



MAX-PLANCK-GESELLSCHAFT

Wetting Transitions: A New Look at an Old Problem

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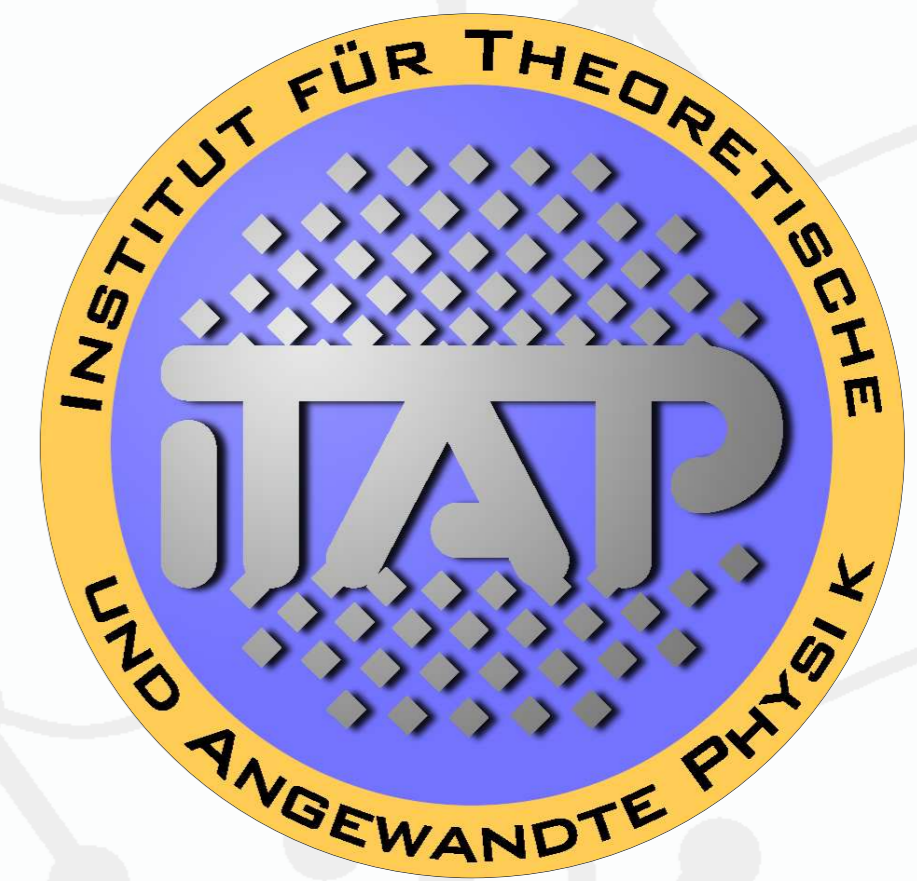
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1. Abstract

- ◆ The theory of the short-range wetting transition in 3D has been in *disagreement with simulations* for over 20 years [1]! It also fails for non-planar substrates and does not satisfy exact sum-rules.
- ◆ A *Nonlocal Model* [2] patches all the shortcomings of the standard theory.
- ◆ Analysis of a microscopic model reveals a *new lengthscale* ξ_{NL} [3]. This new lengthscale is implicit in the structure of the Nonlocal Model, is absent in previous theories and is crucial for the correct description of the wetting transition.
- ◆ Fluctuations with wavelength smaller than ξ_{NL} are suppressed, *restoring agreement with simulations* [3].

2. Wetting Transitions in a Nutshell

- ◆ A *wetting transition* [1] happens when the thickness l of an adsorbed liquid film becomes *infinite* (macroscopic). See Fig. 1 below.

