An Efficient Algorithm for Contact Angle Estimation in Molecular Dynamics Simulations

Sumith YD *ydsumith@gmail.com*
Research Assistant/Mechanical & Aerospace Engineering Department
Syracuse University
Syracuse, NY, USA

Abstract

It is important to find contact angle for a liquid to understand its wetting properties, capillarity and surface interaction energy with a surface. The estimation of contact angle from Non Equilibrium Molecular Dynamics (NEMD), where we need to track the changes in contact angle over a period of time is challenging compared to the estimation from a single image from an experimental measurement. Often such molecular simulations involve finite number of molecules above some metallic or non-metallic substrates and coupled to a thermostat. The identification of profile of the droplet formed during this time will be difficult and computationally expensive to process as an image. In this paper a new algorithm is explained which can efficiently calculate time dependent contact angle from a NEMD simulation just by processing the molecular coordinates. The algorithm implements many simple yet accurate mathematical methods available, especially to remove the vapor molecules and noise data and thereby calculating the contact angle with more accuracy. To further demonstrate the capability of the algorithm a simulation study has been reported which compares the contact angle influence with different thermostats in the Molecular Dynamics (MD) simulation of water over platinum surface.

Keywords: Molecular Dynamics, Contact Angle, Algorithms, Mahalanobis Technique.

1. INTRODUCTION

It is quite common in the literature to use Berendsen or Nose-Hoover thermostat for liquid molecular dynamic simulations to study different thermodynamic properties of water. In this paper I have investigated the effect of such thermostats on the contact angle of water above platinum substrate.

In the past, Bo Shi et al [1] have simulated the contact angle of water on top of Platinum surface with FCC 111. Their work involved simulating columbic attraction with P3M method and keeping the temperature constant using Berendsen thermostat [2]. Maruyama and et al [3] have also done contact angle studies of water on platinum with truncated potential. Both researchers have used Zhu Philpott (ZP) potential [4] for water platinum interaction. There exists a wide range of literature on contact angle estimation for sessile drops over metallic and non-metallic substrates. However they are not mentioned here since the main focus of the paper is on contact angle estimation method for molecular simulations.

The paper is divided into two main sections, first explaining the MD simulation details and models used; second the new algorithm for contact angle estimation.

2. MD SIMULATION OF WATER ABOVE PLATINUM

A 6 nm3 water droplet (7221 molecules) is kept on top of FCC 111 platinum plate as shown in FIGURE 1. The slab geometry made of water in between platinum walls is applied with periodic boundary condition (PBC) laterally and wall boundary vertically. The platinum walls are of 20 nm^2 square and kept apart at a distance of 14 nm.

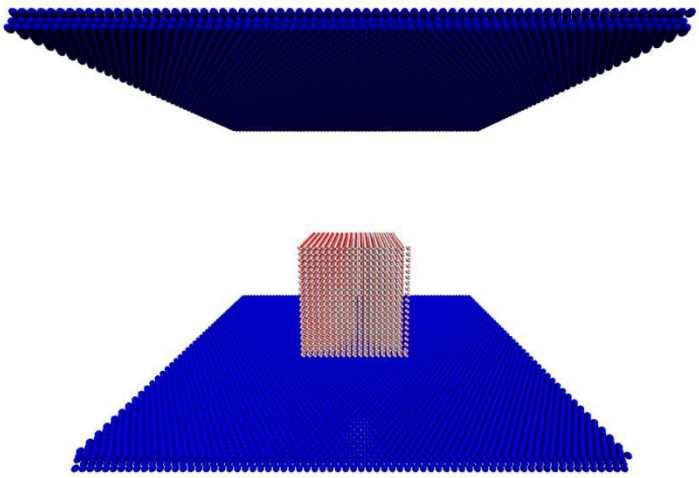

FIGURE 1: Simulation model for contact angle estimation.

