Lattice Gas models including water-surface interactions

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1 Model

We study the interaction of water and surfaces using Monte Carlo simulations in the grand cannonical (GC) ensemble. The lattice-gas is a simplified model where water is reppresented 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:

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

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 humidty) and the critical chemical potential is a known value.

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

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

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		
Temperature, T	298 K	-
Water-water, ϵ	3	[1]
Critical chemical potential, μ_c	3ϵ	[1, 2]
AFM tip simulations		
Number lattice sites horizontal, w	100	-
Number lattice sites vertical, h	100	-
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 heigths y_0 at relatative 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 heigth before the meniscus is broken.

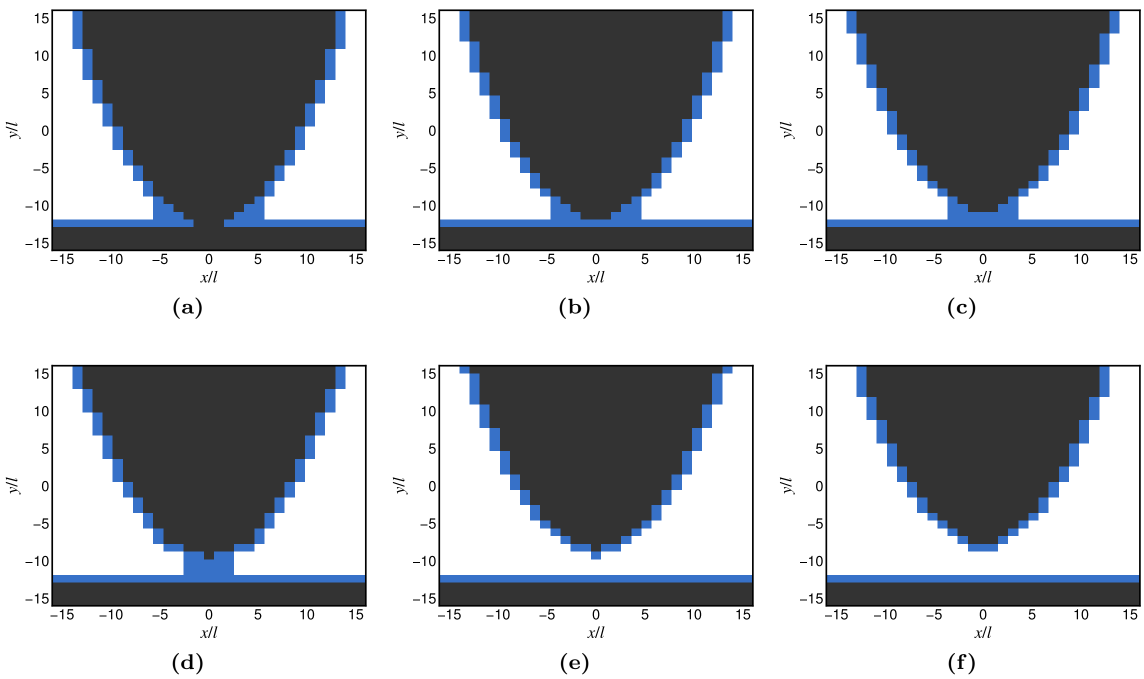

Figure 1: Water meniscus depepending on the distance to surface
Retraction from $y_0 = 0$ to $y_0 = 5$ in steps of l ($y_0 = 0, l, 2l, 3l, 4l, 5l$). The blue areas corresponds to regions with a probability of occupancy $\rho(x, y) > 0.75$ obtained from 2000 Monte Carlo steps equilibration. Saturation $s = 0.30$.

