Self-avoiding walks pulled at an angle from a surface

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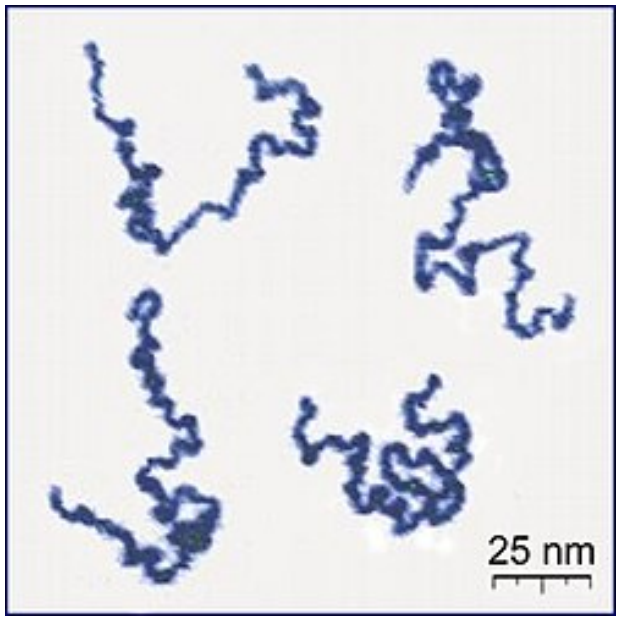
Introduction

Polymers are ubiquitous in the world around us – natural (e.g. DNA, rubber) and synthetic (e.g. plastics)

Adsorption of polymers at surfaces is important for adhesives, protective coatings, sensors, etc.

Polymers can take many forms – here we look at long-chain linear polymers.



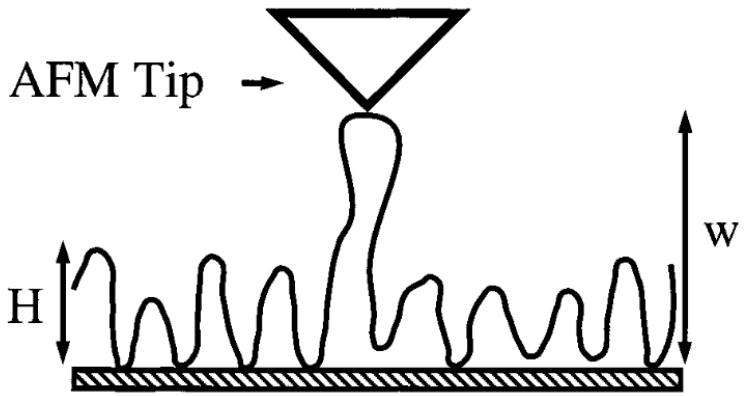
Roiter & Minko, *J. Amer. Chem. Soc.* (2005)

Pulling polymers

Atomic force microscopy (AFM) is usually used for very high-resolution imaging.

However an individual polymer can be picked up or grafted to the AFM tip and adsorbed onto the surface. Then by raising the AFM tip, the elastic properties of the polymer can be measured, as well as the force required to desorb the polymer from the surface.

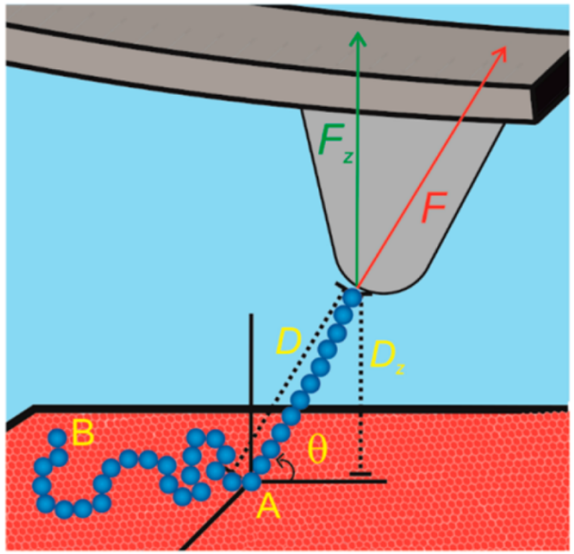
This approach dates back to the 1990s, e.g. Haupt, Ennis & Sevick, *Langmuir* (1999).



Pulling polymers at an angle

The AFM tip only moves vertically. However if the *surface* is simultaneously moved horizontally then the polymer is being pulled at an angle θ to the surface, where θ depends on the relative velocities.

This was employed by Grebíková, Whittington & Vansco, *J. Amer. Chem. Soc.* (2018). They used multiple kinds of polymers and substrates, and pulled at angles between 30° and 90°.



Quantitatively the results depend on the polymer and substrate, but in general the desorption force always increases as the angle decreases. That is, the more vertical the direction of pulling, the easier it is to detact the polymer from the surface.

