INPE – National Institute for Space Research
São José dos Campos – SP – Brazil – May 16-20, 2016

IRREGULAR DYNAMICS OF THE CENTER OF MASS OF DROPLETS

Alexandre B. Almeida[1], *Nicolas Giovambattista*[2], *Sergey V. Buldyrev*[3], *Adriano M. Alencar*[4]

[1]Sao Paulo University, Sao Paulo, Brazil, alebaal@if.usp.br
[2]Brooklyn College of the City University of New York, New York City, EUA, ngiovambattista@brooklyn.cuny.edu
[3]Yeshiva University, New York City, EUA, buldyrev@yu.edu
[4]Sao Paulo University, Sao Paulo, Brazil, aalencar@if.usp.br

Abstract: The understanding of droplets is important to different applications, ranging from wetting to diagnosis of airways condition in the lung. In this work, we performed molecular dynamics and Monte Carlo simulations to solve the displacement of center of mass (CM) of droplets, in order to calculate the Hurst exponent in z-coordinate and in the xy-plane. Depending on the confinement condition, the CM motion, can be persistent, anti-persistent, Brownian or confined.

keywords: Time Series Analysis; Modeling, Numerical Simulation and Optimization; Fluidodynamics, Plasma and Turbulence; Droplet; Liquid Bridge

1. INTRODUCTION

Capillary geometries, for example axis symmetric droplets (AS droplets) and axis symmetric bridges, are important to different problems and applications, like the wetting [1] and the diagnosis of airways condition in the lung [2]. Capillary geometries are supposed to not have any fluctuation, as can be found in the movement of pollen grains suspended on the water surface and in the stock market indicators. Though, it is not true at the nanoscale, since the ration between area and volume is bigger than at the macroscale. Molecular dynamics (MD) studies of AS droplet and capillary bridges [3, 4] show that the macroscopic capillary equations, obtained from the minimization of energy, can be applied to nanoscale once considered the fluctuation of the interface. In other study, these capillary geometries were solved by lattice gas model with Monte Carlo (MC) simulations for the understanding of a specific sound, called crackle sound, related to the obstruction of lung air ways [5, 6].

2. PURPOSE

The goal of this work is to understand the fluctuations involved in this capillary geometries. Therefore, we study two simple capillary geometries, droplet and AS droplet, by means of MD and MC. From the configurations generated by the simulations, we build the time series of dynamic of the center of mass (CM) for each geometry. The Hurst analysis is implemented to understand the movement of the CM at z-coordinate and in the xy-plane, and the movement is classified as persistent, anti-persistent, Brownian or confined.

3. METHODS

3.1. Atomistic simulation

The simulations of water droplet and AS droplet are performed using the LAMMPS software package [7]. The water molecules are represented by the SPC/E model. The periodic boundary conditions are applied along the x, y, and z-coordinates. All simulations are performed for a cubic system of side length $L = 138.6\,\text{Å}$, at constant volume, number of water molecules $N = 2725$, and temperature $T = 300\,\text{K}$. Coulomb and Lennard-Jones interactions are cut off at distance $r_{\text{cutoff}} = 10\,\text{Å}$ and long-range electrostatic interactions are calculated using a particle-particle particle-mesh solver with an accuracy value of 10^{-5}. For the simulation of AS droplet, we insert a hydrophobic silica wall, with null po-

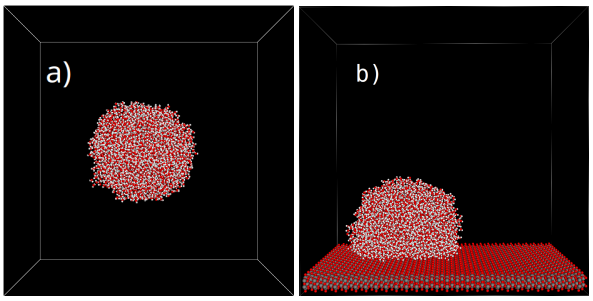

Figure 1 – Snapshots from MD computer simulations of (a) droplet and (b) AS droplet over hydrophobic wall.

larization, that reproduce a contact angle of 109.4°. The hydrophobic silica wall expand across the entire xy-plane, and its O and Si atoms are not allowed to move. We performed 10 ns of simulation printing the configuration after every 1000 fs. More details about the model can be find at refs. [3, 4].

