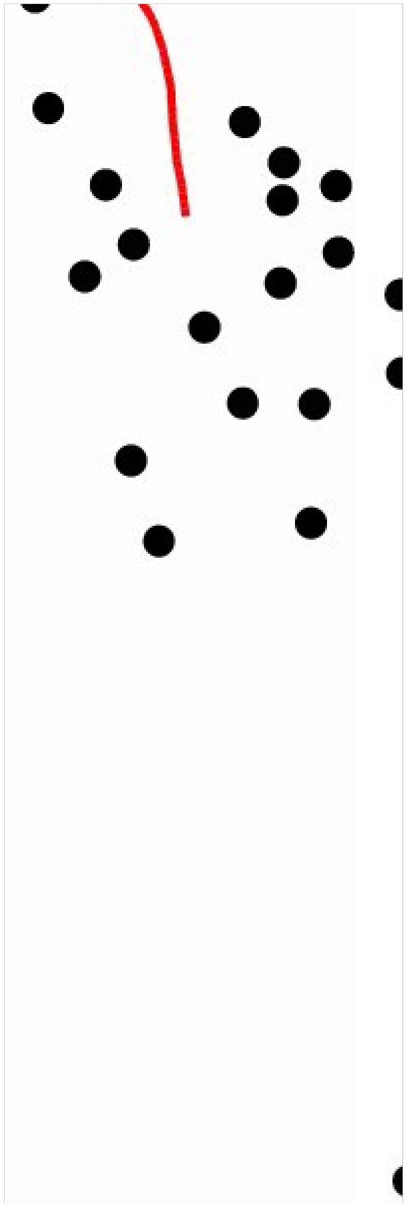
5. Friction force $-\xi \vec{v}$ acts on each bead. Free draining approximation.

6. Electric field assumed uniform – same force on all beads

7. Brownian noise.

8. Overdamped equations of motion.

Details of the model (cont'd):



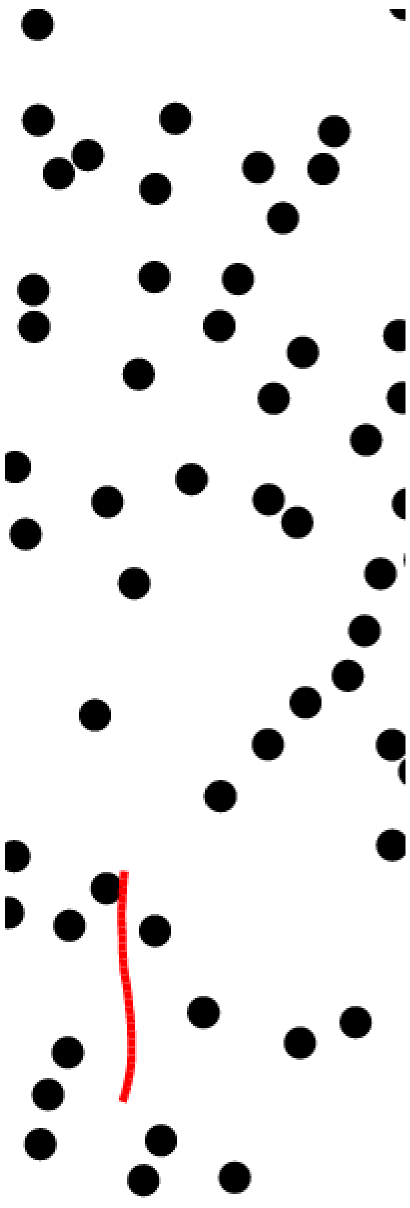
Obstacles are generated on the fly

N = 30 in this example

Random placement of obstacles (as in a gel), rather than an ordered array (as in a microfabricated device)

Periodic boundary conditions orthogonal to the field

Details of the model (cont'd):



Obstacles are generated on the fly

N = 30 in this example

Random placement of obstacles (as in a gel), rather than an ordered array (as in a microfabricated device)

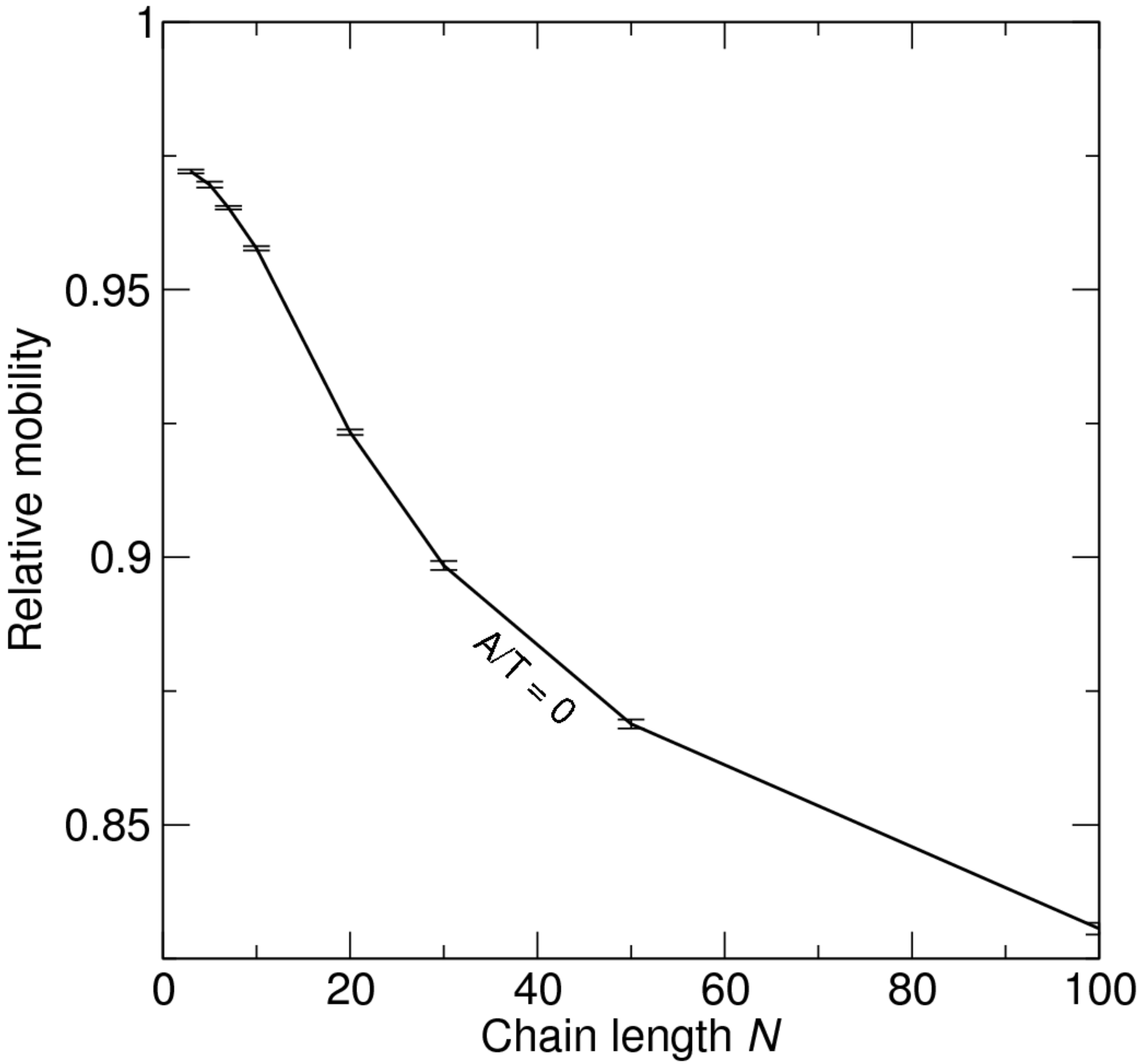
Periodic boundary conditions orthogonal to the field

Mobility $\mu = \langle v \rangle / E$

Plot the relative mobility μ/μ_0

Free solution mobility μ_0 is independent of both the field and the chain length.

