Confinement-Driven Translocation of Polymers

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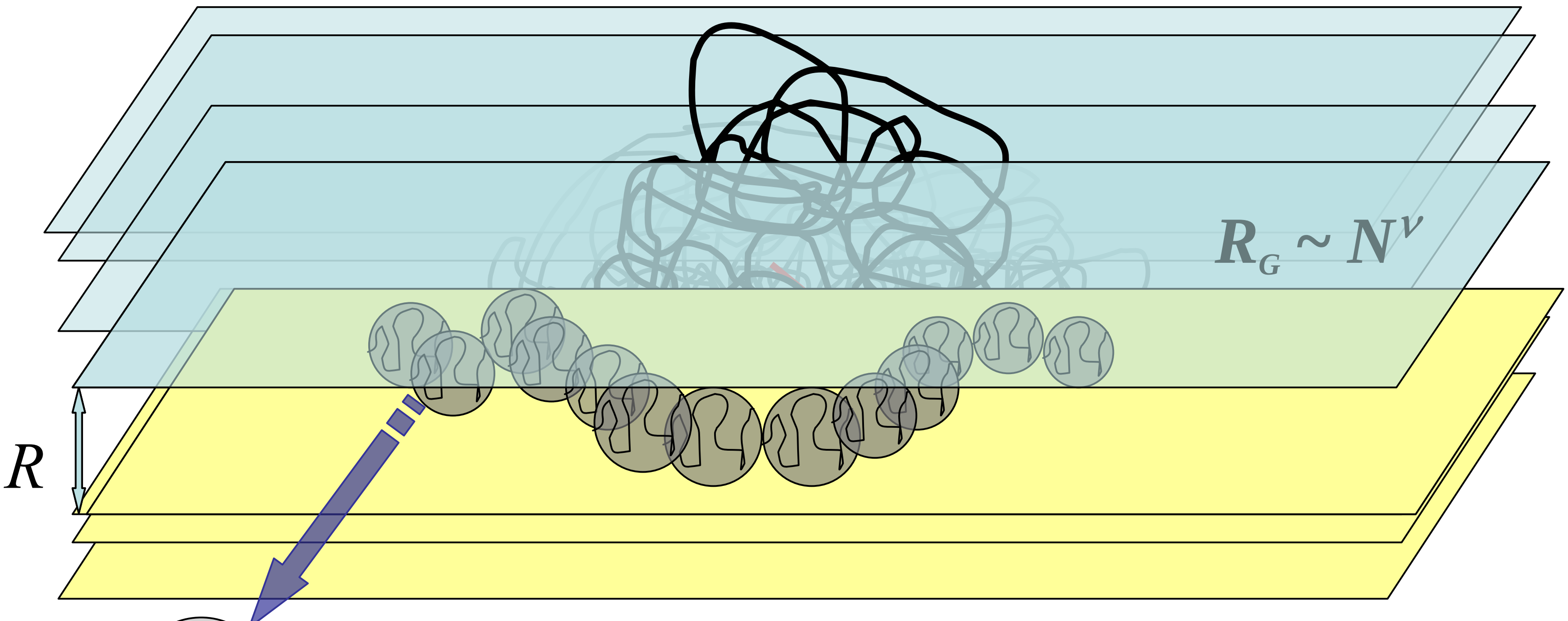
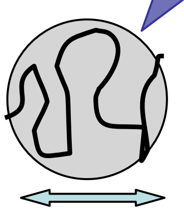
Polymers under confinement

- Behavior of polymers in confined geometries is relevant for many practical applications
  - packing of DNA in virus capsids
  - colloidal stabilization
  - flow-injection problems
  - filtration
  - stability of folded proteins?
- Reduced entropy creates excess free energy.
  This is well understood and covered in standard texts…?
- Specific application: entropy-driven translocation of a polymer out of confinement

What to expect for planar confinement?

Self-avoiding neutral chain of length N





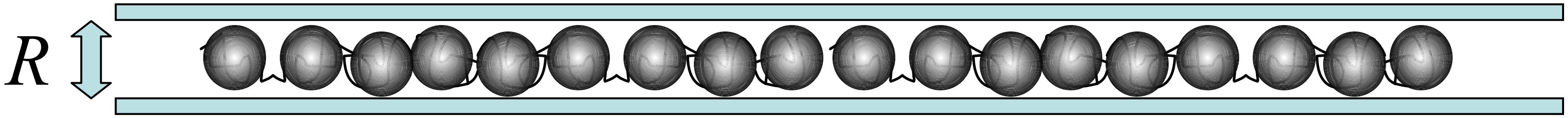
$\xi \sim R$

$$R \sim \xi \sim a n^{\nu} \Rightarrow n \sim (R/a)^{1/\nu}$$

$$\Delta F \sim k_B T\,(N/n) \Rightarrow \beta \Delta F \sim N(a/R)^{1/\nu}$$

Other geometries…

- Cylindrical confinement (e.g., nanotube):
  Identical result $\beta \Delta F \sim N(a/R)^{1/\nu}$



- Spherical geometry:
  "This analysis can be extended [….] to other geometries provided that the confining object is characterized by a single length"
  P. G. de Gennes, *Scaling Concepts in Polymer Physics*
- Indeed, this result is employed in a wide variety of problems!