3.2. Lattice gas model simulation

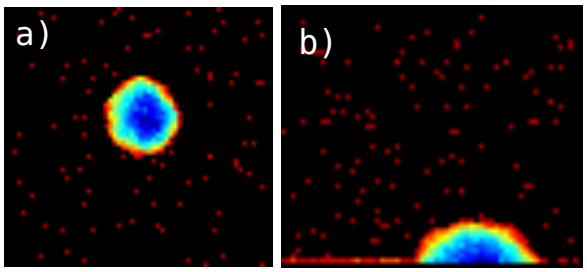

Figure 2 – Snapshots from MC computer simulations of (a) droplet and (b) AS droplet over hydrophilic wall.

Basically, it is a 3D model with lattice size $60 \times 60 \times 52$ (a^3), in which a is the lenght unit of the site. Each site of the lattice can be occupied by particles of three types: liquid (l), solid (s), and gas (g). The total amount of liquid particles used to simulate the droplet and AS droplet is 2575. We simulate the droplet and AS droplets using the MC method with the Metropolis algorithm at temperature $0.93J/k_{\mathrm{B}}$. For each MC step, the total exchanges is equal to the number of liquid particles. There is no exchange between identical particles, and the exchange between gas and liquid particles are performed randomly according to the Kawasaki dynamics and weighted by the Boltzmann factor. The exchange between liquid and gas particles may happen between any site in the lattice. The solid particles are not exchanged, and they are used to create the wall, in which the AS droplet is attached. According to the interaction between liquid and solid particles, it is generate the contact angle of interest. After 500 MC steps have been concluded, the last configuration is printed at the time T (τ), in which τ is the time unit of MC simulation. More details about the model can be find at refs. [5, 6].

3.3. Center of mass calculation

From the configurations generated from the MC and MD we calculate the projections of CM $\overrightarrow{CM} = \frac{1}{N}\sum_i^N \vec{r_i}$, at the z-coordinate and at the xy-plane, for AS droplets and droplets, in which $\vec{r_i}$ is the position of the molecule/particle, and N is the total number of molecule/particle. We have to have attention to the periodic boundary conditions of the simulations box. If the simulation is too long, the droplet can be splitted at the border, and it affects the CM calculation. The procedure that fix it is the following. First, we calculate the $\overrightarrow{CM'}$ of the droplet or the AS droplet. Then, each molecule/particle is displaced of $-\overrightarrow{CM'}$, in order to put the droplet or AS droplet near the origin of the box simulation. During this process, the following condition is applied to coordenates x, y and z of the molecule/particle i:

$$x_i = \begin{cases} x_i - CM_i' & \text{if} \quad 0 < (x_i - CM_i') < L \\ x_i - CM_i' + L & \text{if} \quad (x_i - CM_i') < L \\ x_i - CM_i' - L & \text{if} \quad (x_i - CM_i') > L \end{cases} \tag{1}$$

Then, all molecules/particles are moved again to the original position, now without the periodic boundary condition, by increasing $\overrightarrow{CM'}$ to their position. Finally, we calculate again the CM, obtaining now the correct value $\overrightarrow{CM}$. It must be emphasised that this method is only valid if there are a small number of molecule crossing the boundary.

3.4. Hurst exponent (H) calculation

The Hurst exponent is calculated from the time series generated from MC and MD simulations of the displacements of CM of AS droplets and droplets in z-coordinate and xy-plane. For a time window of size T_S, it is calculated the average of the square of the absolute distance $B(T_S)$ between two points in this size window T_S. From the scale relation between $\langle B(T_S)^2 \rangle$ and T_S we calculate the Hurst exponent as:

$$\langle B(T_S)^2 \rangle \propto T_S^{2H}, \tag{2}$$

in which H is the Hurst exponent [8, 9]. The value of H is obtained from the linear regression of Eq. 2 in a log-log graph. If $H = 1/2$, $H < 1/2$, $H > 1/2$ or $H = 0$, the movement is Brownian, anti-persistent, persistent or confined, respectively.

