Title: Quantized contact angles in the dewetting of a structured liquid

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Abstract: A thin partially wetting layer of liquid will dewet from an unfavourable substrate resulting in spherical cap shaped droplets next to a microscopically thin residual wetting layer of the liquid. We have measured a discrete spectrum of contact angles for dewetted droplets of a lamellar diblock copolymer in its disordered phase instead of the single unique contact angle that is usually observed. The different contact angles coexist with various thicknesses of wetting layer and the spectrum of measured contact angles shifts as the temperature is raised. The contact angle at the base of the droplets is a direct probe of the energy minimum of the film-thickness dependent effective interface potential. Self-consistent field theory was used to calculate the effective interface potential as a function of film thickness for a lamellar diblock copolymer. The results of the calculation show multiple minimums in the potential energy caused by substrate induced ordering within the liquid. The locations and depths of these minimums in the effective interface potential correspond to the wetting layer thicknesses and contact angles of the dewetted droplets respectively. The qualitative behaviour of the calculated contact angles at higher temperature agrees well with the experimental results. Since the contact angles wetting layer thickness are such a sensitive probe of the free energy of the film over a wide range of film thickness this system provides an excellent testing ground for quantitative theoretical predictions as well.

Quantized contact angles in the dewetting of a structured liquid

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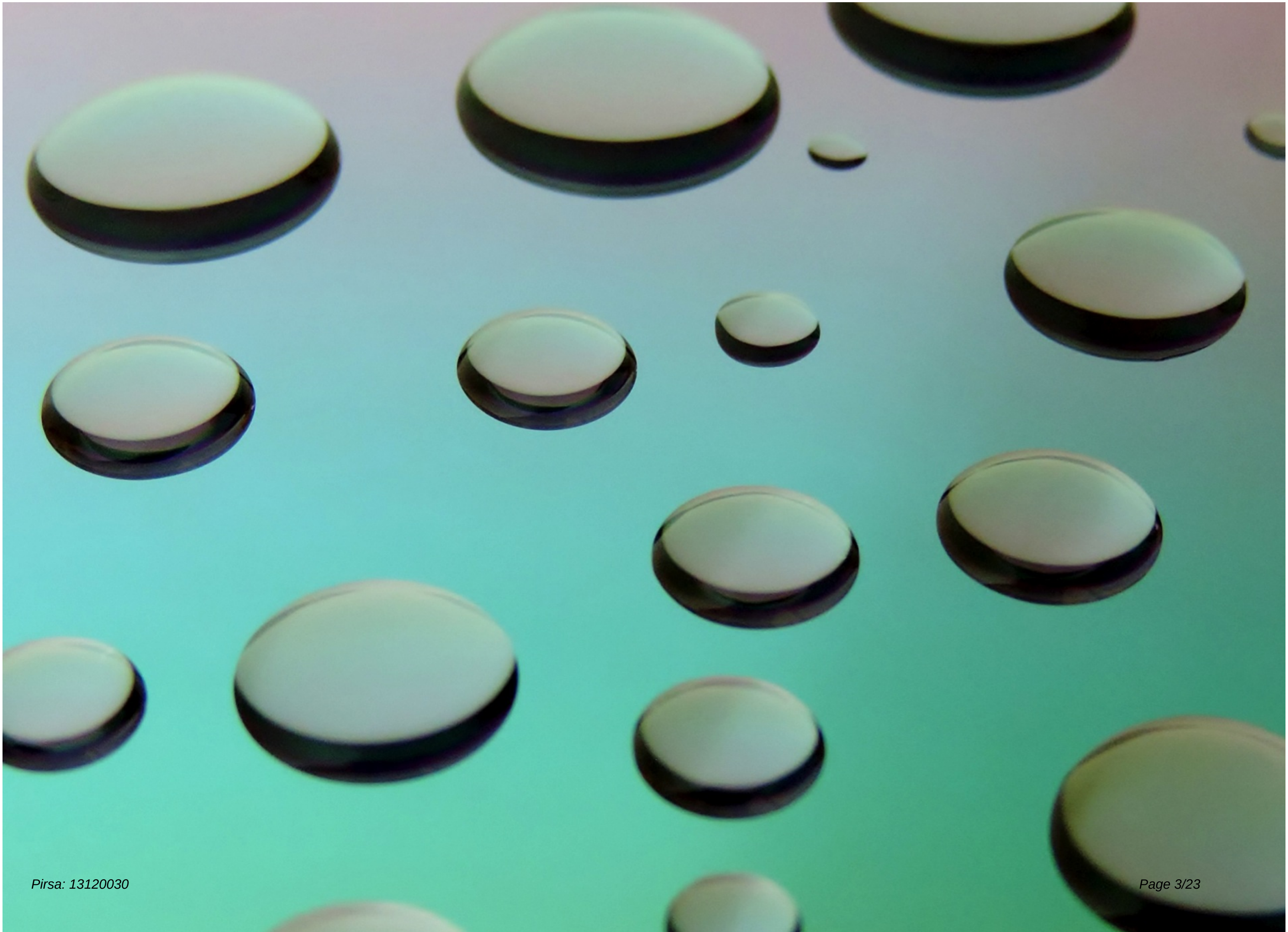
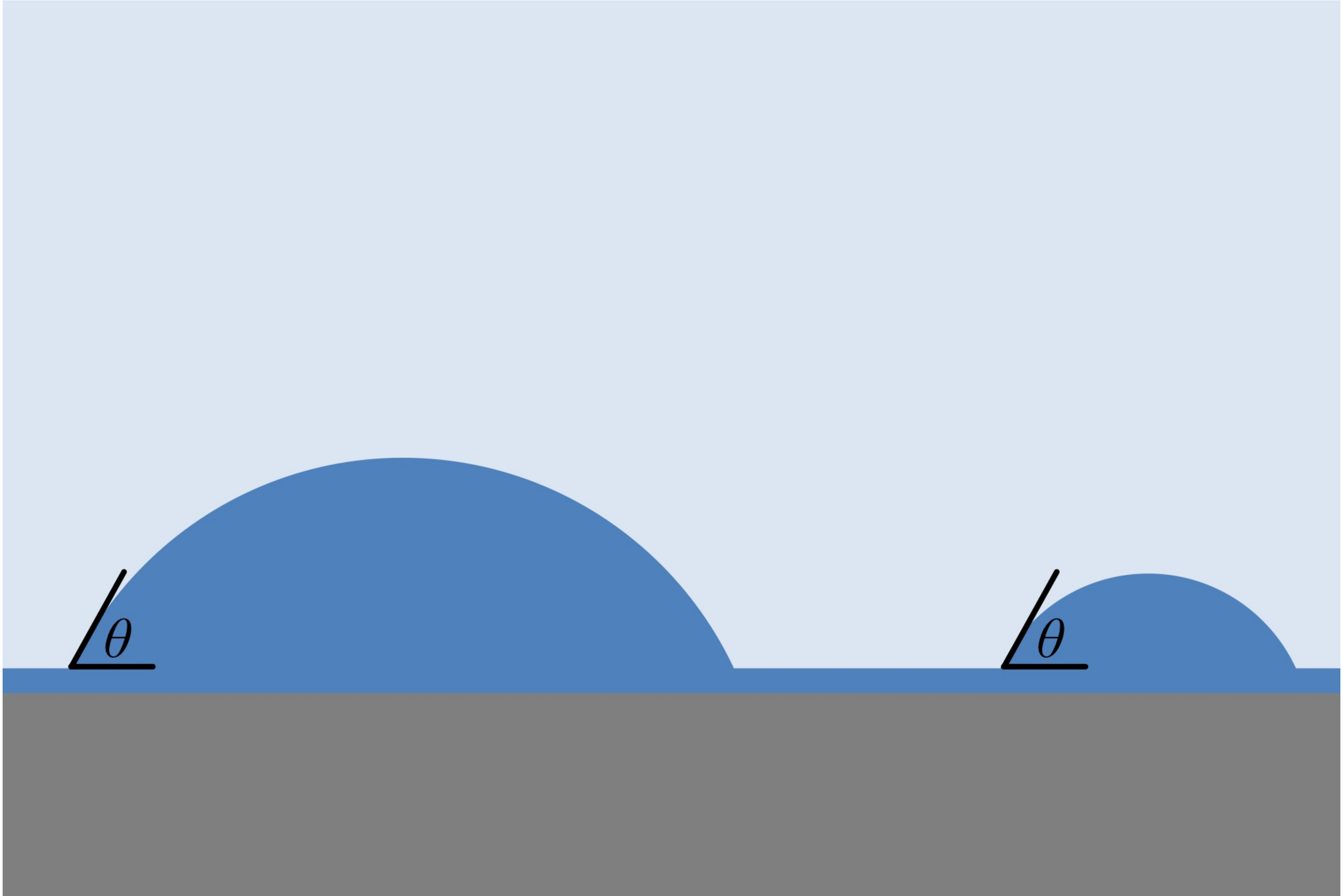
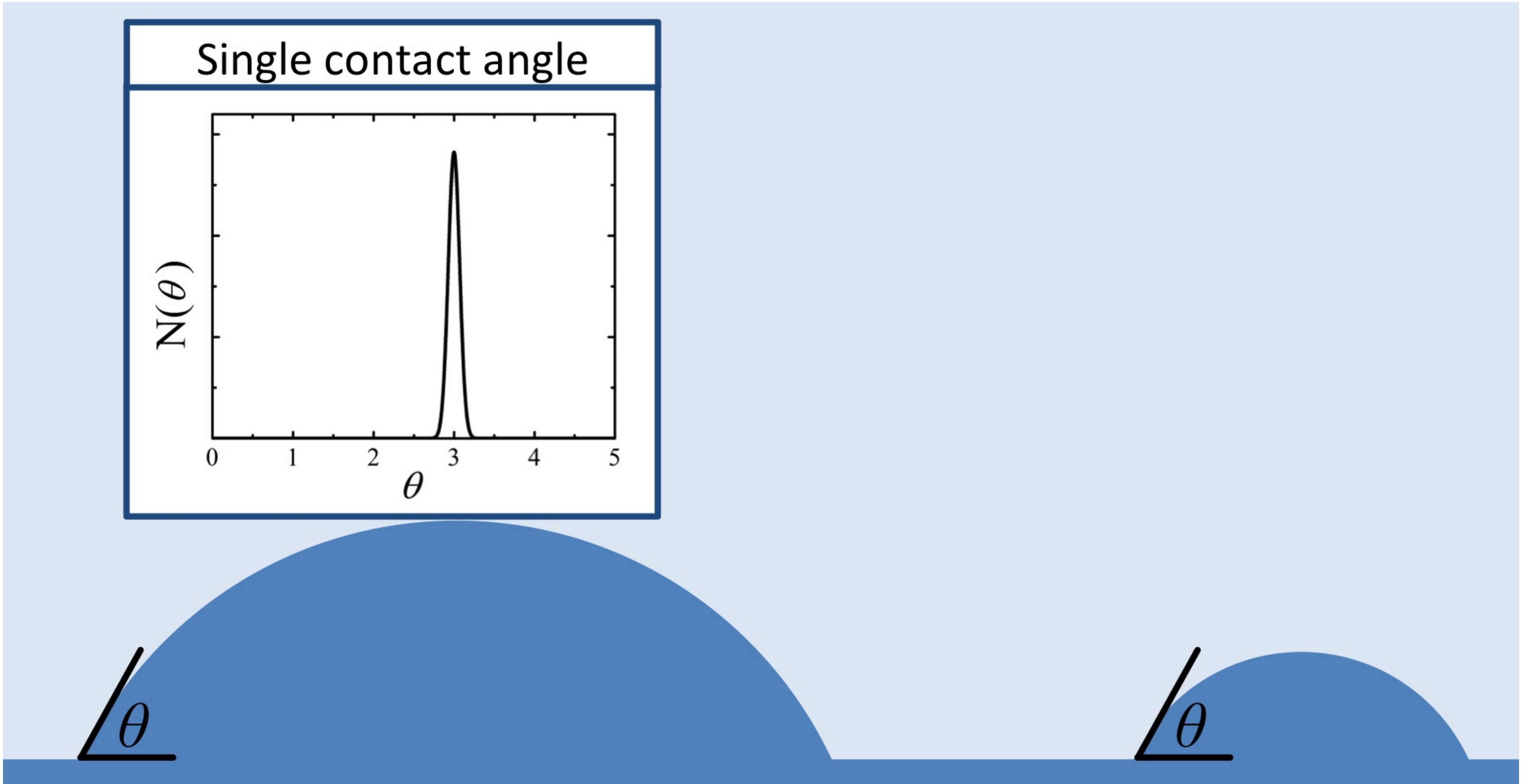
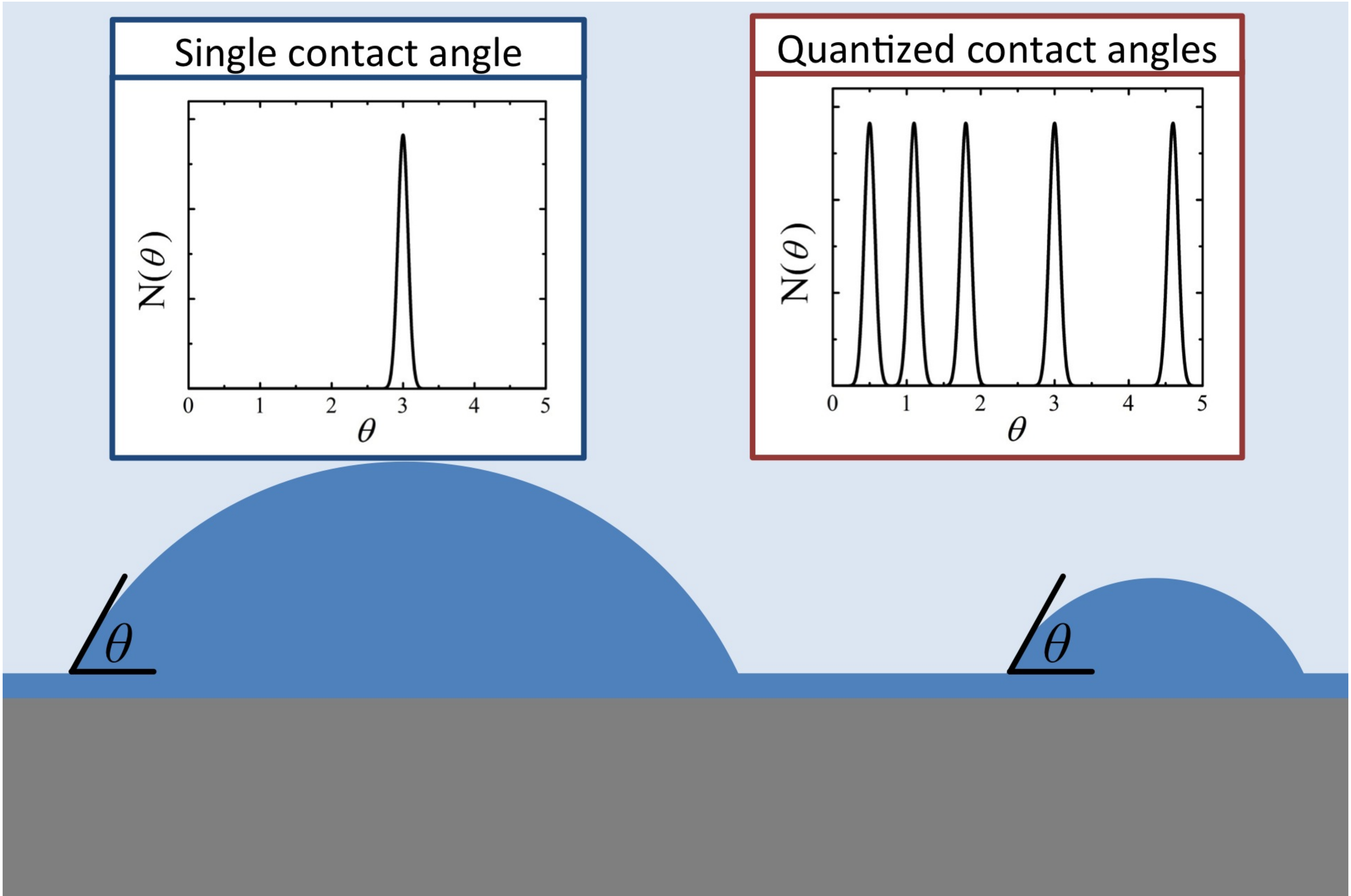
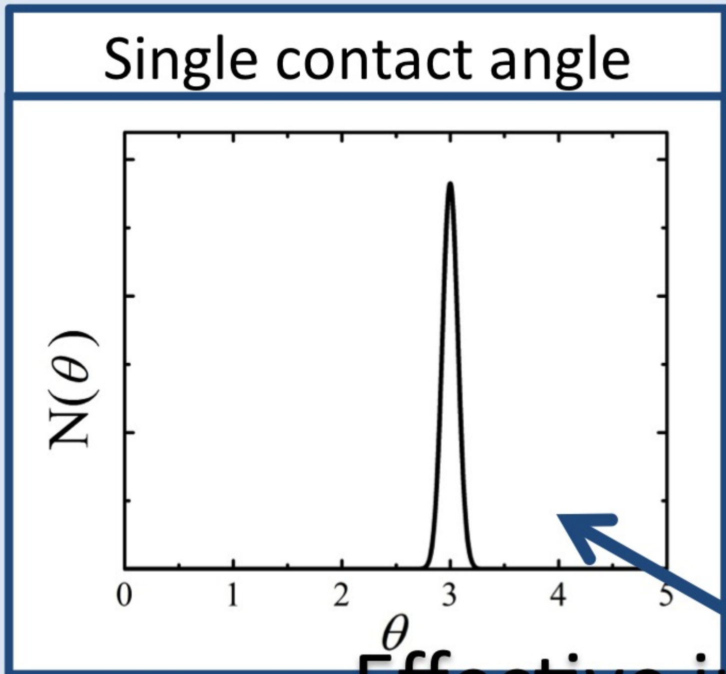
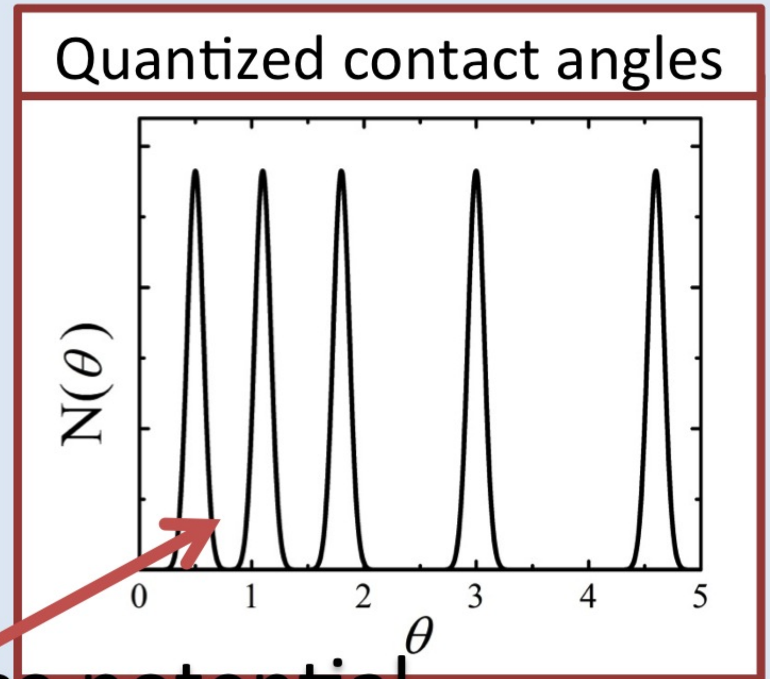