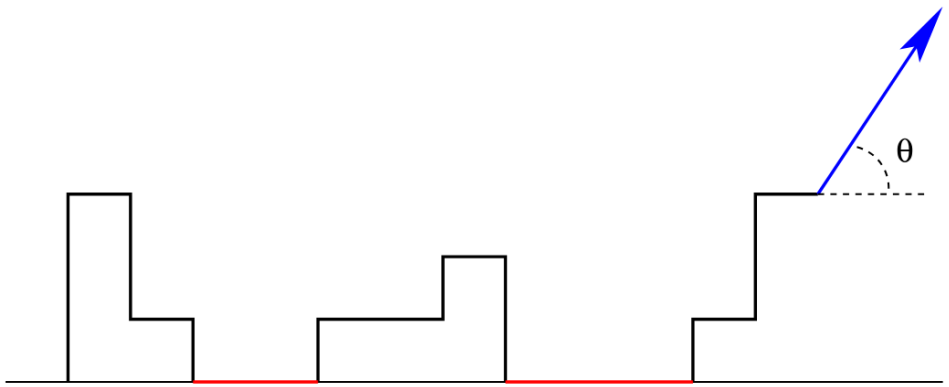
Previous theoretical work: partially directed walks

Self-avoiding walks (SAWs) are the canonical model in statistical mechanics for modelling long-chain polymers. However, SAWs are not solvable, so simpler models are sometimes used.

Partially directed walks (PDWs) are SAWs with a restricted step set, making them tend to walk in a "preferred" direction.

- 2D: allowed steps $+x$, $\pm y$
- 3D: allowed steps $+x$, $+y$, $\pm z$.

Exactly solvable, depending on which physical interactions are included.



Two independent works Osborn & Prellberg, *J. Stat. Mech.* (2010) and Orlandini & Whittington, *J. Phys. A* (2010) looked at these models (same models, different solution methods).

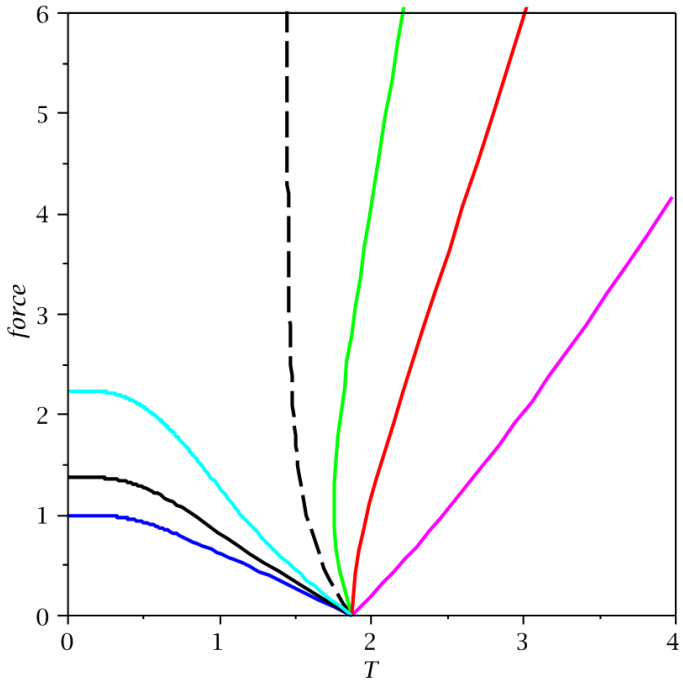
PDWs in 2D

Walks accrue weights

- $b = \exp(-\epsilon/kT)$ with each step on the surface
- $x = \exp(f_x/kT)$ and $y = \exp(f_y/kT)$ when at endpoint (x, y).

For simplicity set $\epsilon = -1$ and $k = 1$, and take $f_x = F\cos\theta$ and $f_y = F\sin\theta$.

Then for each θ we get a phase diagram in the F-T plane: (adsorbed on the left, desorbed on the right; all phase transitions except $\theta = 0°$ are first order)



- $\theta = 0$ (magenta)
- $\theta = \arctan(1/2) \approx 26.6°$ (red)
- $\theta = \arctan(3/4) \approx 36.9°$ (green)
- $\theta = 45°$ (dashed)
- $\theta = \arctan(2) \approx 63.4°$ (cyan)
- $\theta = \arctan(4) \approx 76°$ (black)
- $\theta = 90°$ (dark blue)

(Figure from Orlandini & Whittington, *J. Phys. A* (2010).)

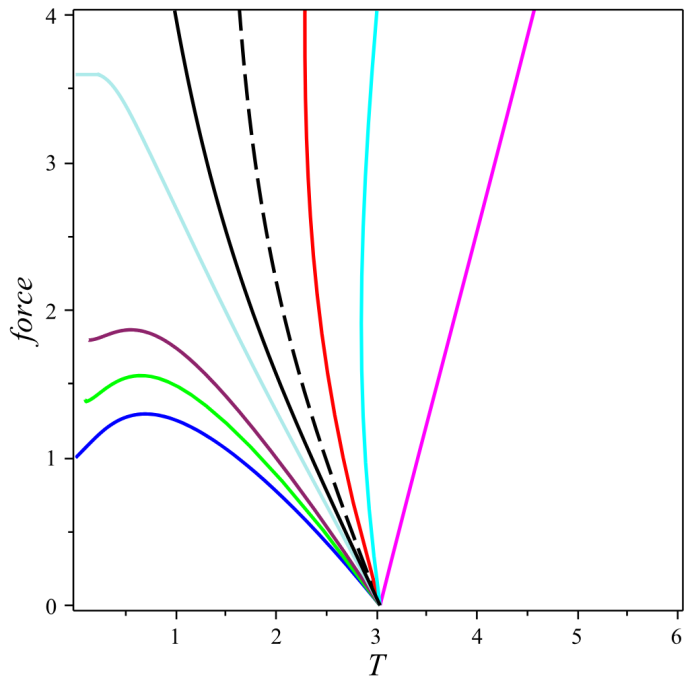
For $\theta < 45°$ and low T, always adsorbed regardless of F.