Mobility for flexible and semiflexible chains



Flexible

Angular potential

$$U = A\cos\alpha$$

Bond length l = 1

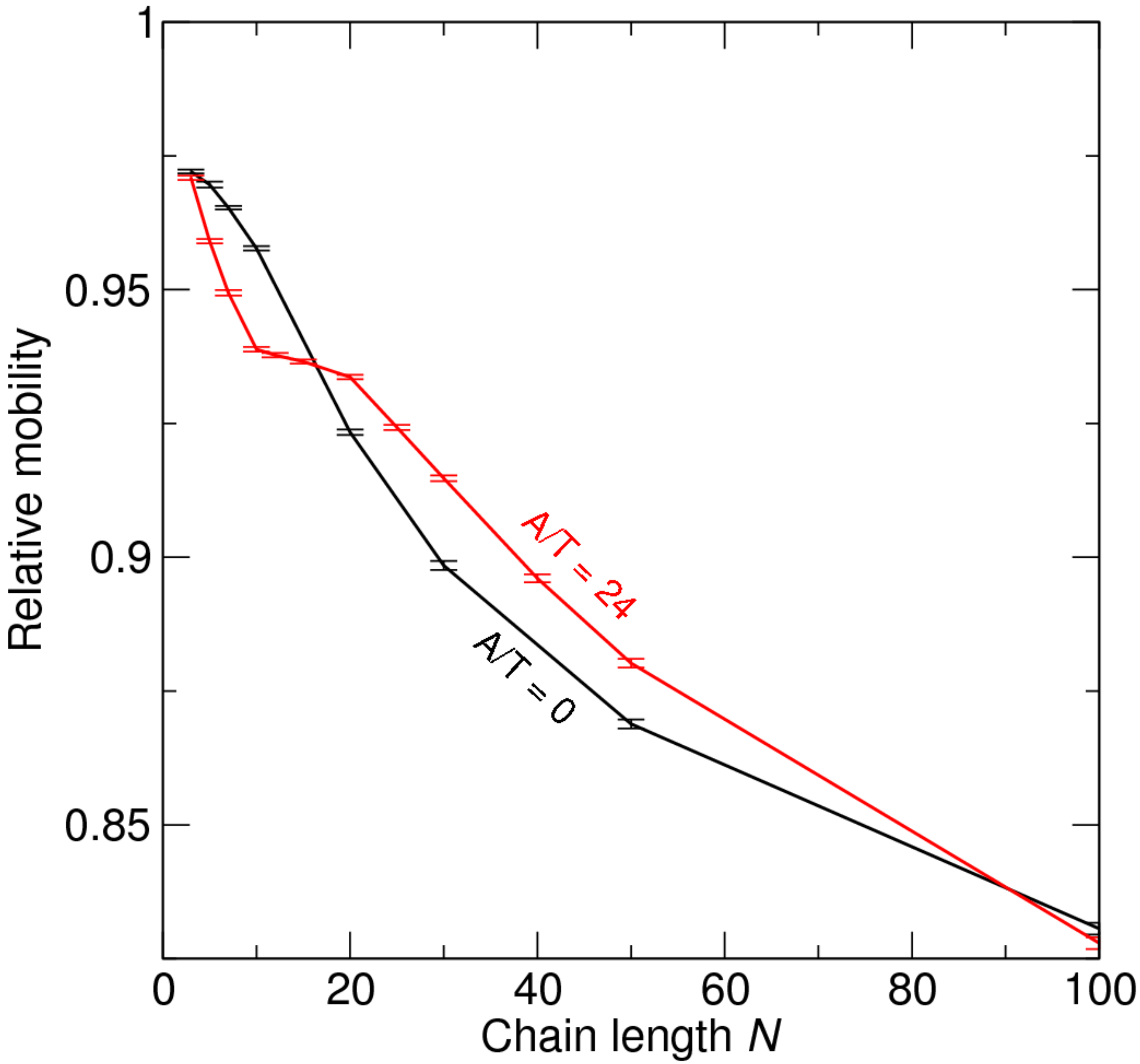
Obstacle radius = 2

Mean distance between obstacles (pore size) ≈ 17

Reduced field qEl/T = 2.4

Persistence length ≈ $2A/T$

Mobility for flexible and semiflexible chains



Angular potential

$$U = A \cos \alpha$$

Bond length l = 1

Obstacle radius = 2

Mean distance between obstacles (pore size) ≈ 17

