# TORN POLYMER LIQUIDS

using tricks from the quantum world to understand them


GT Paul M. Goldbart, Zeb Rocklin → Michigan → Cornell → GT

GT Shina Tan, Anton Souslov → Leiden

GT Benjamin Loewe

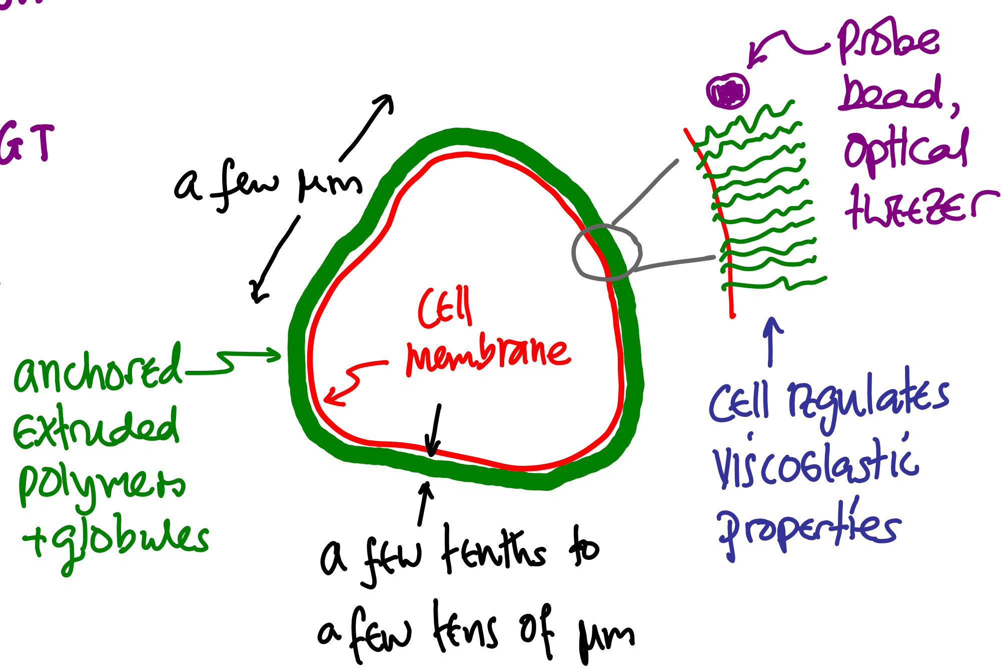

Phys Rev B (2012, 2013), Phys Rev Lett (2013), Phys Rev E (2015)

2D directed, 3D directed, 2D Dirac

Inspired by experiments on the pericellular coat by Jennifer Curtis' group at GT

- chain/globule aggregate enshrouding certain mammalian cells
- impact on cell motility, adhesion

eg. Hyaluronan (polysaccharide chain)
Aggrecan (proteoglycan globule)



# SOME WELL-KNOWN CONSEQUENCES OF POLYMER SEGMENT REPULSION

POLYMERS: characteristic equilib. size, good solvent, dilute

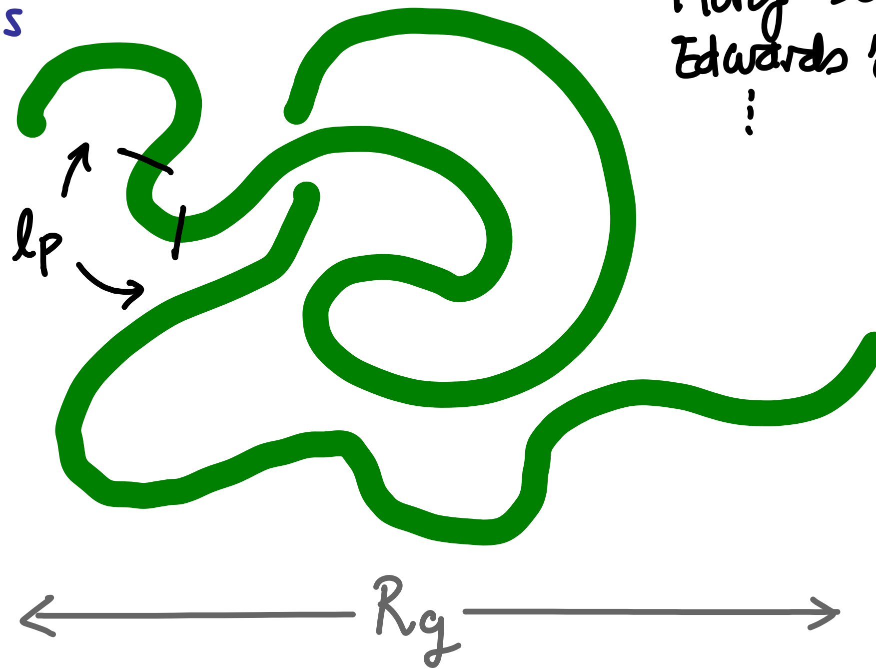
- long flexible molecules
- persistence length
- arc length $N \ell_p$

  # of indep segs

- radius of gyration

  $R_g \sim \ell_p N^{\nu}$

Flory '50s
Edwards '65
⋮



# POLYMERS: characteristic equilib. size, good solvent, dilute

- no self-avoidance

  $\nu = 1/2$

- self-avoidance

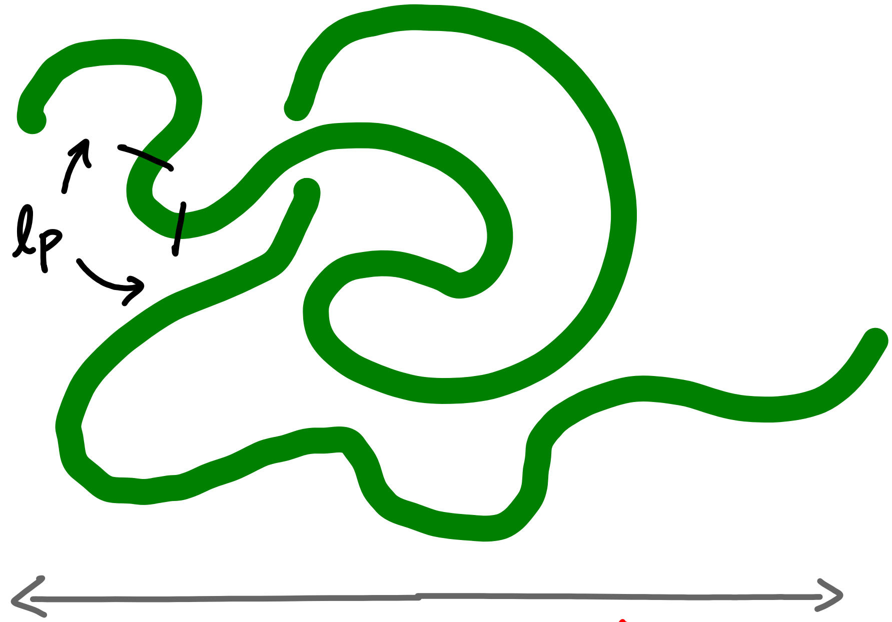
  $(D=3)$ $\nu \approx 3/5$

  $(= 1/2 + 1/10)$

Example:

$$\left.\begin{array}{l}\text{arclength} \sim \mu m \\ \text{persist. length} \sim nm\end{array}\right\} N \sim 2^{10}$$

$$R_g^{\text{with}} / R_g^{\text{w/out}} \sim \boxed{2} \;!!$$




$$R_g \sim \ell_p N^{\nu}$$

# MELT DYNAMICS: REPTATION

deGennes '71, Doi-Edwards '78

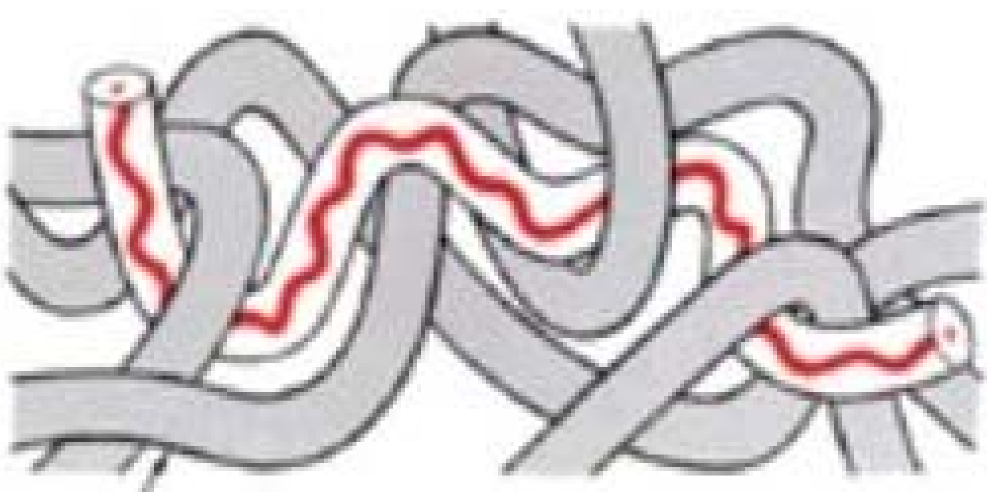


fig: www.nobelprize.org

simple theory $\mu = 3$

measured $\mu \approx 3.3$

$$\tau \sim N^{\mu}$$

time to exit tube

silly putty visco-elasticity

## KEY THEMES FOR TODAY

fluctuating objects
+ low dimensions
+ interactions

well-known triptych in quantum hard condensed matter

eg fractional quantum Hall effect, high-temperature supercond....

⇒ qualitatively new phenomena

e.g. topological constraints, torn fluids

**KEY INSPIRATION:** de Gennes, J Chem Phys (1968)

UNDERLYING
SCHEMA

PROGRESSING...

FROM MICROSCOPIC DESCRIPTIONS
TO EMERGENT COLLECTIVE PROPERTIES

from...

- electrons to superconductivity (eqm state, excitations, response)
- rodlike molecules to liquid crystallinity (structure, elasticity)
- atoms to solids (rigidity, phonons)
- electrons to topological insulators, quantum Hall effects
  (charge fractionalization, new quantum numbers)

DERIVING THE MACRO FROM THE MICRO

Boltzmann & Gibbs

Helmholtz thermodynamic free energy

Energy of a micro. configuration

$$\boxed{e^{-F/T} = \sum e^{-H/T}}$$

temperature
(units: $k_B = 1$)

independent micro. configs
(in phase space, coords & momenta)

- Have H
- Perform sum
- Get thermodynamic potential
- Mechanics, treated statistically

Origin: Entropy of composite system (reservoir at temp T & system of interest)

# DERIVING THE MACRO FROM THE MICRO

## Boltzmann & Gibbs

**Example:**
**Particle in a box**
$$H = \frac{p^2}{2m}$$

$$e^{-F/T} = \underset{\text{independent micro. configs}}{\sum} e^{-H/T}$$

NB: all numbers = 1

$$\frac{1}{2m}\left(\frac{\hbar}{\lambda_{dB}}\right)^2 = k_B T$$

← thermal deBroglie wavelength

$$e^{-F/T} = \underbrace{\int dq\, dp}_{1/\hbar^3} \exp\left\{-\frac{1}{T}\frac{p^2}{2m}\right\} \sim V/\lambda_{dB}^3$$

Entropy $\quad S = -\frac{\partial F}{\partial T} = \ln\left[e^{3/2} V/\lambda_{dB}^3\right]$

Energy $\quad U = F + TS = 3T/2$

Heat capacity $\quad C = T\frac{\partial S}{\partial T} = 3/2$

} Classical equipart.