For $\theta < \arctan(1/2)$, it becomes impossible to desorb the polymer by pulling, at any T.

PDWs in 3D

Same surface weight b as in 2D.

For the force there are now two angles to consider (vertical θ and horizontal ϕ), but the dependence on ϕ is weak so set $\phi = 0$, i.e. direction of pulling in the x-z plane.



- $\theta = 0$ (magenta)
- $\theta = \arctan(1/2) \approx 26.6^\circ$ (cyan)
- $\theta = \arctan(3/4) \approx 36.9^\circ$ (red)
- $\theta = 45^\circ$ (dashed)
- $\theta = \arctan(5/4) \approx 51.3^\circ$ (black)
- $\theta = \arctan(3/2) \approx 56.3^\circ$ (turqoise)
- $\theta = \arctan(5/2) \approx 68.2^\circ$ (purple)
- $\theta = \arctan(4) \approx 76^\circ$ (green)
- $\theta = 90^\circ$ (dark blue)

(Figure from Orlandini & Whittington, *J. Phys. A* (2010).)

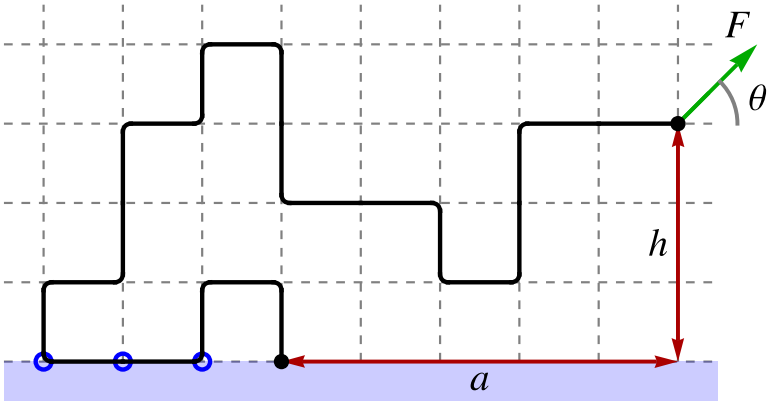
Similar behaviour, except at low temperatures and large θ, there is re-entrance.

This occurs here because in the adsorbed state the walk is effectively a 2D directed walk which still has entropy. But in 2D, the adsorbed walk is just a 1D straight rod with no entropy.

Pulling SAWs: Monte Carlo sampling

How much of this is still true if we move to SAWs instead of PDWs?

SAWs are not solvable but we can use Monte Carlo methods. Let c_{nmah} be the number of SAWs of length n, with m contacts with the surface, vertical displacement h and x-displacement a.



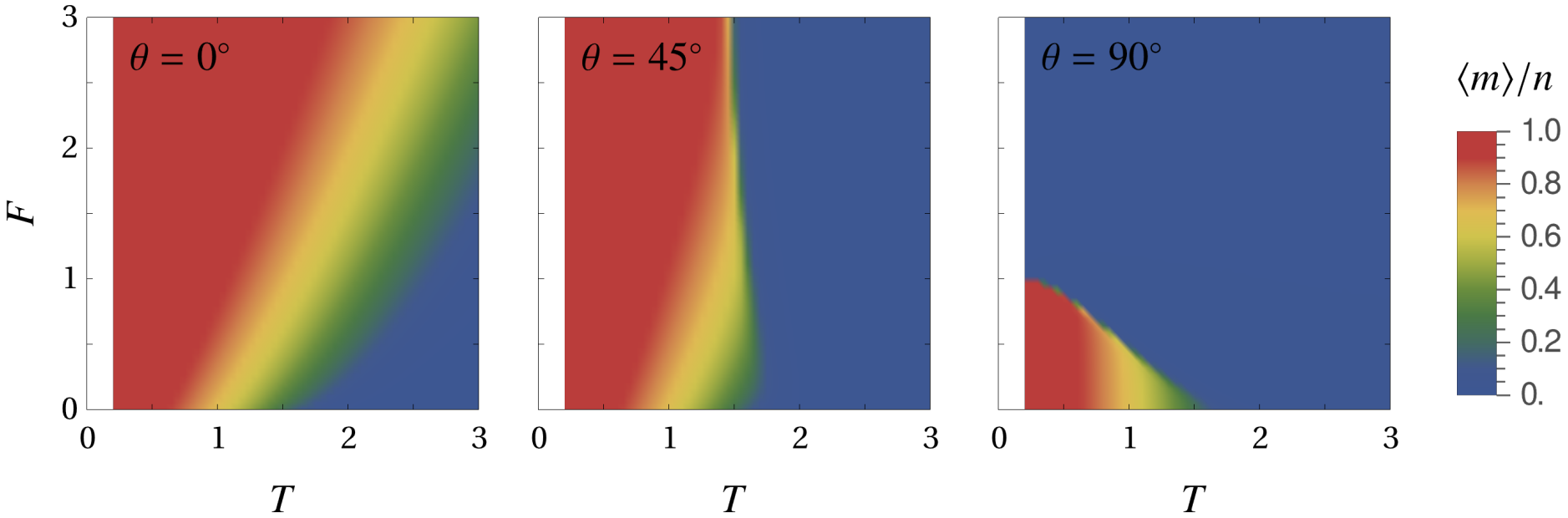
We use the pruned-enriched Rosenbluth method (PERM) which grows and shrinks SAWs in order to sample across a range of n, m, a, h, producing estimates of each microcanonical c_{nmah}.

