Collapse transition in the presence of an applied force

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Lattices and Trajectories:
A Symposium of Mathematical Chemistry
in honour of
Ray Kapral and Stu Whittington

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Motivation of Research

Research is based on R Brak, AJ Guttmann and SG Whittington, J. Phys. A.: Math. Gen. 25 (1992) 2437-2446.

With the advancement of scientific technology,
it is possible to investigate
the collapse transition of a single molecule
in dilute solution.

REVISIT THE PROBLEM

Scientific Approach

What is the "nature" of the problem?

System conditions → linear polymer in dilute solution

→ phase transitions only in the infinite polymer limit

How will you approach the problem?

Configuration model → Directed walk model

Interacting partially directed walk model (IPDSAW)

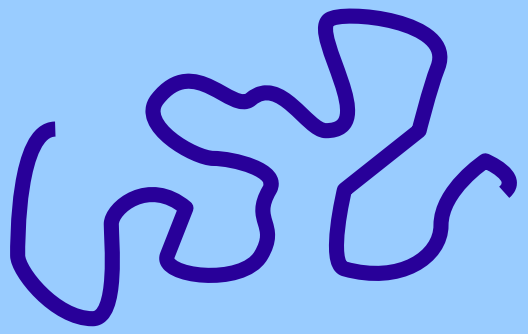
Why choose this approach to solve the problem?

The IPDSAW model a subset of self-avoiding walks (SAW)

a *solvable* model of a polymer collapse

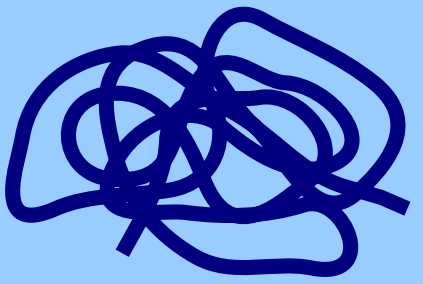
Polymer Conformation

extension



Repulsive “effective” interaction

collapse



Attractive “effective” interaction

Polymer conformation depends on:

- Temperature variable
- Applied force variable

Statistical Mechanics

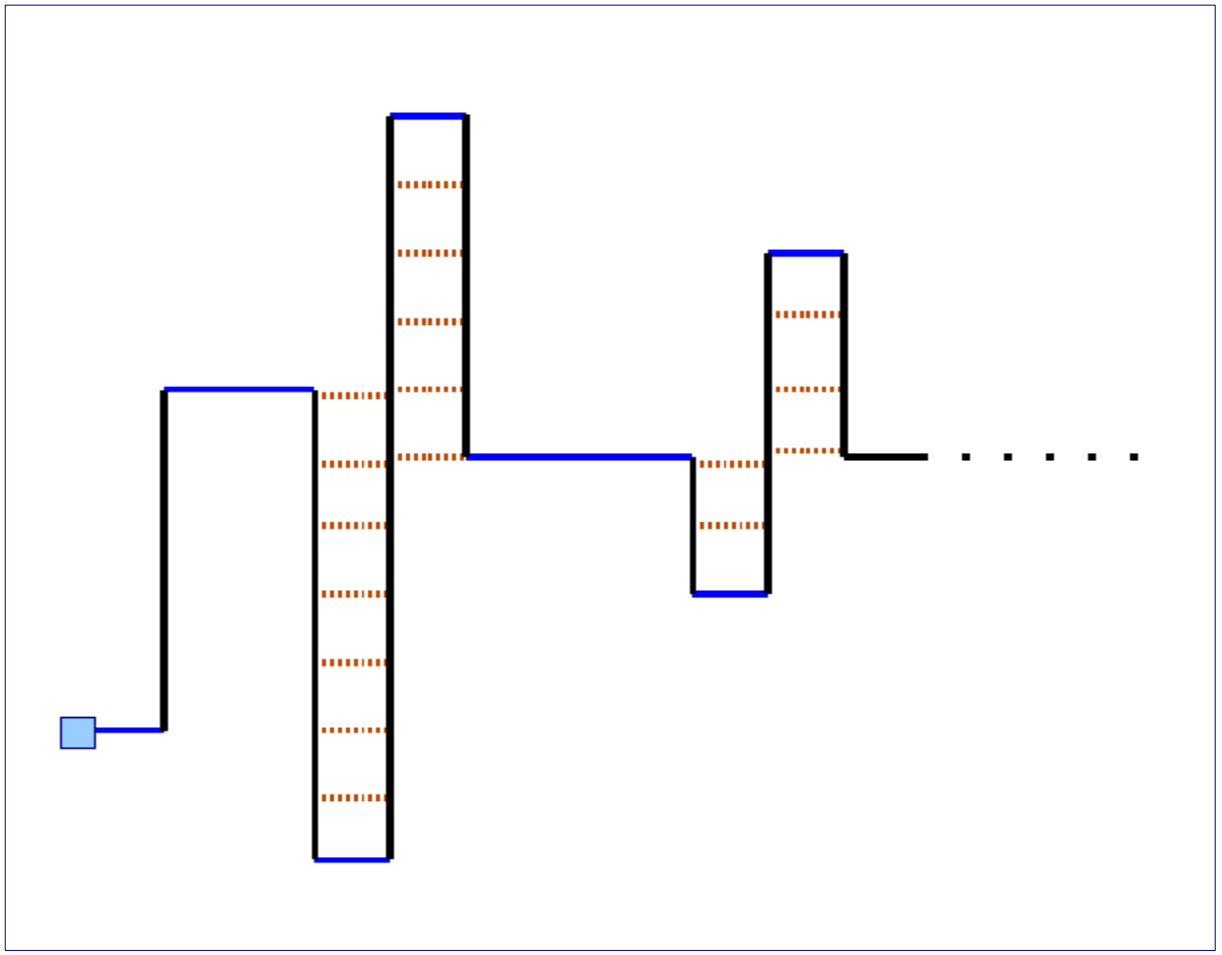
Partition function $$Z_n(x,y)=\sum_{m,s\le 0} c_n(m,s)\,x^m\,y^s$$