# DERIVING THE MACRO FROM THE MICRO

**Boltzmann & Gibbs**

$$e^{-F/T} = \sum e^{-H/T}$$

independent micro. configs

> **Example:**
> **Classical Harmonic Oscillator**
> $$H = \frac{p^2}{2m} + \frac{m}{2}\omega^2 q^2$$

$$e^{-F/T} = \int \underbrace{dq\,dp}_{1/\hbar} \exp\left\{-\frac{1}{T}\left[\frac{p^2}{2m} + \frac{m}{2}\omega^2 q^2\right]\right\} = 2\pi \frac{T}{\omega}$$

$T \to kT$, $\omega \to \hbar\omega$

Entropy $\quad S = -\frac{\partial F}{\partial T} = -\frac{\partial}{\partial T}\left[-T \ln \frac{2\pi T}{\omega}\right] = \ln(2\pi e T/\omega)$

Energy $\quad U = F + TS \quad = T \quad$ Classical equipart.

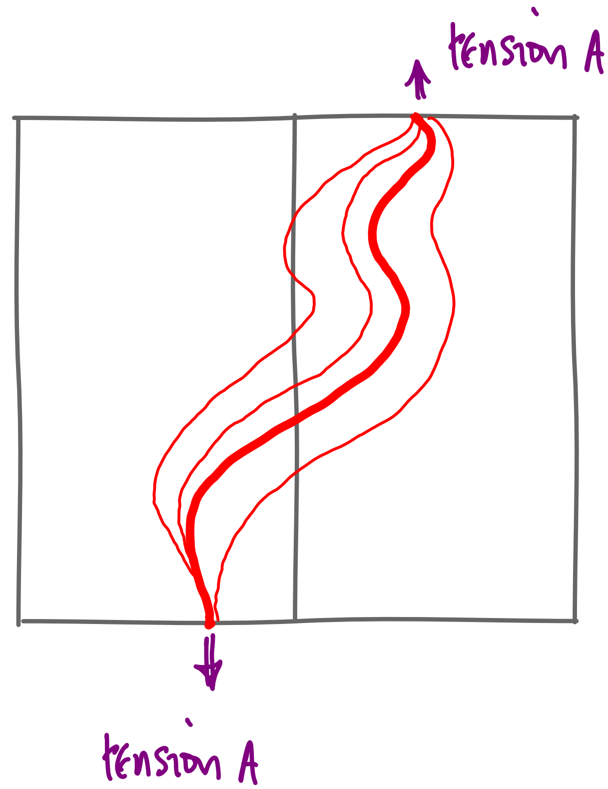
Heat Cap $\quad C = T\frac{\partial S}{\partial T} \quad = 1 \quad \left(= \underset{KE}{\frac{1}{2}} + \underset{PE}{\frac{1}{2}}\right)$

# SINGLE DIRECTED FIBER UNDER TENSION

- almost straight
- small deflections
- thermally excited

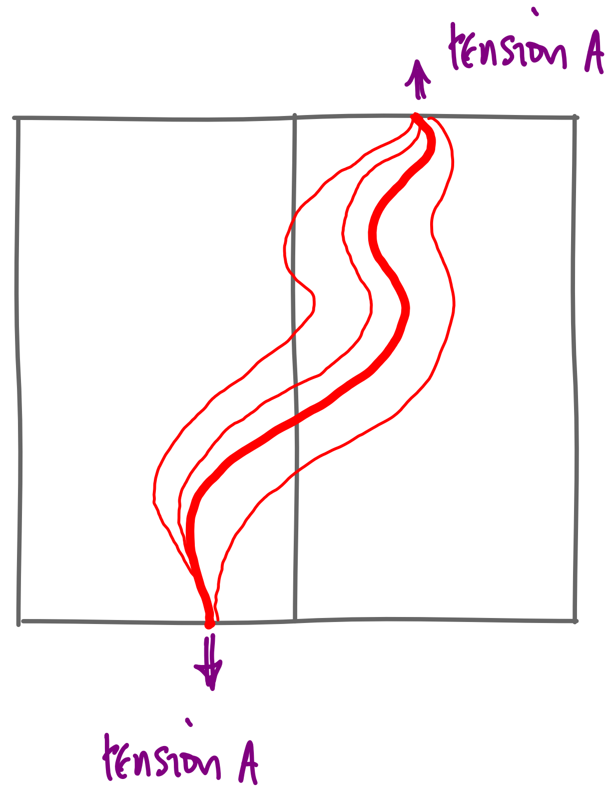
Aim: derive thermodynamics (and correlations, response) using statistical mechanics

Note: focus on configs, not kinetic energy



SINGLE DIRECTED FIBER UNDER TENSION – but also...

- polymers in a nematic background
- wandering step edges on crystal surfaces
- vortex lines in planar Type II superconductors
- KPZ growing interfaces



# SINGLE DIRECTED FIBER UNDER TENSION: ENERGETICS

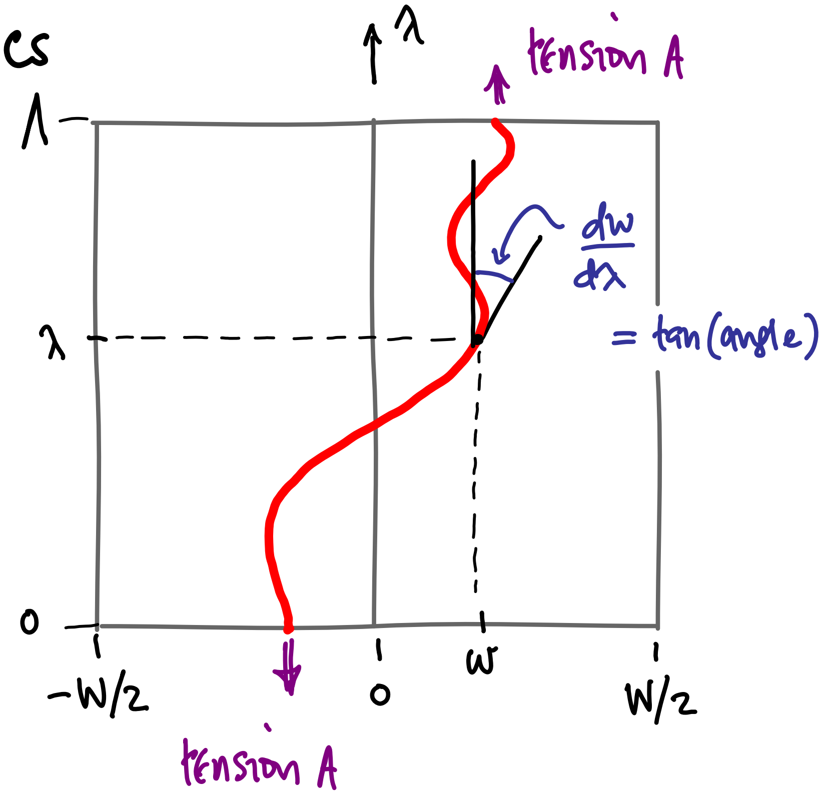
- describe by
  deflection $w$ at height $\lambda$
- increase in length

$$\delta \ell = \sqrt{\delta\lambda^2 + \delta w^2} - \delta\lambda$$

$$\approx \frac{1}{2}\left(\frac{dw}{d\lambda}\right)^2 \delta\lambda$$

- potential energy

$$A \int_0^\Lambda d\lambda \, \frac{1}{2}\left(\frac{dw}{d\lambda}\right)^2$$



# FIBER STATISTICAL MECHANICS

– sum over configurations

$$e^{-F/T}$$

free energy

temperature

$$=$$

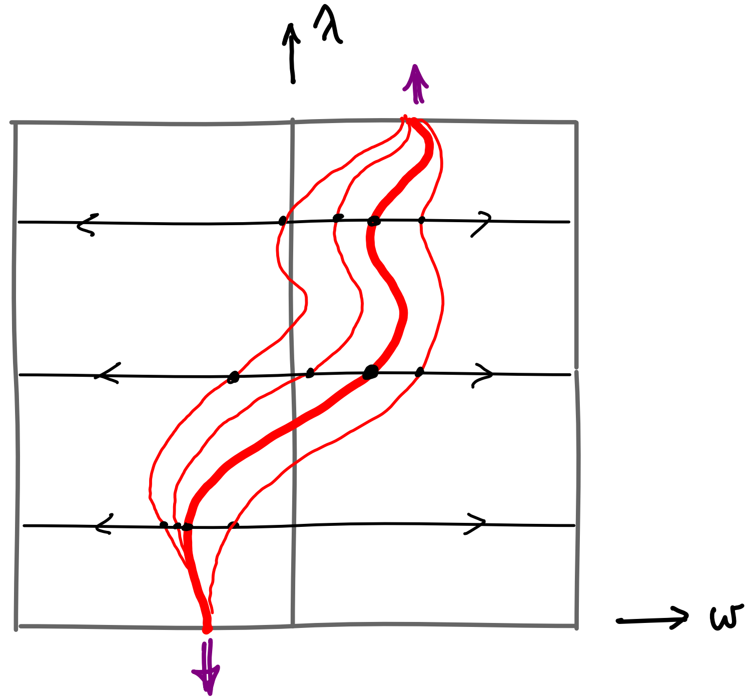
$$Z$$

partition function

$$=$$

$$\int \mathcal{D}w(\cdot)\, \exp\left\{ \underbrace{-\frac{A}{2T}\int_0^{\Lambda} d\lambda \left(\frac{dw}{d\lambda}\right)^2}_{\text{tension x excess length / temperature}} \right\}$$

an integration for each $\lambda$



NOW LET'S LOOK AT A SUPERFICIALLY COMPLETELY DIFFERENT QUESTION:

A QUANTUM PARTICLE MOVING IN ONE SPATIAL DIMENSION

## QUANTUM ANALOGY —
probability amplitudes


particle here at time 0

What is the probability amplitude to be here at time T ?