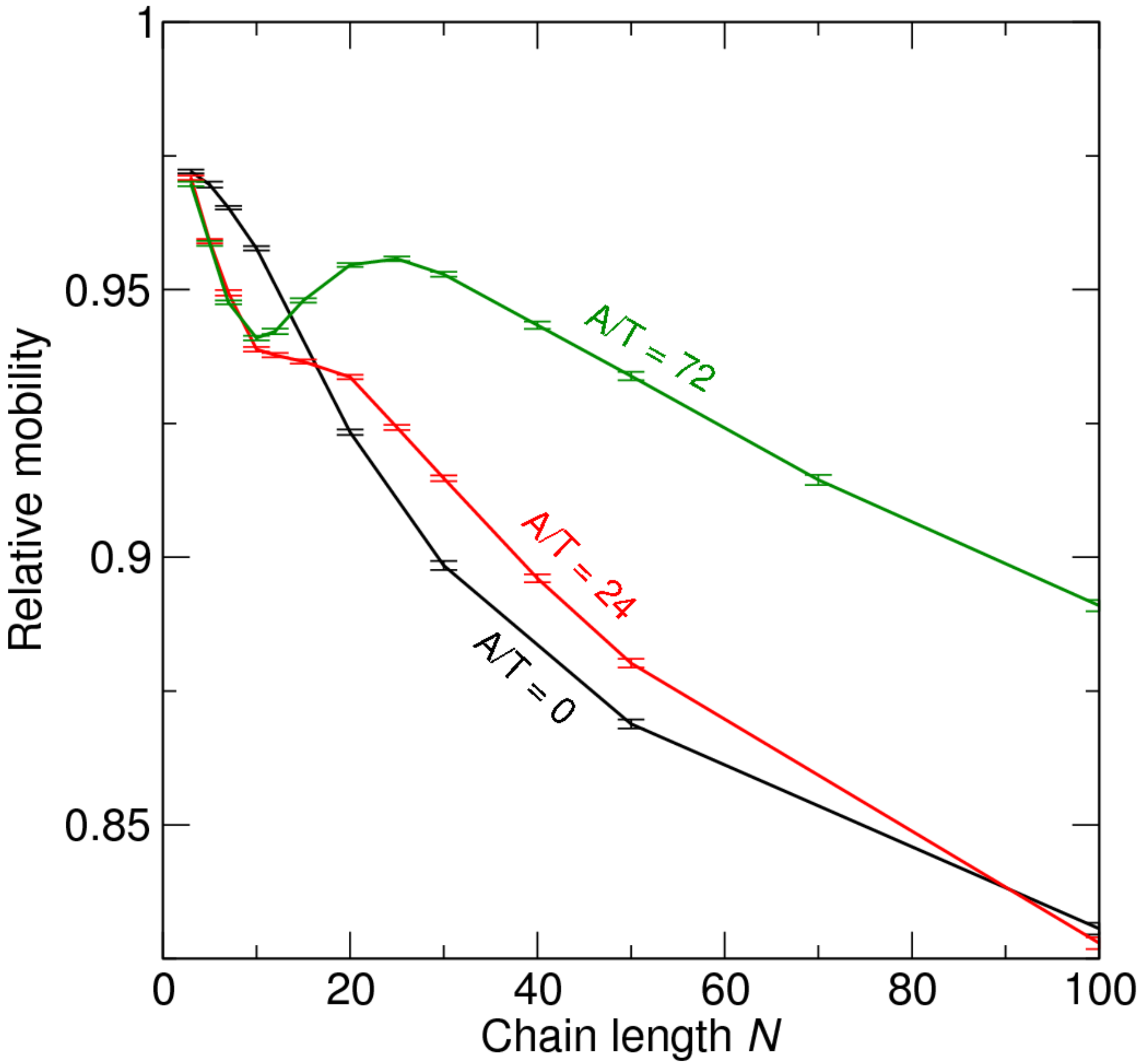
Reduced field qEl/T = 2.4

Persistence length ≈ $2A/T$

Shoulder

Persistence length ~ 3 pores

Mobility for flexible and semiflexible chains



Angular potential
$$U = A\cos\alpha$$

Bond length l = 1

Obstacle radius = 2

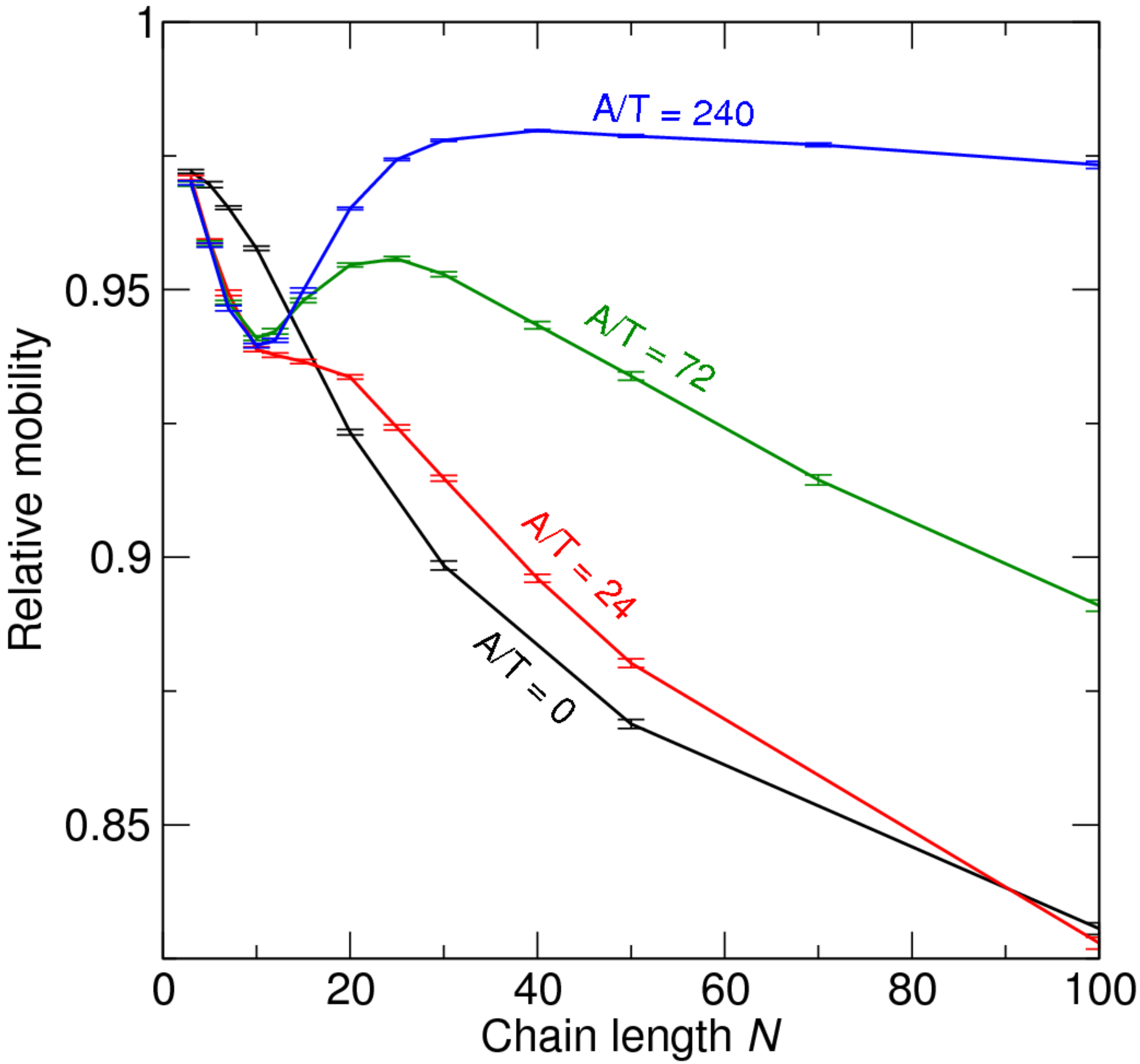
Mean distance between obstacles (pore size) ≈ 17

Reduced field qEl/T = 2.4

Persistence length ≈ $2A/T$

Minimum!