The equations of motions are solved using Velocity Verlet [5] scheme. A shifted truncation scheme is used instead of Ewald summation methods or P3M. The feature of this scheme is that both potential and force goes smoothly to zero at the cut off radius.

$$U(r) = \frac{1}{4\pi\varepsilon_0}\left[\frac{1}{r} - \frac{5}{3r_c} + \frac{5r^3}{3r_c^4} - \frac{r^4}{r_c^5}\right] \tag{1}$$

The water molecules are modeled using Simple point charge extended (SPCE) model introduced by Berendsen et al [6]. The intra molecular bonds are kept rigid throughout the simulation using the SHAKE algorithm [7].

Since we are not modeling a contiguous array of droplets we can safely ignore the long range effects of the single water droplet. Simulation of droplet and films with SPME method will be studied extensively and will be published in another work.

Three cases of simulations with different thermostats are considered here. Berendsen [2], Nose-Hoover [8] and Velocity rescaling [9]. All the cases are run from 0ps to 1000ps using 2fs time integration steps. Gromacs [10] is the software package used for simulation.

At the end of simulation the trajectory files are processed and using the algorithm mentioned in the next section contact angles is determined. The time evolution of contact angle is shown in FIGURE 2. (a) and (b). The results indicate a transient behavior for contact angle.

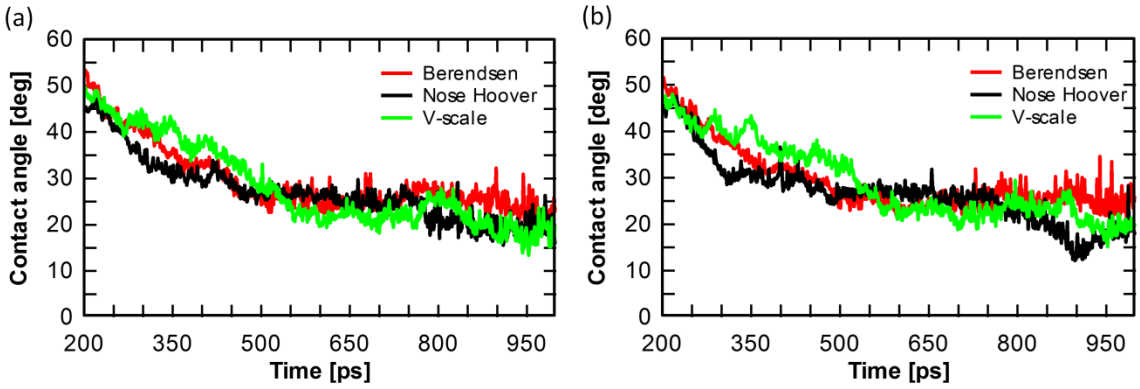

FIGURE 2: (a) Contact angle vs. time in XZ plane (b) Contact angle vs. time in YZ plane.

The contact angles seem to be fluctuating and never reaching a steady state. This is because of the nature of the potential function that we used for wall- water interaction (LJ potential). However this can be accounted by using ZP potential for water platinum interaction.

With the enormous amount of result data estimation of contact angle using visual or manual methods becomes a tedious process. There are not much algorithms which suit well for the direct post processing of molecular simulations. Hence the need for such algorithm raised and I have explained it in the next section.