Standard approach:
spreading Schrödinger wave packet

(cf diffusion as imaginary-time Schrö eqn)

$t=0$ gaussian at $w^i$, spread $\delta$

$\Rightarrow$ gaussian at $w^i$, spread $\Delta$

$$\frac{m\Delta}{t} = \frac{\hbar}{2\delta}$$

defines spread $\Delta$ at (late) times $t$

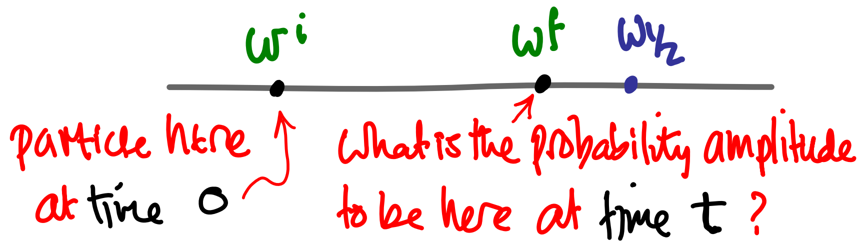
characteristic momentum in initial packet

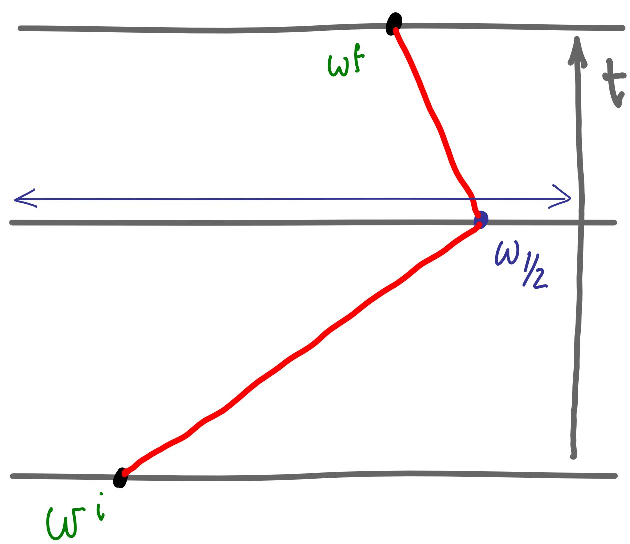
## QUANTUM ANALOGY –

Probability amplitudes via Feynman's sum over histories

$$\langle w^f | e^{-iHt/\hbar} | w^i \rangle \quad \leftarrow \text{prob. ampl.}$$

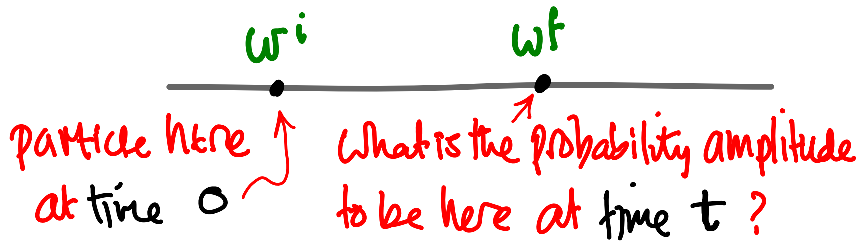
$$= \int dw_{\frac{1}{2}} \, \langle w^f | e^{-iHt/2\hbar} | w_{\frac{1}{2}} \rangle \times \langle w_{\frac{1}{2}} | e^{-iHt/2\hbar} | w^i \rangle$$



## QUANTUM ANALOGY —

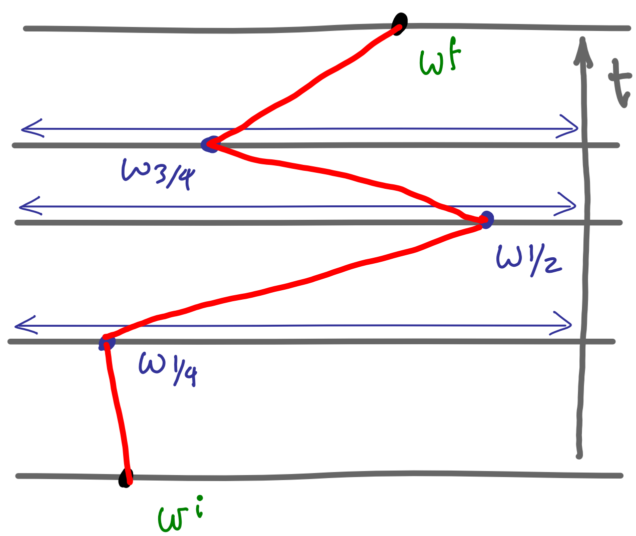
probability amplitudes via Feynman's sum over histories




prob. ampl.

$$\langle w^f | e^{-iHt/\hbar} | w^i \rangle$$

$$= \int dw_{\frac{1}{4}}\, dw_{\frac{1}{2}}\, dw_{\frac{3}{4}} \; \langle w^f | e^{-iHt/4\hbar} | w_{\frac{3}{4}} \rangle$$
$$\times \langle w_{\frac{3}{4}} | e^{-iHt/4\hbar} | w_{\frac{1}{2}} \rangle$$
$$\times \langle w_{\frac{1}{2}} | e^{-iHt/4\hbar} | w_{\frac{1}{4}} \rangle$$
$$\times \langle w_{\frac{1}{4}} | e^{-iHt/4\hbar} | w^i \rangle$$

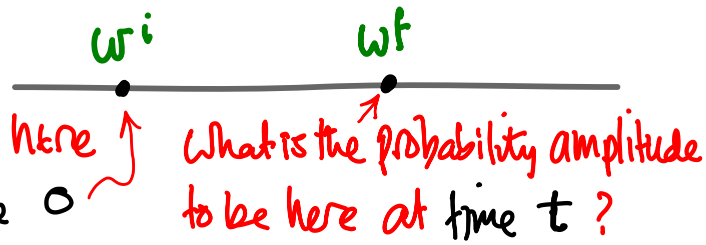


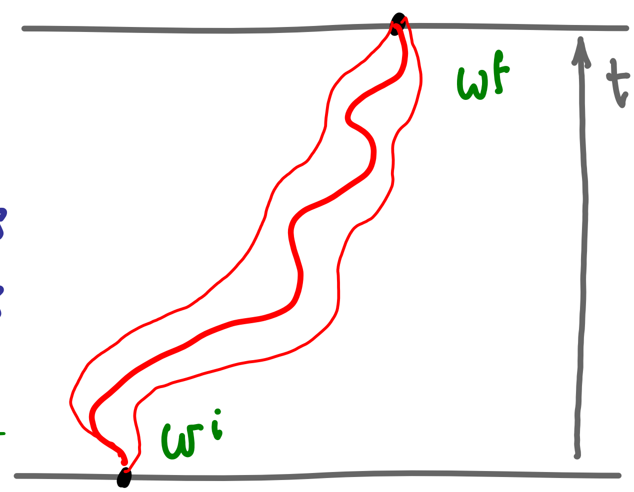
## QUANTUM ANALOGY —

probability amplitudes via Feynman's sum over histories

$$\langle w_f |\, e^{-iHt/\hbar} \,| w_i \rangle$$

prob. ampl.




Repeating infinitely many times leads to infinitely many integrals

— a sum over the continuous history of the particle's location

## QUANTUM ANALOGY –

probability amplitudes via Feynman's sum over histories

prob. ampl.

$$\langle w^f | e^{-iHt/\hbar} | w^i \rangle =$$

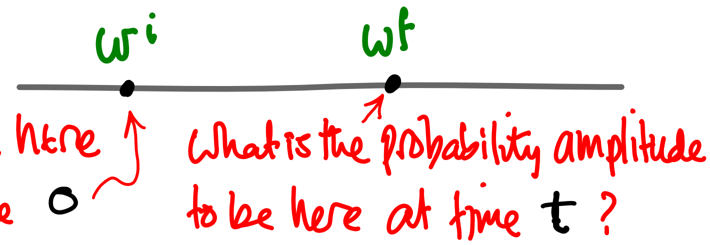
$$\int \mathcal{D}w(\cdot)\ \mathrm{Exp}\left(i\, S[w(\cdot)]/\hbar\right)$$

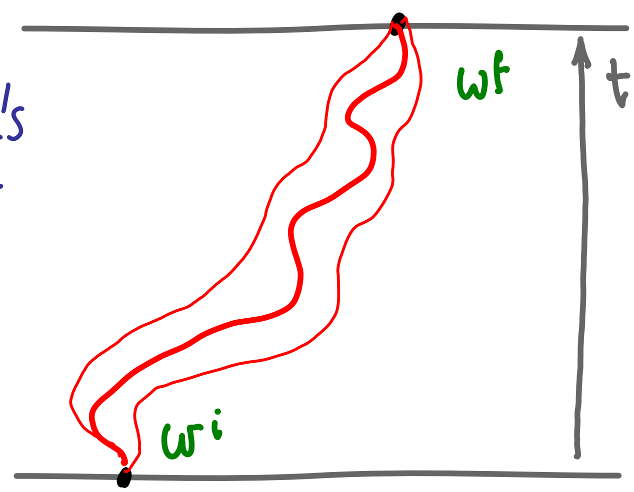
Planck's const.

real time, not imaginary time

action – not just stationary value

– We'll need QM in imaginary time



LOGIC: WE WANT FREE ENERGIES

THEY* LOOK LIKE QUANTUM PATH INTEGRALS

AND THOSE CAN BE GOT VIA THE SCHRÖDINGER EQN#

* really their exponentials do

\# but in imaginary time

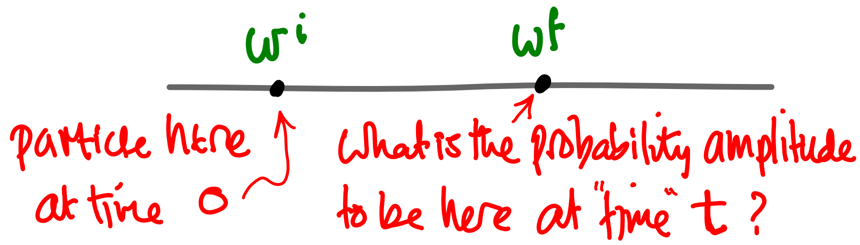
QUANTUM ANALOGY —

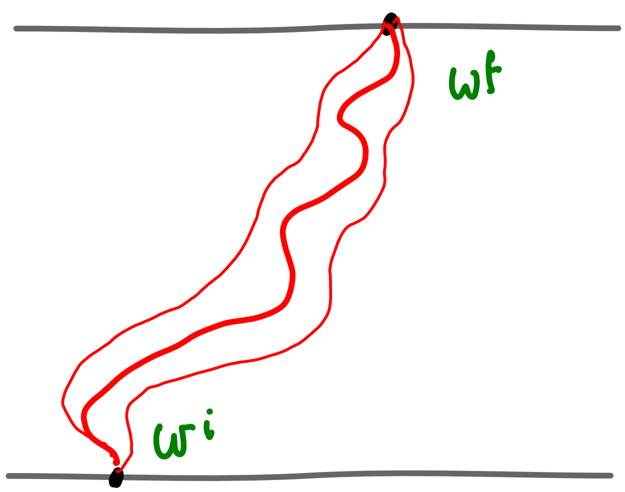
probability amplitudes via Feynman's sum over histories — imaginary time

$$\langle w^f | e^{-H/T} | w^i \rangle \approx$$

$$\Psi_{gs}(w^f)\, e^{-E_{gs}/T}\, \Psi^*_{gs}(w^i)$$

- Ground-state dominance
- Good for <u>long</u> fibers



now let's turn to...