→ **temperature variable**
monomer-monomer interaction energy, ϵ $$x=e^{-\epsilon/k_BT}$$

→ **'*span*' variable**
elastic force, f $$y=e^{f/k_BT}$$

Generating function $$\sum_n Z_n(x,y)\,z^n=G(x,y,z)$$

The configuration model partially directed walks



Possible steps on
a 2-D square lattice

north or south step

east step

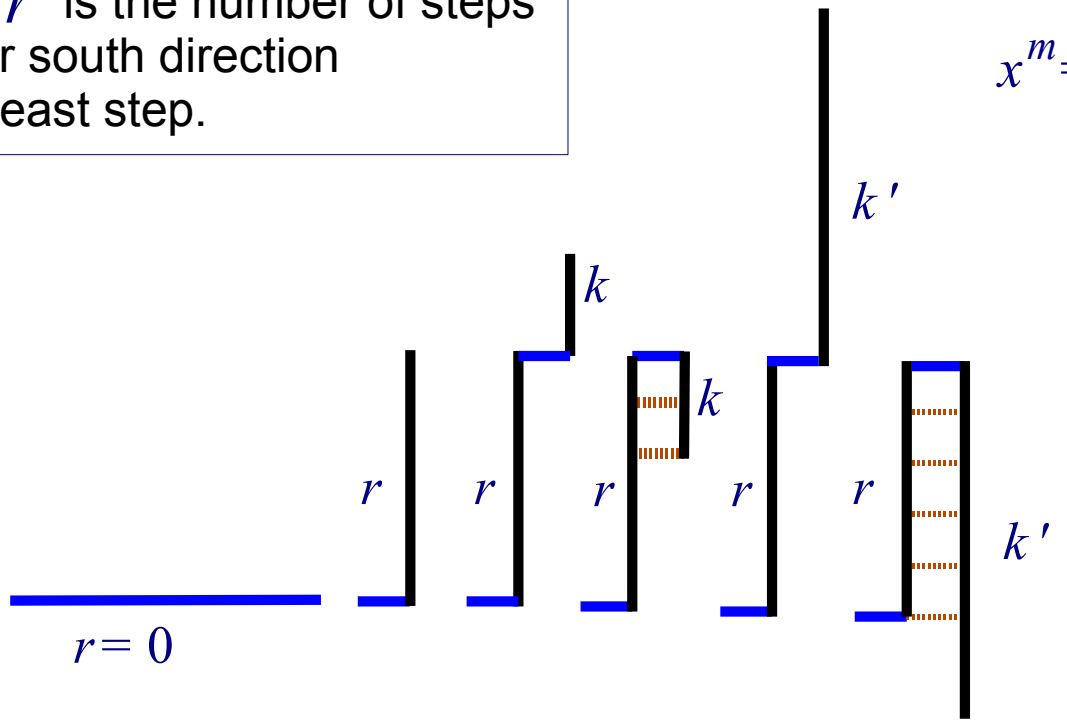
near-neighbour contact

Temperley method

$$G(x,y,z) = \sum_r g_r(x,y,z)$$

The variable r is the number of steps in the north or south direction after the first east step.