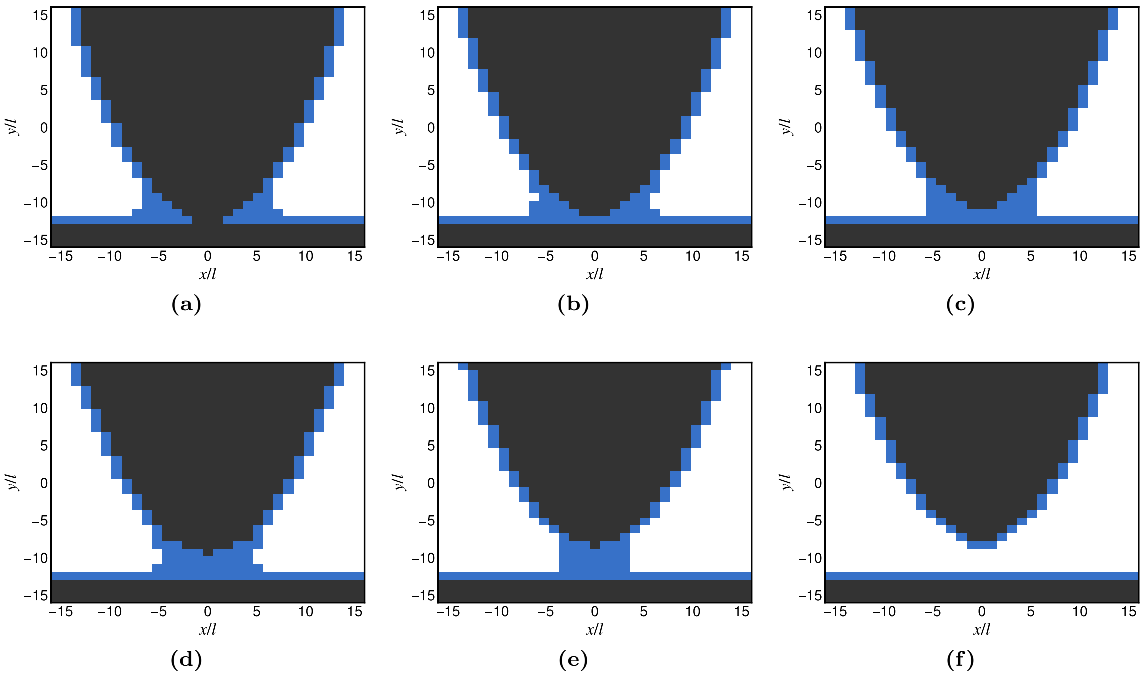

Figure 2: Water meniscus depepending on the distance to surface
Retraction from $y_0 = 0$ to $y_0 = 5$ in steps of l ($y_0 = 0, l, 2l, 3l, 4l, 5l$). The blue areas corresponds to regions with a probability of occupancy $\rho(x, y) > 0.75$ obtained from 2000 Monte Carlo steps equilibration. Saturation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

