Hopping Transport in a Ring of Sites:

A Semi-Analytical Study of a Diffusion Process

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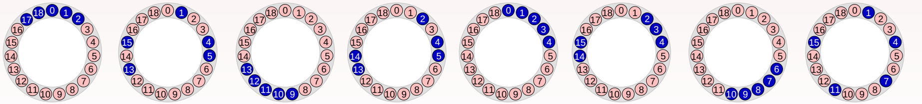

Acknowledgments

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Prologue: A Jack of Many Trades?

Some of the topics I've dabbled with (and published about) in the past:

- **Foundations of quantum theory:**
  Tunneling time problem, uncertainty relations
- **Applied quantum mechanics:**
  Scanning Tunneling Microscopy,
  Photodetachment process, "atom laser"
- **Semiclassical approximation:**
  Quantum Ballistic Motion (QBM!),
  Charged-particle waves in electromagnetic fields
- **Statistical physics:**
  Persistent random walk, "micromaser," diffusion problems

A topic I have *not* dabbled specifically with in the past:

- **Biophysics**

Erwin Schrödinger's Apology

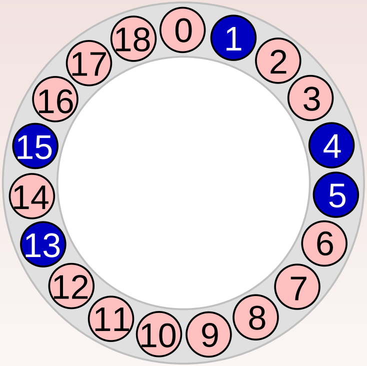
"A scientist is supposed to have a complete and thorough knowledge, at first hand, of *some* subjects, and therefore, is usually expected not to write on any topic of which he is not a master. This is regarded as a matter of *noblesse oblige*. For the present purpose, I beg to renounce the *noblesse* ...

... some of us should venture to embark on a synthesis of facts and theories, albeit with second-hand and incomplete knowledge of some of them — and at the risk of making fools of ourselves.

So much for my apology."

Preface, *What is Life? The Physical Aspect of the Living Cell* (1944).

Diffusion on a Closed Loop — Setup



Circular chain with

- p equivalent sites,

hosting

- k identical objects.

(Here, $p = 19$ and $k = 5$.)

Occupation rules:

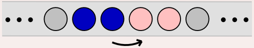
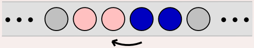
- Sites are occupied or empty.
- Objects cannot share sites.

Diffusion on a Closed Loop — Rules of the Game

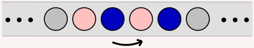
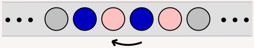
- Objects can "jump" to empty neighboring sites.
- Jump rates depend on occupation of adjacent sites:
  - Motion of isolated objects (rate A)

 or 

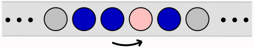
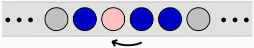
  - Separation from a "block" (rate B)

 or 

  - Fusion of object to "block" (rate C)

 or 

  - Transfer between "blocks" (rate D)

 or 

Diffusion on a Closed Loop — Analysis

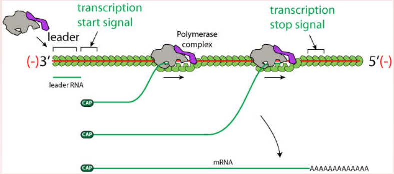
Quantities of interest:

- The "dead" loop: Equilibrium properties
  - Partition function
  - Pattern averages
- The "alive" loop: Kinetics
  - Symmetry properties
  - Master equation
  - Numerical approach
  - Sample results

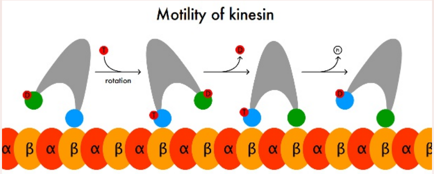
Publication: J.-S. McEwen, S. H. Payne, H. J. Kreuzer, C. Bracher, Int. J. Quant. Chem. **106**, 2889 (2006).

