

Lattice Gas models including water-surface interactions

Cesar L. Pastrana

1 Model

We study the interaction of water and surfaces using Monte Carlo simulations in the grand canonical (GC) ensemble. The lattice-gas is a simplified model where water is represented as two-dimensional lattice with a spacing given by the average distance between water molecules, l [1, 2]. Each lattice site can be either occupied or empty. The GC Hamiltonian in the presence of surfaces is given by:

$$H = -\epsilon \sum_{\langle i,j \rangle} c_i c_j - b_s \sum_{i \in S} c_i - \mu \sum_i c_i \quad (1)$$

where c_i is the occupancy state of lattice site i ($c = 1$ for a occupied site and $c = 0$ for empty site) and ϵ is the attractive energy between water molecules. The chemical potential is given by μ and b_s is the interaction energy between water and surfaces, where $b_s > 0$ for hydrophylic surfaces and $b_s < 0$ for hydrophobic surfaces. The chemical potential is given by $\mu = \mu_c + k_B T \log s$ where s is the water saturation (relative humidity) and the critical chemical potential is a known value.

After appropriate algebraic manipulation, Equation 1 can be modified to map with the Ising model, where the spins are in states ± 1 , resulting in [1]:

$$H = -\epsilon \sum_{\langle i,j \rangle} s_i s_j + \frac{2\epsilon + \mu}{2} \sum_i s_i - \frac{b}{2} \sum_{i \in S} (1 - s_i), \quad (2)$$

where ϵ is analogous to the coupling constant and the term $\frac{2\epsilon + \mu}{2}$ is analogous to the magnetic field. In that form, $s_i = -1$ indicates an occupied lattice site nad $s_i = 1$ is an empty site.

We use periodic boundary conditions and a von Neumann neighborhood for the interaction between water-water and water-surface. Minimisation proceeds by randomly selecting lattice locations and comparing the energy change following the Metropolis criterion.

Parameter	Value	Refs.
General parameters		
Water-water, ϵ	9 kJ/mol	[1]
Water-surface, b_s	3ϵ	[4]
Critical chemical potential, μ_c	-2ϵ	[1, 2]
Lattice spacing, l	3.24 Å	[1]
Temperature, T	298 K	-
AFM tip simulations		
Tip radius r	10 nm	[3]
Tip surface distance y_0	$0.6l$	-
Relative humidity, s	0.30-0.65	-
Icosahedral virus simulations		
Virus radius, R_c	25 nm	[4]
Virus shell thickness, t	3 nm	[4]

Table 1: Simulation parameters.

General and simulation-specific parameters for the Monte-Carlo simulations of AFM tip and virus capsid. A detailed description of the model and parameters can be found in the seminal works by Jang [1, 2].

2 Meniscus between surface and AFM tips

We consider the AFM tip as the values above the parabola given by $y(x) = ax^2 + y_0$, where y_0 is the distance to the surface and $a = \frac{1}{2r}$, with r the desired radius of the tip. The later is determined from the second derivative of $y(x)|_{x=0}$.

The results of the simulation for different heights y_0 at relative humidities, $s = 0.30$, $s = 0.50$, and $s = 0.65$ are shown in Figures 1, Figure 2 and Figure 3. The larger the humidity the wider the water meniscus as well as the maximum height before the meniscus is broken.