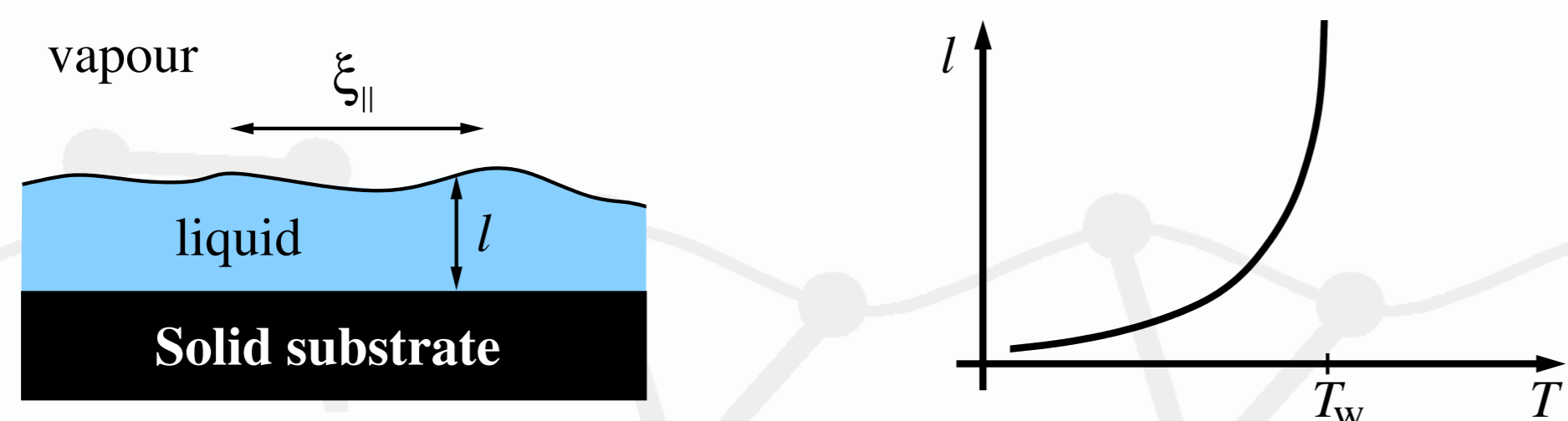


Fig. 1. The thickness of a liquid film l diverges to infinity at the wetting temperature T_w .

- ◆ If the transition is continuous (*critical wetting*) the divergence is characterised by *critical exponents* describing the asymptotic behaviour of the thickness l , and the parallel correlation length $\xi_{||}$ close to T_w :

$$l \sim (T_w - T)^{-\beta},$$

$$\xi_{||} \sim (T_w - T)^{-\nu_{||}}.$$

3. The Standard Model

- ◆ The standard interfacial model considers the *surface tension* Σ of the interface and an *effective interaction* with the substrate $W(l)$:

$$H_1 = \int d\mathbf{x} \left\{ \frac{\Sigma}{2} (\nabla l(\mathbf{x}))^2 + W(l) \right\} \quad \text{with} \quad W(l) = -a(T_w - T)e^{-\kappa l} + be^{-2\kappa l}$$

where a , b and κ are positive constants.

- ◆ In 3D, the upper critical dimension, the standard theory predicts *nonuniversal critical exponents*, dependent on a *wetting parameter* $\omega = \frac{k_B T \kappa^2}{4\pi \Sigma}$.

- ✓ The Standard Model is correct for dimension $d \neq 3$.
- ✗ Ising model ($\omega \approx 0.8$, $\nu_{||} \approx 3.7$) Monte Carlo simulations could not observe the predicted non-universality. The results are *consistent with a smaller wetting parameter* $\omega = 0.27 \pm 0.12$.
- ✗ Fails for *non-planar substrates*, e.g. a sphere or a wedge.
- ✗ Doesn't satisfy an exact sum-rule, thus being *thermodynamically inconsistent*.

4. The Nonlocal Model

- ◆ The derivation of the Interfacial Model from a microscopic model [2] reveals a *nonlocal interaction functional* [2]:

$$W[l] = -a(T_w - T) \text{ (diagram)} + b_1 \text{ (diagram)} + b_2 \text{ (diagram)} + \dots$$

with a , b_1 and b_2 constants.

- ◆ The diagrams represent integrations over the surfaces (black dots) with the kernel $K(\mathbf{r}_1, \mathbf{r}_2)$ proportional to the bulk correlation function:

$$\text{(diagram)} = \int d\mathbf{s}_{r_3} \int d\mathbf{s}_{r_2} K(\mathbf{r}_2, \mathbf{r}_3) \int d\mathbf{s}_{r_1} K(\mathbf{r}_1, \mathbf{r}_2).$$

- ◆ This diagram has an *implicit two-body interaction* with range $\xi_{NL} = \sqrt{l/\kappa}$, present in microscopic models.
- ◆ The diagrammatic formalism has an appealing physical interpretation and is easily extensible, with new classes of diagrams appearing (seen in the *background*).