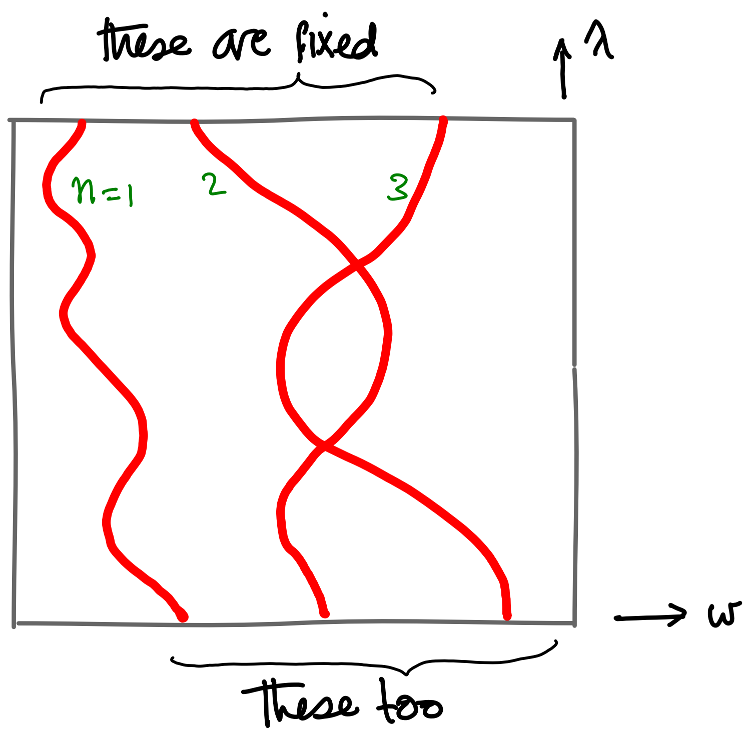
MANY DIRECTED FIBERS UNDER TENSION

## MANY DIRECTED FIBERS UNDER TENSION – noninteracting

$$e^{-F/T} =$$

$$\int \prod_{n=1}^{N} \mathcal{D}\omega_n \quad \exp\left\{ -\frac{A}{2T} \sum_{n=1}^{N} \int_0^{\Lambda} d\lambda \left( \frac{d\omega_n}{d\lambda} \right)^2 \right\}$$

sum over the independent configurations of fibers 1 to N

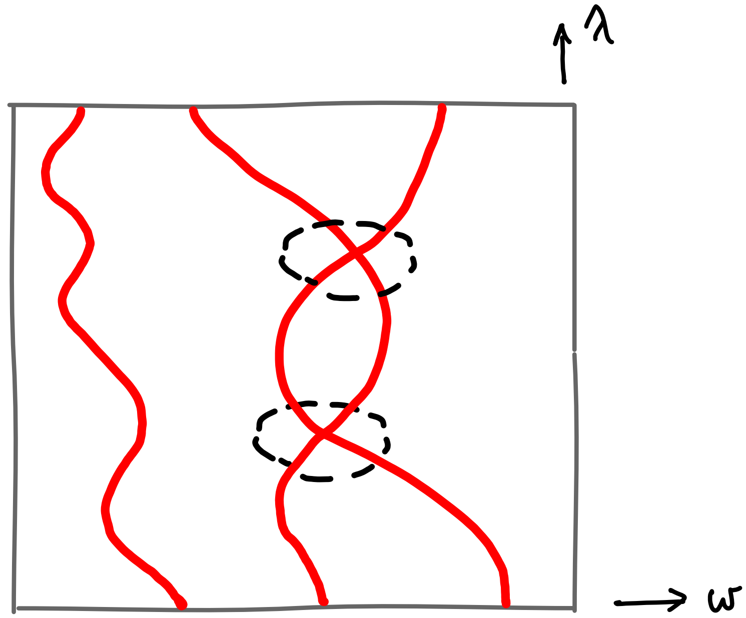


## MANY DIRECTED FIBERS UNDER TENSION – interacting

$$e^{-F/T} =$$

$$\int \prod_{n=1}^{N} \mathcal{D}\omega_n \ \exp\left\{ -\frac{A}{2T} \sum_{n=1}^{N} \int_0^{\Lambda} d\lambda \left(\frac{d\omega_n}{d\lambda}\right)^2 - \sum_{n<n'} \int \frac{d\lambda}{\Lambda} V\left(\omega_n(\lambda) - \omega_{n'}(\lambda)\right) \right\}$$

short-ranged interaction




- What are the consequences of this interaction?

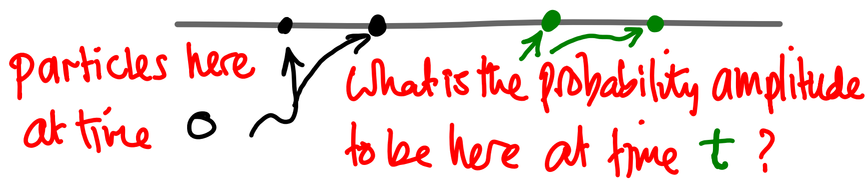
## DE GENNES' ELEGANT IDEA:

Harness the Pauli exclusion principle to implement strong repulsion

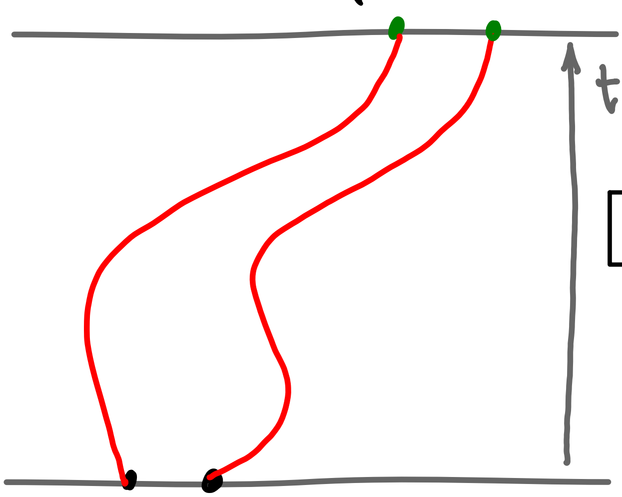
- PEP (aka Fermi-Dirac statistics):
  - no two particles can occupy the same quantum state
- Think: atomic structure
  electrons in metals

  - So how does this bring strong repulsion?

Back to Feynman's sum over histories – with his twist for identical fermions

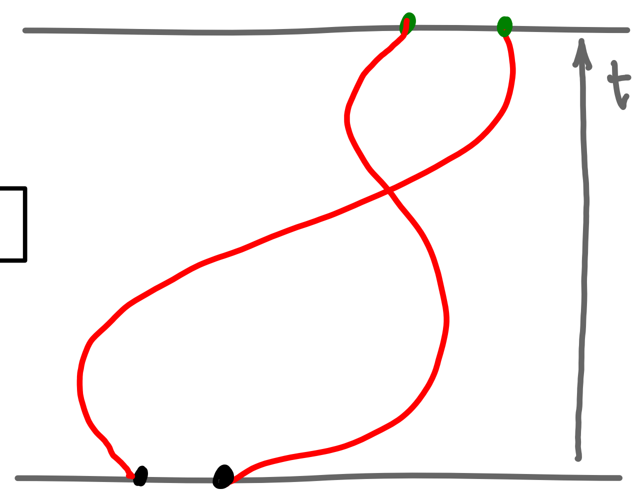



sum over these paths

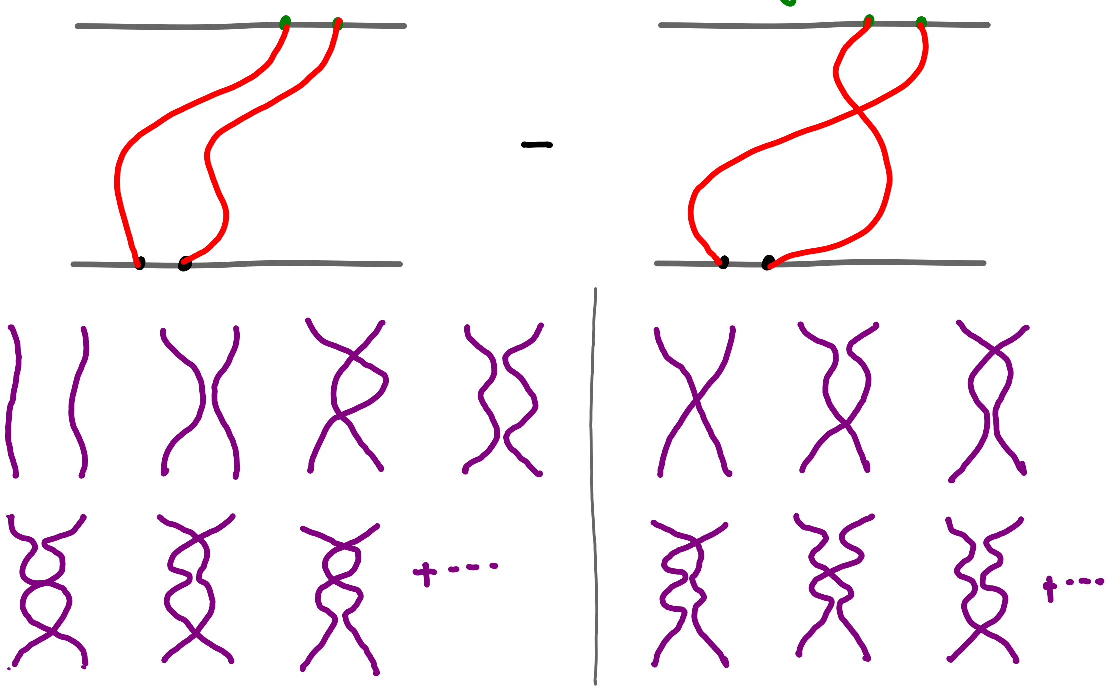



minus

sum over these paths



Now for some combinatorial magic – organize diagrams by numbers of <u>kisses</u> and <u>crossings</u>