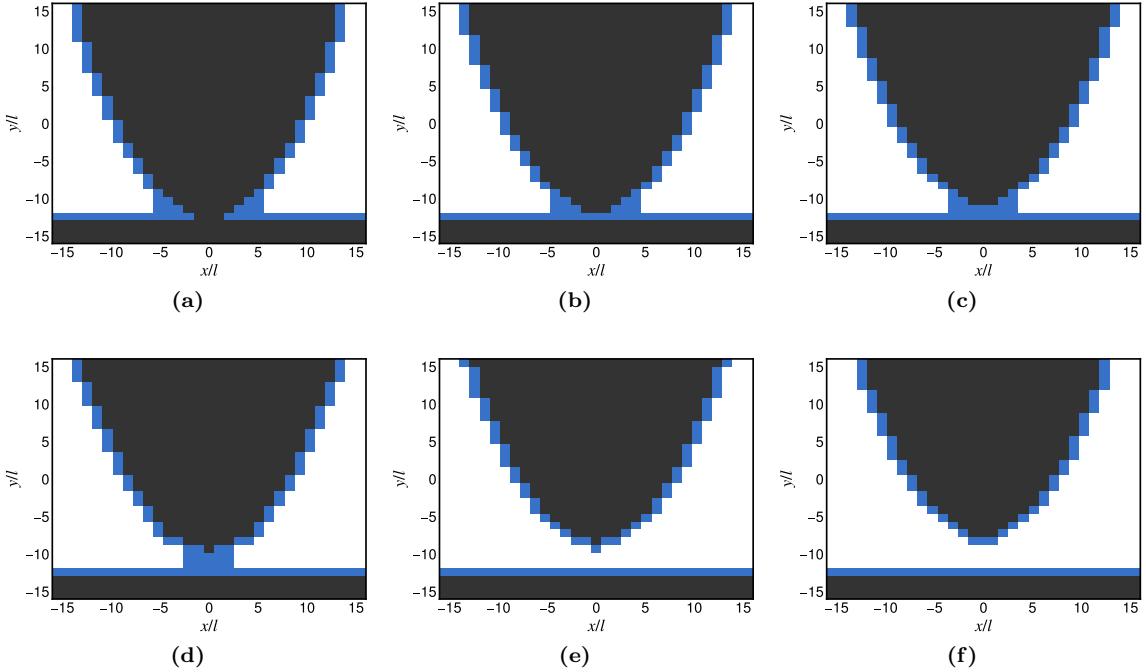


Figure 1: Water meniscus depending on the distance to surface

Retraction from $y_0 = 0$ to $y_0 = 5$ in steps of l ($y_0 = 0, l, 2l, 3l, 4l, 5l$). The blue areas correspond to regions with a probability of occupancy $\rho(x, y) > 0.75$ obtained from 2000 Monte Carlo steps equilibration. Saturation $s = 0.30$.

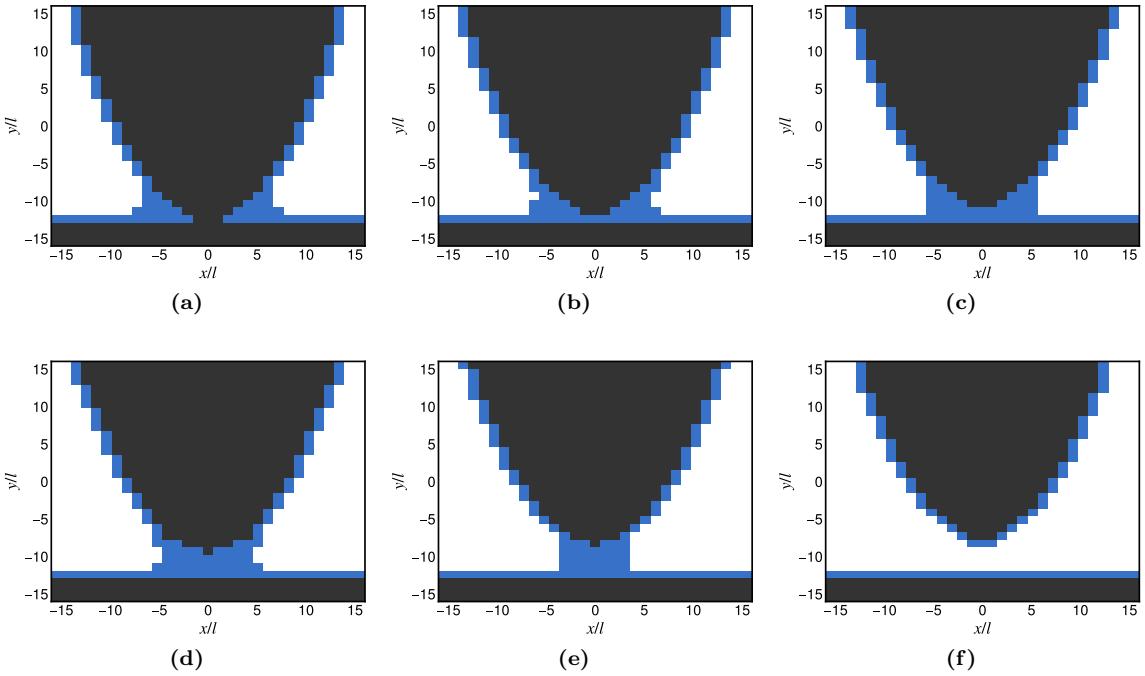


Figure 2: Water meniscus depending on the distance to surface

Retraction from $y_0 = 0$ to $y_0 = 5$ in steps of l ($y_0 = 0, l, 2l, 3l, 4l, 5l$). The blue areas corresponds to regions with a probability of occupancy $\rho(x, y) > 0.75$ obtained from 2000 Monte Carlo steps equilibration. Saturation $s = 0.50$.