Competing predictions

- Self-consistent field theory: $\beta \Delta F \sim N\varphi \sim N^2 \left(\frac{\sigma}{2R}\right)^3$

- Revised blob scaling (Grosberg & Khokhlov, 1994): take into account that—under triaxial confinement—the monomer concentration increases upon compression

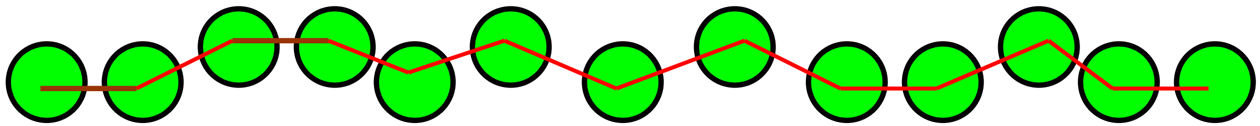
$$\beta \Delta F \sim \left(\frac{R_G}{R}\right)^{3/(3\nu-1)} \sim N\varphi^{1/(3\nu-1)}$$

- Unresolved controversy:

$$\boldsymbol{\beta \Delta F \quad \sim R^{-1.70} \quad \sim R^{-3} \quad \sim R^{-3.93}}$$

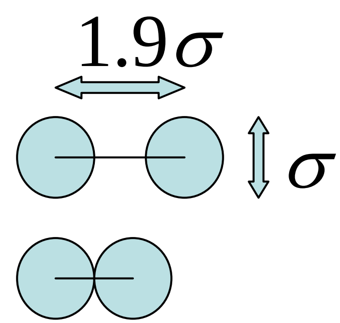
Step 1: Resolve the controversy

- Monte Carlo simulations of bead–spring model



- Monomers act via hard-core repulsions;
  nearest neighbors are connected by stretchable bonds

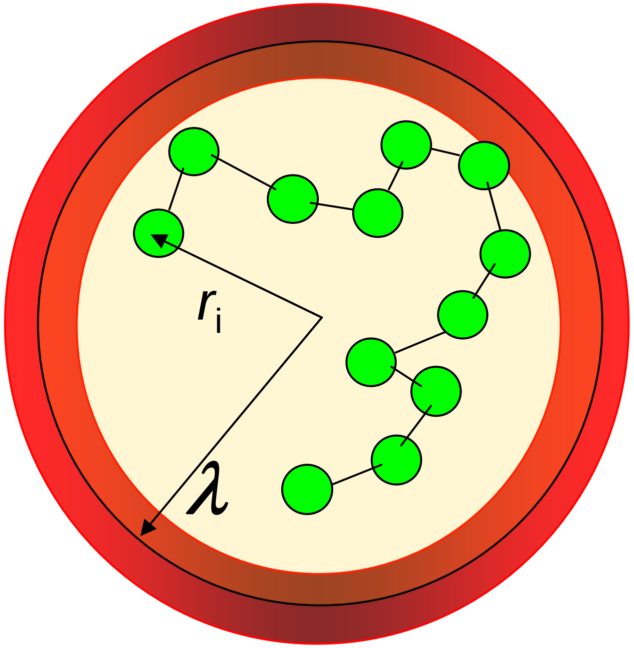
$$u_{\mathrm{b}}(r_{i,i-1}) = \begin{cases} 0 & \text{if } r_{i,i-1} \le l_{\max} \\ \infty & \text{if } r_{i,i-1} > l_{\max} \end{cases}$$



Method

Thermodynamic integration

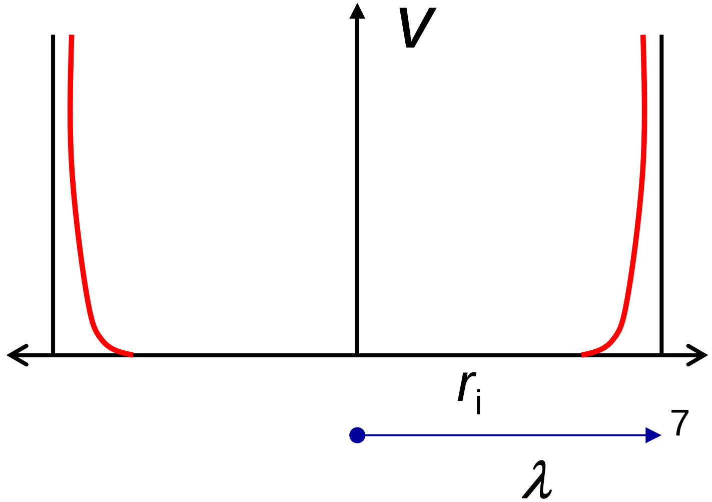
$$\Delta F \equiv F(\lambda_2) - F(\lambda_1) = \int_{\lambda_1}^{\lambda_2} \left\langle \frac{\partial u_\alpha(\lambda)}{\partial \lambda} \right\rangle_\lambda \mathrm{d}\lambda$$