4. RESULTS

In both MD and MC simulations there are 2575 water molecules and liquid particles, respectively. The amount of points generated from MC and MD simulations to create the time series are 20000 and 10000, respectively.

First, we study the droplet with MD and MC simulation. For the MC simulation, we observe that the droplet movement are Brownian in both projections z-coordinate and xy-plane with exactly same slope 1.03. The Hurst exponent, obtained from Eq. 2, is equal to $H = 0.51$. For the MD, it is observed that $\langle B(T_S)^2 \rangle \approx 0$ independent of T_S, or in other

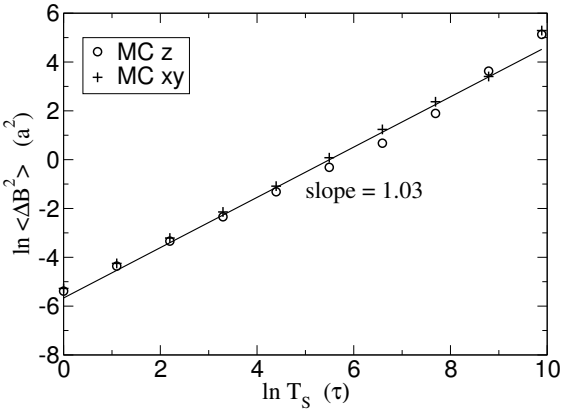

Figure 3 – The mean square of the absolute separation $\Delta B(T_S)$ of the droplet CM at the z-coordinate and xy-plane as a function of the time window T_S, for MC simulations. The line shows the linear regression, and the Hurst exponent obtained from Eq. 2 is $H = 0.51$.

words, the droplet do not move in the scale of time observed. These results are seen in Fig 3.

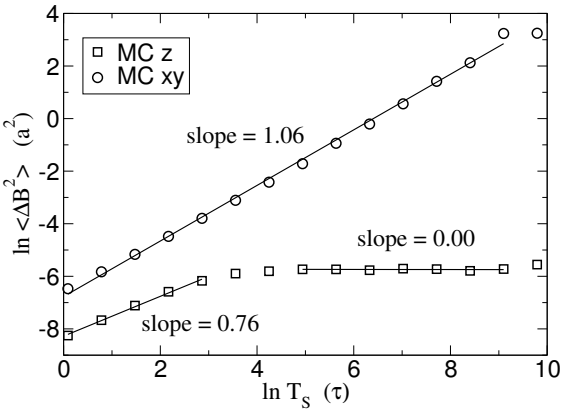

Figure 4 – The mean square of the absolute separation $B(T_S)$ of the AS droplet CM at the z-coordinate and xy-plane as a function of the time window T_S, for MC simulations. The line shows the linear regression. The movement at the xy-plane is Brownian, and Hurst exponent obtained from Eq. 2 is $H = 0.53$. The movement at the z-coordinate has two regimes: anti-persistent, $H = 0.38$, and confined, $H = 0.00$.

Next, we studied the CM movement of AS droplet and it is observed an interesting behavior. The CM movement of AS droplet changes its regime around $T_S \propto e^4\ \tau$, as can be observed in Fig. 4. For the MC simulation, the CM displacement at the z-coordinate has two regimes, anti-persistent, $H = 0.38$, and confined, $H = 0.00$. At the xy-plane it is not seen any difference of regime and the movement is Brownian, $H = 0.53$.