5. Nonlocal effects at the 3D wetting transition

- ◆ Capillary-wave fluctuations with wave-number $q > 1/\xi_{NL}$ are damped, inducing an *effective wetting parameter* dependent on the film thickness.
- ✓ *Agreement with simulations*: Monte Carlo simulations of the Nonlocal Model show that full nonuniversal behaviour can only be observed for very large systems and extremely close to the transition (see Fig. 2 below): the Ising model simulations probed a *pre-asymptotic regime*.

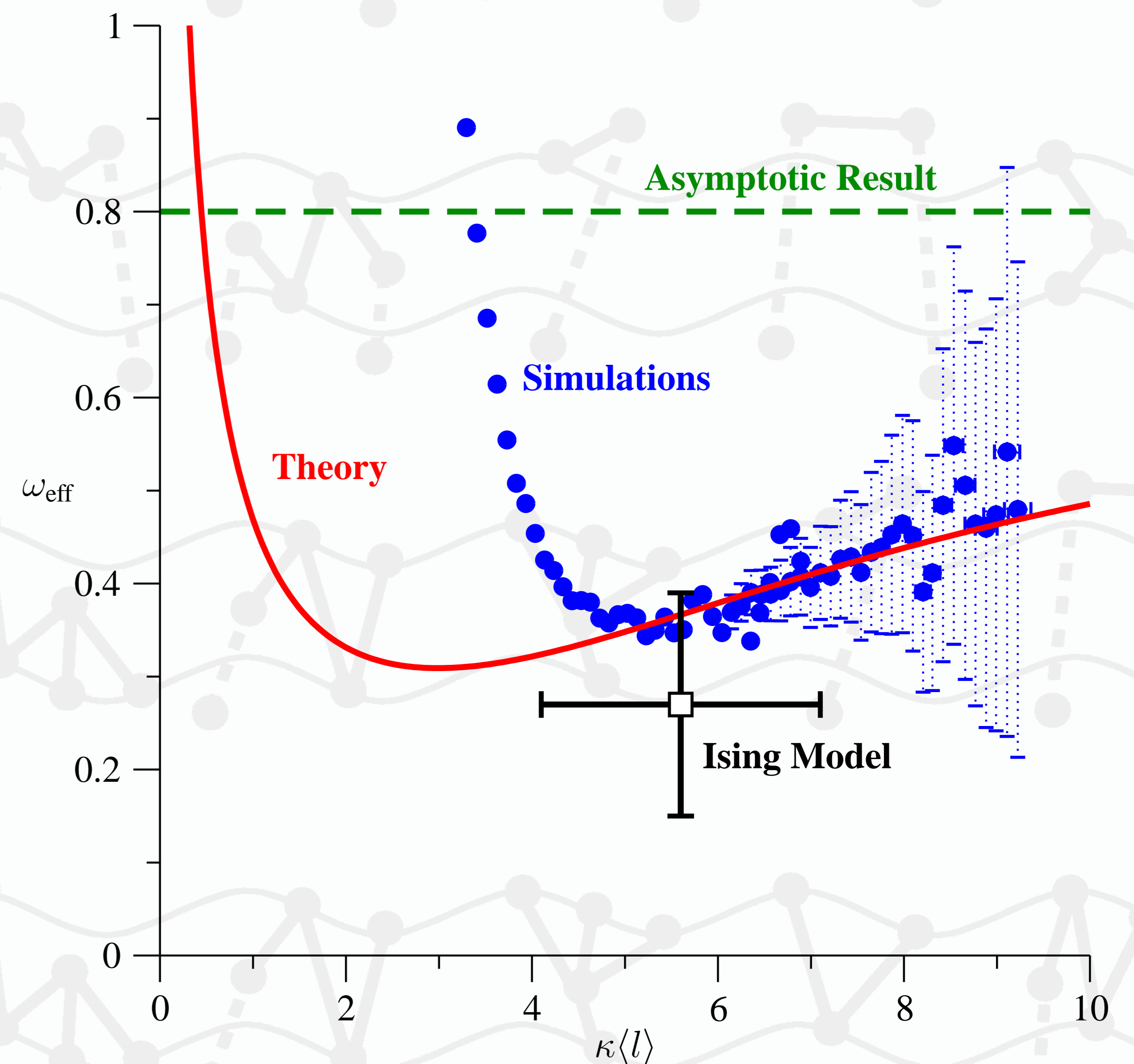
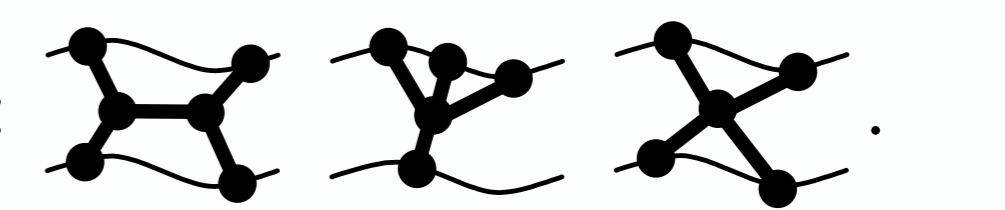