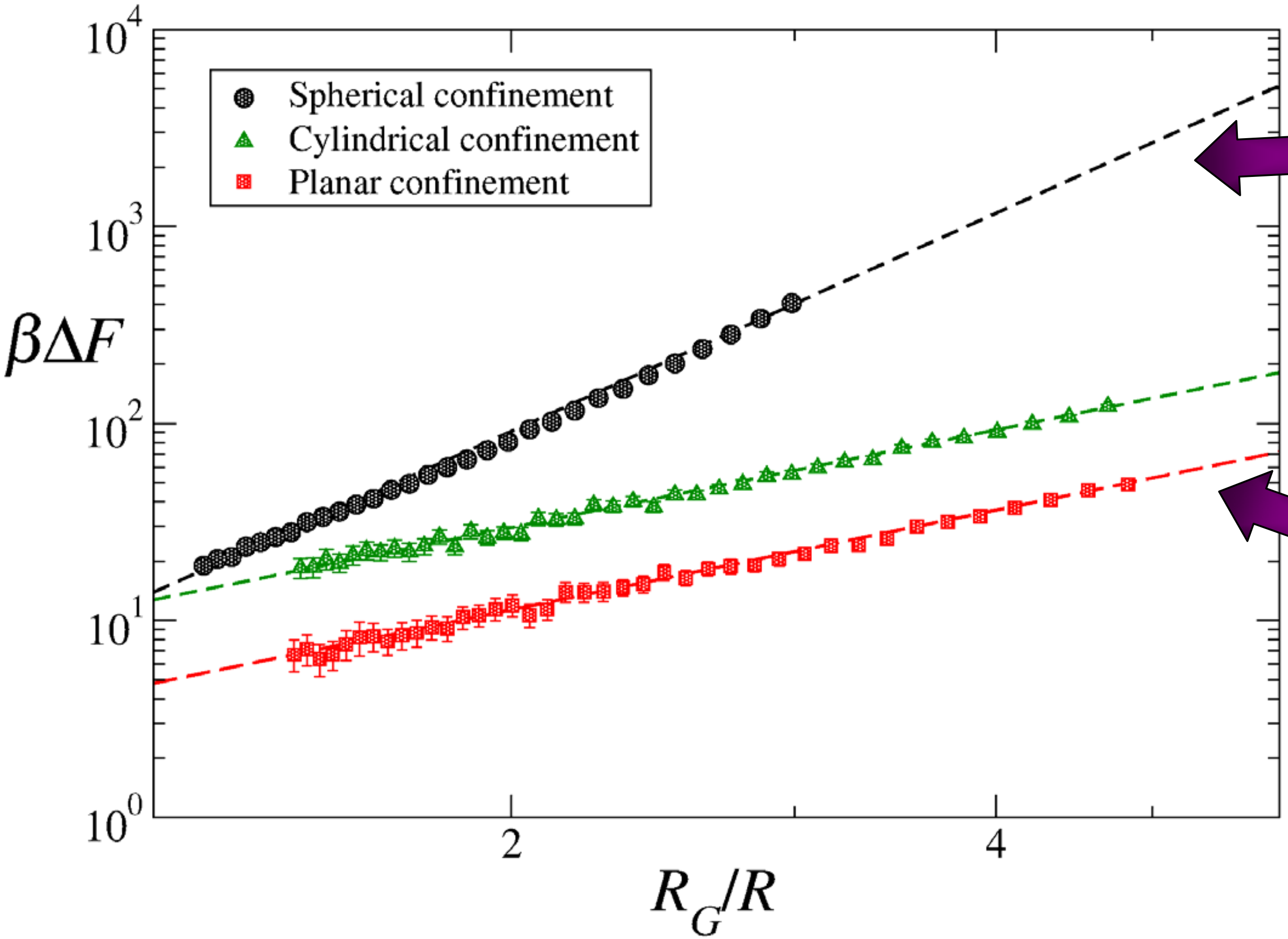
External potential (in the *NVT* ensemble)

$$u_\alpha(\lambda) = k_B T \sum_{i=1}^{N} \frac{1}{(\lambda - r_i)^\alpha} \quad (\alpha > 0)$$

$\alpha = 12$



Results for N=256



Polymers in spheres exhibit much stronger dependence on R!