However in practice this is infeasible because we would be trying to flatten over a 4-dimensional histogram. Instead we use a "thermal" version: first choose T, F, θ and then only need to flatten across n. Tradeoff is that we must run a new simulation for every point in the phase diagram.

Typically ran up to $n = 500$ for each point in a 37×37 (T, F) grid. Some additional simulations up to only $n = 128$ for very small T. Total approx. 50,000 CPU hours for each of $d = 2, 3$.

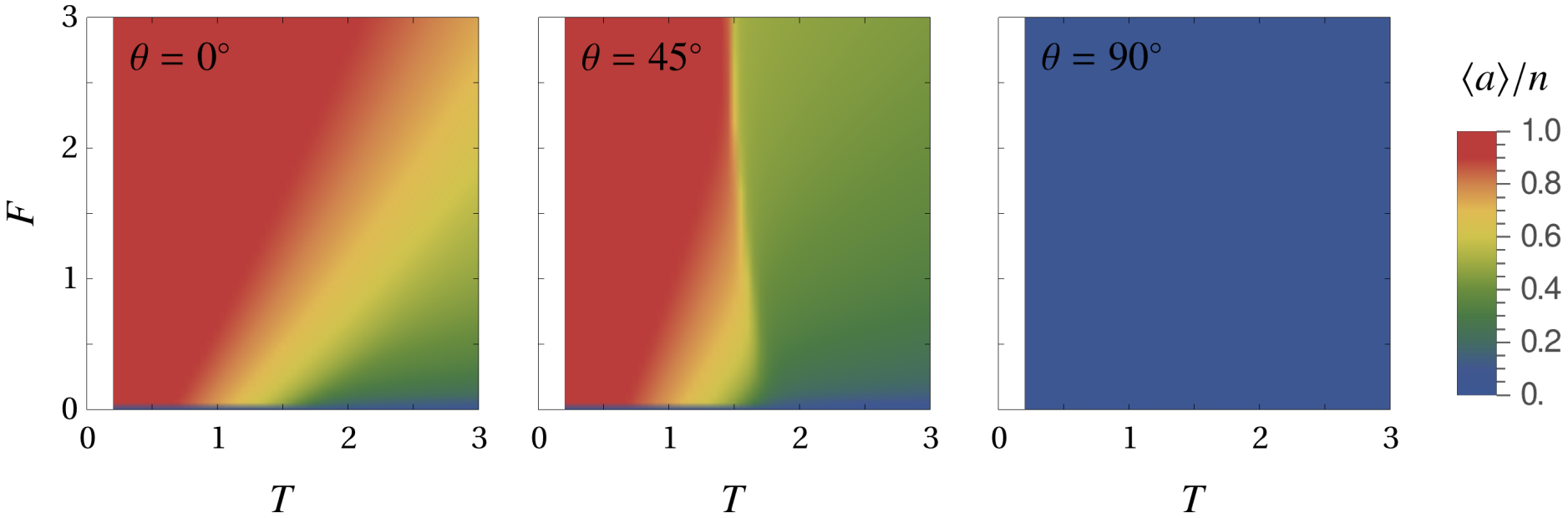
Pulling SAWs: 2D results

Plotting the order parameters: surface contacts



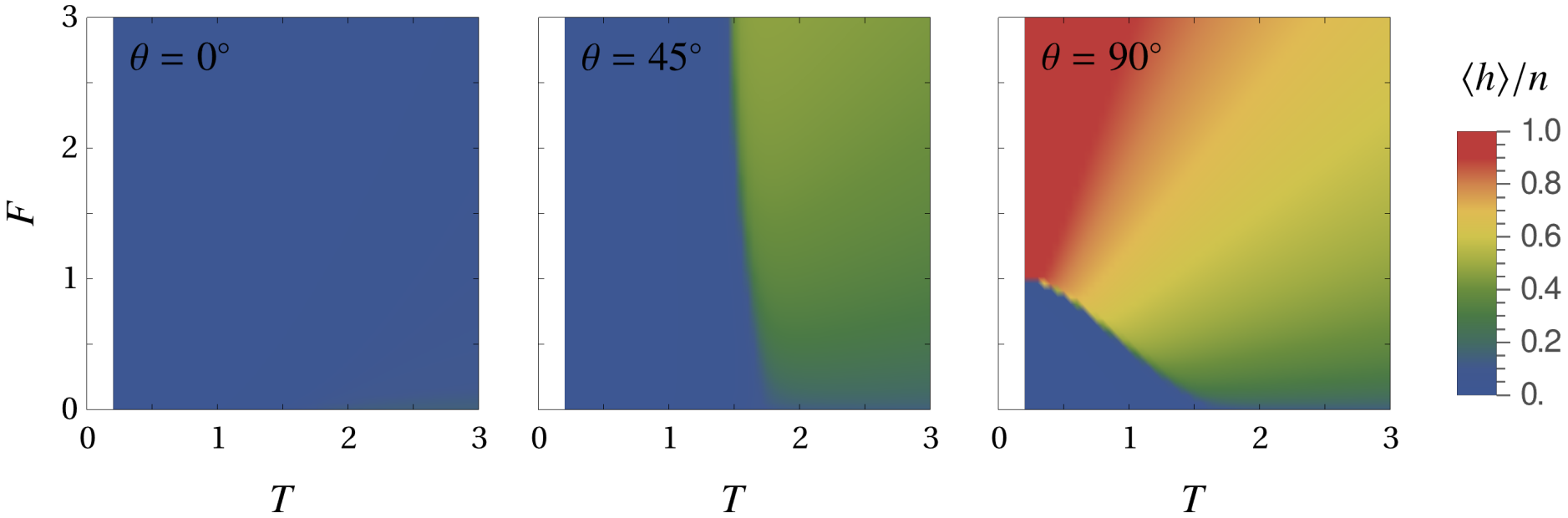
Pulling SAWs: 2D results

Plotting the order parameters: x-displacement



Pulling SAWs: 2D results

Plotting the order parameters: vertical displacement