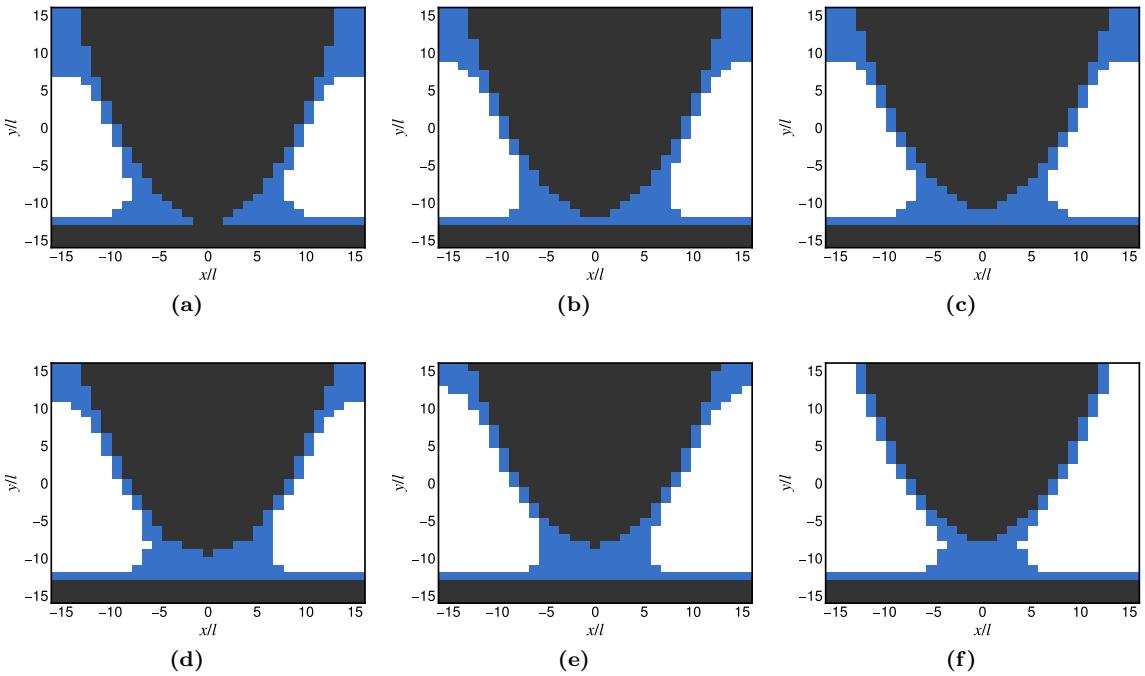


Figure 3: Water meniscus depending on the distance to surface

Retraction from $y_0 = 0$ to $y_0 = 5$ in steps of l ($y_0 = 0, l, 2l, 3l, 4l, 5l$). The blue areas corresponds to regions with a probability of occupancy $\rho(x, y) > 0.75$ obtained from 2000 Monte Carlo steps equilibration. Saturation $s = 0.65$. Note the artifact on the upper part due to the limited size of the mesh in the horizontal direction.

3 Icsaohdral viruses

We draw the icosahedrum from the polar function:

$$r = R_c(1 + A \sin 6\theta), \quad (3)$$

where R_c is the radius of the icosahedron, A is a shape parameter set to $A = 0.06$ and θ spans a range between θ_0 and 2π . A virus with a cavity can be draw by considering $\theta_0 > 0$. In addition, viruses with multiple cavities can be constructed by restricting the domain of θ . The thickness of the shell is enlarged by considering a range of radii R in the domain $R_c - t/2 < R < R_c + t/2$. We consider the radius and shell thickness of the Minute Mouse Virus (MVM) [4]. The results of the simulation are shown in Figure 5. The results of the simulations shown in [4] are not precise. The authors show the evolution in terms of Monte Carlo steps which is variable between realisations and dependent on the arbitrariness of the initial configuration. A rigorous analysis requires to consider the statistics after equilibration, as is shown in Figure 5. Only for a relative humidity $s > 0.95$ there is a significant proportion of water inside the capsid.

We also explored the response of capsids with cavities. In that case, bridge meniscus can be generated connecting the tips of the cavities, but only for large humidities $s > 0.90$.