Polymers in cylinders and between plates exhibit identical R dependence

A. Cacciuto and E. Luijten, Nano Letters ***6****, 901 (2006)*

Determine power law from N=2048

Lines are theoretical predictions

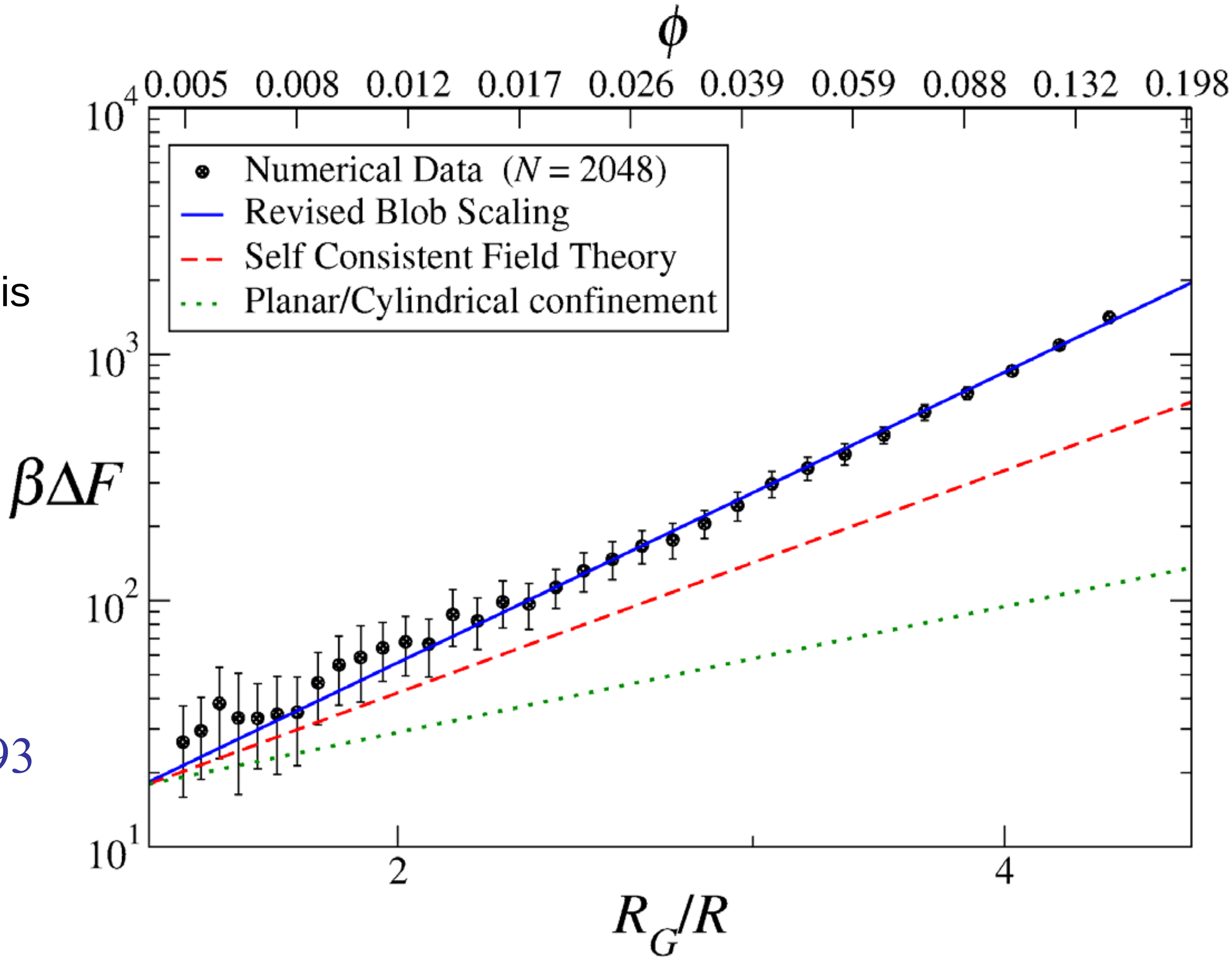
Statistical analysis yields

$\beta\Delta F \sim (R_G/R)^\gamma$

with γ=3.8±0.1

Revised blob scaling predicts

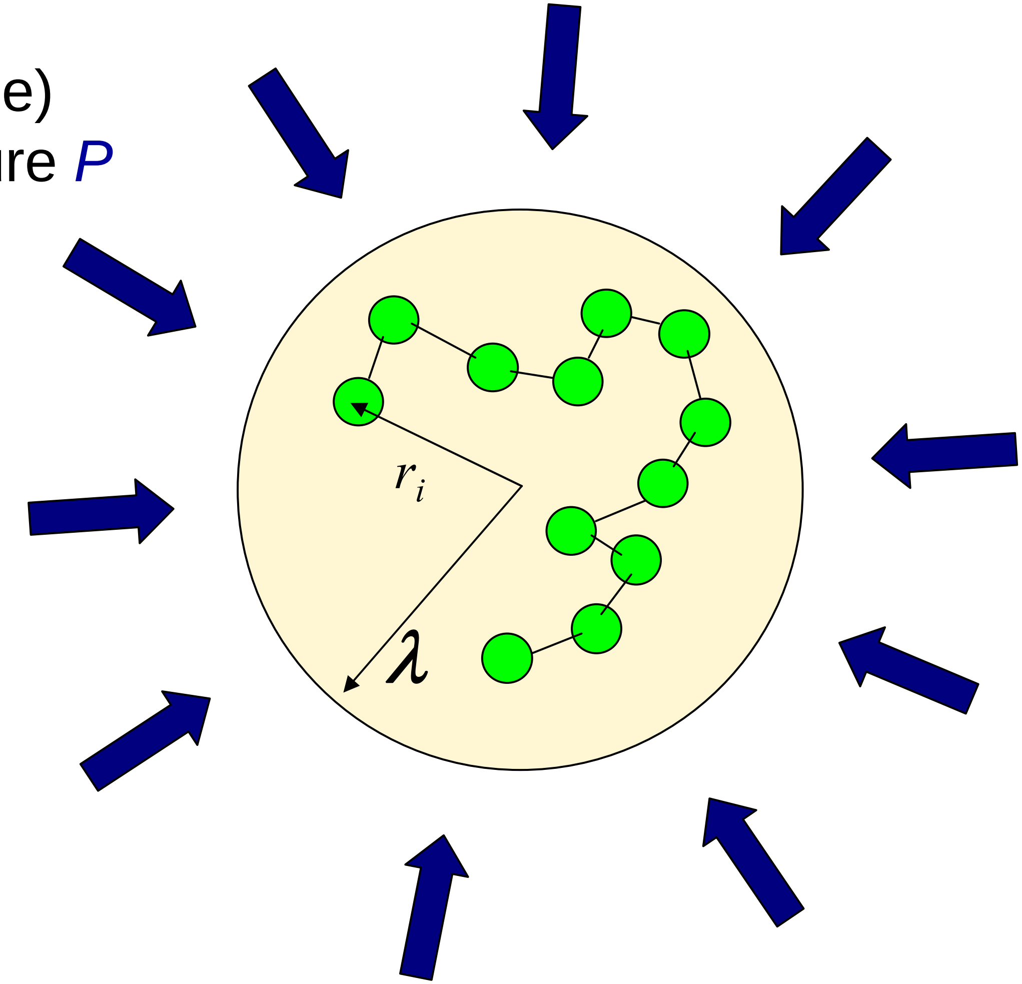
$\gamma=3/(3\nu-1)=3.93$



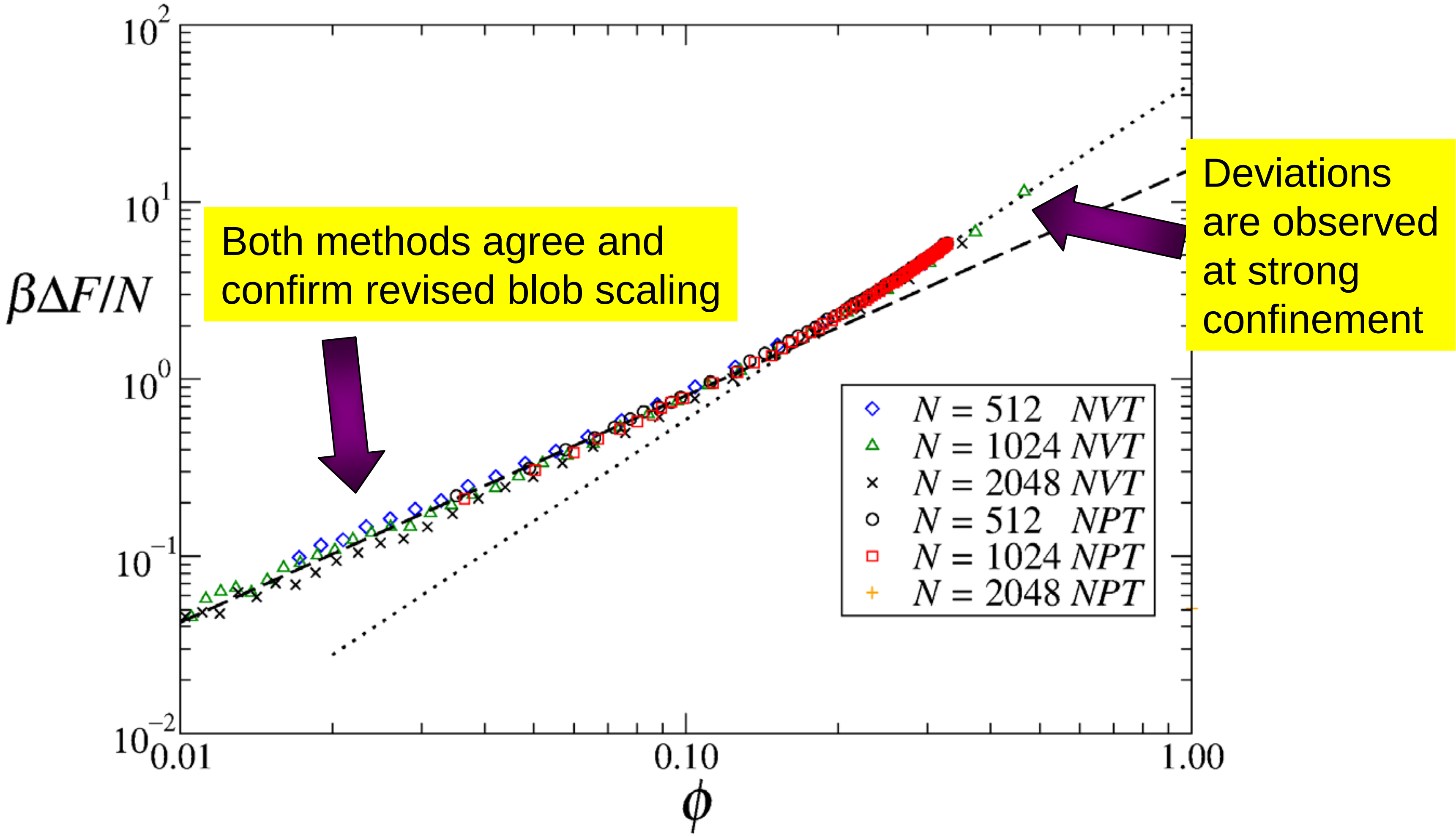
Alternative: constant pressure

Hard wall (in the *NPT* ensemble)
Homogeneous external pressure *P*

$$\frac{\Delta F}{N} = \int_0^{\rho} \frac{P(\rho')}{\rho'^2} d\rho'$$