Then, we compare the behavior of the CM displacement of AS droplet obtained from MD simulations with the MC data discussed previously, see Fig. 4. First we compare the displacement at the z-coordinate. Both AS droplet from

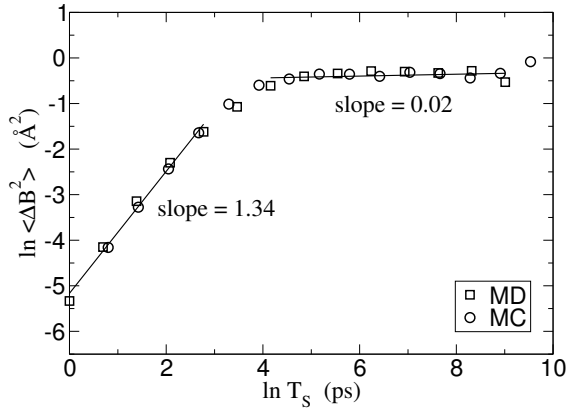

Figure 5 – The mean square of the absolute separation $B(T_S)$ of the AS droplet CM at the z-coordinate as a function of the time window T_S, for MD and MC simulations. The line shows the linear regression, and the Hurst exponents obtained from Eq. 2 for the persistent and confined regimes are $H = 0.67$ and $H = 0.01$, respectively. The MC data is obtained from the data shown on Fig. 4, applying Eq. 3.

MC and MD simulations have the same behavior with two regimes. This fact allow us to convert the units between MC and MD simulations using the equations below:

$$\begin{cases} \Delta B^2[\text{Å}^2] = & \Delta B^2[a^2] 1.51 \left[\frac{\text{Å}^2}{a^2}\right] + 5.5[\text{Å}^2] \\ T_S[\text{ps}] = & T_S[\tau] 0.9 \left[\frac{\text{ps}}{\tau}\right] + 0.8[\text{ps}] \end{cases} \quad (3)$$

These results are shown on Fig. 5, and we can observe that the regimes are persistent, $H = 0.67$, and confined, $H = 0.01$. Finally, we compare the displacement at the xy-plane applying Eq. 3. We observed an interesting behavior, as can be seen in Fig. 6. Differently from the MC, in the MD simulation the CM displacement at the xy-plane has also two regimes, persistent $H = 0.85$ and anti-persistent $H = 0.31$.

5. DISCUSSION

From Figure 3, we can conclude that the first neighbor interaction and the Kawasaki dynamics are the responsible for the CM displacement. During the Kawasaki dynamic with exchange between liquid and gas particles, the exchange can happen between any two site in the lattice, generating the Brownian behavior. However, the same behavior is not observed for MD simulations. Once the intermolecular interactions are internal forces, they will not cause a CM displacement of the system.

From Figure 4, we can observe the behavior of CM movement of AS droplet for MC simulation. Once there is no restriction at the xy-plane, the displacement of CM is Brownian, like the droplet. However, once the droplet is attached to the hydrophilic wall, the movement at the z-coordinate has two regimes. It can be anti-persistent, and for long time confined.

From Figures 5 and 6, we compare the results obtained from MC and MD simulations, by applying Eq. 3. In the MD

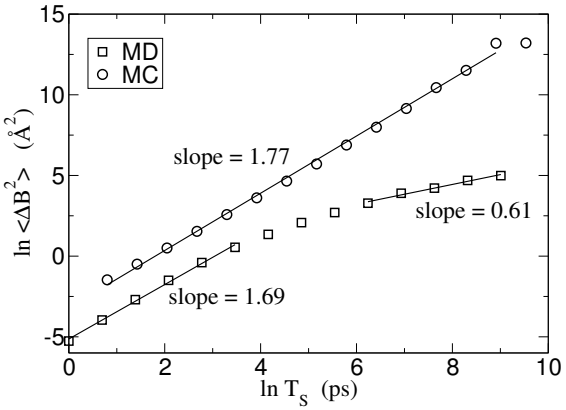

Figure 6 – The mean square of the absolute separation $B(T_S)$ of the AS droplet CM at the xy-plane as a function of the time window T_S, for MD and MC simulations. The line shows the linear regression. For the MD, the movement can be persistent and anti-persistent, and the and Hurst exponents obtained from Eq. 2 are $H = 0.85$ and $H = 0.31$, respectively. For the MC, it is not seen any difference of regime and the movement is persistent, and Hurst exponent is $H = 0.89$. The MC data is obtained from the data shown on Fig. 4, applying Eq. 3.

simulation, differently from the motion of droplet, the motion of the CM is observed because the silica surface is not allowed to move. The movement at the z-coordinate shows the same behavior as observed in MC simulation. However, at the xy-plane the MD shows also two regimes: anti-persistent and persistent.