Pulling SAWs: 2D results

Set partition function

$$Z_n(T, F, \theta) = \sum_{m,a,h} c_{nmah} \kappa^m \lambda^a \tau^h$$

and $A_n = \frac{1}{n} \log Z_n$, where

$$\kappa = e^{1/T}, \quad \lambda = e^{F \cos\theta / T}, \quad \tau = e^{F \sin\theta / T}.$$

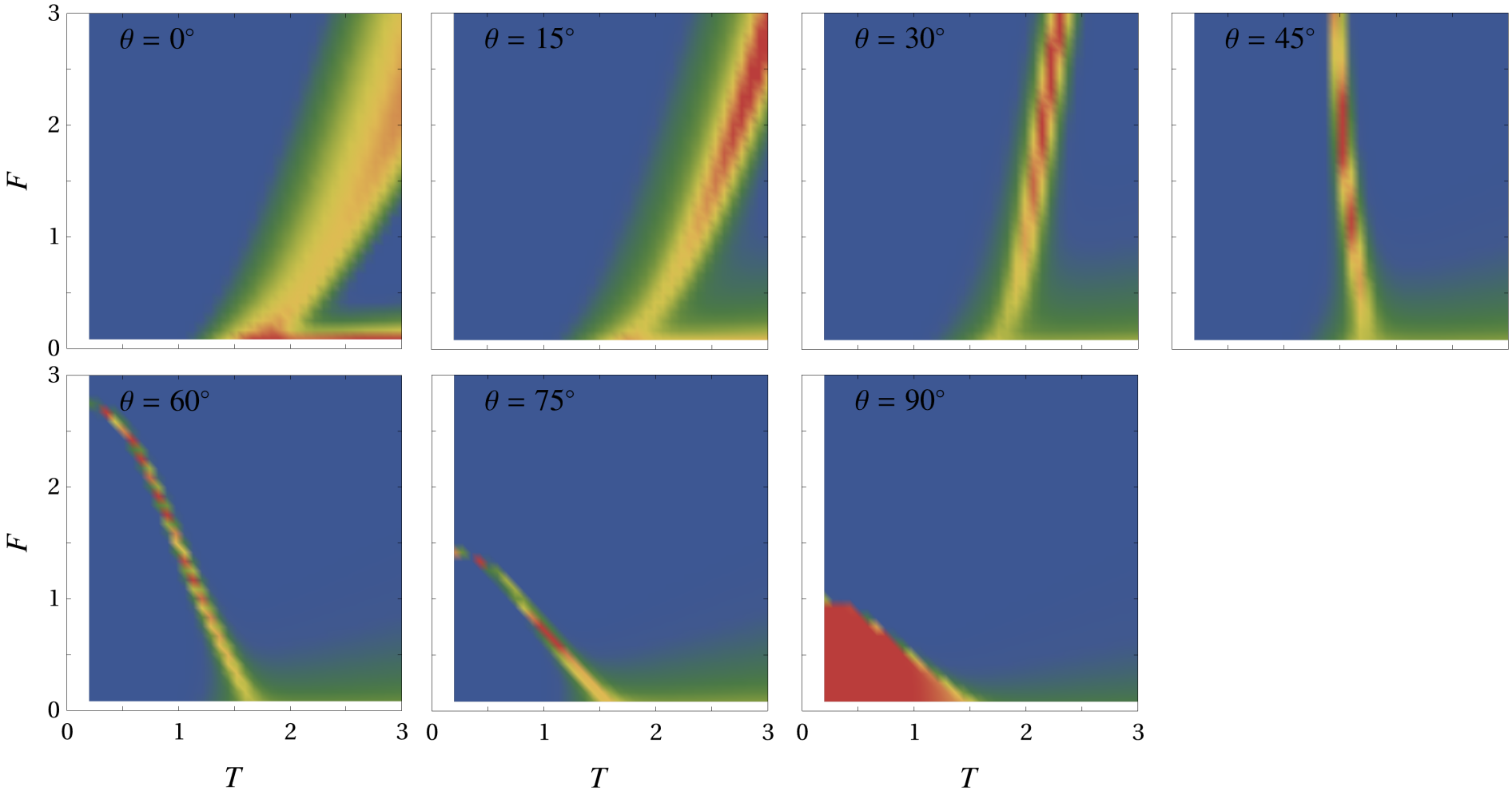
Then the Hessian matrix

$$H_n = \begin{pmatrix} \partial_\kappa^2 A_n & \partial_\kappa \partial_\lambda A_n & \partial_\kappa \partial_\tau A_n \\ \partial_\lambda \partial_\kappa A_n & \partial_\lambda^2 A_n & \partial_\lambda \partial_\tau A_n \\ \partial_\tau \partial_\kappa A_n & \partial_\tau \partial_\lambda A_n & \partial_\tau^2 A_n \end{pmatrix}$$

has largest eigenvalue χ, and we can associate large values of χ (or $\log \chi$) with the locations of phase transitions.