$x^m = x^r$ where $k' > r$



Recurrence Relations

Partial generating functions

$$g_0 = yz + yz\left(g_0 + g_1 + g_2 + \cdots\right)$$

$$g_r = yz^{r+1}\left(2 + \sum_{k=0}^{r}\left(1+x^k\right)g_k + \left(1+x^r\right)\sum_{k=r+1}^{\infty} g_k\right)$$

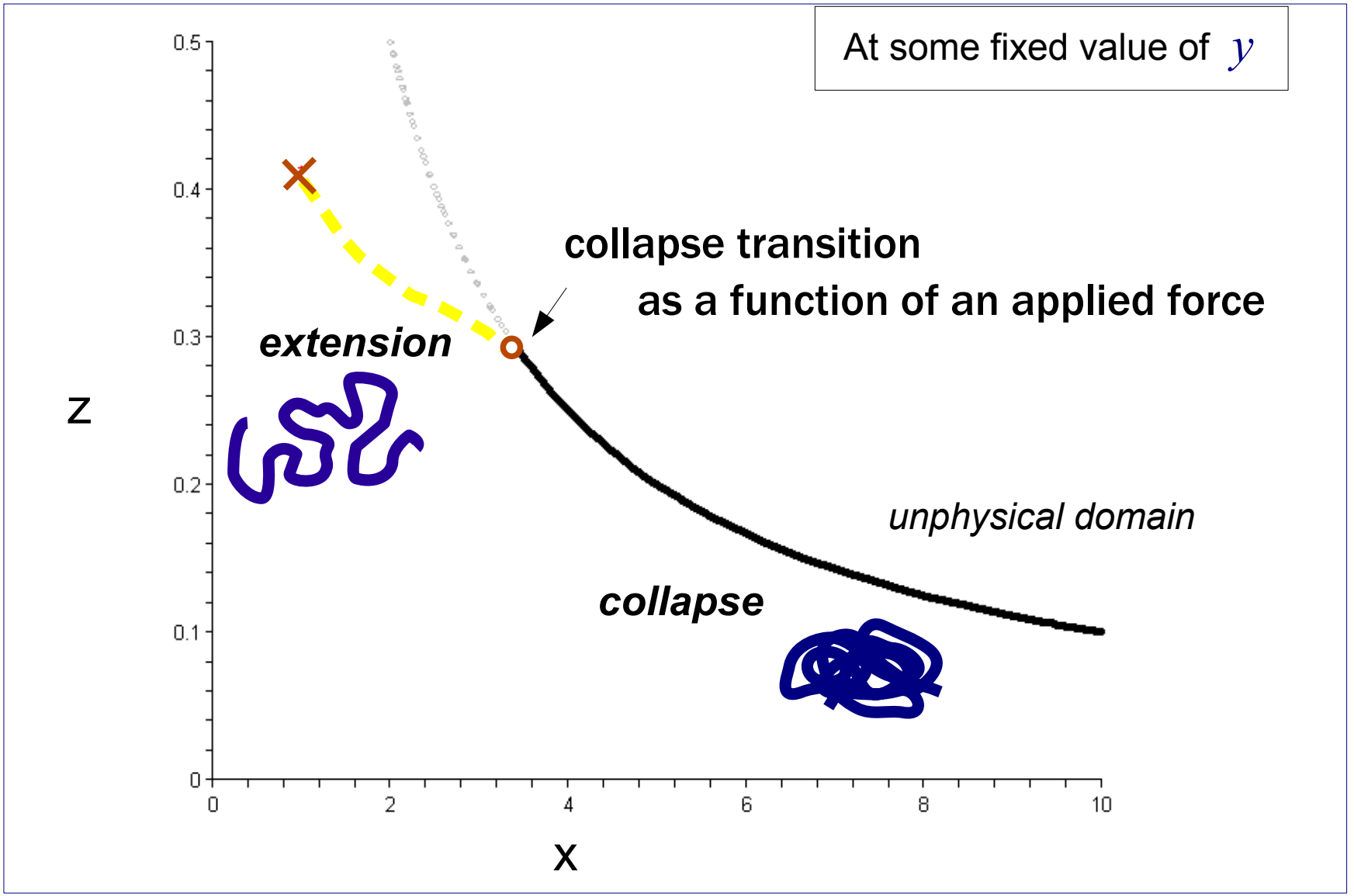
Difference equation

$$g_{r+1} - \left(z+xz\right)g_r + x^r y z^{r+2}\left(x-1\right)g_r + x z^2 g_{r-1} = 0$$

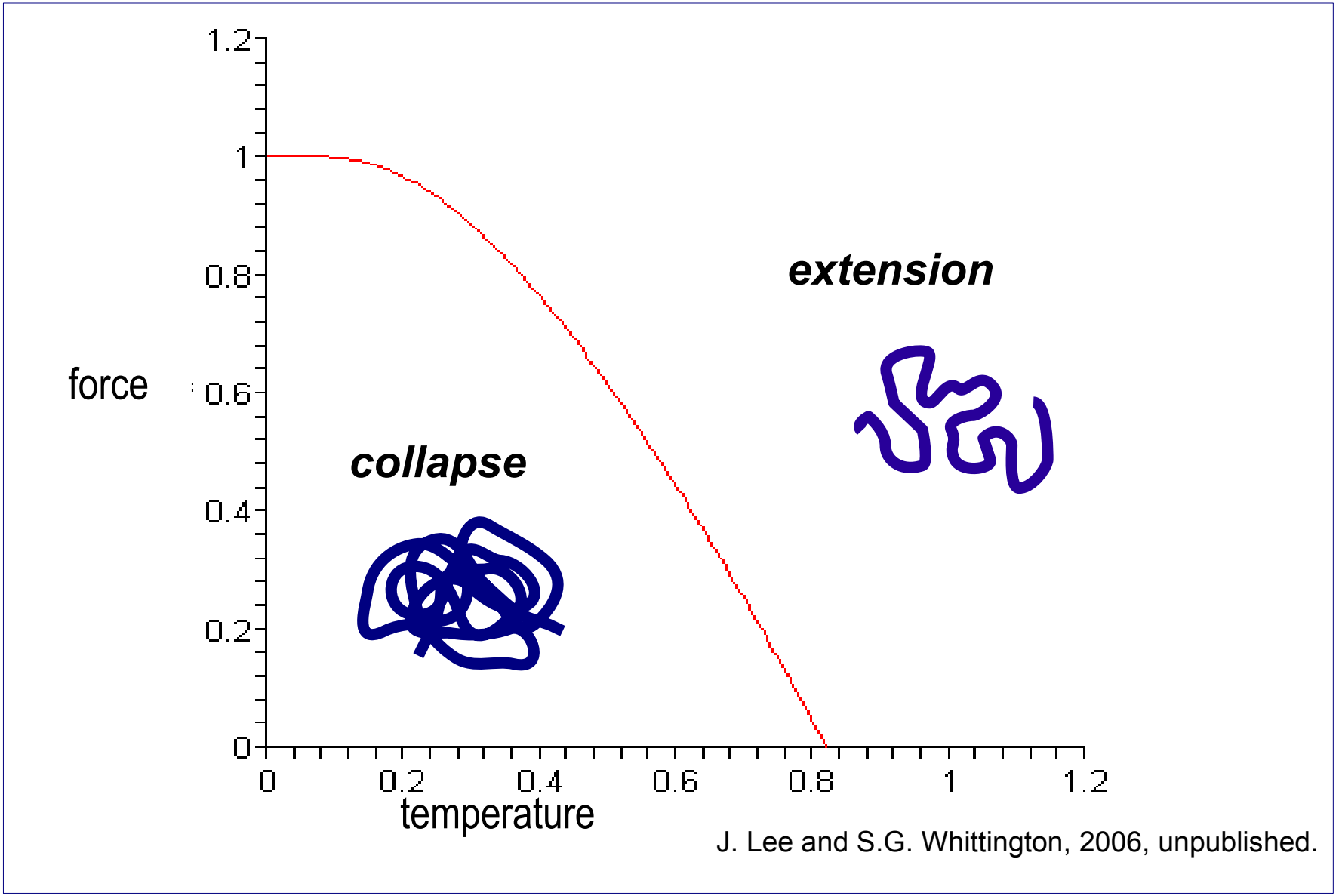
The difference equation can be solved and determines $G\left(x, y, z\right)$