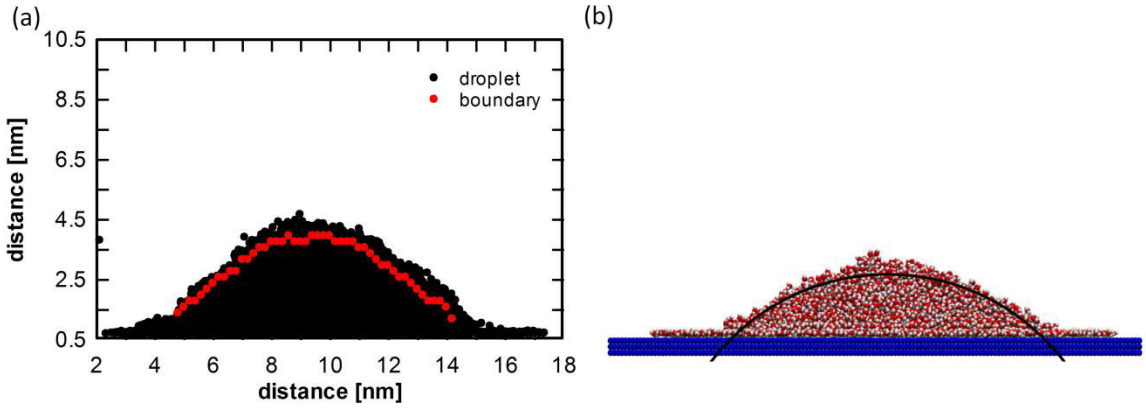

FIGURE 3: (a) Droplet particles (in black) and detected boundary (in red) (b) water molecules on top of platinum, black line shows the fitted circle from liquid vapor interface.

FIGURE 3. (a) shows a screenshot of molecular centroid after 300 ps simulation using case1 (Berendsen). The red dots show the location of liquid vapor interface detected using the new algorithm.

3. ALGORITHM DETAILS

Once obtaining the coordinate data (center of mass in case of water molecule) from the molecular simulations another challenge is to process the data to get a quality sample. Here a new method is explained to systematically find the boundary or edge of water droplet using simple mathematical methods and without using any image processing algorithms. For the convenience of the reader the whole process is divided into 5 steps.

We can process the data by projecting it normal to X-Z plane and also normal to Y-Z plane. (x, y) represents (X,Z) and (Y,Z) coordinates respectively for the data processing. FIGURE 4 shows screenshot of water above platinum surface after 500ps simulation.

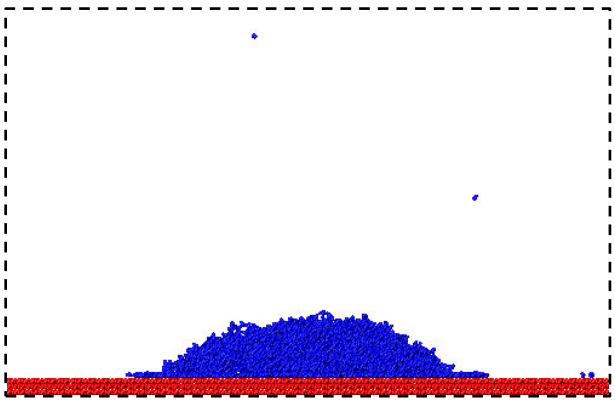

FIGURE 4: Water on top of Platinum [Berendsen 500ps].

3.1. Step 1: Preparing the Sample for Processing

The unwanted vapor molecules (outliers) in the data can be removed effectively using Mahalanobis Distance [11] technique.

If $X_c$is the $n \times 2$ column centered vector consisting of $(x - \bar{x}, y - \bar{y})$data of n points then variance-covariance matrix C_x is defined as:

$$C_x = \frac{1}{(n-1)}(X_c)^T(X_c) \tag{2}$$

Then the Mahalanobis Distance (MD) is calculated as:

$$MD_i = \sqrt{X_i {C_x}^{-1} {X_i}^T} \tag{3}$$

Where $X_i$is the mean centered data of i[th] data point. From this list of MD we can neglect those data points with considerably high MD values. For current study I have neglected all values above 4. Again this can be changed and fine-tuned according to the data.

The effectiveness of MD technique can be visualized from FIGURE 5. (a) and (b). The two vapor molecules which would have been a hindrance to estimate the contact angle accurately was removed easily with MD method.