Mobility for flexible and semiflexible chains



Angular potential
$$U = A\cos\alpha$$

Bond length l = 1

Obstacle radius = 2

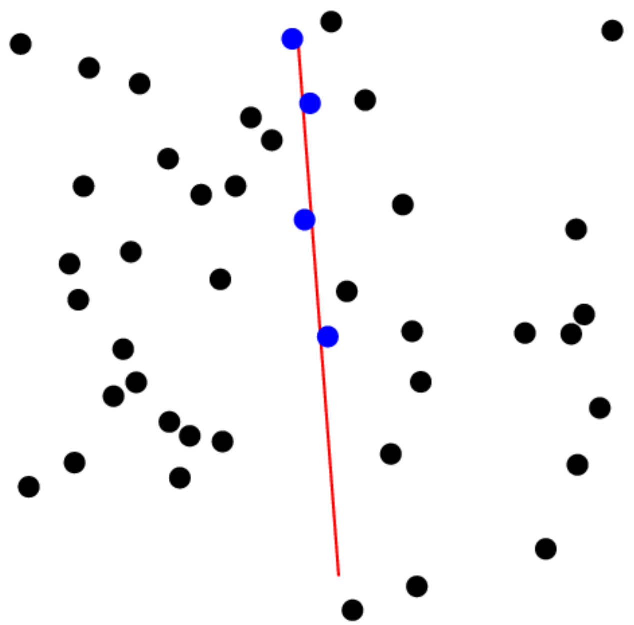
Mean distance between obstacles (pore size) ≈ 17

Reduced field qEl/T = 2.4

Persistence length ≈ $2A/T$

Minimum!

Perfectly stiff rods



- Get trapped! To escape, need to move against the field by distance up to O(N) – escape time is exponential in both the field and N^2.

But probably not important in practice: in simulations for semiflexible polymers trapping only happens for extremely stiff rods (persistence length ~ hundreds of beads) and at very strong fields.

Avoiding trapping:

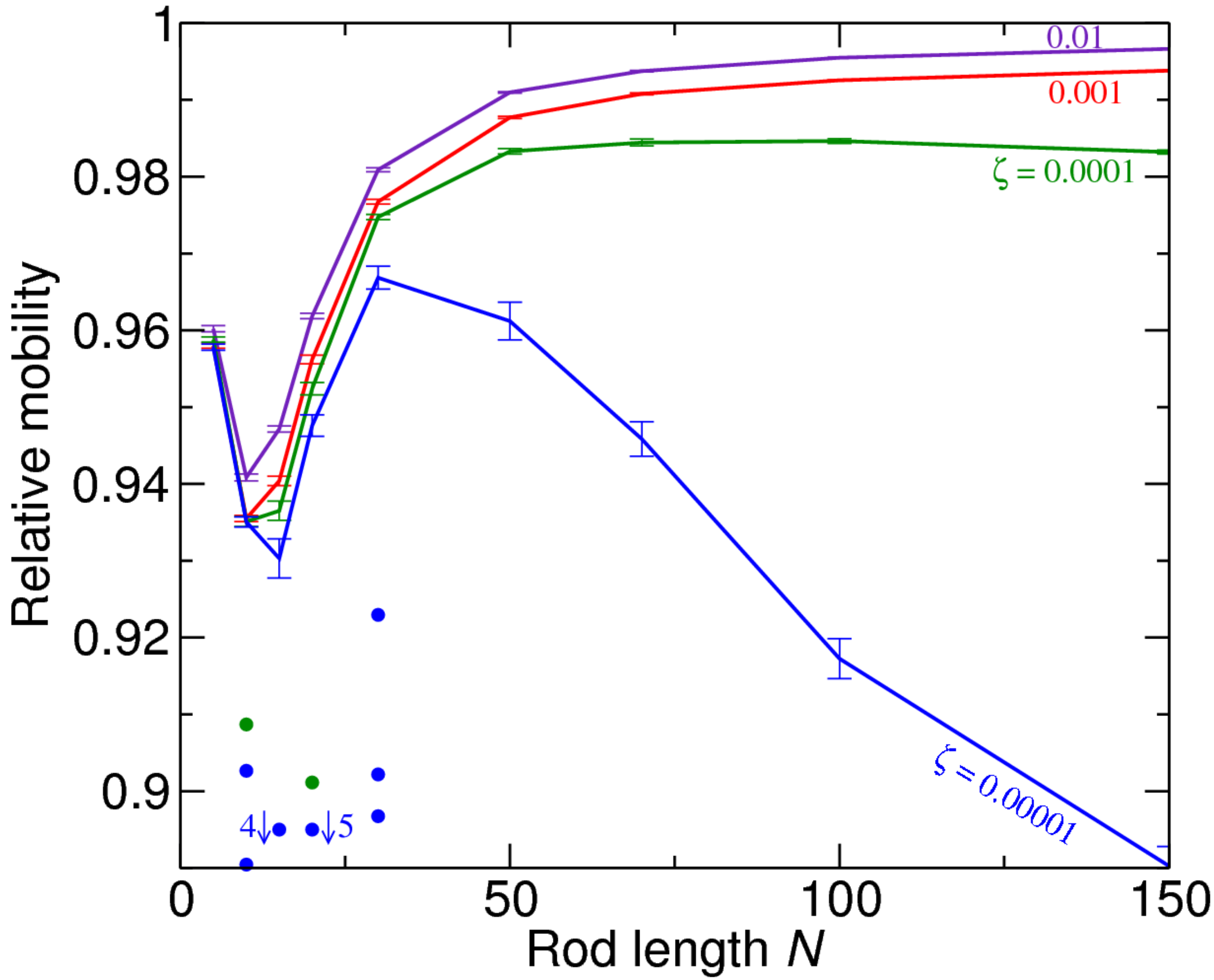
Can go back to slightly flexible rods – but much more computationally costly!

Trick: movable ("draggable") obstacles. Obstacles move with velocity $\vec{v}_{obs} = \zeta \vec{F}_{obs}$

"Draggability" ζ should be low enough so it does not affect motion between trappings, but high enough to de-trap rapidly.

Not unrealistic: in gels and polymer solutions, the "obstacles" are not perfectly immobile (not true for microfabricated arrays, though).