The thermodynamics of the model is determined by the singularity structure of $G\left(x, y, z\right)$

Singularity diagram



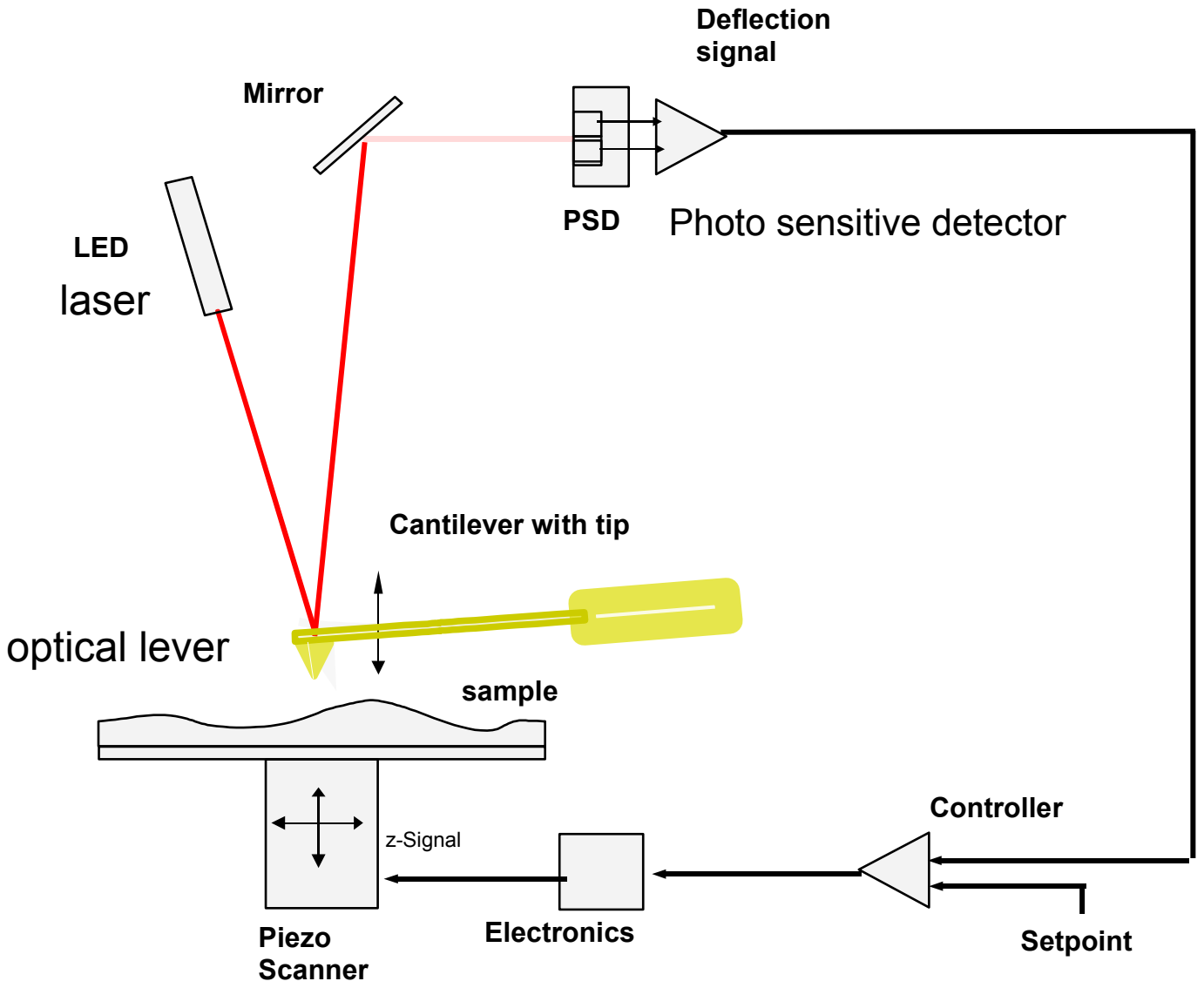