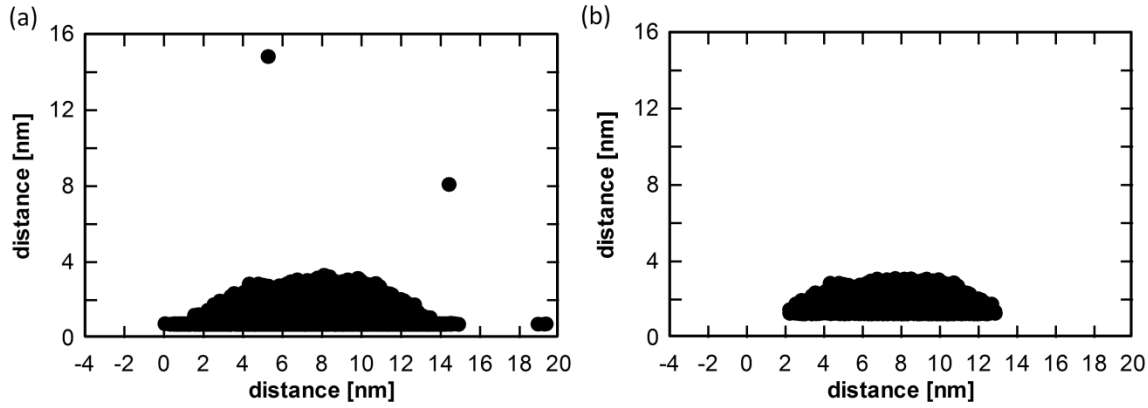

FIGURE 5: (a) Before removing the outliers (b) After removing the outliers and monolayer.

3.2. Step 2: Mesh based Contour Conversion using B-Splines

In this step a 2D mesh is generated and the entire droplet data is smeared into the grids using 4[th] order B-spline function. This makes it easier to find a smooth transition between the liquid core and the vacuum or vapor.

The Nearest Grid Point (NGP) method is a traditional first order method used to assign data to the grid points. Inspired from Hockney and Eastwood [12] the density of the molecules at every grid point can be calculated by the below equation.

$$\rho_{ij} = \sum_{p=1}^{N} W\left(\frac{|x_i - x_p|}{dx}\right) * W\left(\frac{|y_i - y_p|}{dy}\right) \tag{4}$$

Where the weight function is defined as

$$W(x) = \begin{cases} 1, & x < \frac{1}{2} \\ 0, & otherwise \end{cases} \tag{5}$$

The B-spline method is inspired from Smooth Particle Mesh Ewald [13]. Reproducing the definition gives, for any real number u, let $M_2(u)$ denote the linear hat function given by $M_2(u) = 1 - |u - 1|$ for $0 \leq u \leq 2$ and $M_2(u) = 0$ for $u < 0$ or $u > 2$. For n greater than 2, define $M_n(u)$ by the recursion

$$M_n(u) = \frac{u}{n-1} M_{n-1}(u) + \frac{n-u}{n-1} M_{n-1}(u-1) \tag{6}$$

For our case $n = 4$ and u is in fractional coordinates.

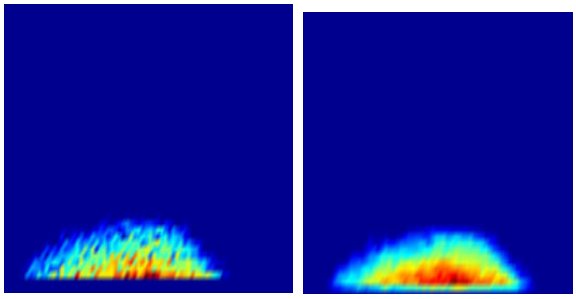

FIGURE 6: a) NGP assignment, b) B-spline assignment.

FIGURE 6. (a) and (b) shows the graphical representation of 2D density using NGP method and B-spline method. It can be seen easily that B-spline assignment scheme provides a smooth transition between liquid and vapor. Hence it is the recommended method for smearing.

3.3. Step 3: Filter Out the High and Low Density Data

As the next step towards the identification of the droplet boundary the grid points with high densities which resemble the liquid region and low densities that resemble the noise is eliminated based on the threshold densities defined as below.

$$Threshold_{MAX} = w1 * Mean \tag{7}$$
$$Threshold_{MIN} = w2 * Mean \tag{8}$$

$w1$ and $w2$ are weights which can be fine-tuned according to the data. For present analysis I have taken them as 2 and 0.5 respectively. Now all the data which meets the below criteria will be used for further analysis.