Comparison between different draggabilities

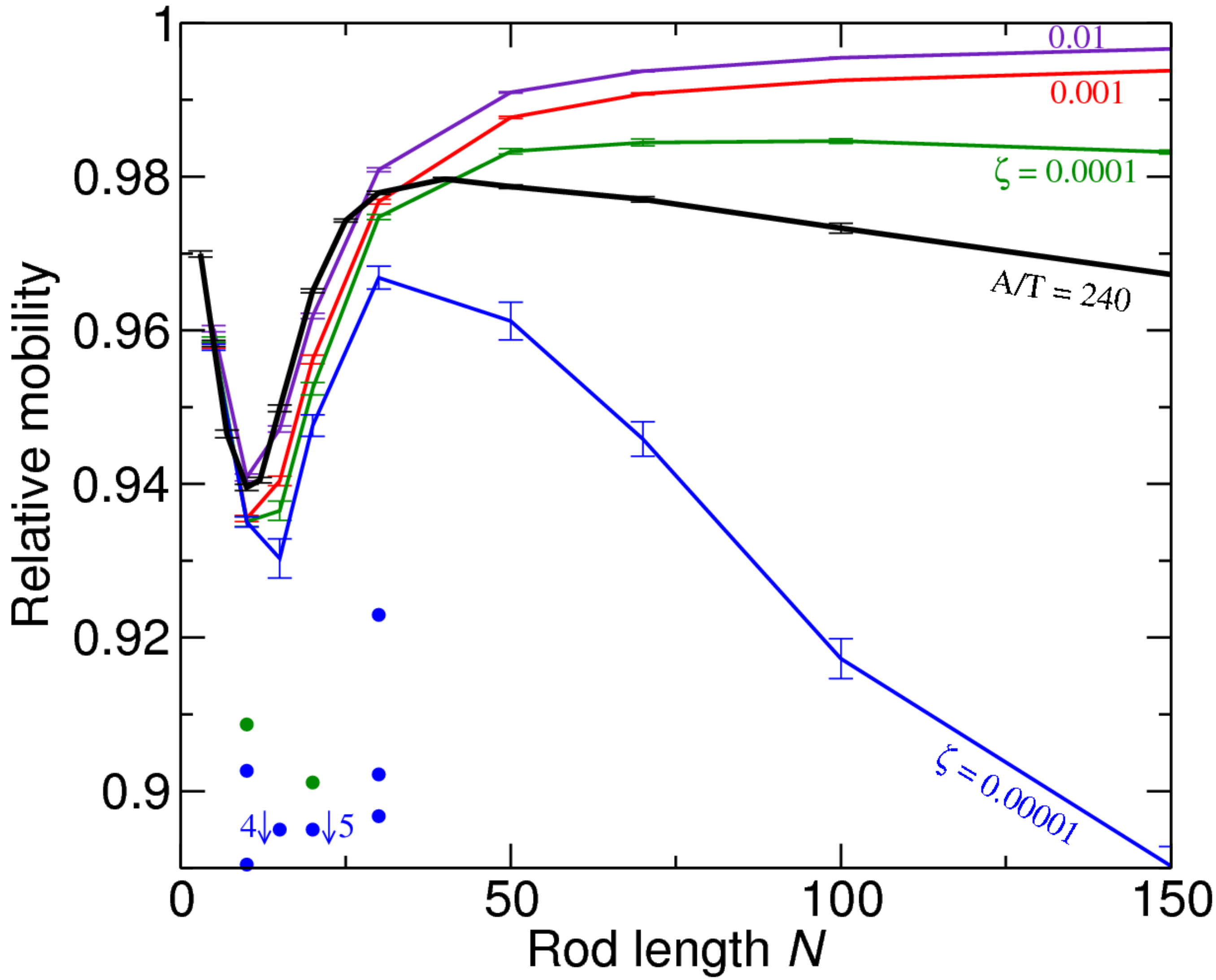


Mobility minimum is reproduced for 3 orders of magnitude of ζ

Some "outliers" for the lowest ζ

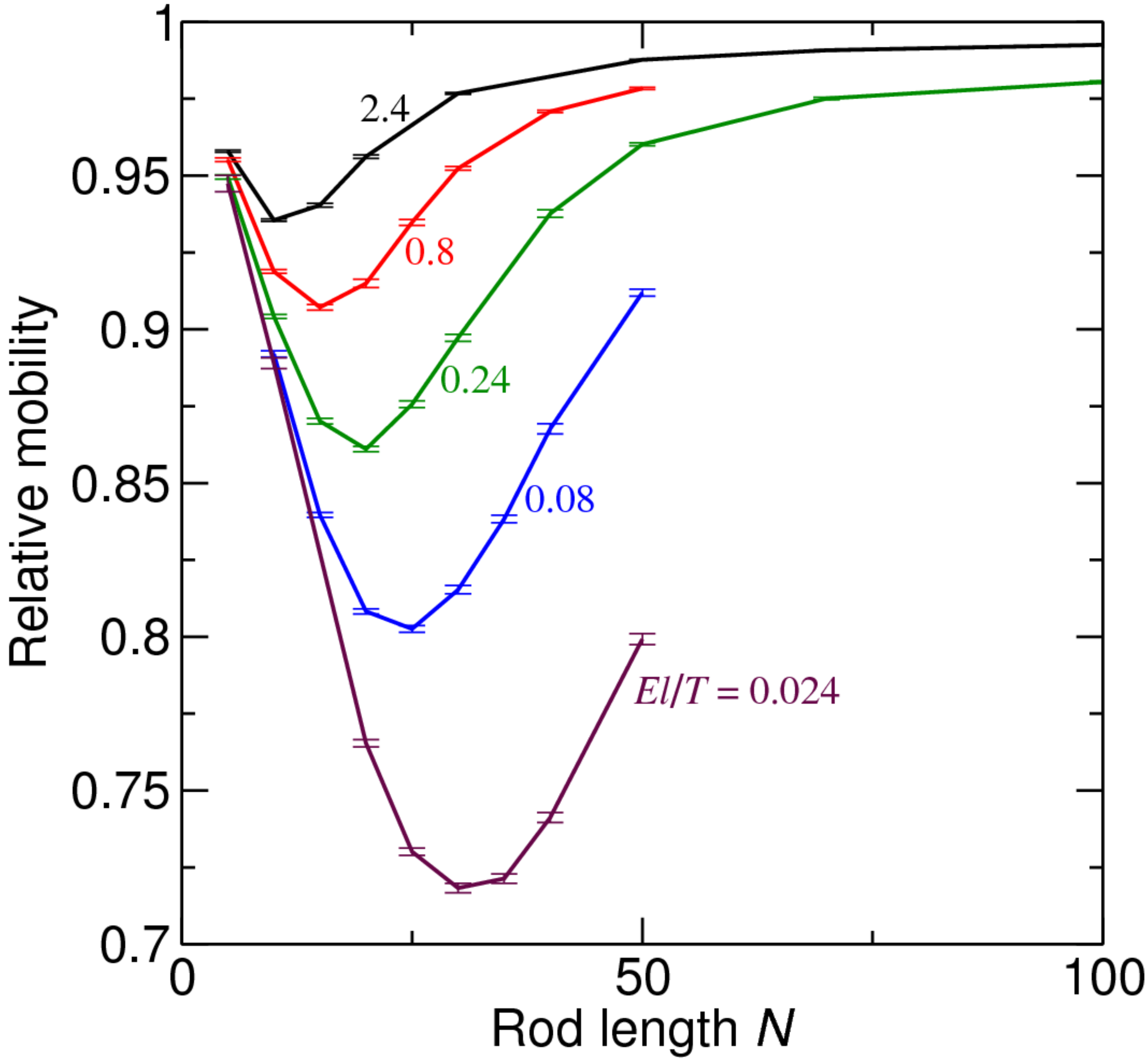
Usually works even better (here, the field and the obstacle density are high)

Comparison to a slightly flexible rod with immobile obstacles



Use this approach to obtain the rest of the data in this talk.

Different fields



Bond length l = 1

Obstacle radius = 2

Mean distance between obstacles (pore size) ≈ 17

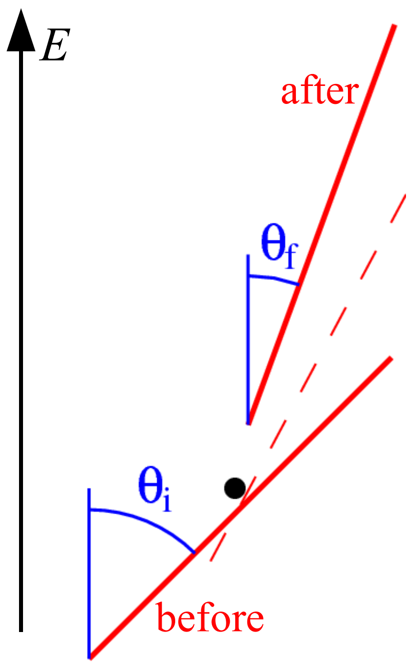
Field-independent for small N (equilibrium). The mobility minimum is a field-dependent non-equilibrium effect.