Force and critical temperature



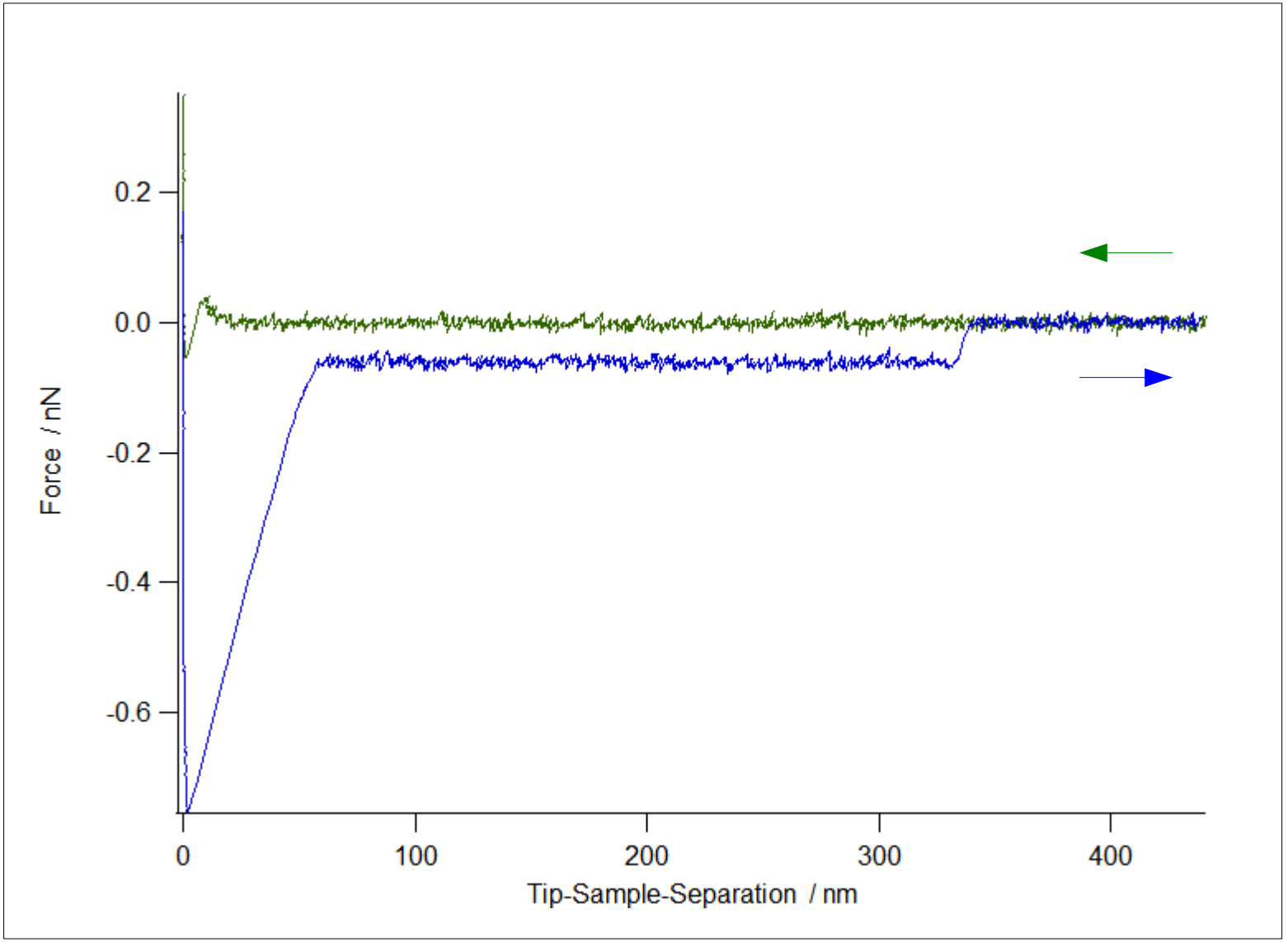
J. Lee and S.G. Whittington, 2006, unpublished.

cf. Rosa, Marenduzzo, Martin and Seno, Phys Rev E **67** 041802 (2003).