θ
θ

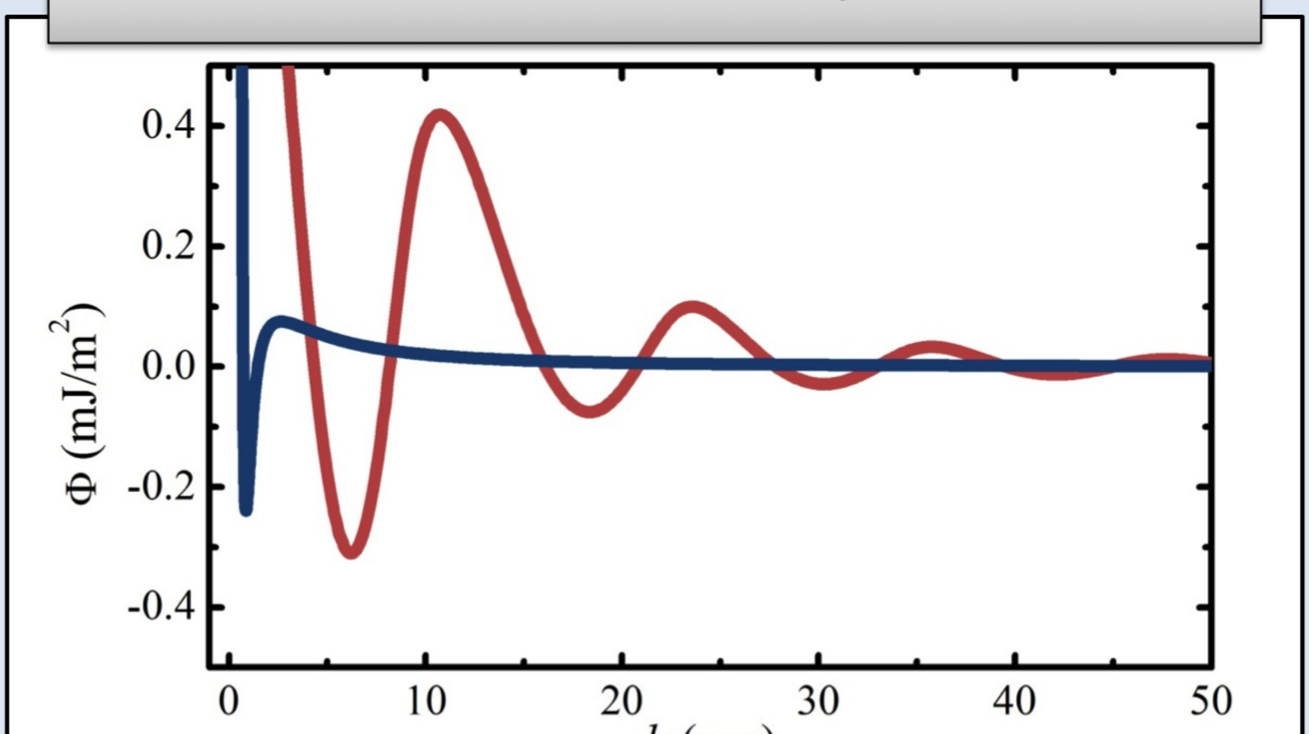

Single contact angle
N(θ)
0
1
2
3
4
5
θ
θ
θ


Single contact angle
N(θ)
0 1 2 3 4 5
θ
Quantized contact angles
N(θ)
0 1 2 3 4 5
θ
θ
θ