Collapse of *NVT* and *NPT* data



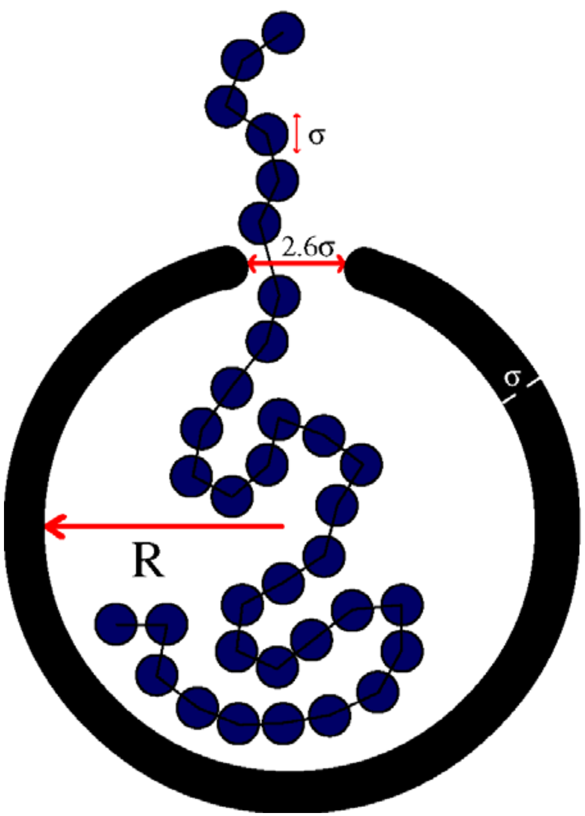
Step 2: Translocation out of confinement

- For chemical potential difference $\Delta\mu$, the predicted translocation time τ scales as

$$\tau \sim \frac{N^{\alpha}}{\Delta\mu} \qquad \begin{cases} \alpha = 2 & \text{diffusive regime} \\ \alpha = 1 & \text{driven regime} \\ \alpha = 1 + \nu & \text{lower bound (unhindered motion)} \end{cases}$$

- Free energy of confinement determines $\Delta\mu$
- ¿Earlier work has numerically “confirmed” the above for spherical confinement, employing incorrect $\Delta\mu$ ...?