Atomic force microscopy (AFM)



Force-distance curve of polystyrene in water



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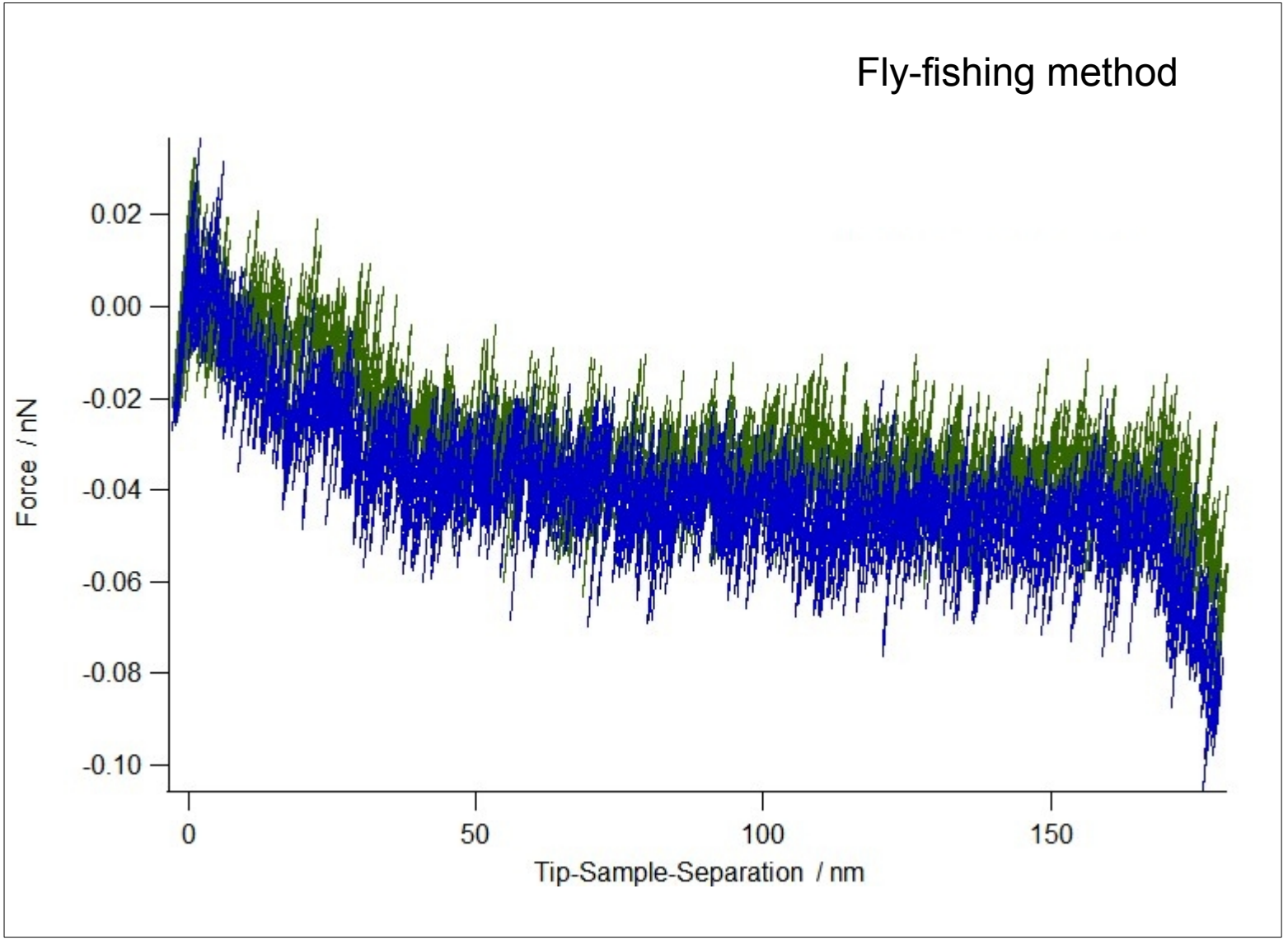

Summary

SCIENTIFIC PROBLEM:

The collapse transition of a linear homopolymer in dilute solution in the presence of an applied force was investigated.

RESULTS AND DISCUSSION:

Exact expression of the generation function $G(x, y, z)$ → All theoretical results are derived from this one mathematical expression

Analytic structure of $G(x, y, z)$:

- singularity diagram → phase diagram- number of monomers in a polymer chain and their interaction
- temperature and critical force diagram → relates the temperature and the applied force with respect to polymer conformation

Force spectroscopy using AFM → Single polymer force curves exhibit characteristic profiles in “poor” solvent conditions; single pulling event has low probability

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Thank you for your time and attention