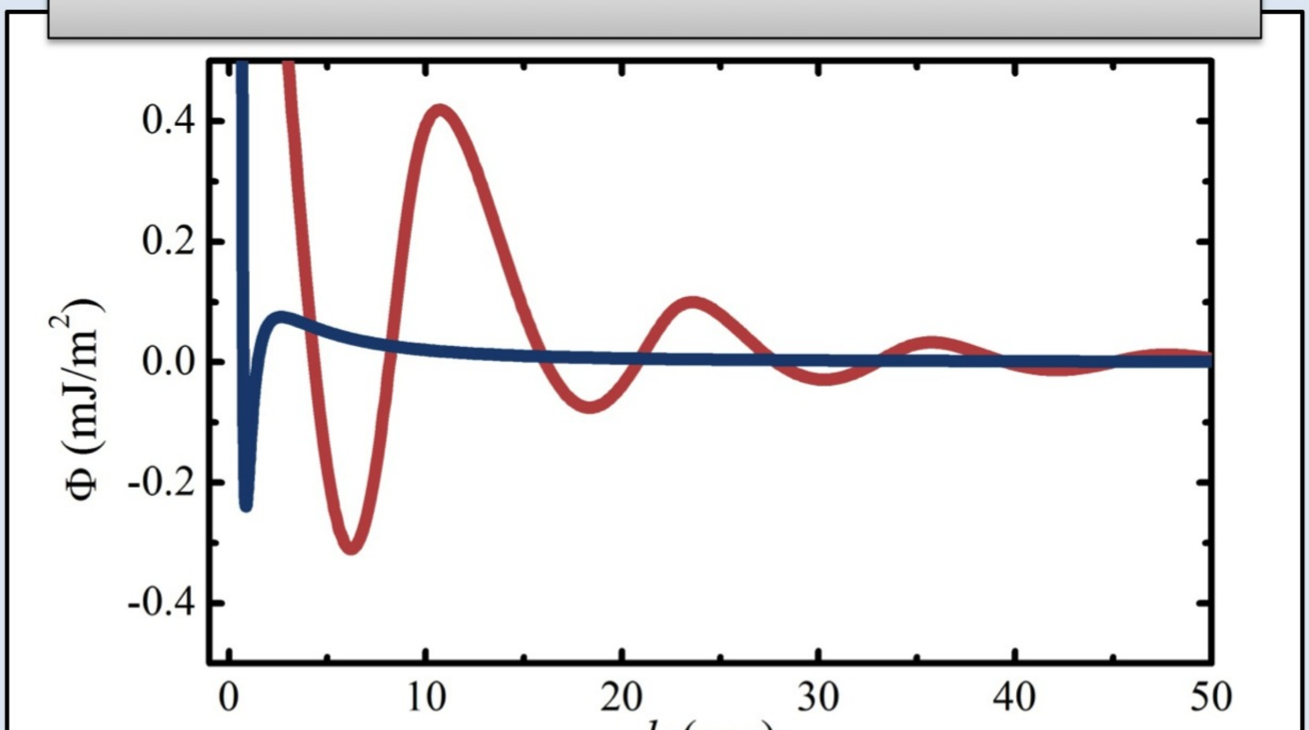
Effective interface potential



Single contact angle

Quantized contact angles

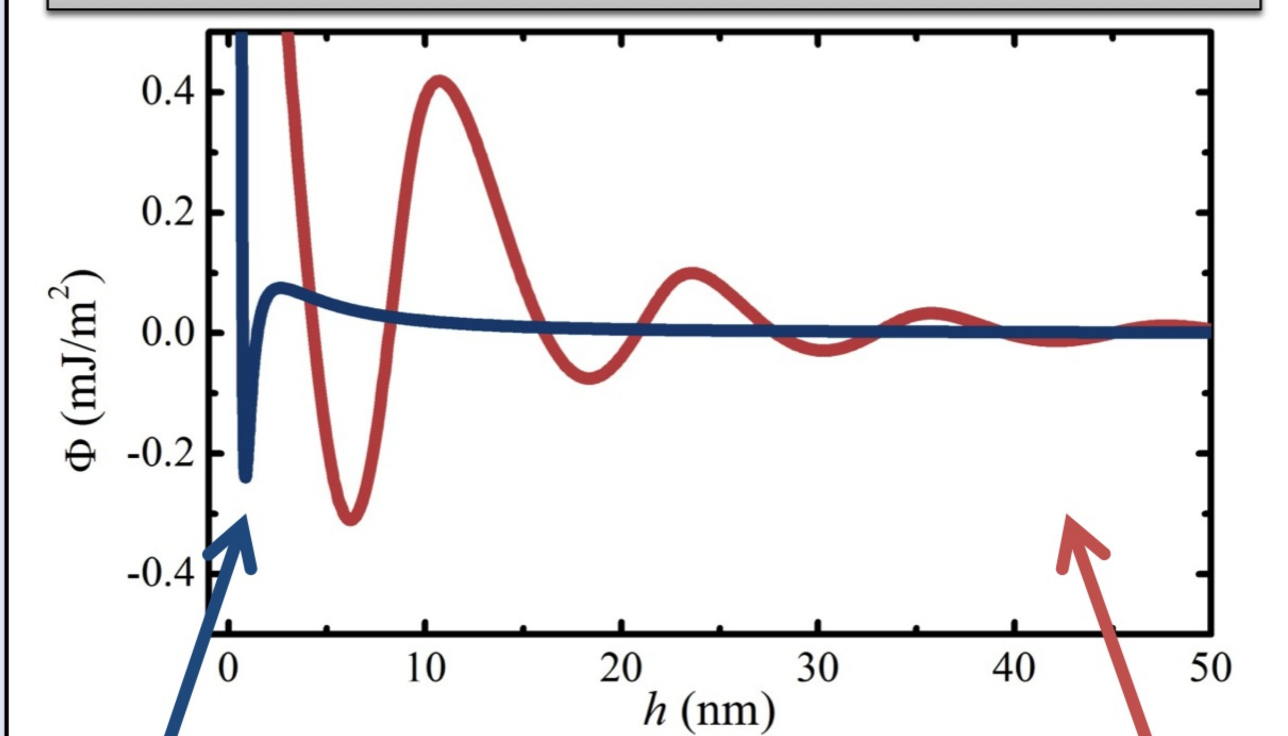
Effective interface potential



Single contact angle

Quantized contact angles

Effective interface potential



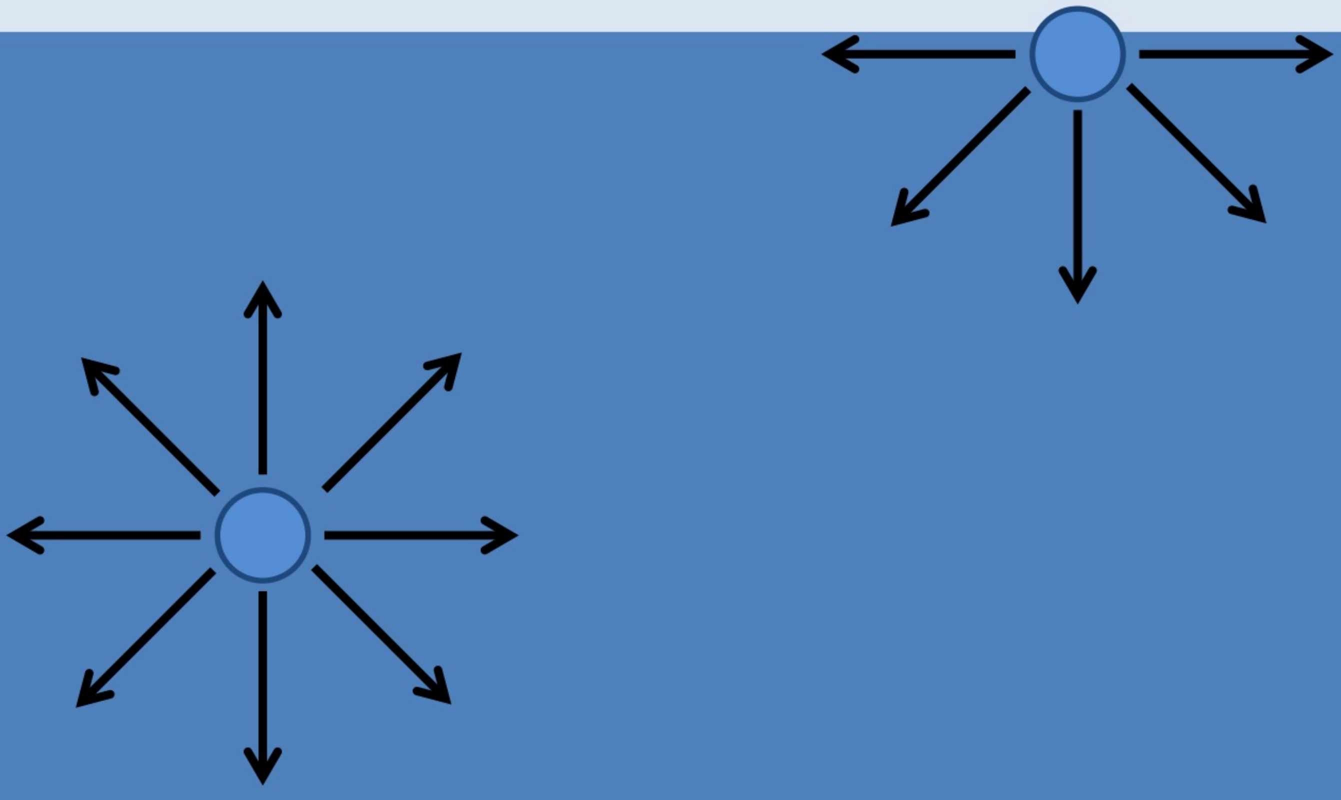
Homopolymer

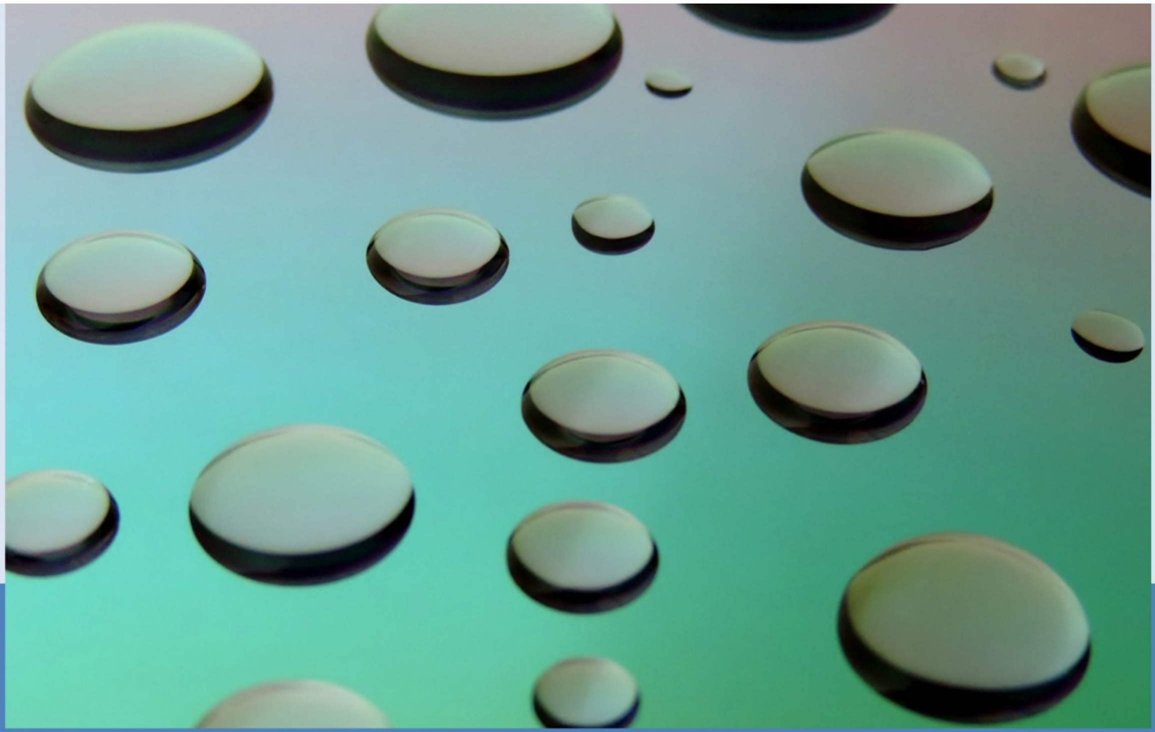
van der Waals

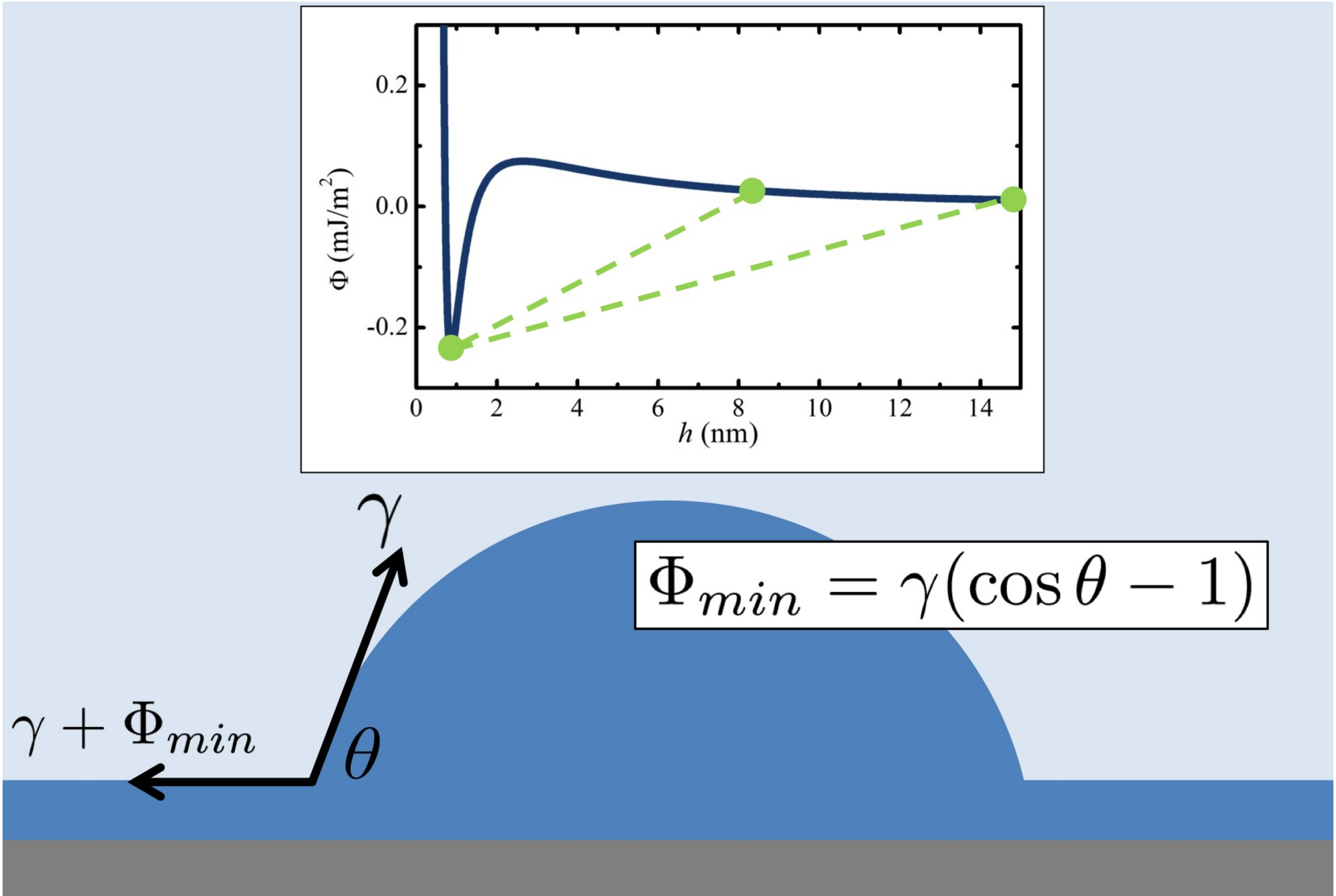
Diblock copolymer

molecular order

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{T,V,n}$$





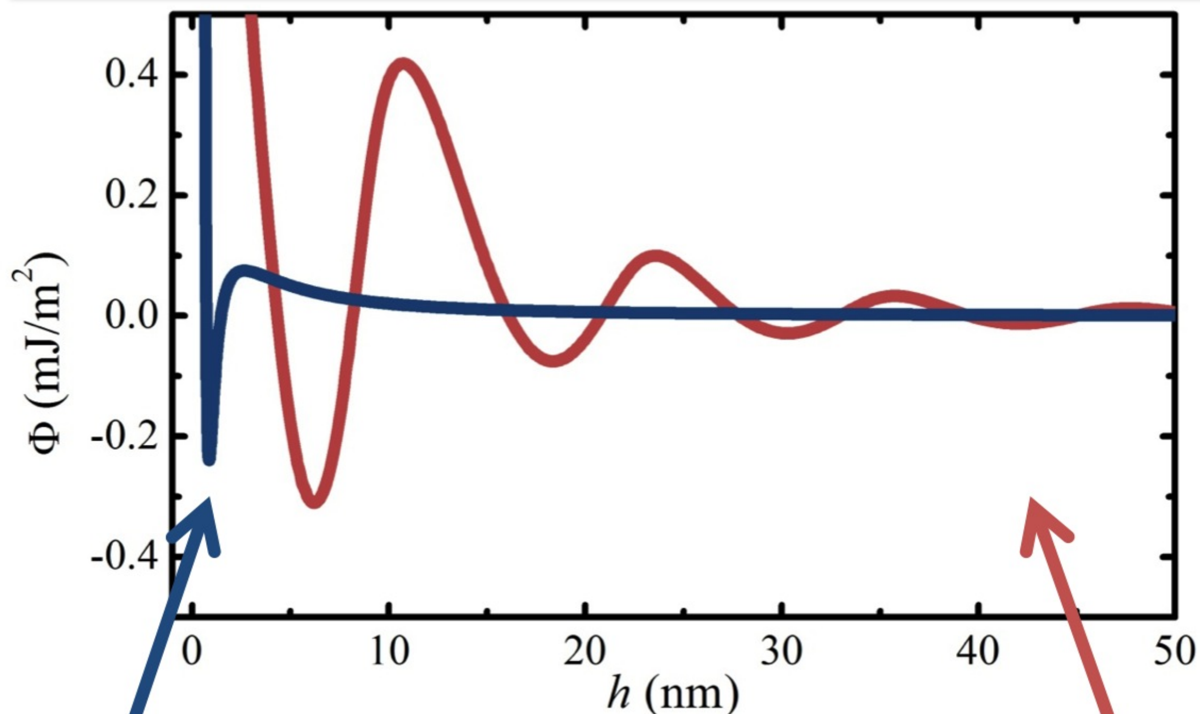


Φ (mJ/m^2)
0.2
0.0
-0.2
0
2
4
6
8
10
12
14
h (nm)
γ
$\Phi_{min} = \gamma(\cos\theta - 1)$
$\gamma + \Phi_{min}$
θ