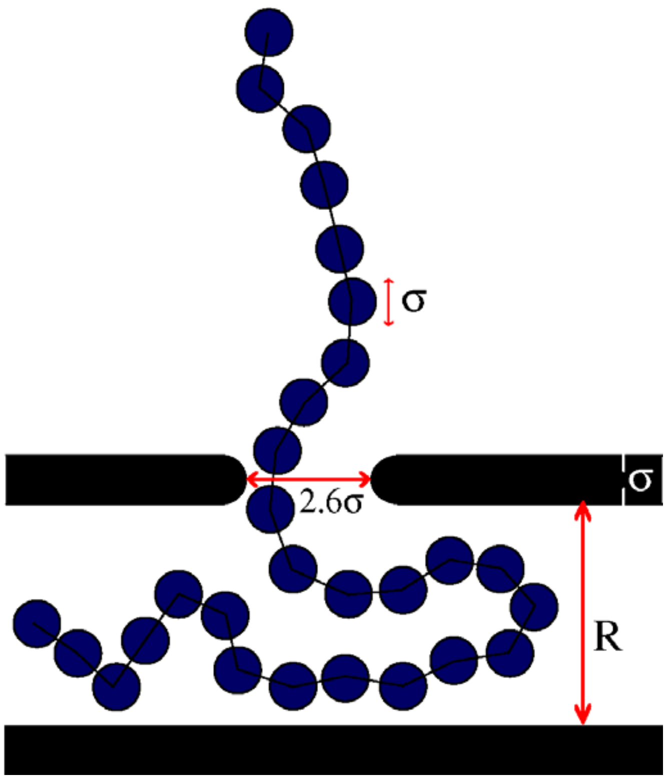
Compare escape out of two geometries



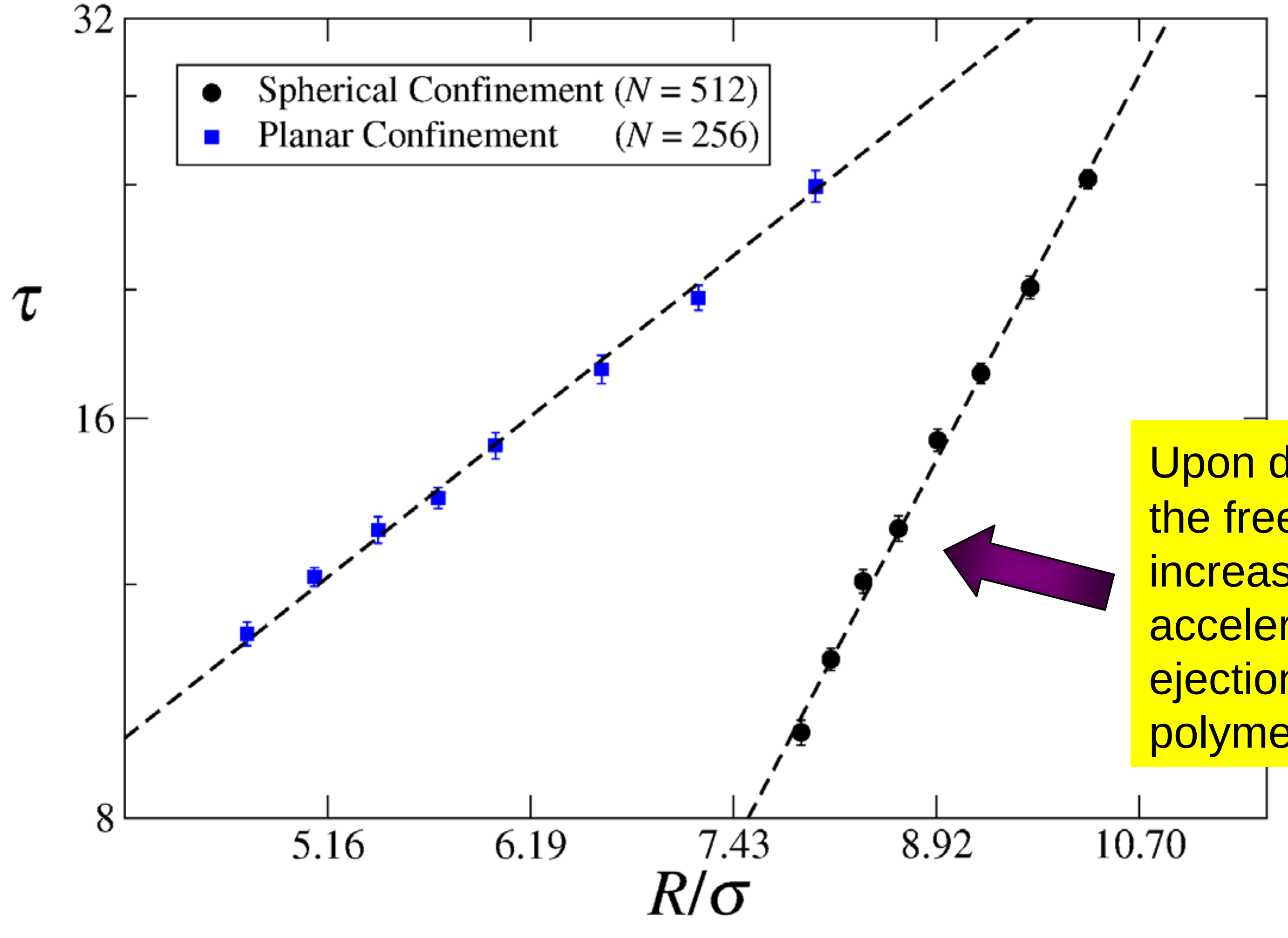
For both systems, MC simulations are used, involving only local monomer displacements

The driven regime ($N\Delta\mu > 1$) requires $R < R_G$, i.e. a large range in R requires long chains

We use $40 < N < 512$, with 400–1400 escape events for each choice of (N, R)