Stiff rods are pretty simple objects, no internal d.o.f. Not a lot of ways to be out of equilibrium.

Rod orientation with respect to the field may be relevant. In equilibrium, all orientations are equally likely.

Theory of rod orientation

Orienting and disorienting effects



Collision with an obstacle. For small θ_i and obstacle size

$$\langle \theta_f \rangle = C\,\theta_i, \text{ where } C = \frac{1}{2} + \frac{\ln(2+\sqrt{3})}{4\sqrt{3}} \approx 0.69 \;\underline{\underline{\leq 1}}$$

Collisions with obstacles orient the rod!

(Special class of "head-on" collisions are disorienting and need to be considered separately, but we don't go into detail here)

On the other hand, thermal rotational diffusion of the rod is disorienting.

Interplay of these two effects determines the orientation of the rod

Calculation of the rod orientation

Characterize the orientation by the width of the angle distribution $\Delta\theta$.

Omit numerical factors. Put $l = q = k_B = \mu_0 = 1$.

Steady-state $\Delta\theta$ is determined by equating its decrease during a collision with its increase due to rotational diffusion between collisions.

During a collision: $-\delta(\Delta\theta)^2 \sim (\Delta\theta)^2$

Between collisions: $\delta(\Delta\theta)^2 \sim D_r t \sim (T/N^3)(1/f)$

The collision frequency f itself depends on $\Delta\theta$: $f \sim vcN\Delta\theta \sim EcN\Delta\theta$.

Final result: $\Delta\theta \sim (T/EcN^4)^{1/3}$

When the above is >1, $\Delta\theta \sim 1$ instead – unoriented regime.

Crossover between unoriented and oriented regimes occurs at

$$N_c \sim (T/Ec)^{1/4}$$

Calculation of the mobility reduction

Due to collisions.

The velocity change (averaged over the whole duration, including periods between collisions) is:

$$\Delta v \sim -v(\Delta\theta)^2 (N/v) f_0 \sim -vcN^2\Delta\theta^3.$$

The mobility change $\Delta\mu \sim -cN^2\Delta\theta^3$.

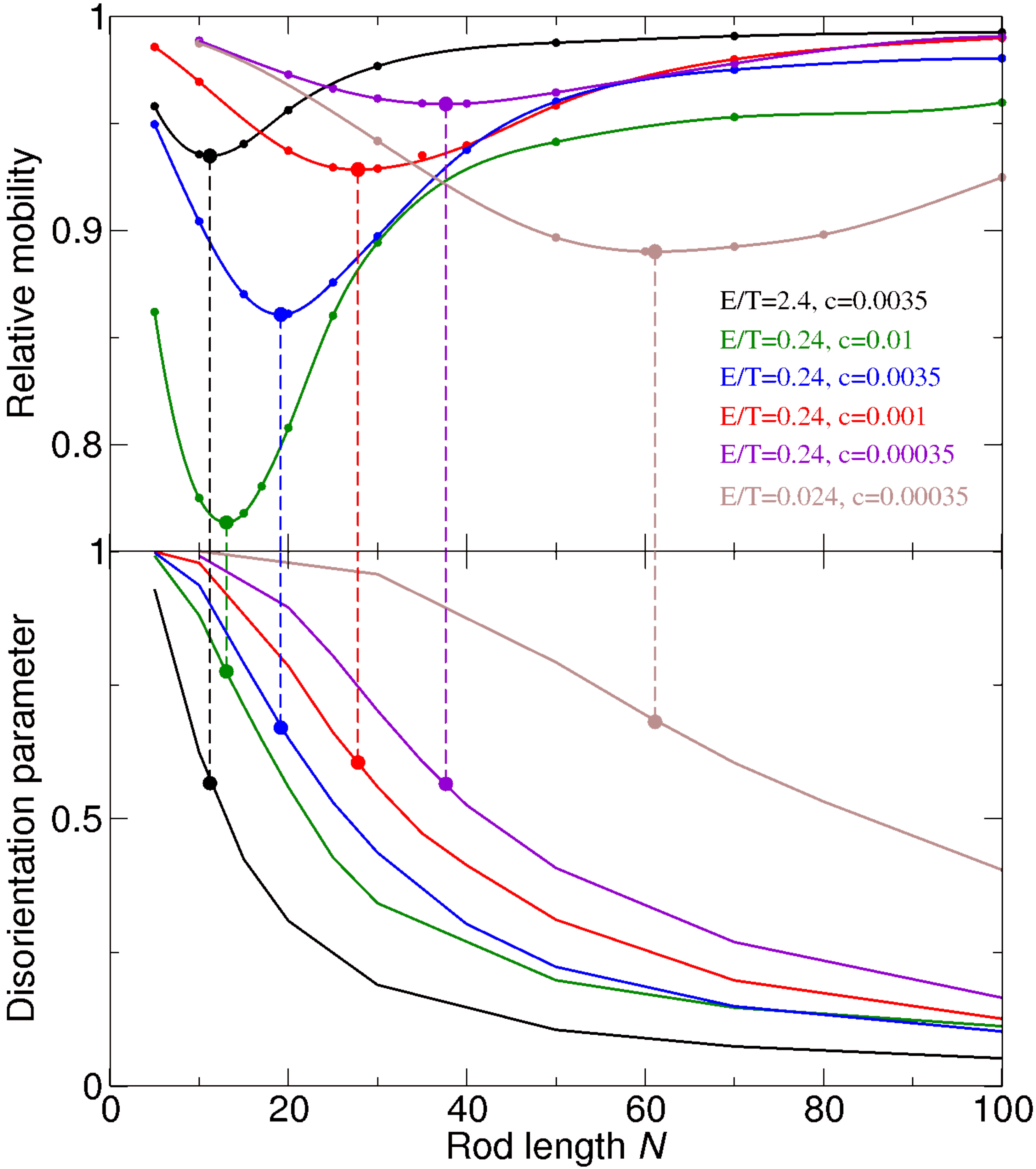
In the unoriented regime ($\Delta\theta \sim 1$), $\Delta\mu \sim -cN^2$. Mobility is field-independent (equilibrium), decreases with increasing N.

In the oriented regime [$\Delta\theta \sim (T/EcN^4)^{1/3}$], $\Delta\mu \sim -T/(EN^2)$. Mobility increases with increasing N.

The mobility minimum coincides with the crossover between the unoriented and oriented regimes.

For short unoriented rods, the longer the rod, the more it collides with the obstacles. But as orientation sets in, longer rods are more oriented and pass more easily without colliding.