$$Threshold_{MIN} \leq Grid.value \leq Threshold_{MAX} \tag{9}$$

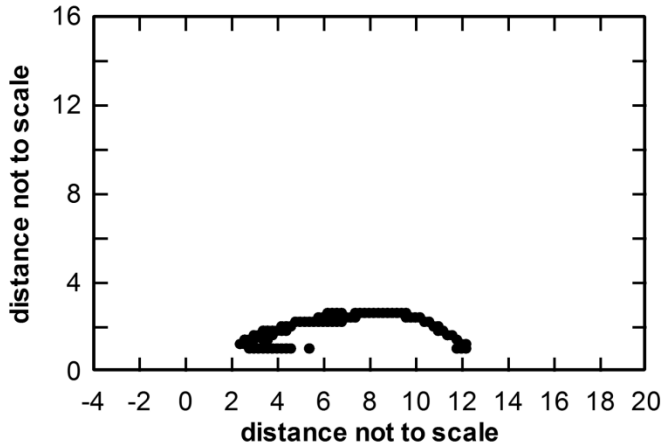

FIGURE 7: Filtered data (not to scale).

FIGURE 7 shows the data points obtained after applying the filter based on threshold density values. We can see that the interior liquid and exterior vapors have been eliminated.

3.4. Step 4: Finding the Ideal Location for Droplet Boundary

In this step we will find the centroid of the data obtained from the Step 3. If centroid lies below y-axis then set the y coordinate as the top of the platinum plate. This is to ensure that we prevent the erroneous semicircle shape which will lead to incorrect contact angle estimation. Then we radially move outwards from that point until we reach the boundary of data as shown in FIGURE 8. (a). This procedure is repeated for $0 \leq \theta \leq \pi$. If the centroid is above in the positive y-axis then the procedure is repeated for $0 \leq \theta \leq 2\pi$.

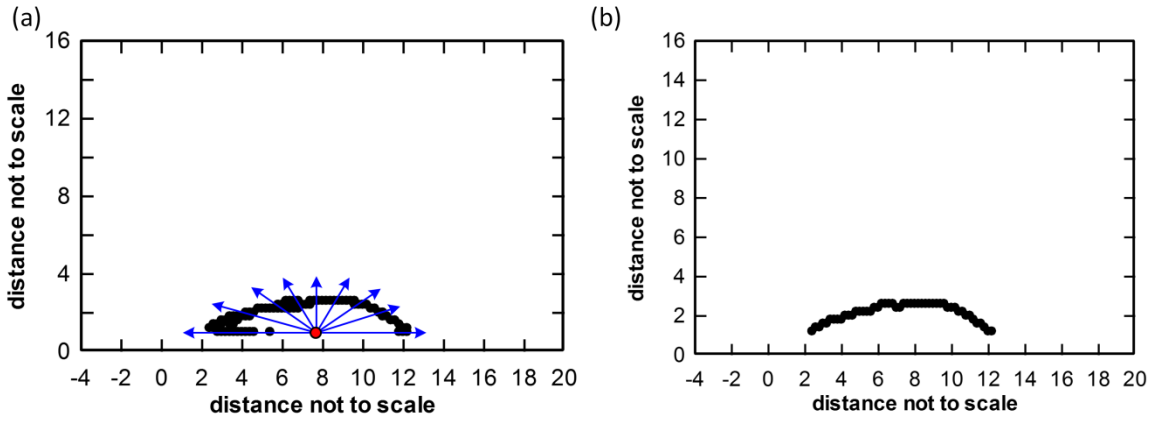

FIGURE 8: (a) Radial rays from centroid to find the extremities (b) Location of the droplet boundary.

At the end we will be left with a collection of points which forms the exterior of the droplet. FIGURE 8. (b) shows the final data points obtained using the algorithm.

3.5. Step 5: Finalizing the Droplet Boundary

These data points from step 4 are suitable candidates for final droplet boundary. Hence we fit them with Landau method [14] and find the circle which represents the droplet boundary. Once we get the equation of circle we can solve it for the angle made by the tangent at the platinum-water interface.