Interlude: A Biological Connection?

Motion along one-dimensional chains is a common motif in cell biology:



Transcription of DNA



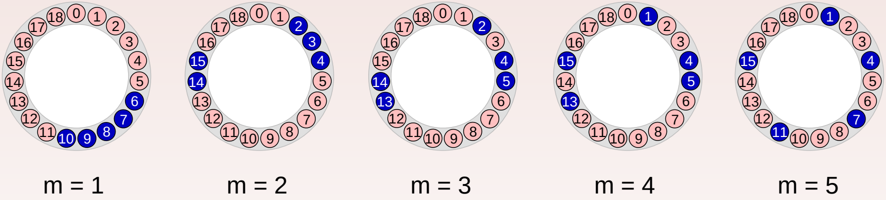
Molecular Motors

Does interaction between “adsorbates” play a role?

Loop in Equilibrium: Block Numbers

- Block number $m[\mathcal{Z}]$ of a configuration $\mathcal{Z}$:

  Number of contiguous “blocks” of objects in loop



- Equilibrium average $p_{\mathrm{eq}}[\mathcal{Z}]$ of configuration depends only on m!
- m changes in fusion and separation processes only ($\Delta m = \pm 1$)

Loop in Equilibrium: Partition Function

- Principle of detailed equilibrium:

$$\frac{p_{\mathrm{eq}}[\mathcal{Z}']}{p_{\mathrm{eq}}[\mathcal{Z}]} = \left(\frac{B}{C}\right)^{m[\mathcal{Z}']-m[\mathcal{Z}]}$$

- Number $N[p,k,m]$ of configurations with m blocks:

$$N[p,k,m] = \frac{p(p-k-1)!(k-1)!}{m!(k-m)!(m-1)!(p-k-m)!}$$

- Partition function $Z[p,k]$:

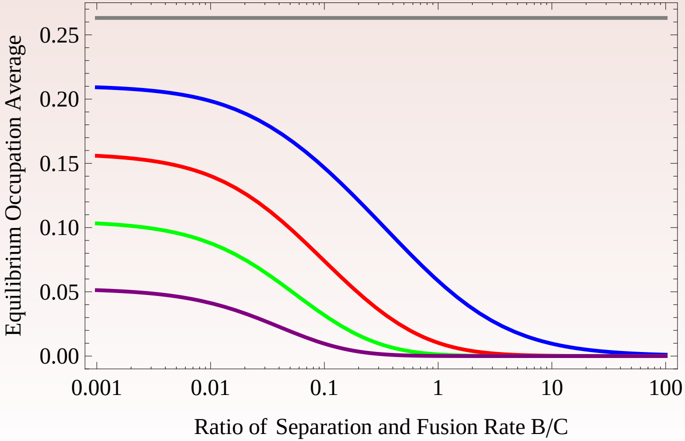
$$Z[p,k] = \sum_{\mathcal{Z}} p_{\mathrm{eq}}[\mathcal{Z}] = \sum_{m=1}^{k} N[p,k,m]\,(B/C)^m$$

can be expressed as a hypergeometric series:

$$Z[p,k] = \frac{B}{C} \cdot {}_2F_1(1-k,\,1-p+k,\,2;\,B/C)$$

Loop in Equilibrium: Correlation Functions

- Correlation functions (pattern averages) follow from $Z[p, k]$
- Example: $\langle \bullet \rangle$, $\langle \bullet\bullet \rangle$, $\langle \bullet\ \bullet\ \bullet \rangle$, $\langle \bullet\ \bullet\ \bullet\bullet \rangle$, $\langle \bullet\ \bullet\ \bullet\ \bullet\ \bullet \rangle$ $(p = 19,\ k = 5)$



Kinetics of the Loop: Three Solution Approaches

Now, consider the loop out of equilibrium. Compare three approaches:

- Monte Carlo Simulation
  - \+ Easy to implement
  - − Not systematic, statistical error, interpretation of results?
- Mean Field Methods (Diffusion Equation)
  - \+ Established method, good for extended, dilute systems
  - − Misses correlations between objects
- Diagonalization
  - \+ Provides exact results
  - − Numerically expensive, complexity grows fast with system size
  - \+ "Borrow" tricks from quantum mechanics

Symmetry and Invariance — A Primer

Some quantum theory in a nutshell:

- Physical state of system is contained in state vector $|\Psi\rangle(t)$
- Time-dependent Schrödinger equation controls state evolution:

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle(t) = \mathcal{H}|\Psi\rangle(t)$$

  $\mathcal{H} = \mathcal{H}^\dagger$ is the Hamilton operator

- A symmetry of the system is represented by a unitary operator $\mathcal{U}^{-1} = \mathcal{U}^\dagger$ that commutes with $\mathcal{H}$:

$$\mathcal{U}\mathcal{H}\mathcal{U}^\dagger = \mathcal{H}$$

- A symmetry $\mathcal{U}$ induces a decomposition of $\mathcal{H}$ into orthogonal parts:

$$\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus \ldots \oplus \mathcal{H}_n$$

  ("block-diagonal form"), associated with the eigenspaces of $\mathcal{U}$.

Physical Symmetries of the Diffusion Problem

Symmetries thus simplify diagonalization, i. e., finding the eigenvalues and -states E_ν, $|\Psi_\nu\rangle$ of $\mathcal{H}$, by splitting $\mathcal{H}$ into smaller, independent parts.

- Idea: Use the same principle to solve the diffusion problem!
- Physical symmetries of the diffusion setup:
  - Rotation of the pattern by an angle $2\pi/p$ (or a multiple)
  - Mirror reflection symmetry
  - Exchange of occupied and empty sites ("particle-hole symmetry")

Classifying Congruent Patterns

Insight (from abstract algebra):

- For prime p, the numbers $0, 1, \ldots, p-1$ form a number field under arithmetics *modulo* p.
- Convenient to choose a prime number of sites p in the loop!

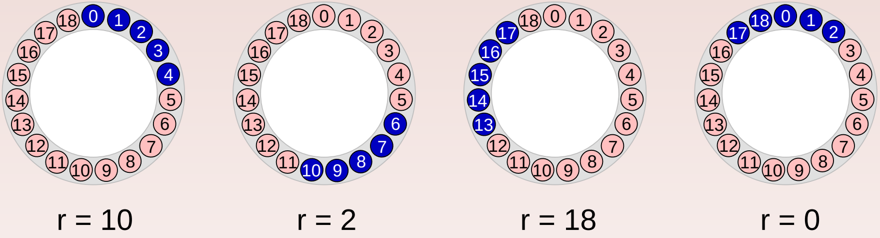
Consequences:

- Every non-trivial rotation of a pattern of k objects yields a congruent, yet distinct pattern.
- Patterns form equivalence classes $\{\mathcal{Z}\}$ with p members each.
- The pattern sum r is a unique identifier of each pattern within a class:

$$r = (\text{sum of occupied site labels}) \mod p$$

(**Note**: None of this holds for composite p.)

Classifying Congruent Patterns — Example

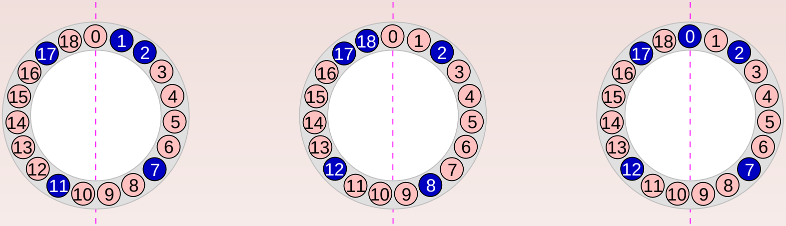


- Primitive pattern with sum $r = 0$ is representative of class.
- Number of distinct primitives:

$$n[p,k] = \frac{(p-1)!}{k!(p-k)!}$$

- Straightforward binary coding scheme

Mirror Reflection Symmetry



mirror image pair

palindrome

- Pattern sum r changes sign under reflection
- Mirror image of primitive configuration is again primitive:
  - Pairs two different primitives $\mathcal{Z}$ and $\mathcal{Z}'$, or
  - has inherent reflection symmetry (palindromic configuration)

Rate Matrices and Master Equation

As objects jump into adjacent sites, their configuration $[\mathcal{Z}|r]$ changes.