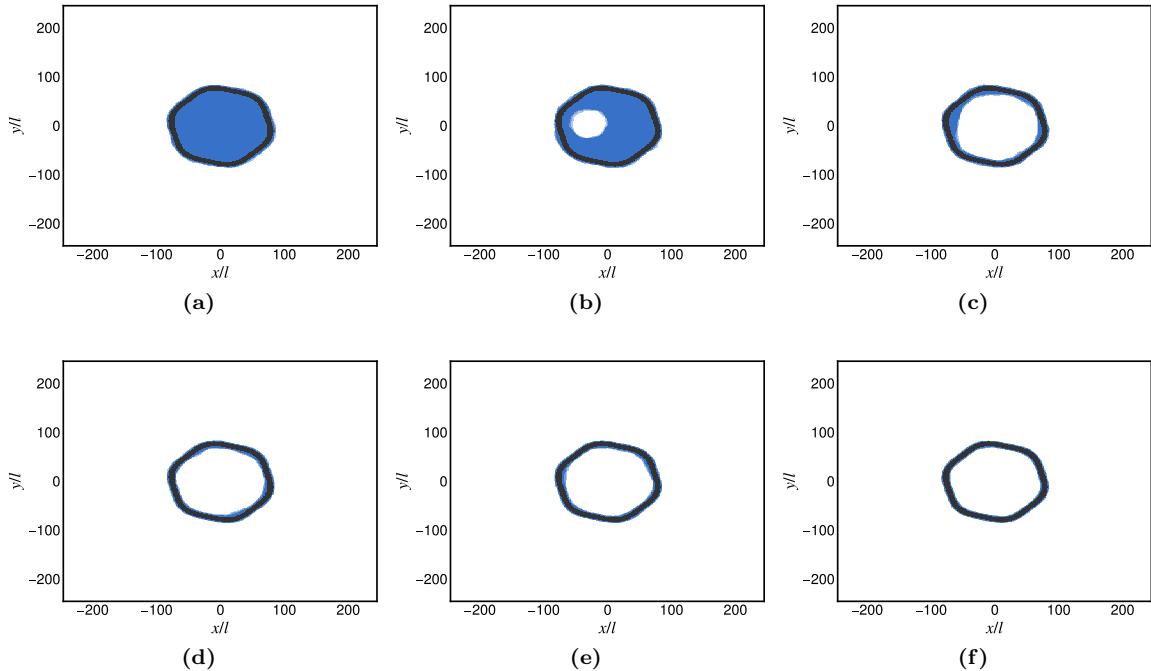


Figure 4: Dessication of icosahedral virus

Dessication of an icosahedral capsid from $s = 0.98$ to $s = 0.90$: $s = 0.98$, $s = 0.97$, $s = 0.96$, $s = 0.95$, $s = 0.94$ and $s = 0.90$. We represent in shades of blues the relative probability of water occupancy $\rho(x, y)$ for the intervals, from lighter to darker: 0, 0.25, 0.50, 0.75, 1.00.

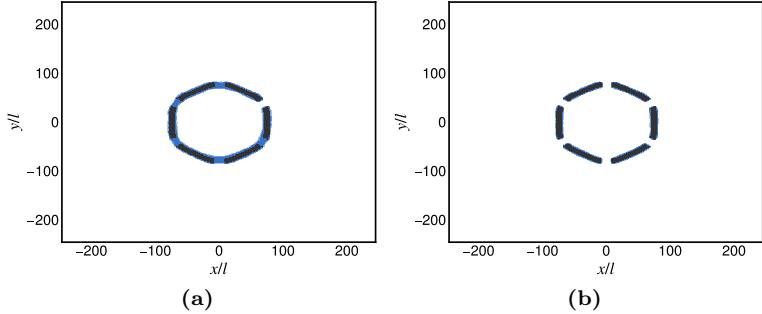


Figure 5: Dessication of icosahedral virus with cavities

a) Humid saturation, $s = 0.95$. b) Humid saturation, $s = 0.90$. The cavities have a side of $\pi/30$. We represent in shades of blues the relative probability of water occupancy $\rho(x, y)$ for the intervals, from lighter to darker: 0, 0.25, 0.50, 0.75, 1.00.

References

- [1] J. Jang, G. C. Schatz, and M. A. Ratner, *The Journal of Chemical Physics* **116**, 3875 (2002).
- [2] J. Jang, G. C. Schatz, and M. A. Ratner, *Phys. Rev. Lett.* **92**, 085504 (2004).
- [3] M. E. Fuentes-Perez, M. S. Dillingham, and F. Moreno-Herrero, *Methods* **60**, 113 (2013).
- [4] C. Carrasco, M. Douas, R. Miranda, M. Castellanos, P. A. Serena, J. L. Carrascosa, M. G. Mateu, M. I. Marqués, and P. J. de Pablo, *Proceedings of the National Academy of Sciences* **106**, 5475 (2009).