Single contact angle

Quantized contact angles

Effective interface potential



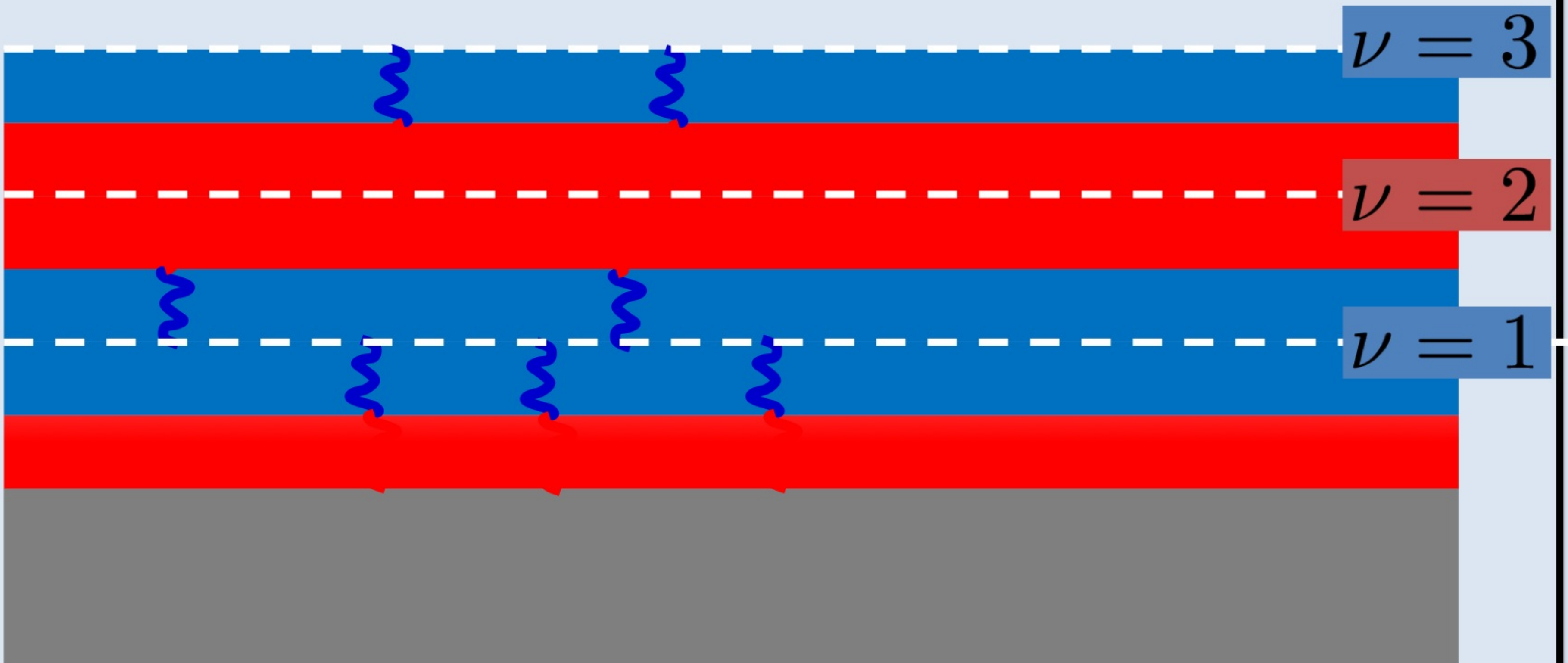
<u>Homopolymer</u>

van der Waals

<u>Diblock copolymer</u>

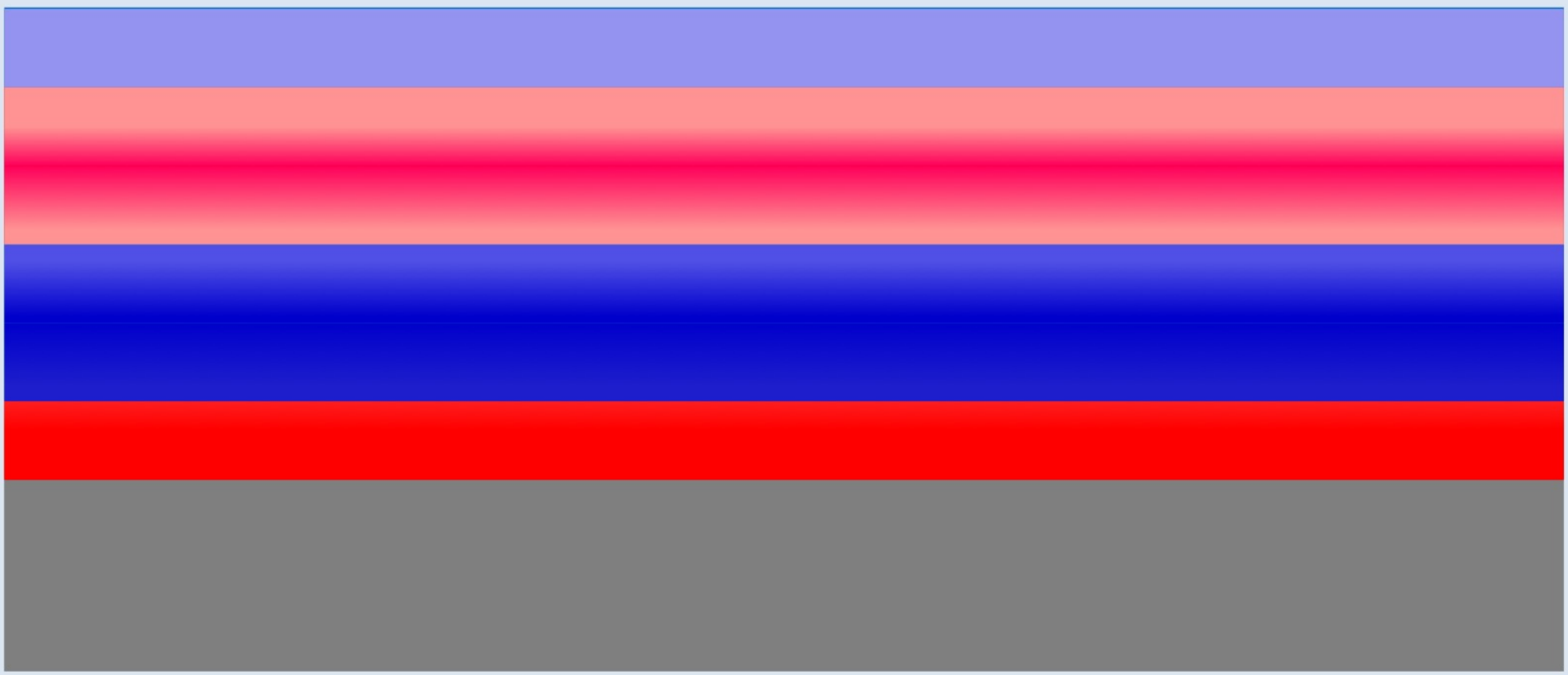
molecular order

Lamellar Diblock Copolymers

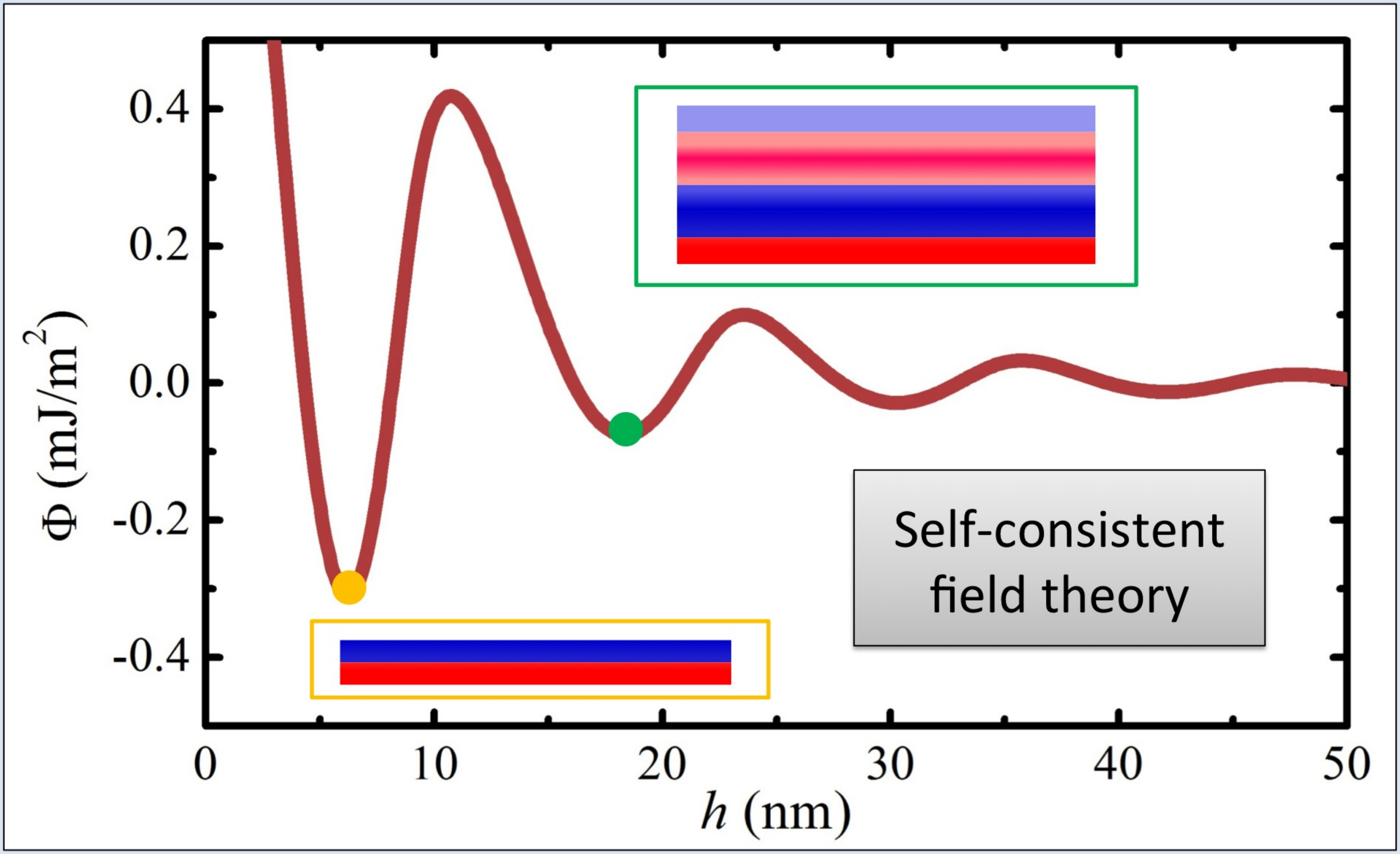