Do some simulations to test the theory



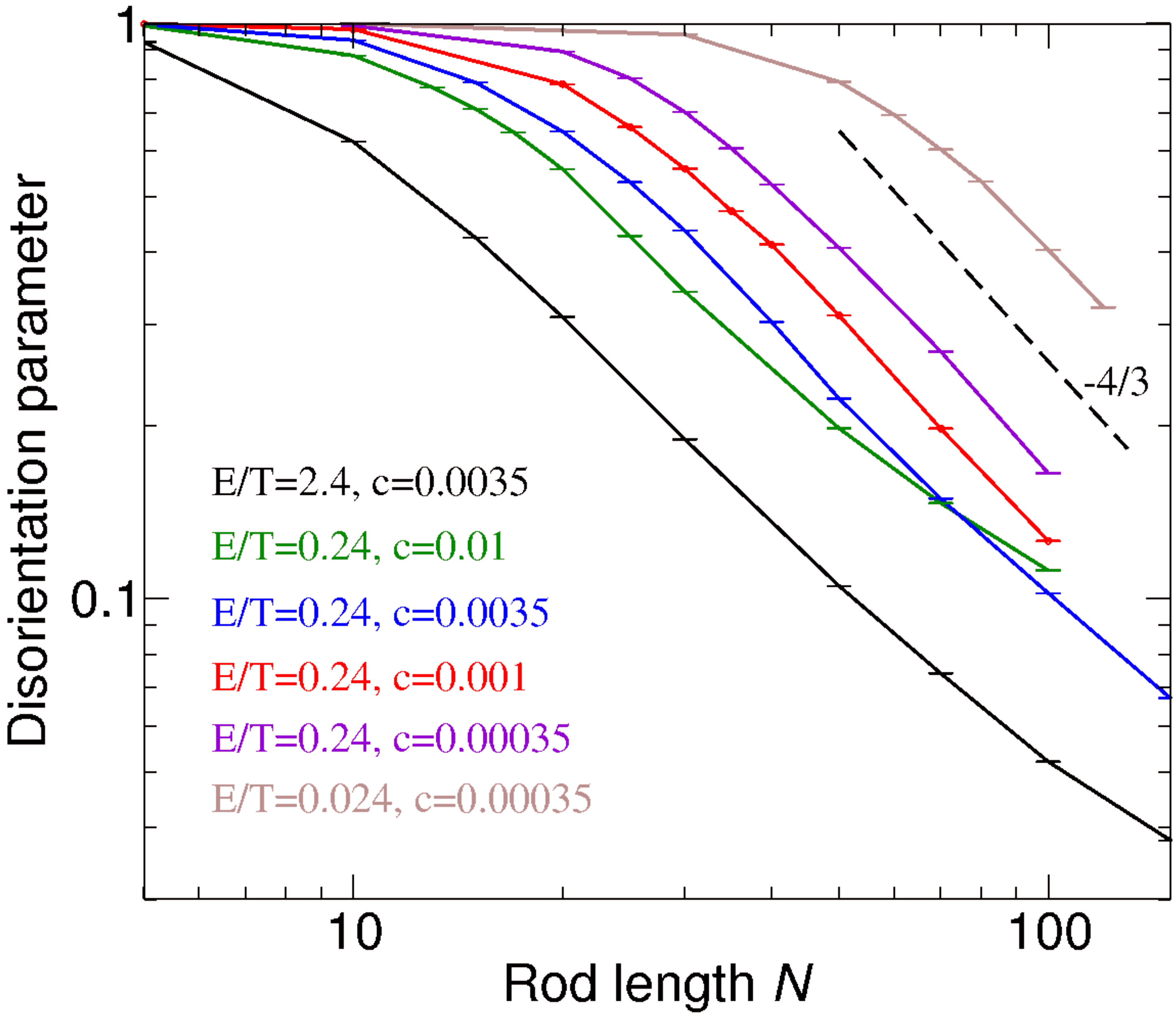
Disorientation parameter:

$$\frac{\langle \theta \rangle}{\pi / 4}$$

0 – perfect orientation

1 – perfect disorientation

Log-log plot of the disorientation parameter



Disorient. parameter:

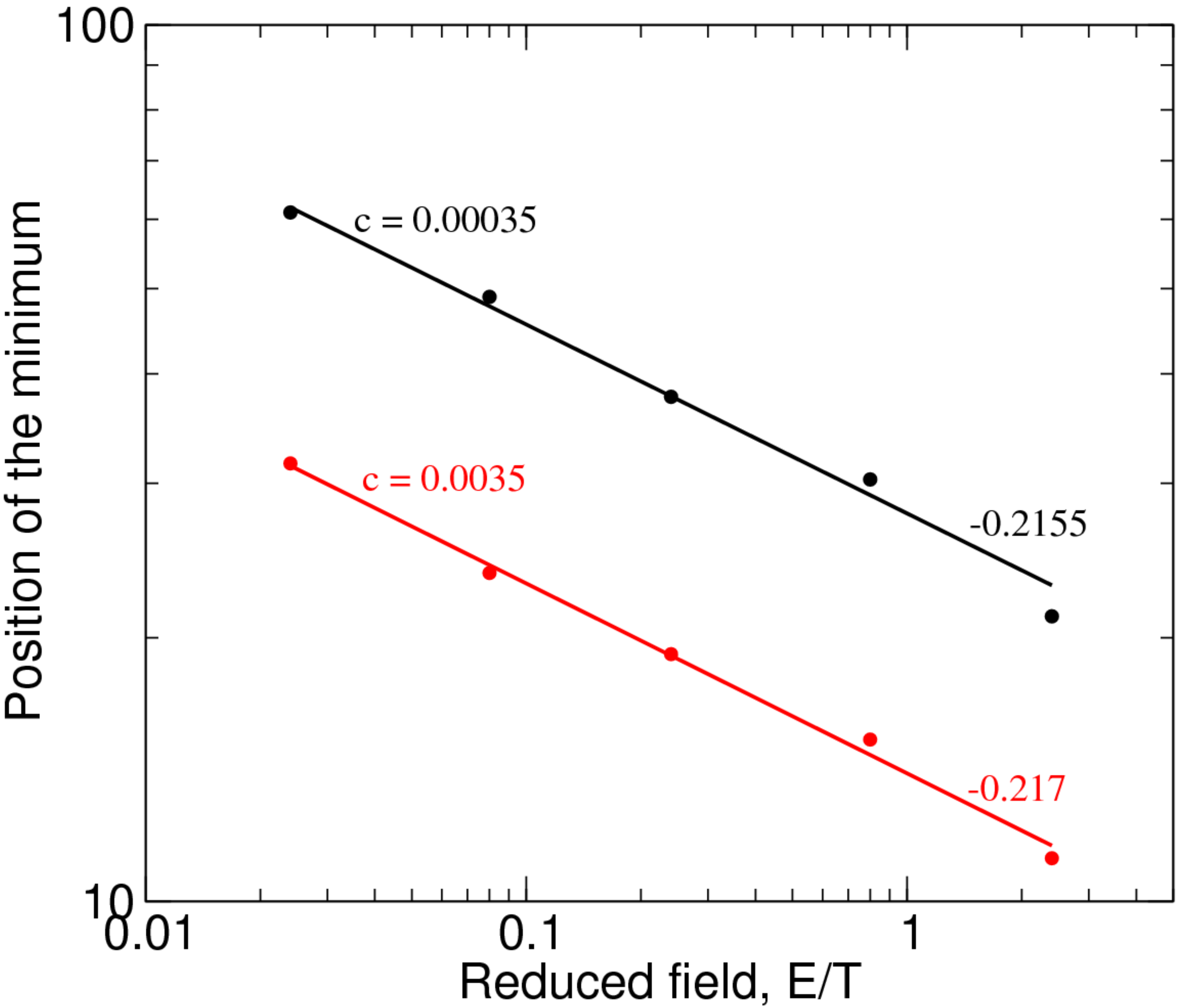
$$\frac{\langle \theta \rangle}{\pi / 4}$$