- A pattern $\mathcal{Z}$ with block number m permits m possible jumps in (counter-)clockwise direction.
- Jump changes the pattern sum r by ± 1
- Jumps target distinct primitive configurations $\mathcal{Y}$:
  Set up rate matrices $\mathbf{R}_{\circlearrowleft}[\mathcal{Y},\mathcal{Z}]$, $\mathbf{R}_{\circlearrowright}[\mathcal{Y},\mathcal{Z}]$

Occupation of a particular configuration $\langle[\mathcal{Z}|r]\rangle$ changes through:

- loss due to jumps leaving $\mathcal{Z}$:

$$R[\mathcal{Z}] = \sum_{\mathcal{Y}} \left(\mathbf{R}_{\circlearrowleft}[\mathcal{Y},\mathcal{Z}] + \mathbf{R}_{\circlearrowright}[\mathcal{Y},\mathcal{Z}]\right)$$

- gain through jumps from accessible configurations $[\mathcal{Y}|r \pm 1]$.

Rate Matrices and Master Equation

Master equation: Rate equation for occupation probability

$$\frac{d}{dt}\left\langle[\mathcal{Z}|r]\right\rangle(t) = -R[\mathcal{Z}]\left\langle[\mathcal{Z}|r]\right\rangle(t) + \sum_{\mathcal{Y}} R_{\circlearrowright}[\mathcal{Z},\mathcal{Y}]\left\langle[\mathcal{Y}|r-1]\right\rangle(t) + \sum_{\mathcal{Y}} R_{\circlearrowleft}[\mathcal{Z},\mathcal{Y}]\left\langle[\mathcal{Y}|r+1]\right\rangle(t)$$

Vector-matrix form:

- Collect $\langle[\mathcal{Z}|r]\rangle$ into state vector $\mathbf{P}(t)$ of probabilities,
- Arrange jumping rates $\mathbf{R}_{\circlearrowleft}[\mathcal{Y},\mathcal{Z}]$, $\mathbf{R}_{\circlearrowright}[\mathcal{Y},\mathcal{Z}]$ into transition matrix $\boldsymbol{\mathcal{A}}$:

$$\frac{d}{dt}\mathbf{P}(t) = \boldsymbol{\mathcal{A}}\,\mathbf{P}(t)$$

- Formally similar to TDSE!

Reciprocal Space Patterns

Idea: Use rotational symmetry to simplify the master equation.

- Rotation of pattern $[\mathcal{Z}|r]$ changes pattern sum by fixed offset
- Define reciprocal space patterns via discrete Fourier transformation:

$$(\mathcal{Z}|q) = \frac{1}{p} \sum_{r=0}^{p-1} e^{-2\pi iqr/p} \, [\mathcal{Z}|r]$$

$$[\mathcal{Z}|r] = \sum_{q=0}^{p-1} e^{2\pi iqr/p} \, (\mathcal{Z}|q)$$

- Reciprocal space patterns $(\mathcal{Z}|q)$ are eigenstates under rotations
- Akin to angular momentum eigenstates in quantum mechanics, reciprocal space in solid state physics