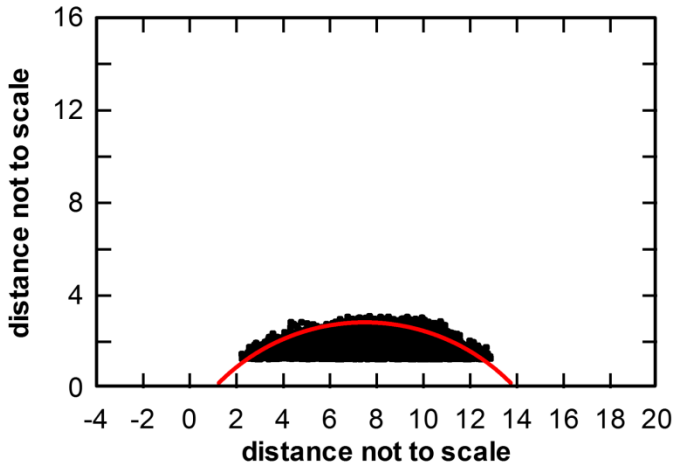

FIGURE 9: Final boundary of the droplet and fitted circle.

$$\theta = \tan^{-1}\left[\frac{(xc - x0)}{(yc - y0)}\right] \quad (10)$$

Where θ is the contact angle, (xc, yc) is the centroid of the fitted circle.

$$y0 = cutoff \quad (11)$$
$$x0 = xc - \sqrt{R^2 - (y0 - yc)^2} \quad (12)$$

Where cutoff is the distance above the platinum plate where we want to ignore the data points related to monolayer (high dense) region. R is the radius of the fitted circle. FIGURE 9 shows a typical droplet snapshot and also its detected boundary (in red) using the algorithm. The droplet is shown as single particles since their center of mass is only considered for analysis.

4. CONCLUSION

A new algorithm to accurately estimate the contact angle of the liquid from the molecular simulation results was presented in the paper. The algorithm is computationally efficient and accurate. Different parameters used in the identification procedure makes it easier to implement to new and different data sets. The different thermostat schemes and its effect on contact angle of water have also been discussed in this work. A MATLAB version of the algorithm will be provided upon request to author.

5. ACKNOWLEDGEMENT

The author would like to thank Prof. Maroo, Department of Mechanical Engineering, Syracuse University, for his helpful support for performing the Molecular Dynamics Simulations.

6. REFERENCES

[1] B. Shi, S. Sinha, and V. K. Dhir, in *ASME 2005 International Mechanical Engineering Congress and Exposition* (American Society of Mechanical Engineers, 2005), pp. 93.

[2] H. J. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. Haak, The Journal of chemical physics 81, 3684 (1984).

[3] T. Kimura and S. Maruyama, Heat Transfer 1, 537 (2002).

[4] S.-B. Zhu and M. R. Philpott, Interaction of water with metal surfaces, 1994.

[5] W. C. Swope, H. C. Andersen, P. H. Berens, and K. R. Wilson, The Journal of Chemical Physics 76, 637 (1982).

[6] H. Berendsen, J. Grigera, and T. Straatsma, Journal of Physical Chemistry 91, 6269 (1987).

[7] B. J. Leimkuhler and R. D. Skeel, Journal of Computational Physics 112, 117 (1994).

[8] W. G. Hoover, Physical Review A 31, 1695 (1985).

[9] G. Bussi, D. Donadio, and M. Parrinello, The Journal of chemical physics 126, 014101 (2007).

[10] B. Hess, C. Kutzner, D. Van Der Spoel, and E. Lindahl, Journal of chemical theory and computation 4, 435 (2008).

[11] R. De Maesschalck, D. Jouan-Rimbaud, and D. L. Massart, Chemometrics and intelligent laboratory systems 50, 1 (2000).

[12] R. W. Hockney and J. W. Eastwood, *Computer simulation using particles* (CRC Press, 2010).

[13] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, The Journal of chemical physics 103, 8577 (1995).

[14] S. M. Thomas and Y. Chan, Computer Vision, Graphics, and Image Processing 45, 362 (1989).