Pulling SAWs: 2D results

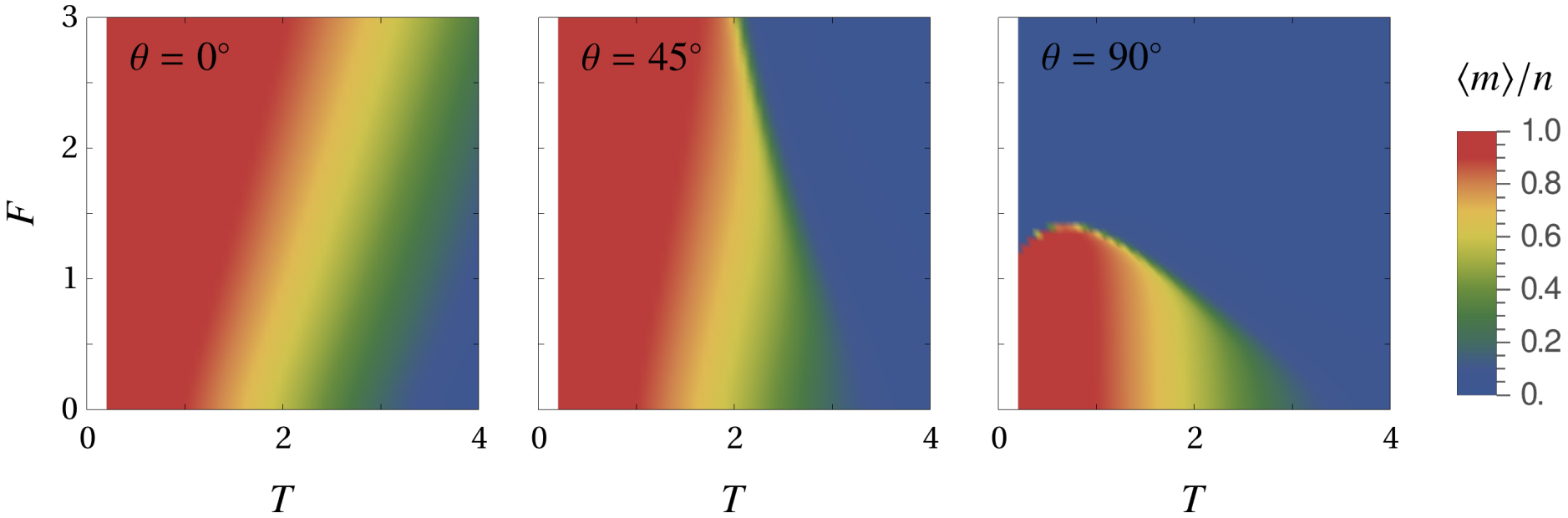
Plots of covariance $\log \chi$ for various angles:



Qualitatively matches PDWs.