Solution in Reciprocal Space

Master equation decouples into p independent equations:

$$\frac{d}{dt}\langle(\mathcal{Z}|q)\rangle(t) = \sum_{\mathcal{Y}} \mathcal{R}_q[\mathcal{Z},\mathcal{Y}]\,\langle(\mathcal{Y}|q)\rangle(t)$$

with reciprocal rate matrix elements:

$$\mathcal{R}_q[\mathcal{Z},\mathcal{Y}] = -R[\mathcal{Z}] + e^{-2\pi i q/p} R_{\circlearrowright}[\mathcal{Z},\mathcal{Y}] + e^{2\pi i q/p} R_{\circlearrowleft}[\mathcal{Z},\mathcal{Y}]$$

- Note: $\mathcal{R}_q[\mathcal{Z},\mathcal{Y}] = \mathcal{R}_{p-q}[\mathcal{Z},\mathcal{Y}]^*$
- Rate matrix $\mathcal{R}_q[\mathcal{Z},\mathcal{Y}]$ is easily transformed into hermitian operator
- Diagonalize matrix using standard methods (QM!)
- Solution is superposition of exponentially decaying modes, decay rates $\lambda_\nu(q)$ are eigenvalues of rate matrices.

Diffusion on a Circle: 5 Objects on 19 Sites

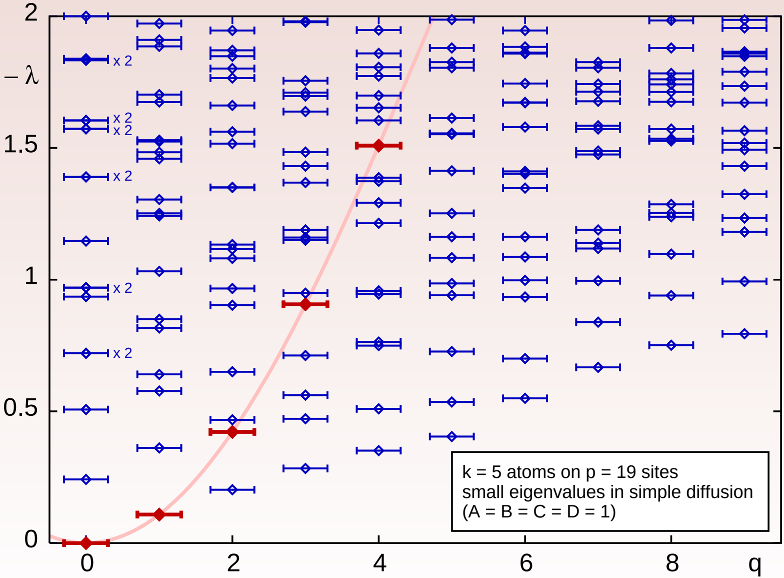
Example: $k = 5$ objects, $p = 19$ sites

- Complexity of the problem:
  - Number of distinct configurations: $N = \binom{19}{5} = 11,628$
  - Number of primitive patterns: $N_p = N/p = 612$ (288 mirror image pairs + 36 palindromes)
  - Primitive patterns $\mathcal{Z}$ by number of blocks m:

m	1	2	3	4	5
$N[p,k,m]$	1	26	156	286	143

- Numerical expense:
  - Find primitive patterns $\mathcal{Z}$, set up rate matrices $\mathbf{R}[\mathcal{Z}, \mathcal{Z}']$
  - Spectral decomposition of hermitian 612×612 matrices for each momentum subspace $q = 0, 1, 2, \ldots, 9$
  - Execution time < 1 min on my laptop (Core i5 processor)