6. CONCLUSIONS

Fluctuations are not supposed to be found in problems concerned to capillarity at macroscale. At the nanoscale, the ratio between area and volume is bigger, and fluctuations can be observed at the interface formed. To study these fluctuations, we analysed projections of the CM movement at the z-coordinate and xy-plane of droplet and AS droplet by MC and MD simulations.

In the droplet study, the MC simulation shown that the CM movements are Brownian in both projections. In MD simulation, it is not observed movement in both projections. This difference between MC and MD happen due the interaction between water molecules in MD and the particles in the MC. In the first case, the intermolecular interactions are internal force, hence it do not cause any displacement in CM. In the second case, the interactions between first, second and third neighbor, plus the exchange between any particle makes the movement to be characterized as Brownian.

In the AS droplet study, the CM movements have two regimes in both projections. From this observation, we find a couple of equations able to convert units from MC to MD simulations. At z-coordinate, the movement can be persistent and confined for both MC and MD, depending on time window size. At xy-plane, the MD shown that the movement can be persistent and anti-persistent, and the MC shown that the movement is only persistent.

We concluded that different behavior of the CM can be found in this preliminary study of droplet and AS droplet. A similar study may be applied to understanding more complex problems related to formation and rupture of liquid bridges.

7. ACKNOWLEDGMENTS

This work was supported Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

References

[1] P. de Gennes, F. Brochard-Wyart, and D. Quèré, Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves, Springer, 2004

[2] R. Notter, Lung Surfactants: Basic Science and Clinical Applications, Marcel Dekker, 2000

[3] N. Giovambattista, P. G. Debenedetti, and P. J. Rossky, "Effect of Surface Polarity on Water Contact Angle and Interfacial Hydration Structure," The Journal of Physical Chemistry B, Vol. 111, No. 32, pp. 9581-9587, June 2007.

[4] N. Giovambattista, A. B. Almeida, A. M. Alencar, and S. V. Buldyrev, "Validation of Capillarity Theory at the Nanometer-Scale by Atomistic Computer Simulations of Water Droplets and Bridges in Contact with Hydrophobic and Hydrophilic Surfaces" The Journal of Physical Chemistry C, Vol. 120, No. 3, pp. 1597-1608, December 2015.

[5] A. M. Alencar, E. Wolfe, and S. V. Buldyrev, "Monte Carlo simulation of liquid bridge rupture: Application to lung physiology," Physical Review E, Vol. 74, pp. 026311, August 2006.

[6] A. B. Almeida, S. V. Buldyrev, and A. M. Alencar, "Crackling sound generation during the formation of liquid bridges: A lattice gas model," Physica A: Statistical Mechanics and its Applications, Vol. 392, No. 16, pp. 3409-3416, August 2013.

[7] Plimpton, S., "Fast Parallel Algorithms for Short-Range Molecular Dynamics," Journal of Computational Physics, Vol. 117, No. 1, pp. 1-19, March 1995.

[8] A. M. Alencar, D. G. V. da Silva, C. B. Oliveira, A. P. Vieira, H. T. Moriya, G. Lorenzi-Filho "Dynamics of snoring sounds and its connection with obstructive sleep apnea" Physica A: Statistical Mechanics and its Applications, Vol. 392, No. 1, pp. 271-277, January 2013.

[9] P. S. Addison, Fractals and Chaos: An Illustrated Course, CRC Press, 1997