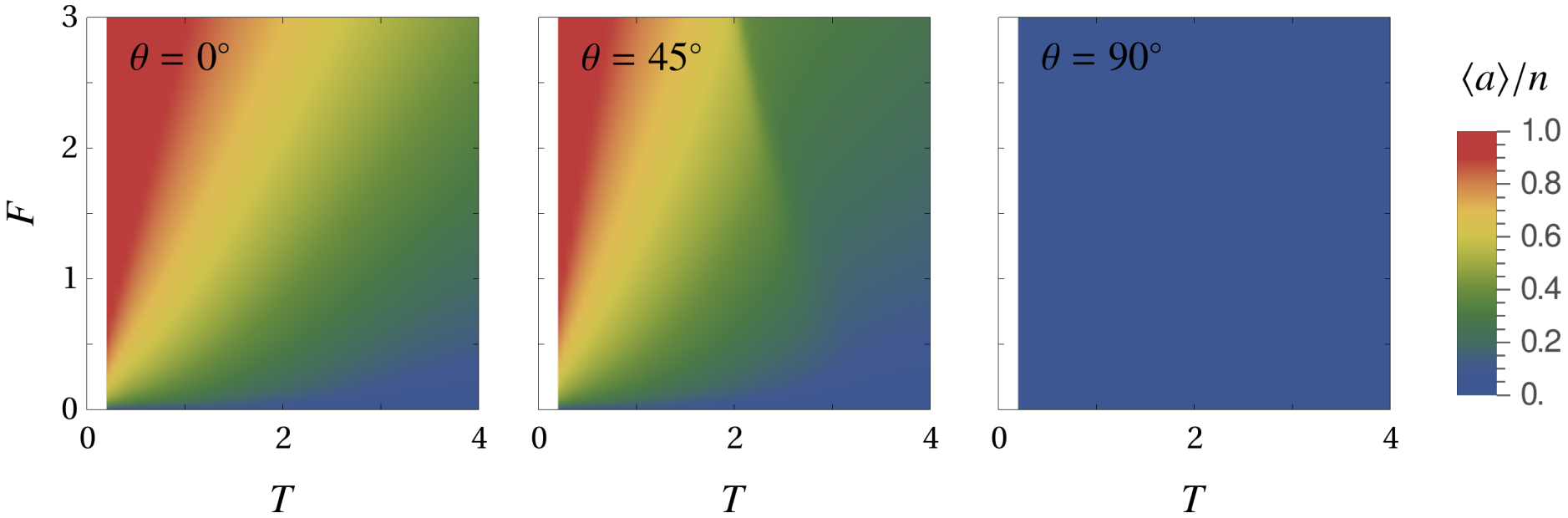
Pulling SAWs: 3D results

Plotting the order parameters: surface contacts



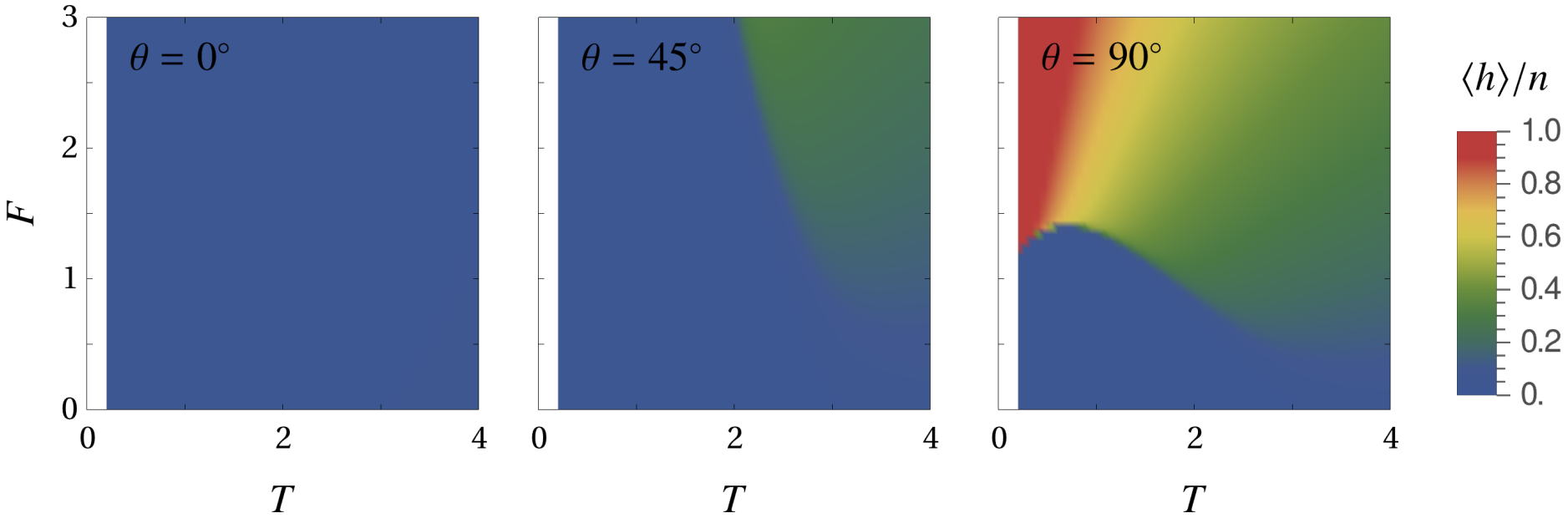
Pulling SAWs: 3D results

Plotting the order parameters: x-displacement



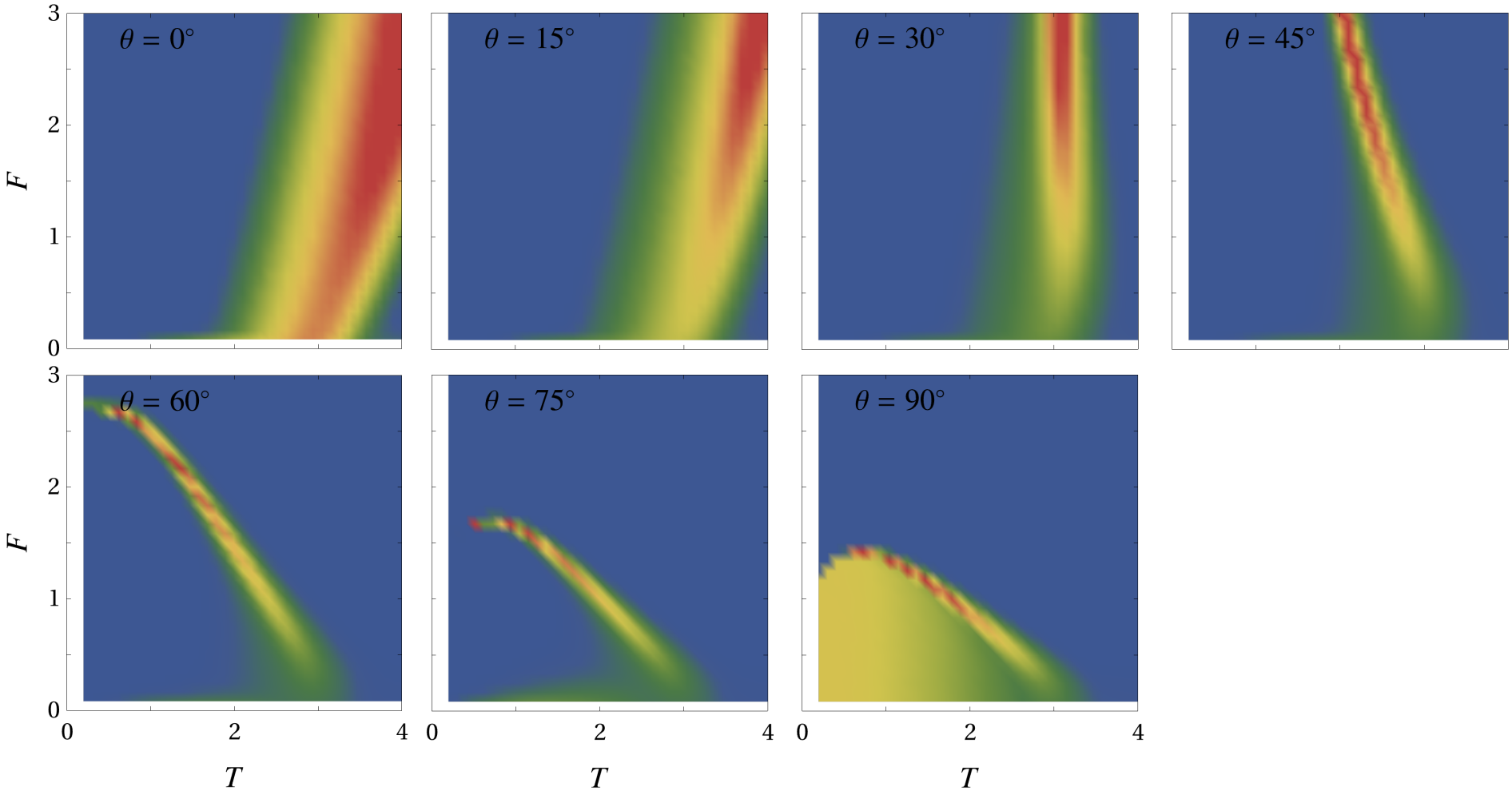
Pulling SAWs: 3D results

Plotting the order parameters: vertical displacement



Pulling SAWs: 3D results

Plots of covariance $\log \chi$ for various angles:



Again qualitatively matches PDWs – re-entrance clearly present for large angles.

Low temperature behaviour

For small T (large κ, λ, τ) can approximate total contributions to energy and entropy. When $\theta = 90^\circ$ the desorbed phase is a straight vertical rod, while the adsorbed phase is completely stuck to the surface, giving the total energy

$$A \approx nF - n - Tn \log \mu_{d-1}$$

where μ is the connective constant of the lattice.

When $\theta < 90^\circ$ the force has a horizontal component. When $F > 0$ and T is very small, there is only one relevant configuration, namely m horizontal steps in the surface followed by $n - m$ vertical steps, where $\tan\theta = (n-m)/m$. The total energy is thus