Diffusion on a Circle: 5 Objects on 19 Sites



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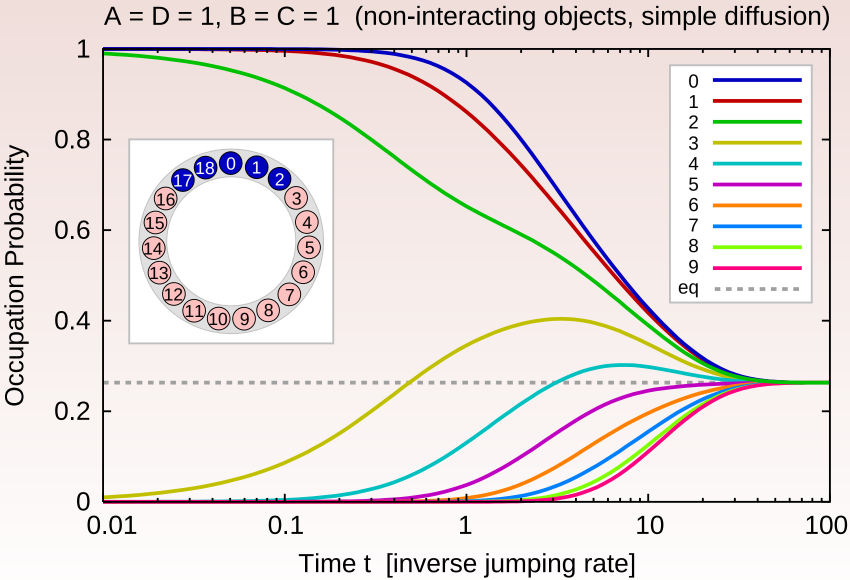
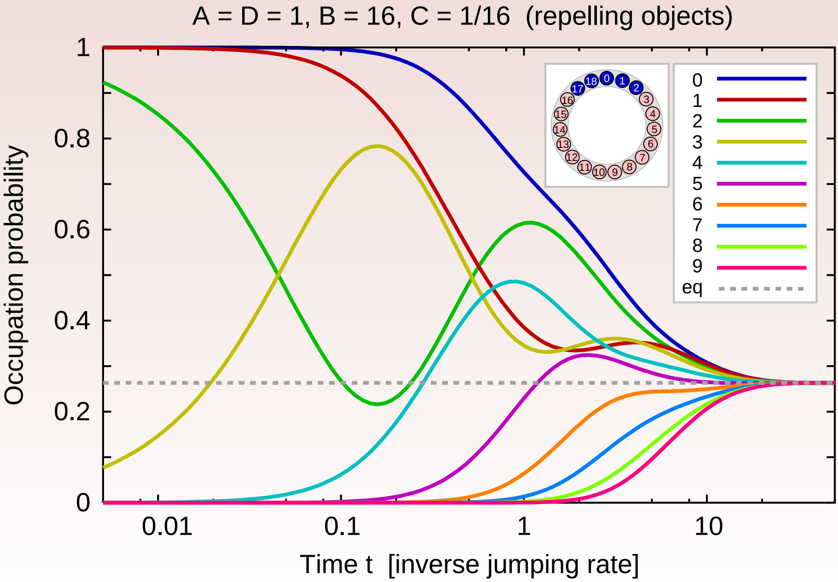


Diffusion on a Circle: 5 Objects on 19 Sites



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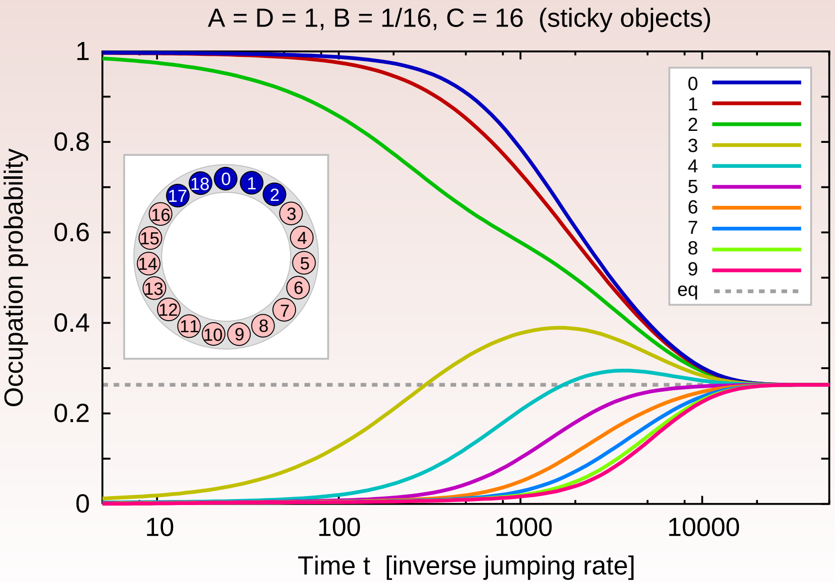
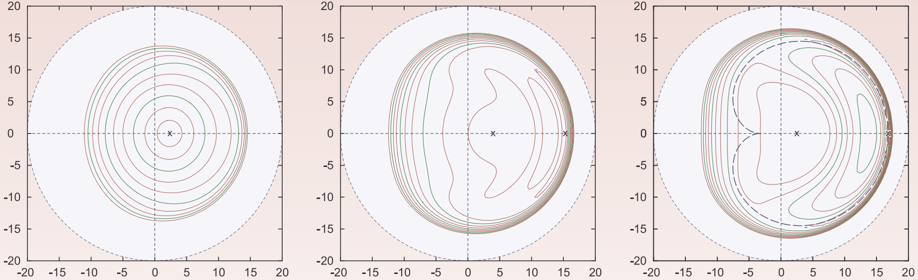