Fig. 2. Effective value of the wetting parameter ω_{eff} as a function of the film thickness $\kappa \langle l \rangle$. The blue circles are the Monte Carlo simulation results of the Nonlocal Model. The square is the Ising model result. The red line is the theoretical description (one fitting parameter).

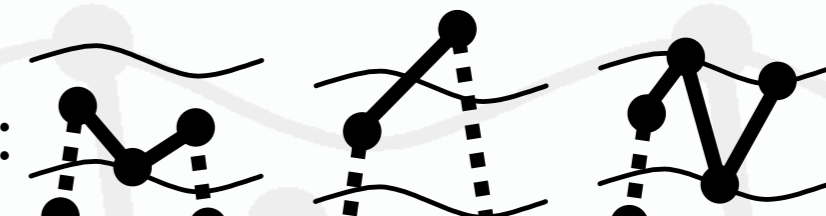
6. Applications of the Nonlocal Model

- ✓ Due to ξ_{NL} the sum-rule is now satisfied: the Nonlocal Model is *thermodynamically consistent*.

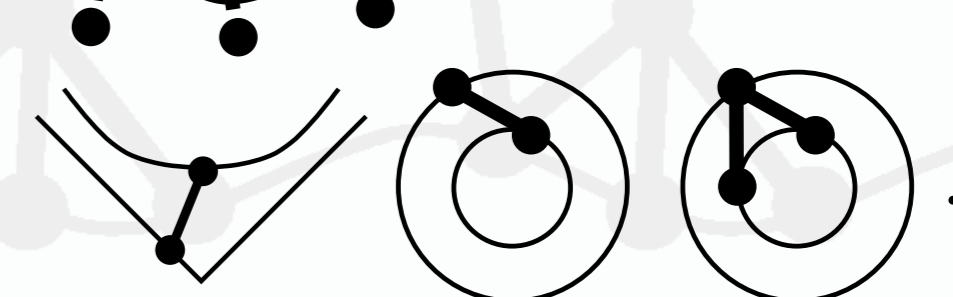
- ✓ Can do *perturbation theory*:



- ✓ Can introduce a *surface potential*:



- ✓ Can do wetting on *non-planar substrates*:



7. Take Home Message

- ◆ The standard model of wetting isn't good enough.
- ◆ The Nonlocal Model solves old problems of the wetting theory:
 - ✓ Agreement with simulations.
 - ✓ Consistent treatment of non-planar interfaces.
 - ✓ Agrees with an exact sum-rule.
- ◆ There is an extra lengthscale ξ_{NL} , related to nonlocal effects and crucial for the explanation of the discrepancies.

8. References & Acknowledgements

- [1] S. Dietrich, in *Phase Transitions and Critical Phenomena*, C. Domb and J. L. Lebowitz (Eds), Academic Press, vol. **12** (1988).
- [2] A. O. Parry, C. Rascón, N. R. Bernardino and J. M. Romero-Enrique, *Journal of Physics: Condensed Matter*, **18**, 6433 (2006).
- [3] A. O. Parry, C. Rascón, N. R. Bernardino and J. M. Romero-Enrique, *Physical Review Letters*, **100**, 136105 (2008).
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