Theory:

$\Delta\theta \sim (T/EcN^4)^{1/3}$

Predicted slope: -4/3

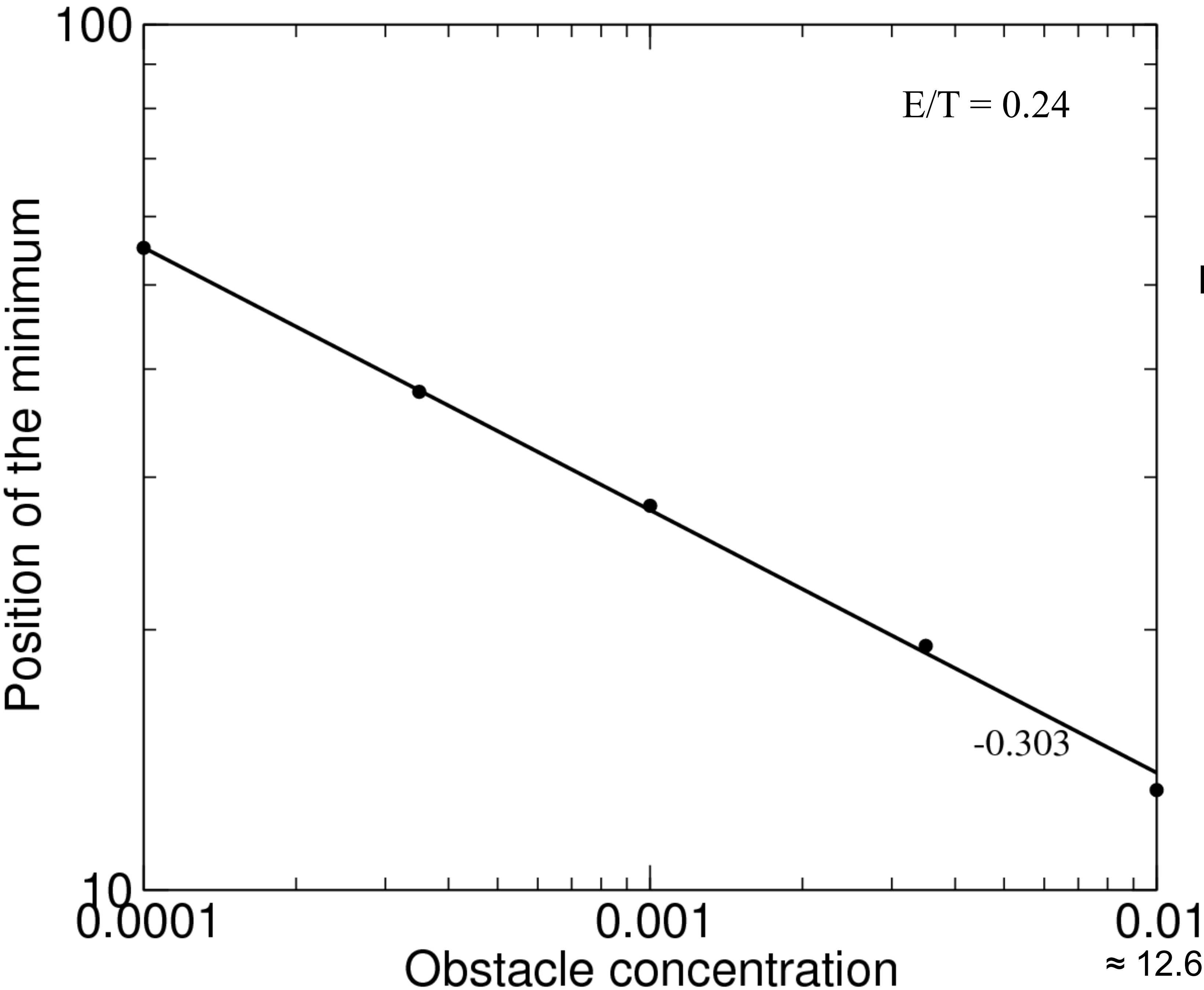
Deviations at large *N* are probably due to failure of the single-obstacle approx.



Theory:

$N_c \sim (T/Ec)^{1/4}$

Predicted slope:
-0.25

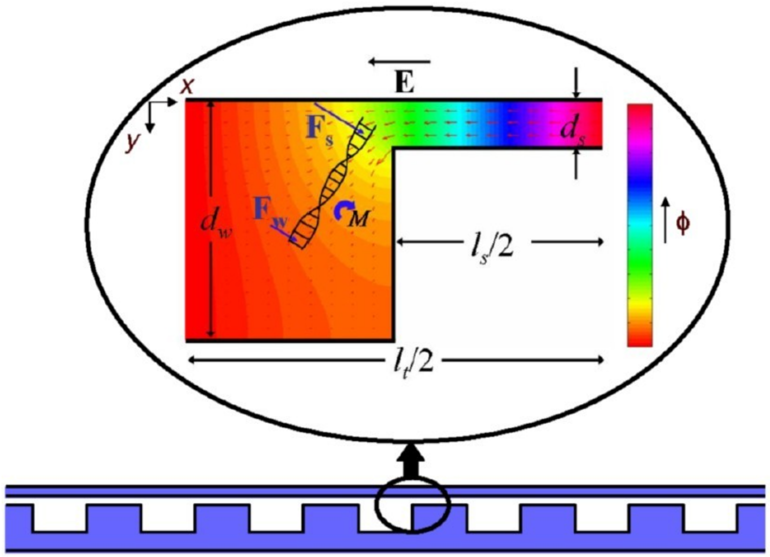


≈ 12.6% occupied by obst.

Theory:

$N_c \sim (T/Ec)^{1/4}$

Predicted slope:
-0.25



Similarity to the work of Laachi *et al.* (2007), where an increase of mobility of rigid rods with length in a nanofilter device due to orientation effects was likewise predicted. In that work, the orienting effect is the non-uniform electric field at the entrance from the deep well to the narrow slit.

Future work

1. 3D. Likely qualitatively similar, even the exponents are probably the same.

2. Ordered arrays of obstacles.

3. Understand better the sources of discrepancies between simulations and theory.

4. Study the regime where the single-obstacle approximation would not be applicable even around the mobility minimum.