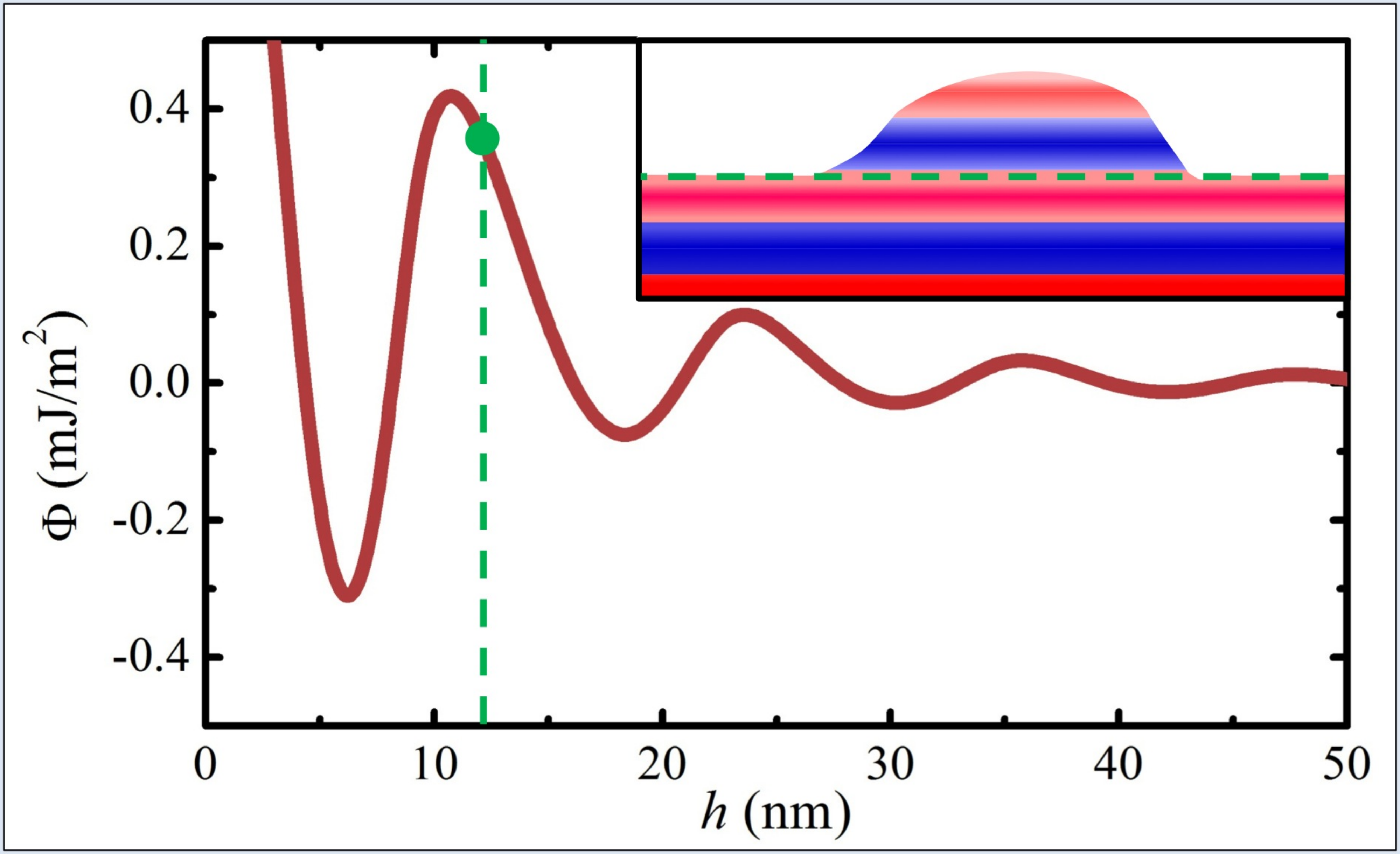
$$T < T_{ODT}$$

Lamellar Diblock Copolymers

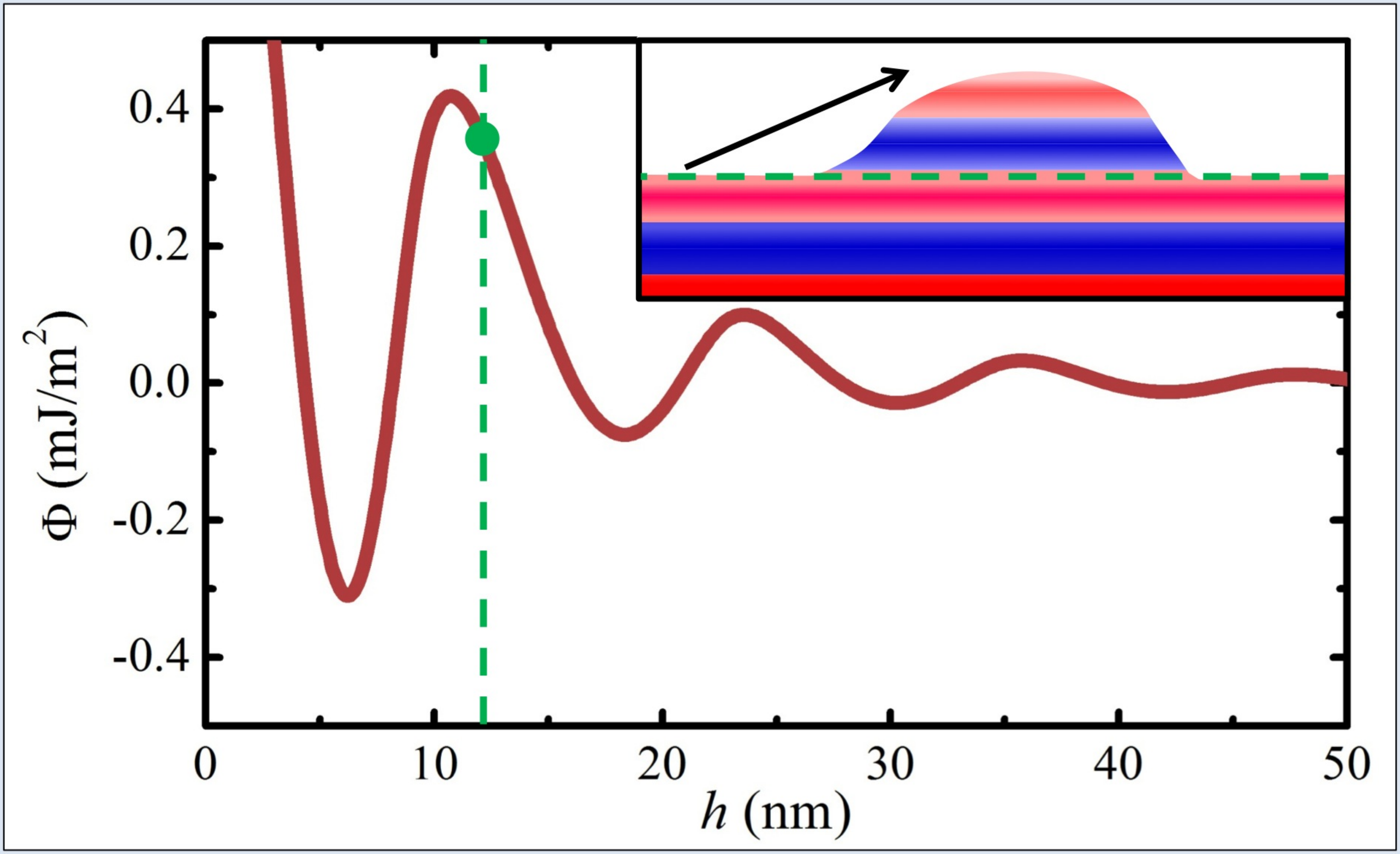


$$T > T_{ODT}$$

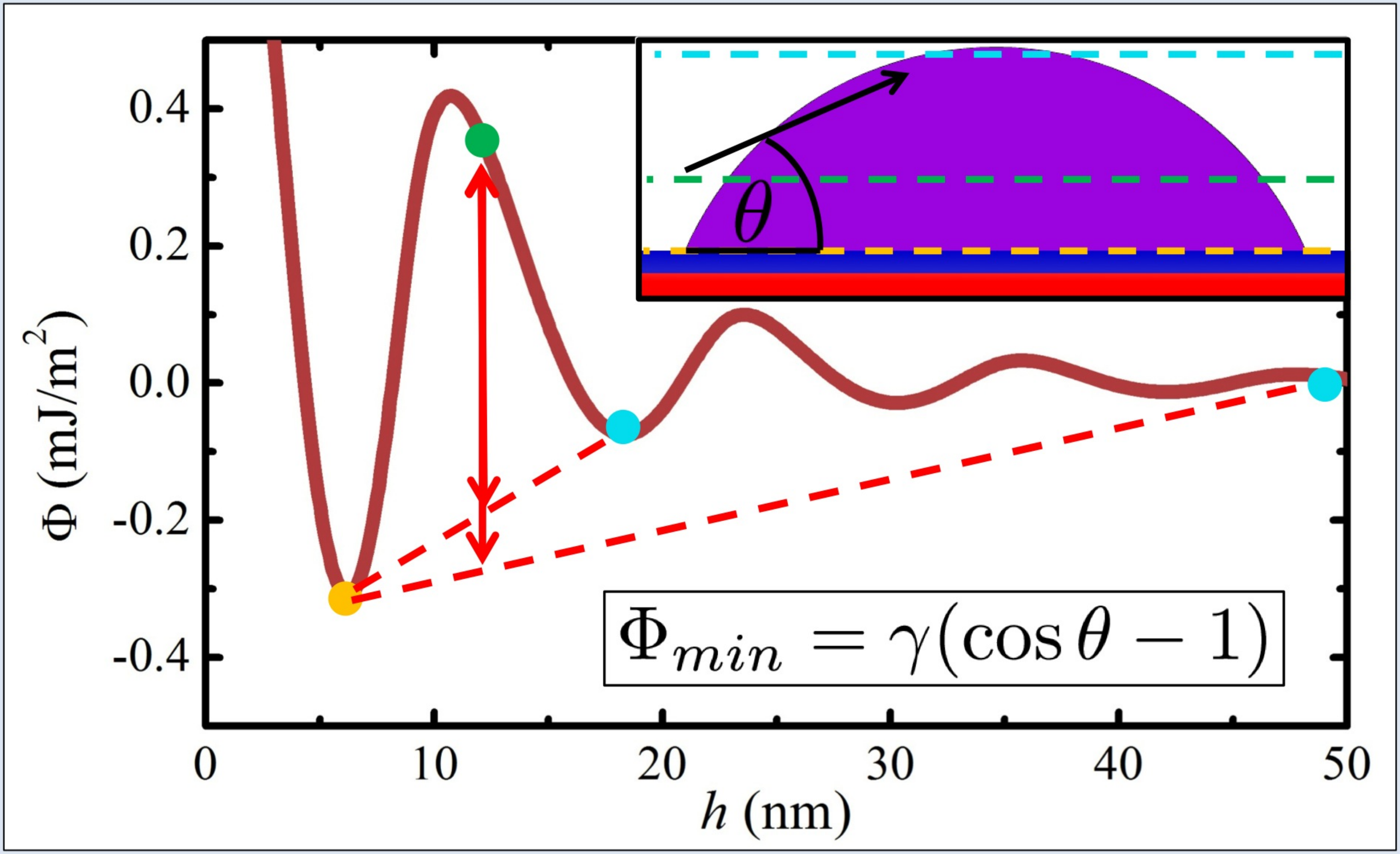

0.4
0.2
0.0
-0.2
-0.4
Φ (mJ/m²)
0
10
20
30
40
50
h (nm)
Self-consistent
field theory



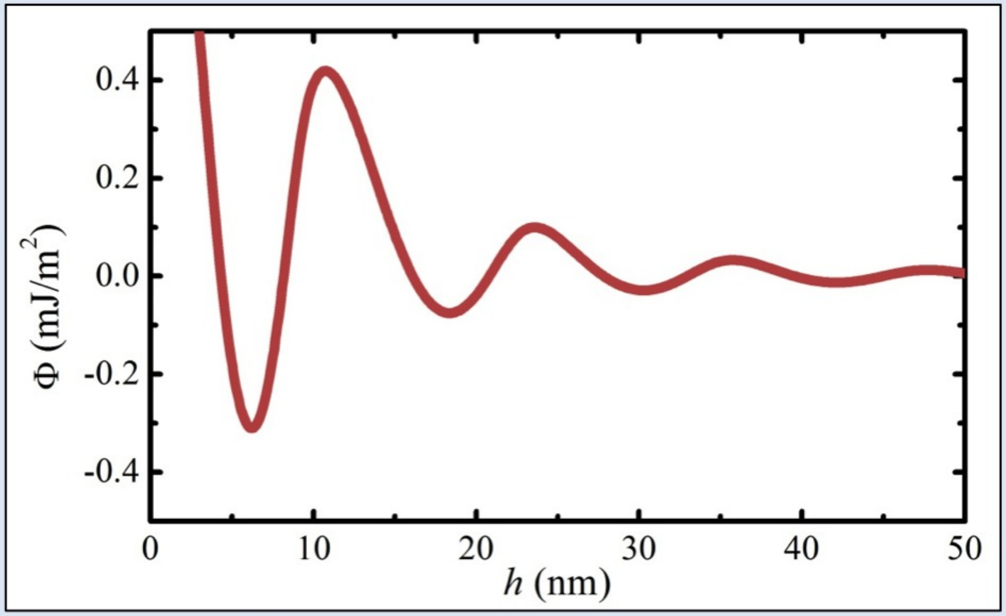