$$A \approx -m + mF\cos\theta + (n-m)F\sin\theta.$$

Minimising w.r.t. m gives the critical force.

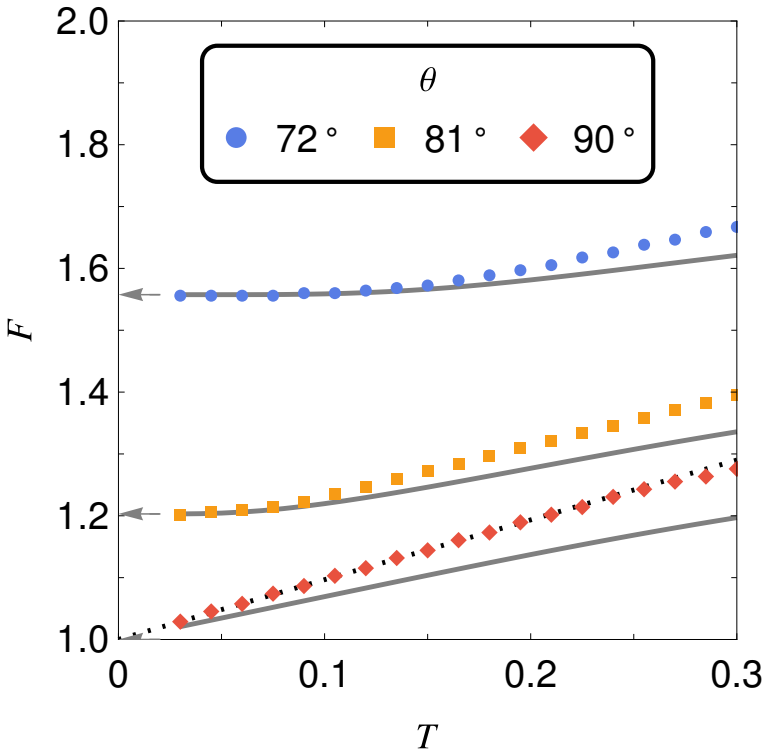
Bringing the above two cases together we get for small T

$$F_c = \begin{cases} T\log\mu_{d-1} + 1, & \theta = 90^\circ, \\ \dfrac{1}{\sin\theta - \cos\theta}, & 45^\circ < \theta < 90^\circ, \\ \text{N/A}, & \theta \leq 45^\circ. \end{cases}$$

Note the T-dependence for $\theta = 90^\circ$ but not for $\theta < 90^\circ$.

Low temperature behaviour

Plotting the critical force for small T:



Grey curves are the boundaries for PDWs.
Dotted line has slope $\log \mu_2$.

Conclusion

Strong qualitative agreement between PDWs and SAWs across a range of T, F and θ, in 2D and 3D.

Behaviour when $\theta = 0^\circ$ is known for PDWs but still unclear for SAWs, especially as $F \to 0^+$. Further work to come!

arXiv:2511.21036 – to appear in J. Phys. A

Thanks for listening!