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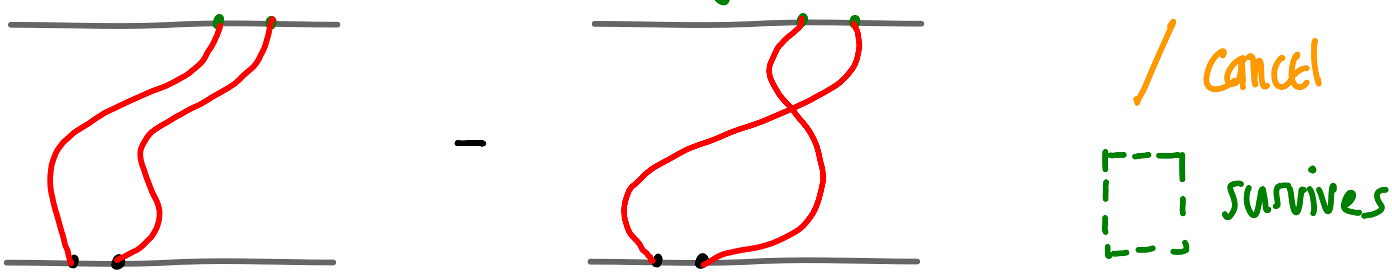
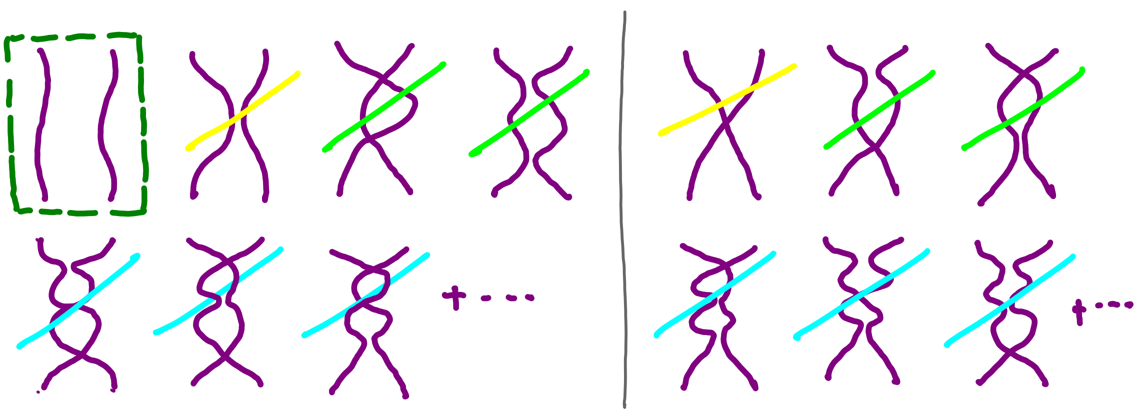



- Only the <u>avoiding</u> paths remain
- Holds for <u>any</u> # of particles

UPSHOT: Gas of many quantum particles* in one dimension provides information about strongly repulsive thermally fluctuating fibers in two dimensions

*identical fermions

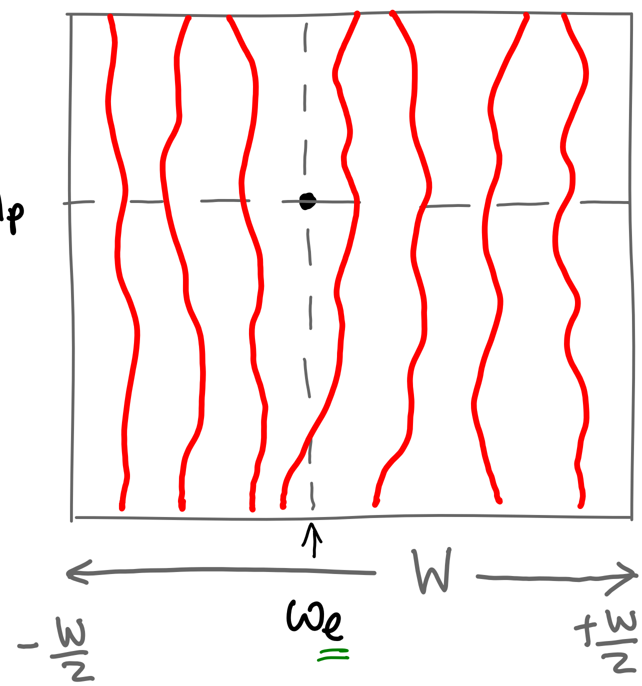
**UPSHOT:** Gas of many quantum particles in one dimension provides information about strongly repulsive thermally fluctuating fibers in two dimensions

**Example:** Response to an impenetrable pin that forces $N_L$ fibers to its left, $N_R$ fibers to its right?

large

equilibrium position: $w_e$

$$\frac{N_L}{\frac{W}{2}+w_e} = \frac{N_R}{\frac{W}{2}-w_e}$$

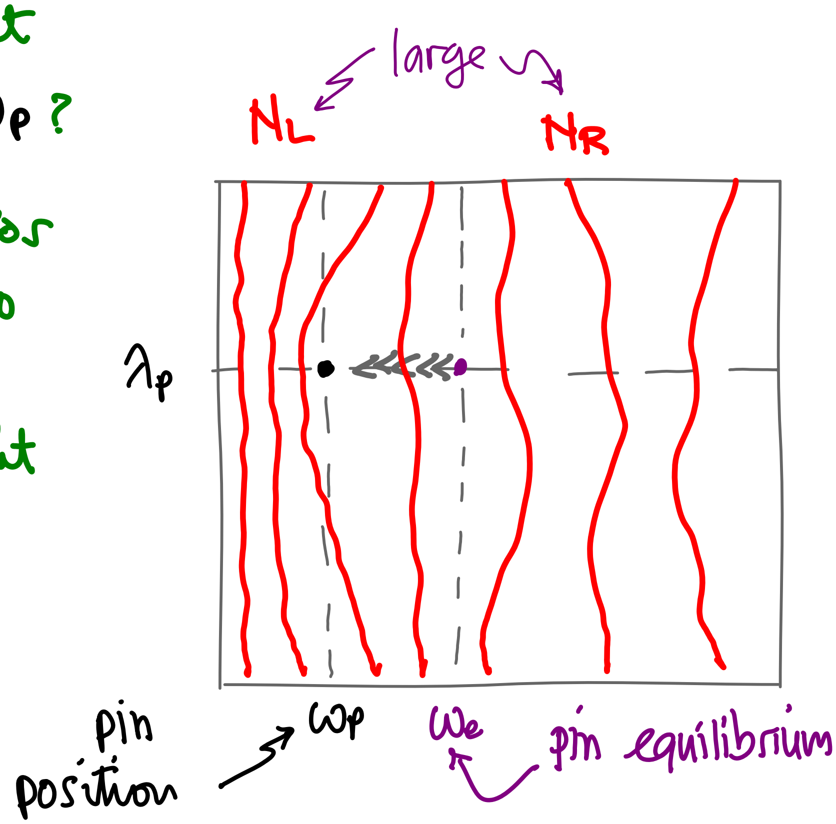


QUESTION: What is the impact of moving pin from $\omega_e$ to $\omega_p$?

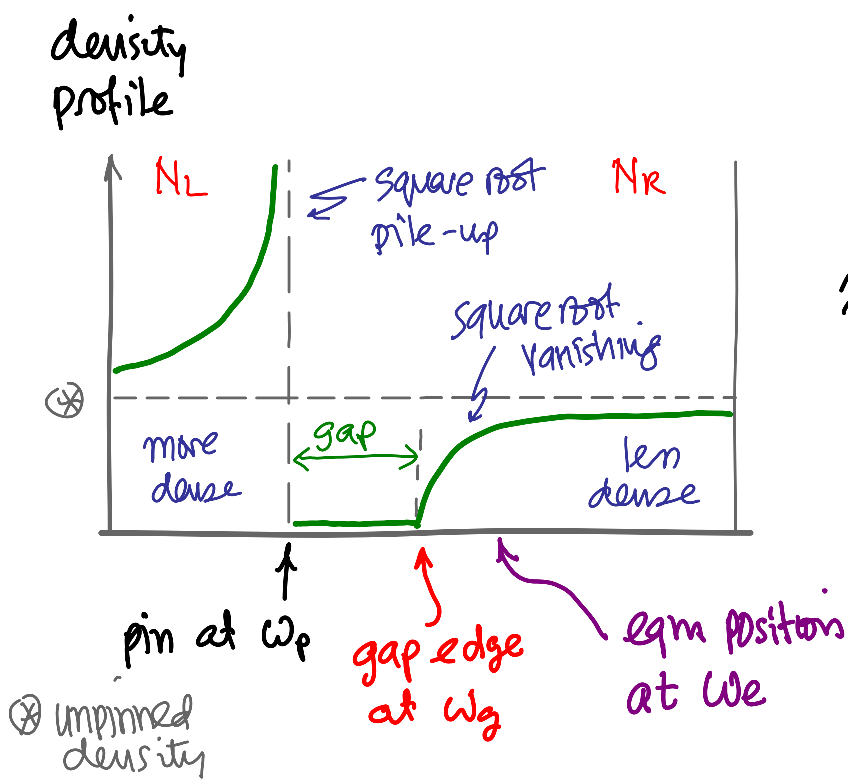
Tool: Probability amplitude for quantum gas ground state to part to have $N_L$ to pin left
$N_R$ to pin right

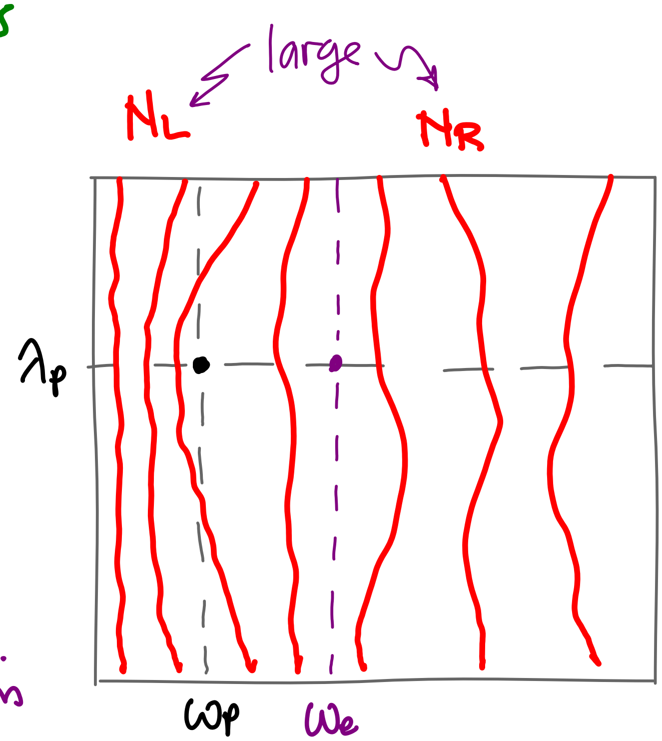
an unusual amplitude

"Red Sea Problems"