Φ (mJ/m²)
0.4
0.2
0.0
-0.2
-0.4
0
10
20
30
40
50
h (nm)



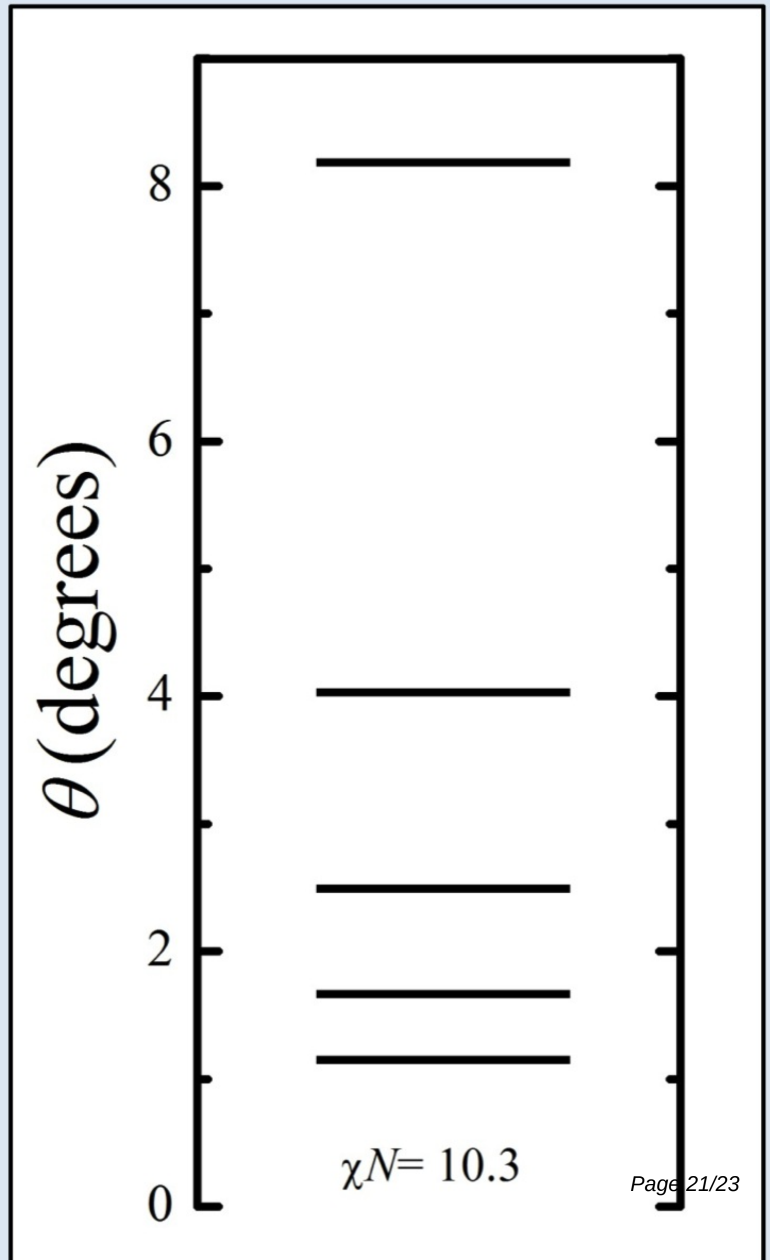
0.4
0.2
0.0
-0.2
-0.4
Φ (mJ/m²)
0
10
20
30
40
50
h (nm)

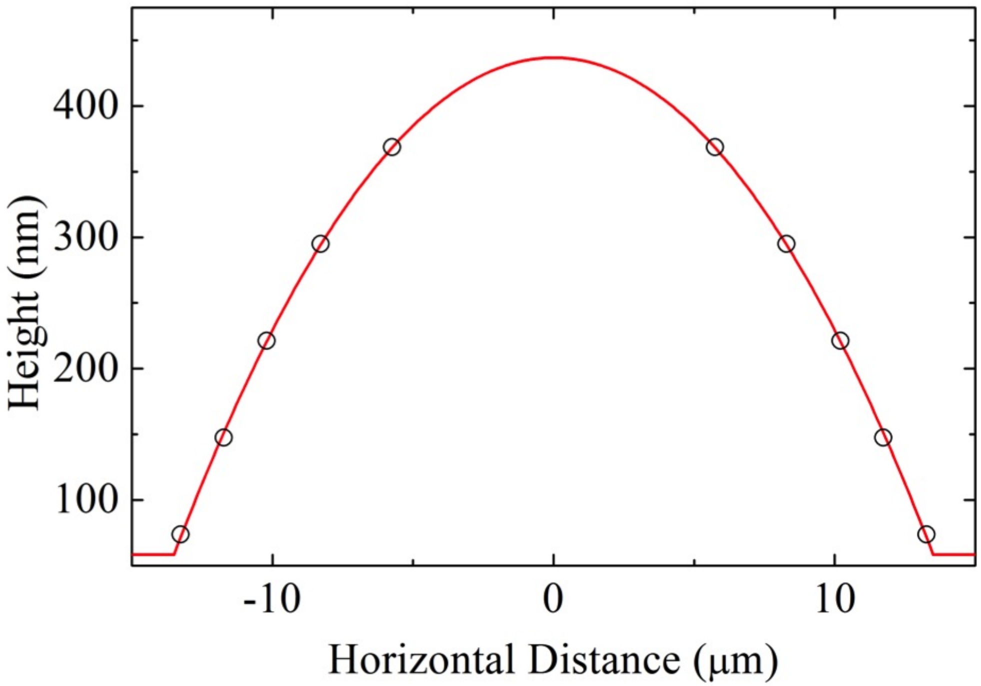


0.4
0.2
0.0
-0.2
-0.4
Φ (mJ/m²)
0
10
20
30
40
50
h (nm)
θ
$\Phi_{min} = \gamma(\cos\theta - 1)$