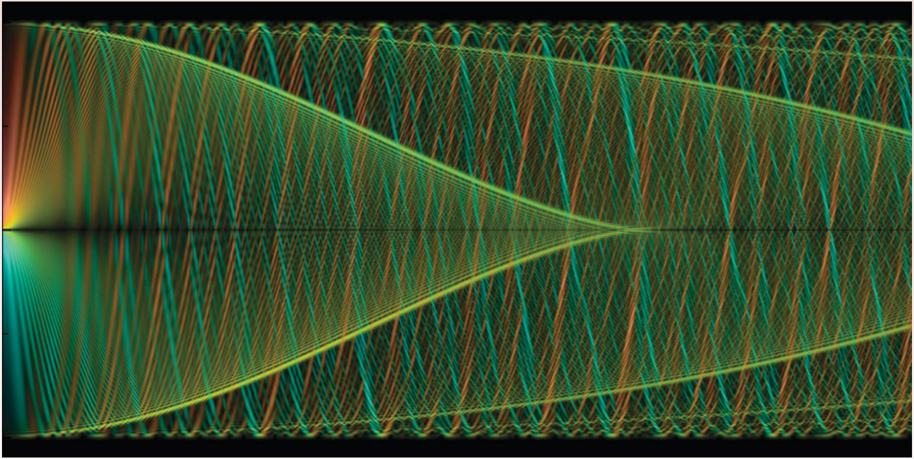
Outlook: Persistent Random Walk



- Persistent random walk in two dimensions
- Interpretation: Simple polymer model
- Shown: Curves of constant entropic force for increasing joint stiffness

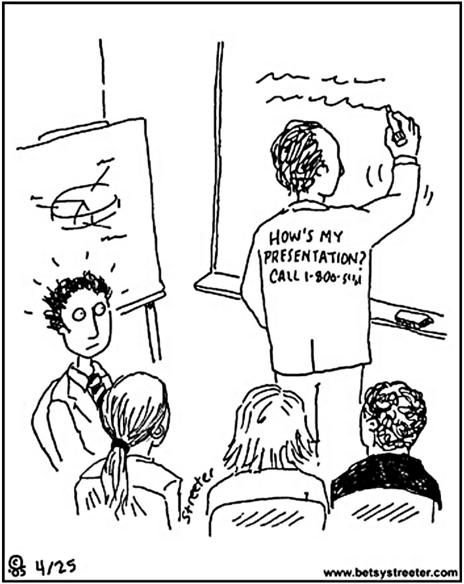
Publication: C. Bracher, Physica A **331**, 448 (2004).

Outlook: Electron Source in a Uniform Magnetic Field



Publication: C. Bracher, A. Gonzalez, Phys. Rev. A **86**, 022715 (2012).

(See also: APS Wall Calendar 2013.)



THANK YOU!

(Questions? Just ask!)