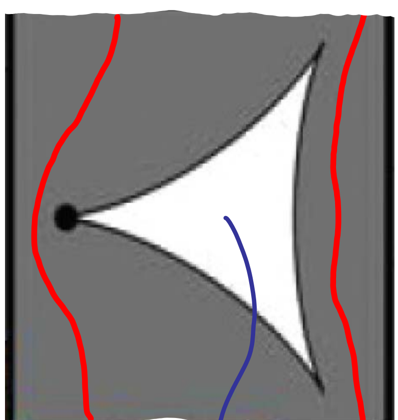


# Impact #1: Gap forms, liquid tears



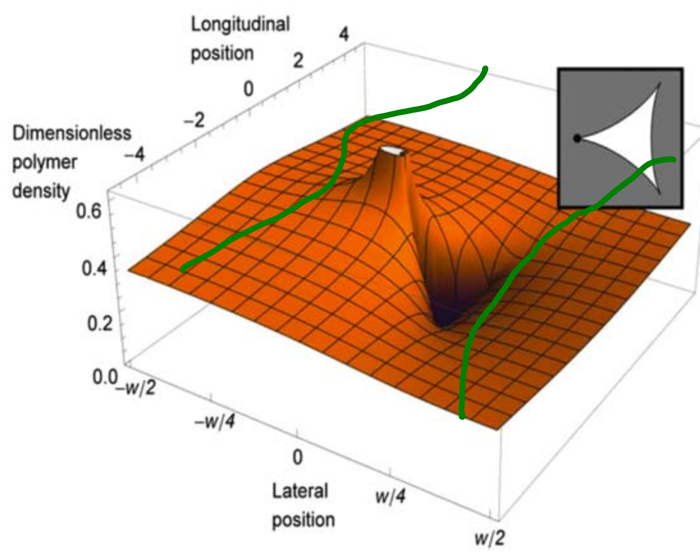
Impact #1: Gap forms, liquid tears



many more polymers

density heavily suppressed

(cf 2D electrostatics)

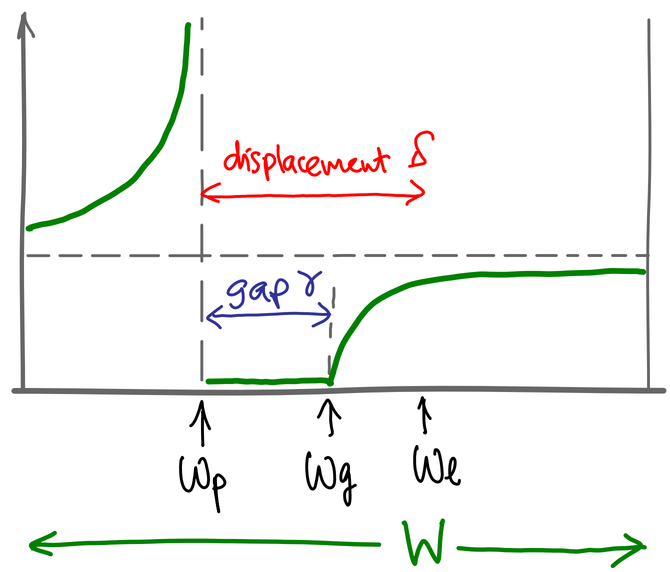


How does the gap vary with pin displacement?

displ $\delta = w_e - w_p$

gap $\gamma = w_g - w_p$

$$\gamma \approx \frac{\delta}{\ln \sqrt{\frac{2}{\delta} \cos^2 \frac{\pi w_p}{W}}}$$




- move the pin away from equilibrium ($\delta$ increases from 0)
- the fluid seeps in, but ...
- a gap opens up (sublinear in $\delta$)

## Impact #2: How does the force vary with displacement?

$$\Delta F = T \, \frac{\pi^2}{2} \, \frac{N^2}{W^2} \, \frac{\delta^2}{\ln \sqrt{\frac{2}{\pi} \frac{W}{\delta} \cos^2 \frac{\pi w_p}{W}}}$$

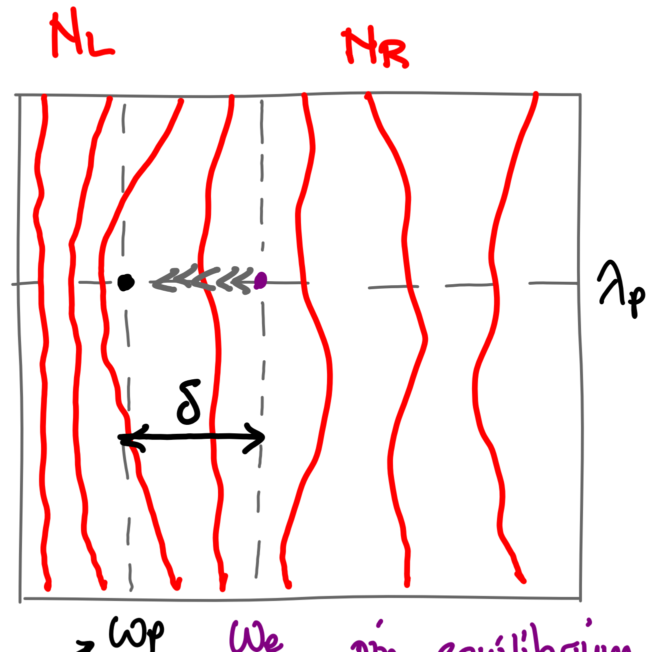
$\Delta F$: free energy

$T$: temperature

$N$: # of fibers

$W$: sample width

$\delta$: displacement



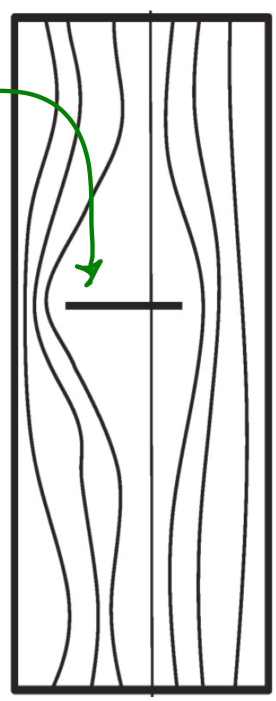

pin position

pin equilibrium

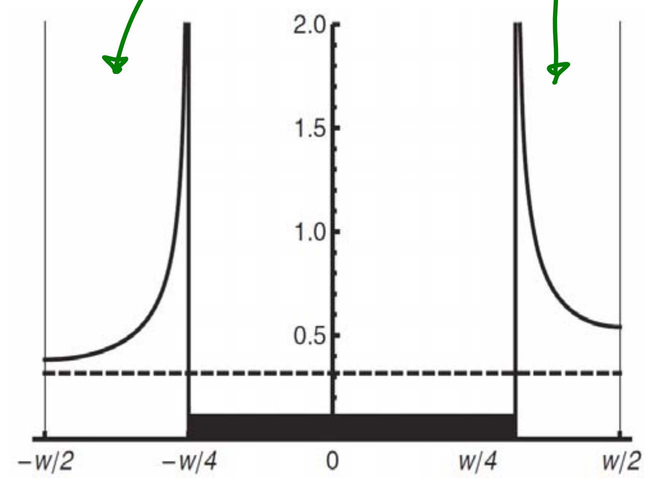
- sub-Hookean (slower than $\delta^2$)

# EXTENDED OBSTACLES

one bar
(could have more)



divergent,
if squeezed




- Interactions between pins and/or bars?

# THREE-DIMENSIONAL POLYMERS

# THREE-DIMENSIONAL POLYMERS

- same challenge: suppress intersections
- remedy: quantum analog

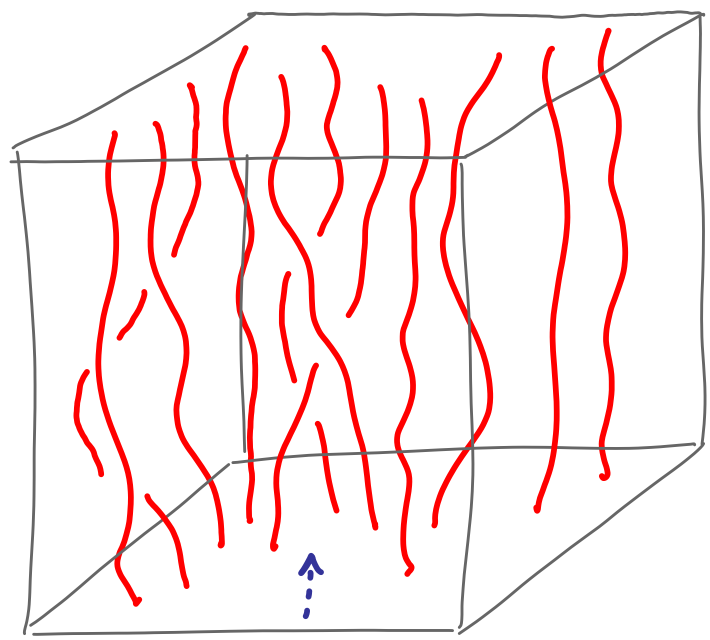
BUT

really have not FERMIONS

but HARD CORE BOSONS

positive statistical weights

- quantum tool: Chern-Simons statistical gauge field, turns HCB into noninteracting fermions + CS field



$$P^i(\{x_n\}) = \langle \{x_n\} | \Psi^i \rangle \; !$$

bosons, positive

# THREE-DIMENSIONAL POLYMERS

- fake magnetic field [$\underline{B} = \underline{\nabla} \times \underline{A}$]

in attached flux tubes: $B(\underline{r}) \propto \rho(\underline{r})$

CS Lagrangian ~ $\int d^2r \, \underline{A} \cdot (\underline{\nabla} \times \underline{A})$

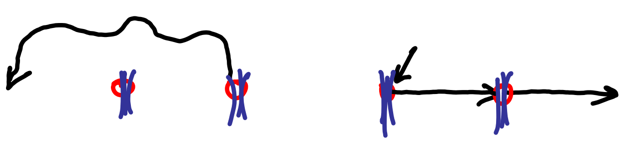
not Maxwell

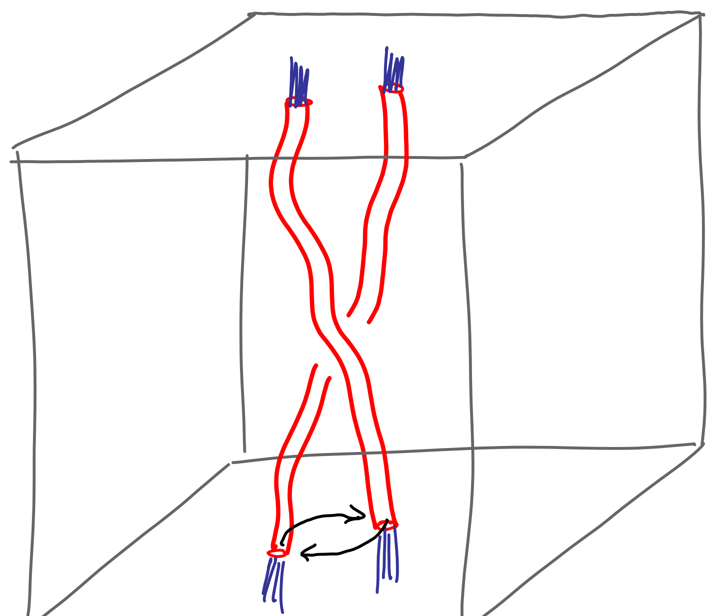
- particles feel it: $\underline{p} \to \underline{p} - q \underline{A}$