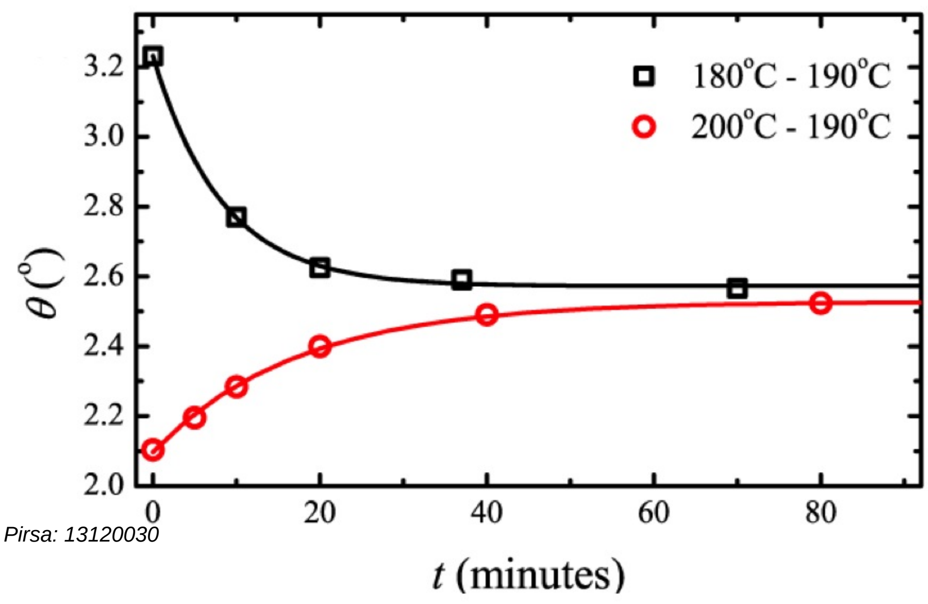


$$\Phi_{min} = \gamma(\cos\theta - 1)$$

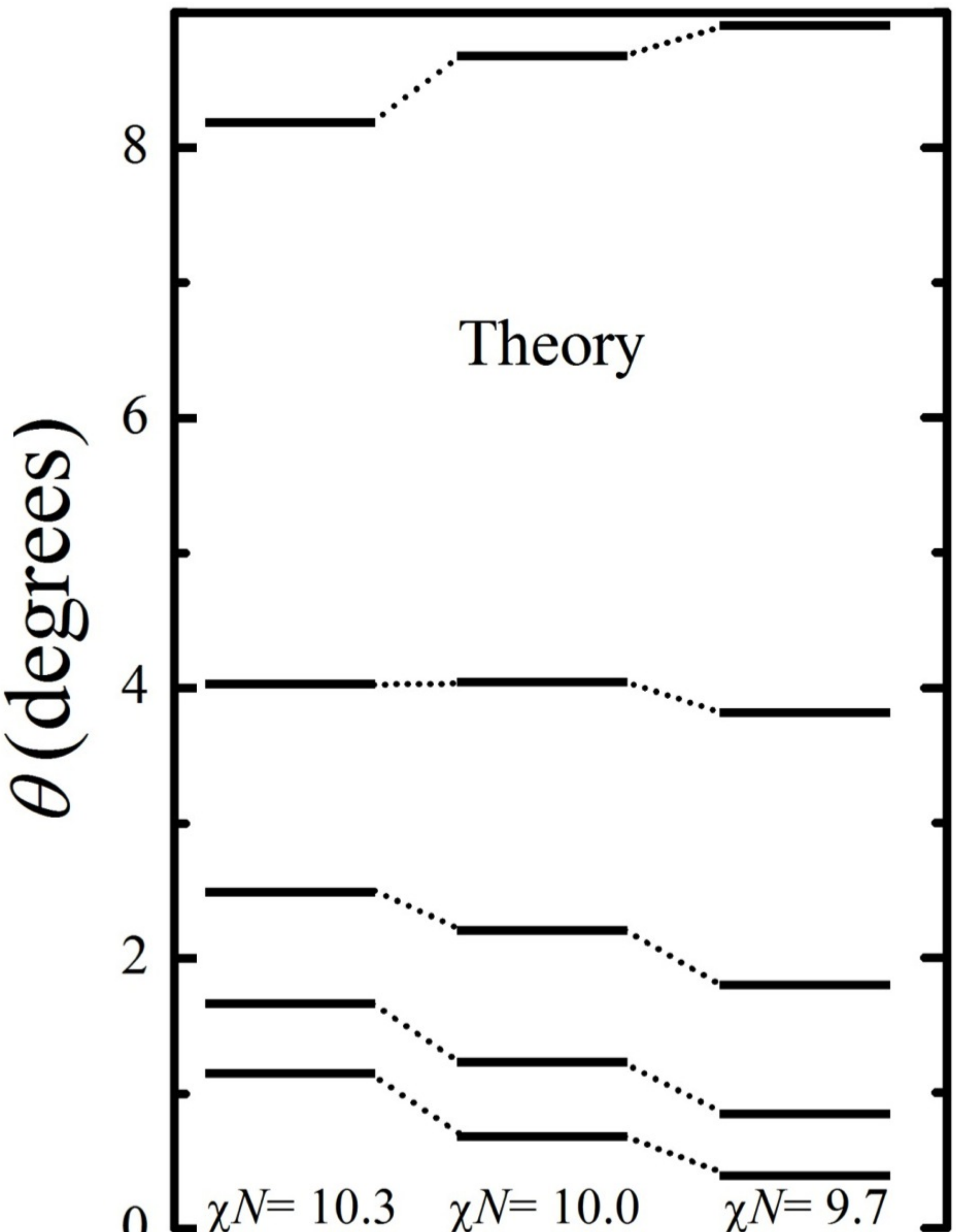




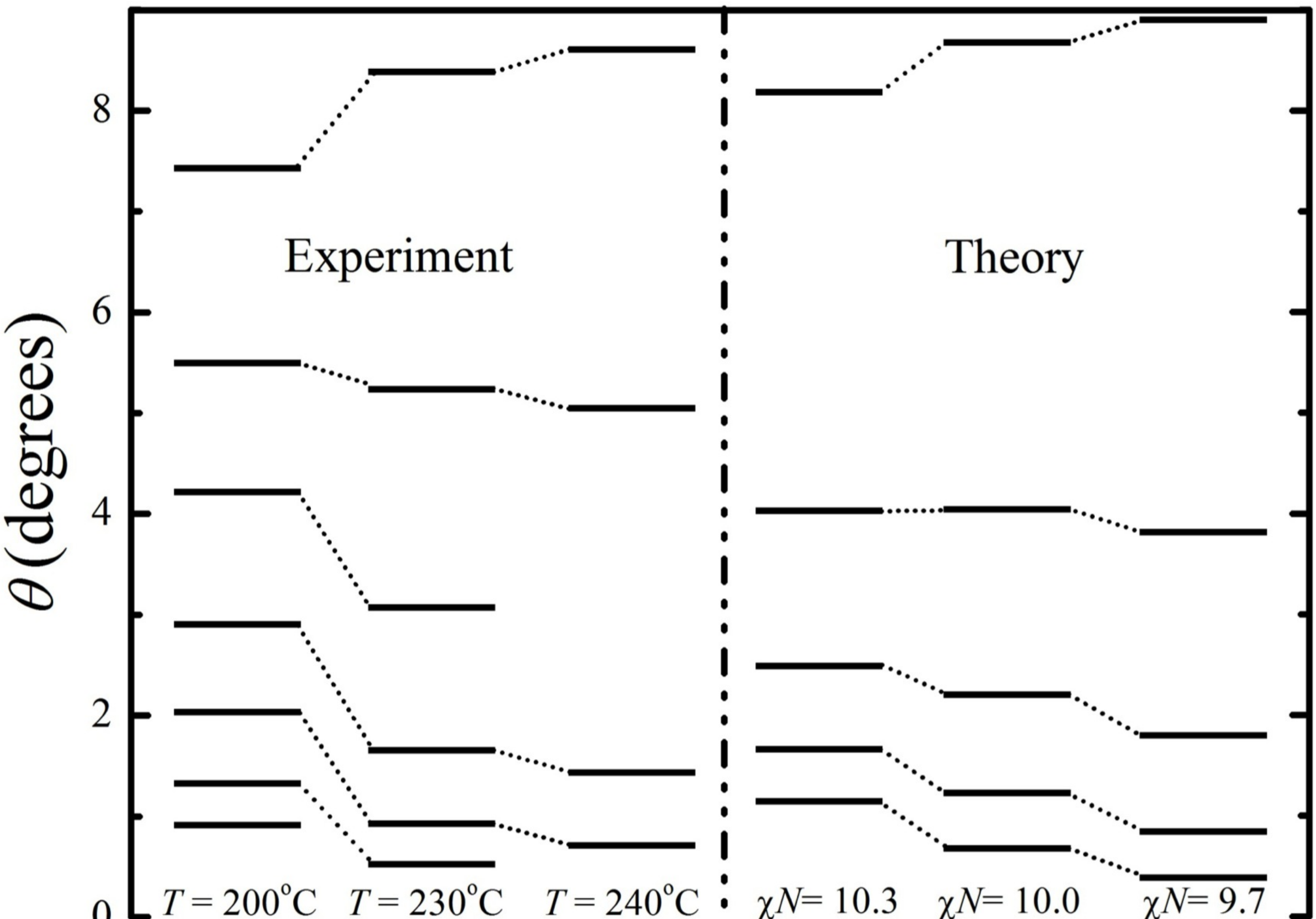
Height (nm)
400
300
200
100
-10
0
10
Horizontal Distance (μm)



θ (°)
3.2
3.0
2.8
2.6
2.4
2.2
2.0
0
20
40
60
80
t (minutes)
180°C - 190°C
200°C - 190°C



θ (degrees)
8
6
4
2
0
Theory
χN= 10.3
χN= 10.0
χN= 9.7



M. Ilton, P. Stasiak, M. W. Matsen & K. Dalnoki-Veress, (submitted to PRL)