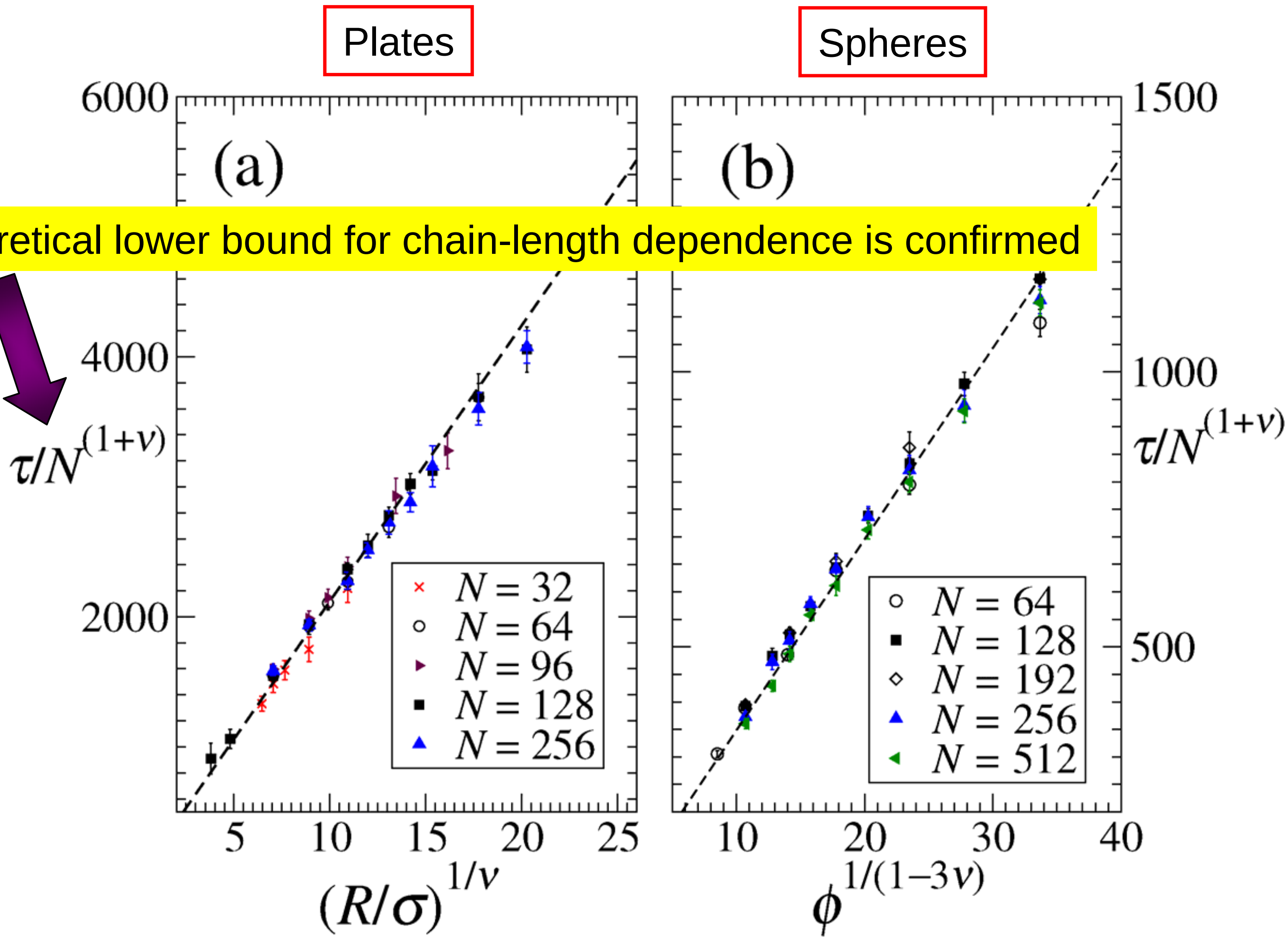
Translocation time



Upon decreasing R, the free energy increases rapidly, accelerating the ejection of the polymer chain

A. Cacciuto and E. Luijten, Phys. Rev. Lett. ***96****, 238104 (2006)*

Data collapse



Theoretical lower bound for chain-length dependence is confirmed

Understanding "confirmation" from wrong ΔF

- Muthukumar (*PRL*, 2001):

$$\tau \sim N(N/\varphi)^{1/3\nu} = N^{1+1/3\nu}\varphi^{-1/3\nu} \neq N^{1+\nu}\varphi^{-1/(3\nu-1)}$$

proper prediction

- Note coincidence in power of N:

$$1+1/3\nu \approx 1.567 \approx 1+\nu!$$

- On the other hand, powers of φ are very different…

$$1/(3\nu) \approx 0.567$$

$$1/(3\nu-1) \approx 1.31$$

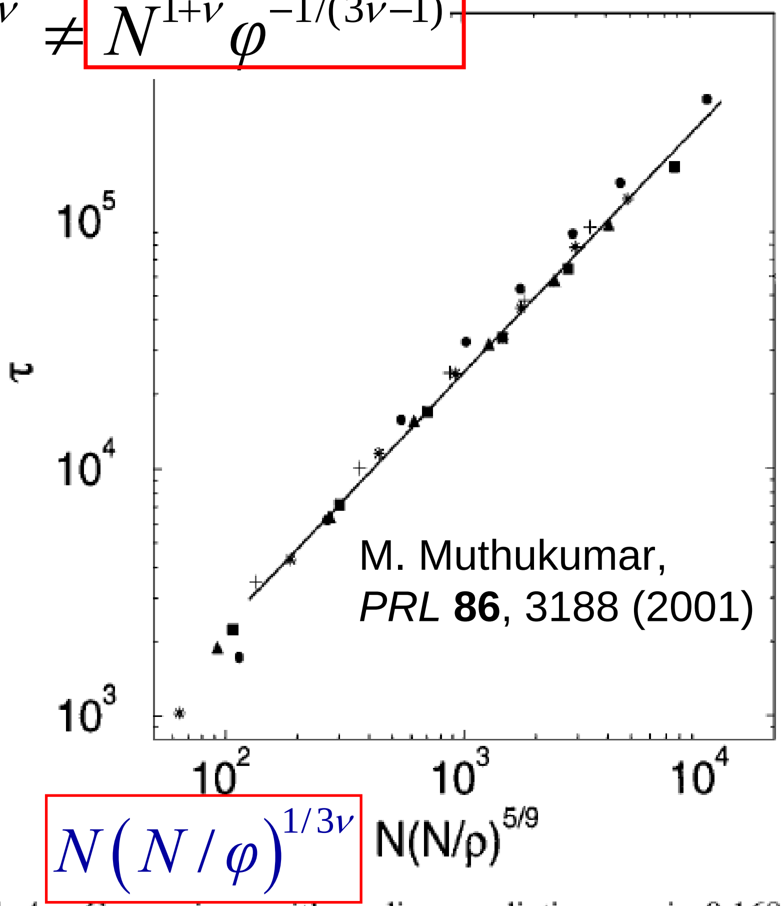
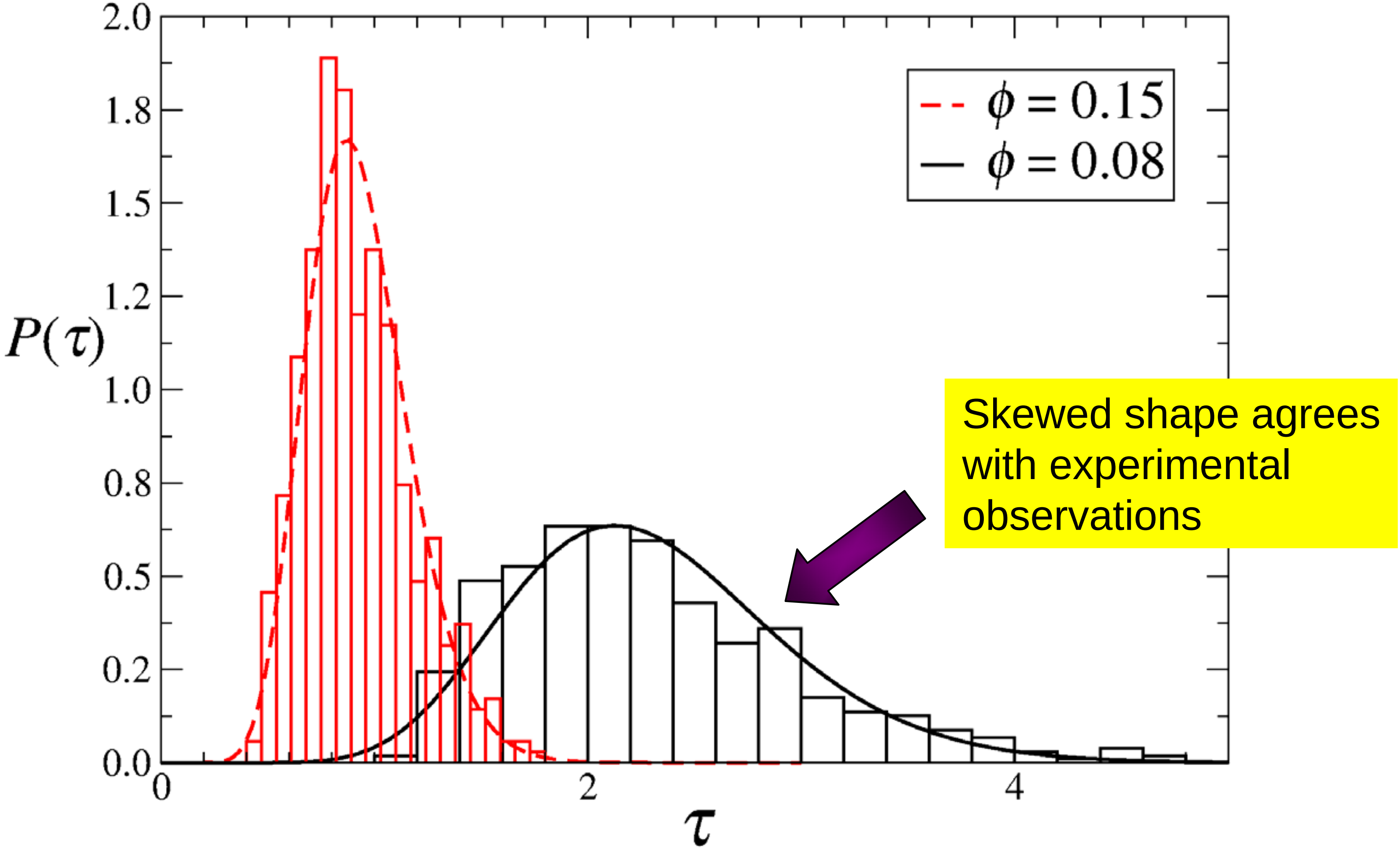


FIG. 4. Comparison with scaling prediction. ρ is 0.168, •; 0.27, ∗; 0.387, ▲; 0.443, ■; and 0.57, +. Solid line, a guide to the eye, has a slope of 1.

Distribution of translocation times



Conclusions

- Monte Carlo simulations combined with thermodynamic integration show that the free energy of confinement sensitively depends on confining geometry
- Widely used generalized expression for ΔF is incorrect, but numerical data accurately confirm revised blob scaling
- Effect on translocation out of confined geometries is confirmed: chains escape much faster out of triaxial confinement than out of cylindrical or planar geometries
- Chain-length dependence of translocation time satisfies theoretical lower bound
- Old confirmation (*PRL* 2001) of incorrect N-dependence and incorrect ΔF can be understood from cancellation of errors and insufficient numerical accuracy

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