Aharonov-Bohm effect

charge

- transmutation of statistics



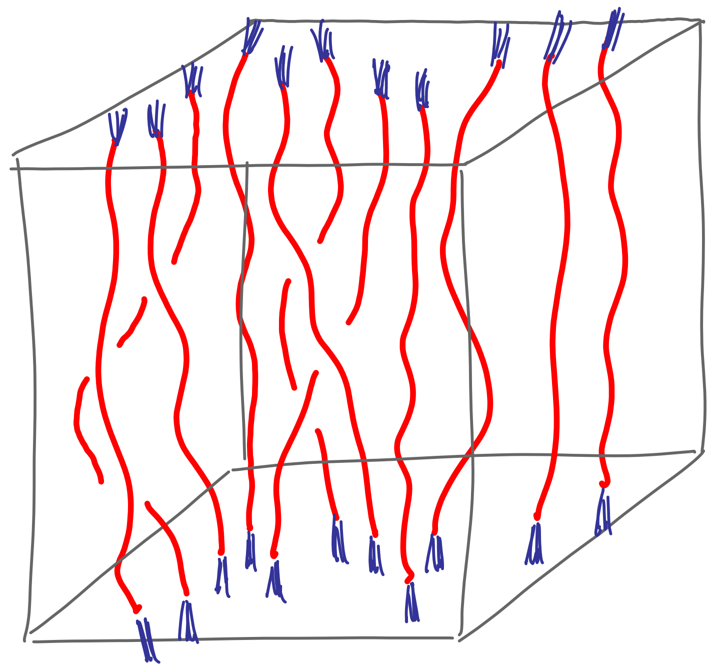


- choose charge to turn bosons into nonint. fermions + CS field

# THREE-DIMENSIONAL POLYMERS

- worldlines of quantum fermions
  + CS flux tubes but otherwise free

- approx: smear CS field

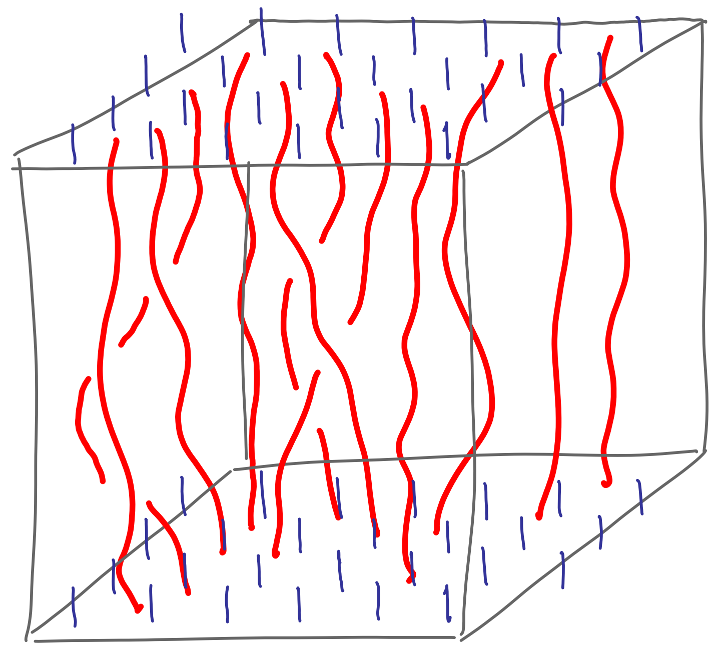


# THREE-DIMENSIONAL POLYMERS

- worldlines of quantum fermions
  + CS flux tubes but otherwise free

- approx: smear CS field

⇒ fermions in uniform mag. field
  - Landau problem
  - Exactly one filled LL
  - Vandermonde type GS WF

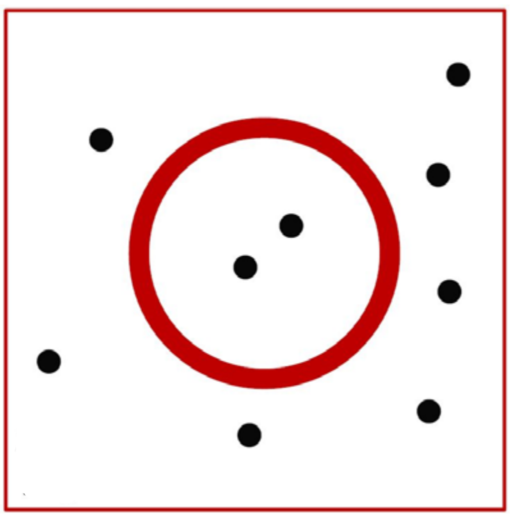


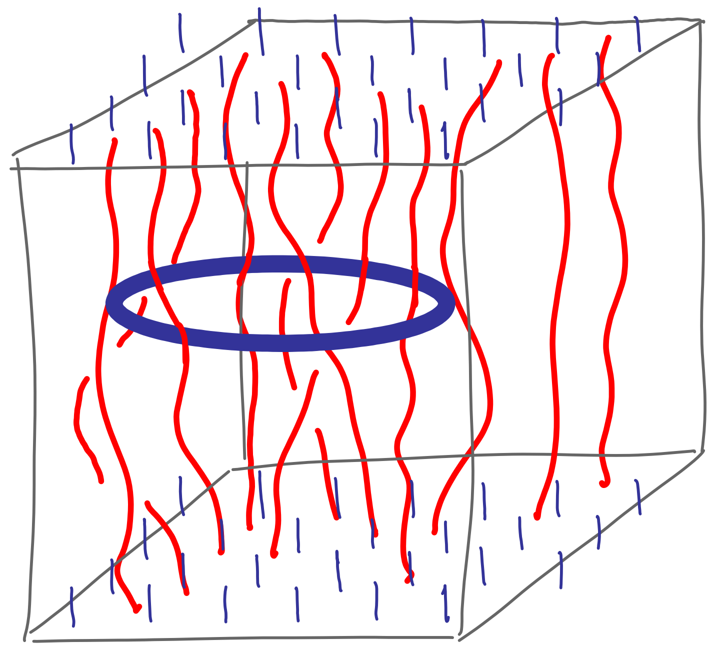
- effectively a 2D one-component plasma

# THREE-DIMENSIONAL POLYMERS

- use wave function to (e.g.) compute impact of constraints

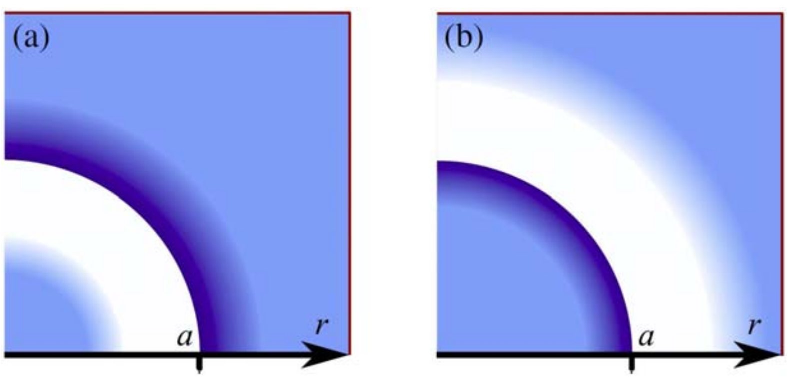
– Red Sea amplitude

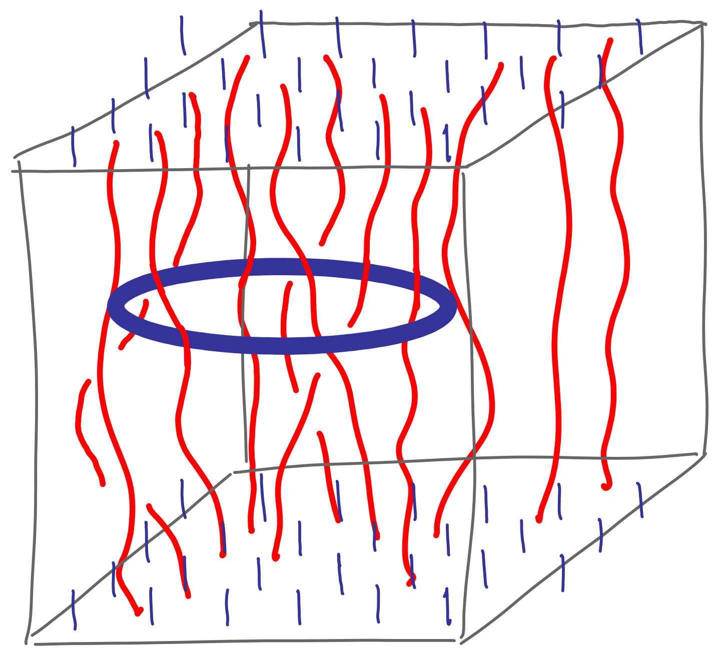




## THREE-DIMENSIONAL POLYMERS

- use wave function to (e.g.) compute impact of constraints



- less pronounced pile-ups and depletion zones
- Brush properties? Densities, correlations, ...?

nonrelativistic QM

$\Longleftrightarrow$ wiggling fibers

# BACK TO TWO-DIMENSIONAL POLYMERS

## WHAT IF WE REPLACE THE SCHRODINGER EQN BY THE DIRAC EQN

- relativity
- spin
- gyromagnetic ratio
- antimatter
- quarks, leptons

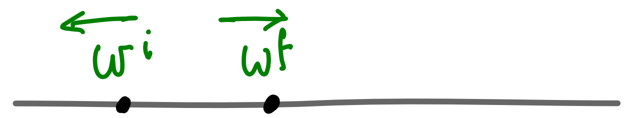
relativistic QM

$\Longleftrightarrow$ what kind of fibers?

# QUANTUM PROPAGATOR —

Feynman's Checkerboard amplitude

$$\langle w^f \pm | e^{-iLh} | w^i \pm \rangle$$




at time 0 / What's the amplitude at L?