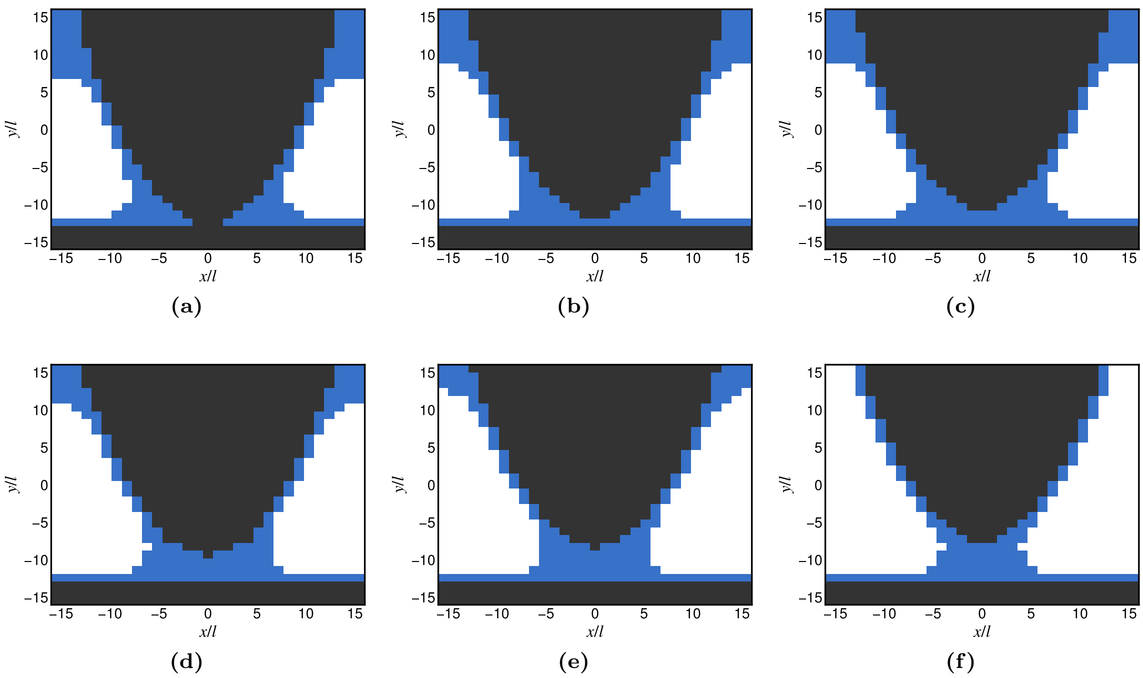

Figure 3: Water meniscus depepending on the distance to surface
Retraction from $y_0 = 0$ to $y_0 = 5$ in steps of l ($y_0 = 0, l, 2l, 3l, 4l, 5l$). The blue areas corresponds to regions with a probability of occupancy $\rho(x, y) > 0.75$ obtained from 2000 Monte Carlo steps equilibration. Saturation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

3 Icsaohedral viruses

We draw the icosahedrum from the polar function:

$$r = R_c(1 + A\sin 6\theta), \tag{3}$$

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 4. 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 4.

References

[1] J. Jang, G. C. Schatz, and M. A. Ratner, The Journal of Chemical Physics **116**, 3875 (2002).

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[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).

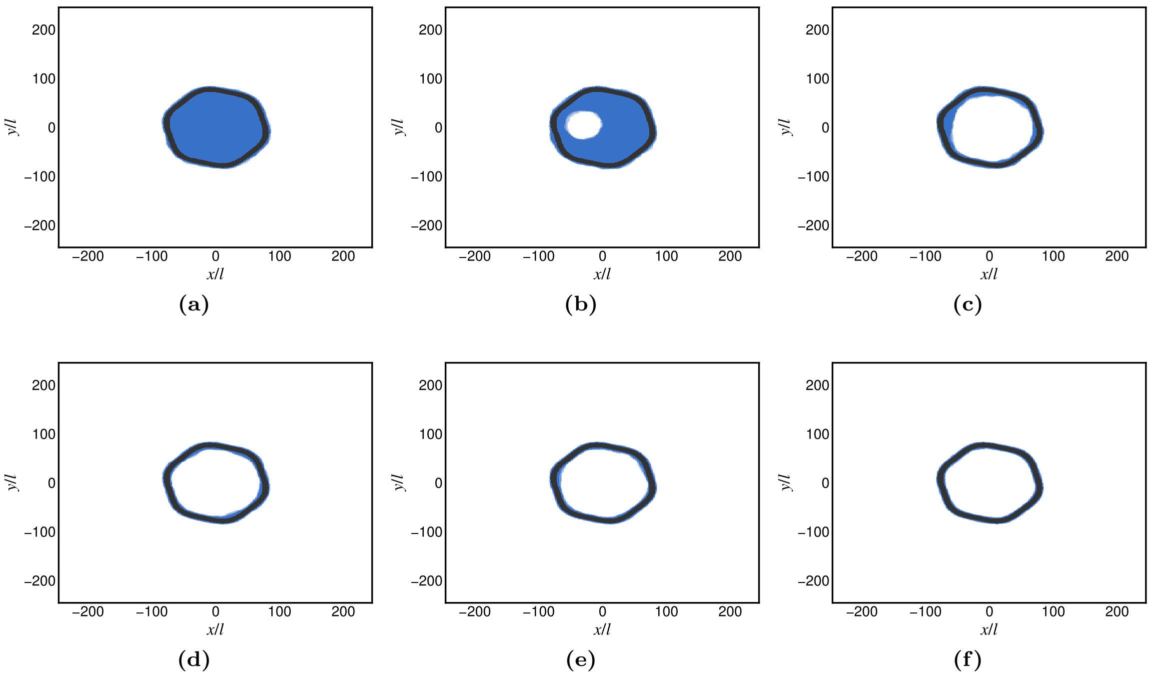

Figure 4: Dessication of icosahedral virus
Dessecation of an icosahedral capside from $s = 0.98$ to $s = 0.90$: $s = 0.98$, $s = 0.97$, $s = 0.96$, $s = 0.95$, $s = 0.94$ and $s = 0.90$. We reppresent in shades of blues the relative probability of water occupancy $\rho(x, y)$ for the intervals, from lighter to darker: 0, 0.25, 0.50, 0.75, 1.00.