Where $h$ is the Dirac 1D Hamiltonian

$$h = \begin{pmatrix} -i\partial_w & -\mu \\ -\mu & +i\partial_w \end{pmatrix}$$

## QUANTUM PROPAGATOR –

Feynman's Checkerboard amplitude

$$\langle w^f \pm | e^{-iLh} | w^i \pm \rangle$$

$$\| $$

$$\lim_{\varepsilon \to 0} \frac{1}{2\varepsilon} \sum \left( \varepsilon \cdot \mu c / \hbar \right)^{\tau} i^{\tau}$$

speed of light

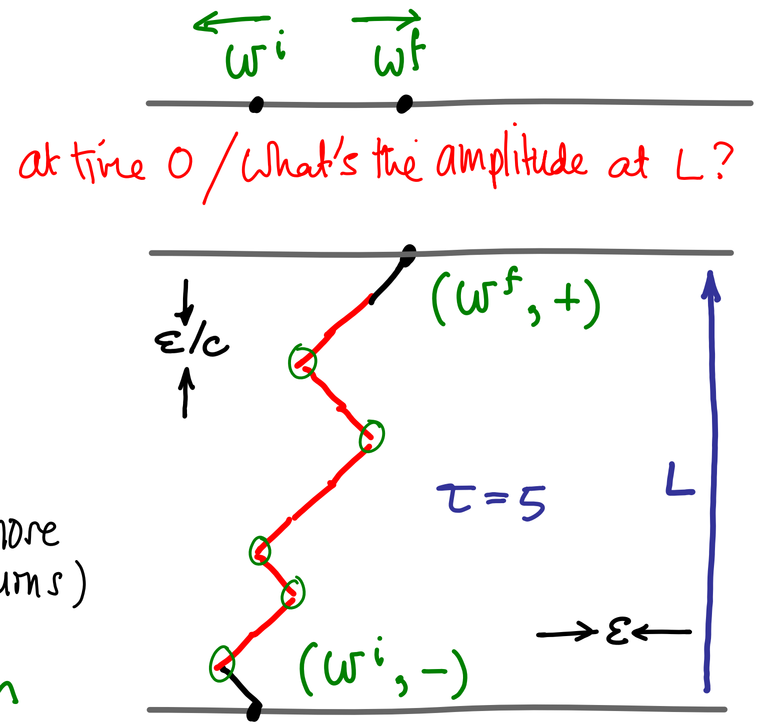
# of turns

particle mass ($\uparrow$ : more turns)

sum over all connecting paths

where $h$ is the Dirac 1D Hamiltonian

$$h = \begin{pmatrix} -i\partial_w & -\mu \\ -\mu & +i\partial_w \end{pmatrix}$$




Can get this ampl. from Dirac eq.

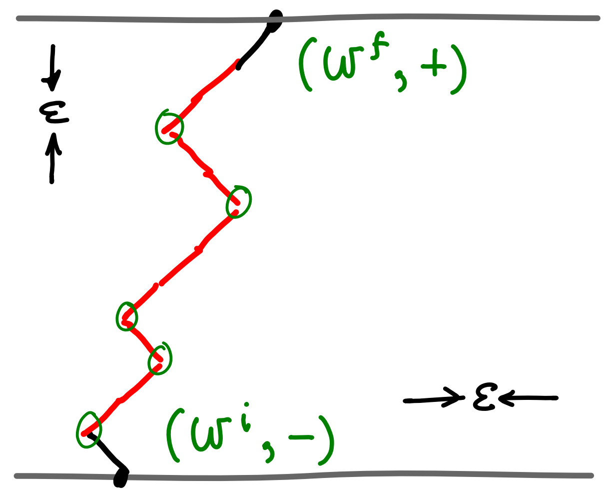
# GETTING TO STAT MECH OF ZIGZAG POLYMERS

- real time → imaginary time
- real mass → imaginary mass

$$e^{-F/\tau} = \lim_{\varepsilon \to 0} \frac{1}{2\varepsilon} \sum (\varepsilon m)^{\tau}$$

Boltzmann factor for bending

Sum over configurations




So can get this free energy via Dirac eq.

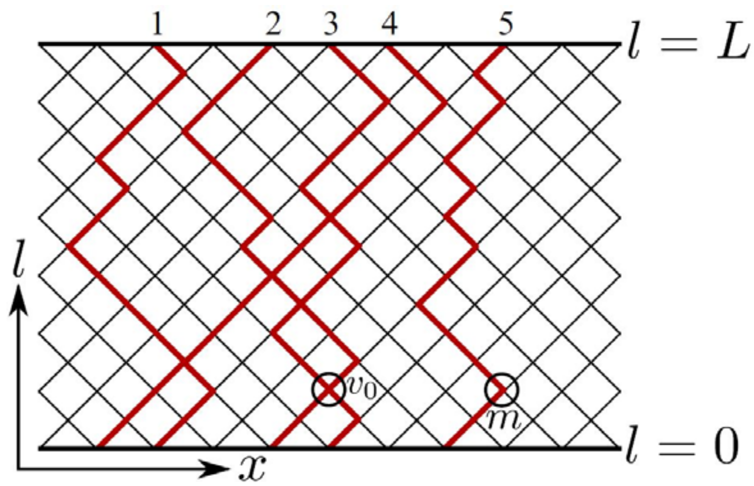
(at imaginary time and mass)

MANY INTERACTING
ZIGZAG POLYMERS

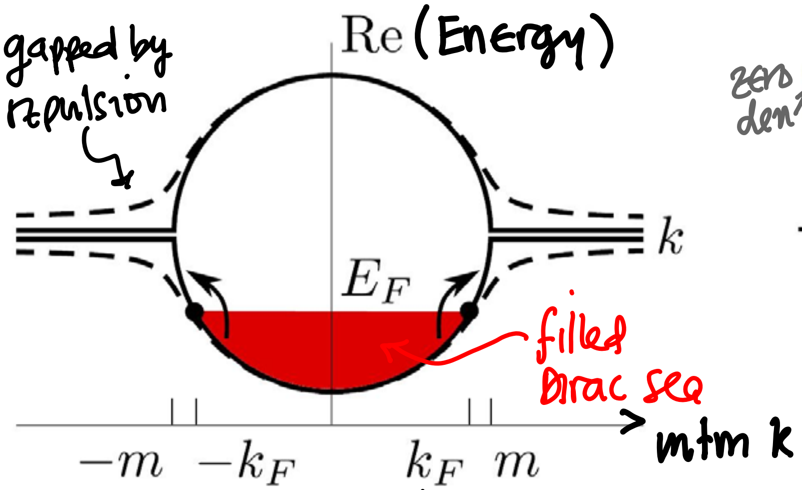
with energy cost for bending
or intersecting

$\approx$ many interacting
Dirac quantum particles

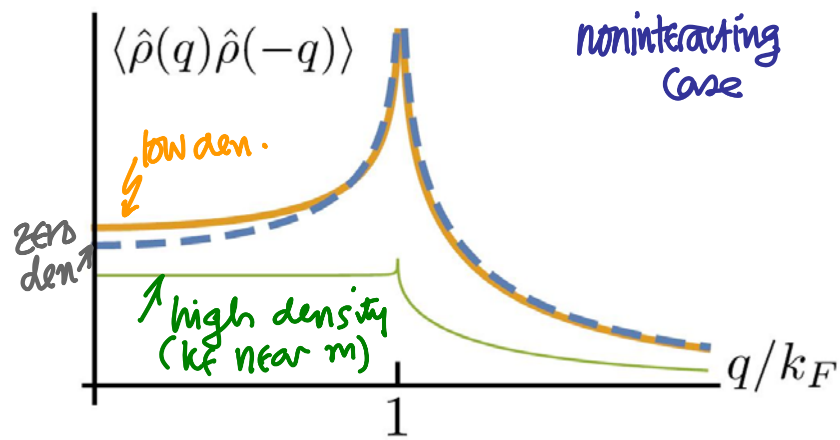
fermions with repulsion $v_0$
and imaginary mass $m$



# PHENOMENOLOGY OF ZIGZAG POLYMERS




- nonhermitian
- strange s.p. energies

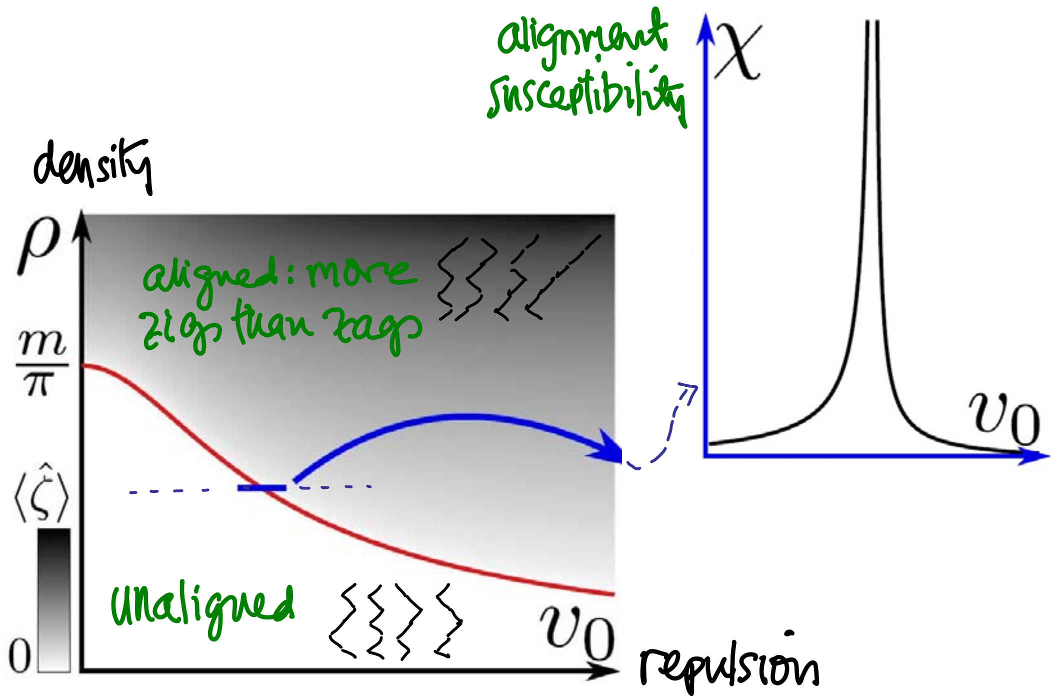



- scattering function (transv.)
- Fermi level → singularity

[cf Carl M. Bender et al. on non-Hermitian Hamiltonians]

# ZIGZAG POLYMERS
## – phase structure

- density & repulsion promote alignment
- fluctuations suppress it, leaving strong correlations



OPPORTUNITIES/ CHALLENGES

Fanning out, nozzles → time-dependent QM

Grafting, curved substrates → QM in curved spacetime

Impurity/blend polymers/grooved substrates → mobile impurities, Kane-Fisher insulation

Realizations? Vortices, crystal step edges

Polymer brushes → proper time, switchbacks

Dirac → Constant-speed agents

new avenues for flocking, schooling, robo-physics, molecular motors, ....

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and NSF & GT