

# Numerical Study of Critical Liquid Droplets Using Density Functional Theory for 2D Lattice Gas with Short-Range Interactions

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**Abstract.** The method of density functional theory (DFT) was used to create a simulation of a droplet inside a supersaturated vapor. This DFT model was based on a two-dimensional lattice structure with short-range interactions. Closest and second-closest neighbor interactions were included. An iterative numerical procedure was used to solve the DFT equation for the density profile of a critical liquid droplet. Droplets of different radii for a wide range of chemical potentials above coexistence were simulated. Surface tension was found to approach a maximum for a planar liquid-vapor interface as droplet radius increased at a constant temperature. Dependencies of surface tension on the radius shifted as temperature changed.

## INTRODUCTION

Density functional theory (DFT) has been widely used in computational physics for solving problems related to interfacial phenomena. An important aspect of a liquid-vapor interface that could be studied with the help of DFT is the surface tension. Surface tension of a critical liquid droplet is one of the key factors that affect the rate of homogeneous nucleation during the first-order phase transition in supersaturated vapor. Original DFT studies of homogeneous nucleation were conducted in the late 1980s and early 1990s.<sup>1,2</sup> Similar DFT models were used in the late 1990s<sup>3,4</sup> to study the dependence of surface tension on the radius of liquid droplets. All these studies involve quite sophisticated DFT approaches that are based on integral equations to account for long-range interactions in fluid and hard sphere approximations to account for short-range interactions. It would have been overly challenging as an undergraduate student to master numerical approaches to solve these DFT equations. However, several years ago a paper devoted to a much simpler two-dimensional (2D) lattice gas version of DFT was published in the *American Journal of Physics*.<sup>5</sup> This work has been studied as part of an upper-division thermodynamics course. The results presented here were obtained in the research project completed during this course. It was surprising to see that results conceptually match the results from much more sophisticated DFT studies, even though a rather simple model was used which did not require very extensive computational work. To obtain a better understanding of these results, it is encouraged to study this work in conjunction with Ref. 5.

## DFT FOR 2D LATTICE GAS

Following Ref. 5, a 2D lattice fluid that consists of circular particles with unit diameter was considered for this project. These particles can fill enumerated (sub index  $i$ ) sites of a rectangular lattice. The number of particles is much smaller than the number of sites, so some sites are going to have one particle (occupation number  $n_i = 1$ ), and some will have none (occupation number  $n_i = 0$ ). Particles can interact by means of the short-range attractions. Only closest neighbor interactions on the four sides of a given particle and second-closest neighbor interactions diagonal to a given particle are accounted for. Corresponding strengths for these interactions are of  $\epsilon$  and  $\epsilon/4$ . The density of the fluid is constant ( $\rho$ ) for the bulk homogeneous fluid (liquid or gas) or varying in space ( $\rho_i$ ) for inhomogeneous fluid, such as liquid droplets inside of gas. This density,  $\rho_i = \langle n_i \rangle$ , is the average value of occupation numbers for a given site over all possible configurations of the system. DFT allows the thermodynamic properties of the fluid to be obtained as a function of this average density. This work considers the fluid to be in grand canonical ensemble, so the following equation was used for grand thermodynamic potential:<sup>5</sup>

$$\Omega = k_B T \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)] - \frac{1}{2} \varepsilon \sum_i \rho_i \sum_j \rho_j - \frac{1}{2} \frac{\varepsilon}{4} \sum_i \rho_i \sum_k \rho_k - \mu \sum_i \rho_i \quad (1)$$

In this equation,  $k_B$  is the Boltzmann constant,  $T$  is thermodynamic temperature, and  $\mu$  is chemical potential. Summation with respect to  $j$  is performed through the closest neighbors, and summation with respect to  $k$  is performed through the next-closest neighbors. The extreme value of this grand thermodynamic potential delivers the density profile of the system at equilibrium, which satisfies this density profile equation:<sup>5</sup>

$$\rho_i = (1 - \rho_i) \exp \left[ \frac{1}{k_B T} \left( \mu + \varepsilon \sum_j \rho_j + \frac{\varepsilon}{4} \sum_k \rho_k \right) \right] \quad (2)$$

This equation must be solved in order to determine the density profile of critical liquid droplets in equilibrium with their supersaturated vapor surroundings. Once determined, this density profile can be used to find other thermodynamic properties of a two-phase system.

## THERMODYNAMICS OF A TWO-PHASE SYSTEM

From the standpoint of classical thermodynamics, the grand thermodynamics potential of a two-phase system can be split into two contributions: the bulk phases and interfacial contribution. In a 2D case, one can assume that a circular liquid droplet is formed in the middle of an open square ( $L \times L$  lattice cells) system, which reduces grand thermodynamic potential:

$$\Omega = -P_l \pi R^2 - P_v (L^2 - \pi R^2) + \sigma 2\pi R \quad (3)$$

Here  $P_l$  is the bulk liquid pressure,  $P_v$  is the bulk vapor pressure, and  $\sigma$  is the 2D analog of the surface tension. The radius  $R$  of the droplet can be calculated assuming an equimolar dividing surface:

$$N = \rho_l \pi R^2 + \rho_v (L^2 - \pi R^2) \quad (4)$$

Here  $\rho_l$  is the density of bulk liquid and  $\rho_v$  is the density of bulk vapor.  $N$  is the total number of particles in the system, and by solving that equation, the radius  $R$  can be found:

$$R = \sqrt{\frac{N - \rho_v L^2}{\pi(\rho_l - \rho_v)}} \quad (5)$$

This radius can then be used in Eq. (3), which gives the 2D analog of the surface tension:

$$\sigma = \frac{\Omega + P_v L^2 + (P_l - P_v) \pi R^2}{2\pi R} \quad (6)$$

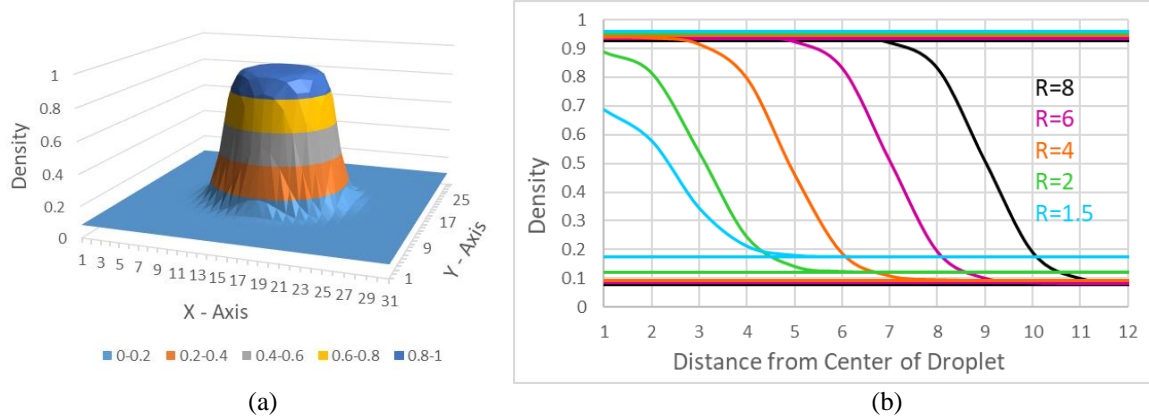
## NUMERICAL PROCEDURE FOR SOLVING DFT EQUATION

The density of the bulk liquid and bulk vapor, as well as the pressure, were found by solving the bulk fluid equations introduced in Ref. 5. This was done for a large range of chemical potentials above the coexistence value but below the spinodal value. One can use bulk fluid phase diagrams and equations from Ref. 5 for numeric values of these thermodynamic properties. An iteration procedure described in Ref. 5, with a mixing parameter in the Picard iteration algorithm of 0.02, was used to solve Eq. (2). Following the approach originally introduced in Ref. 1, an initial approximation for the density profile was set to supersaturated vapor everywhere except inside of a region with a given initial radius, where it was set to the bulk liquid. Since the desired solution would represent an unstable critical droplet inside of a supersaturated vapor, the number of particles in the system was monitored throughout iterations to see if the droplet was growing or decreasing. After the original droplet radius was set to 1, iterations were performed until the iteration procedure started diverging. If the number of particles in the system was decreasing at this point, the original radius was increased by 1 and the entire procedure was repeated. The simulation was stopped when the number of particles started to increase. The number of particles in the system at that point was then used to calculate the radius of the critical droplet and the 2D analog of surface tension according to Eqs. (5) and (6).

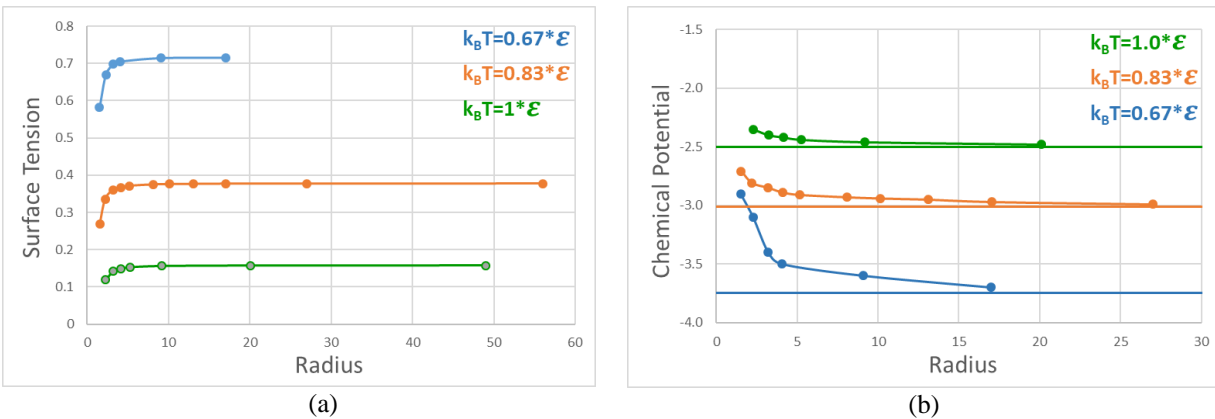
## RESULTS AND CONCLUSIONS

Density profiles of critical droplets inside a 150-lattice cell square matrix were calculated for different chemical potentials (supersaturations) and corresponding droplet radii. Figure 1(a) shows a typical density profile for a droplet with a radius of six lattice cells. Figure 1(b) shows how the density profile changes for decreasing radii. The most interesting result was that for the smallest droplets, the bulk liquid phase is not realized at the center. This points to self-overlapping of the surface layer and is consistent with the results found in more sophisticated DFT models.<sup>1-3</sup> Figure 2(a) shows how surface tension increases to a maximum as the radii increase and how an increasing shift occurs to that maximum as temperature is decreased. This is consistent with the previous findings for small droplets,<sup>3</sup> where

the surface tension would be substantially smaller than that in the planar limit. However, the present model is incapable of predicting nonmonotonic behavior for surface tension as a function of the droplet radius, because no negative Tolman length<sup>3,4</sup> is found for very large droplets. This is not surprising, since liquid and vapor have artificially symmetric bulk properties in this model. This would be considered the weakest feature of this model. Figure 2(b) shows how chemical potential depends on the critical droplet radii and how an increasing shift and change in curvature occur as temperature increases. These dependencies could serve as inputs to study the kinetics of homogeneous nucleation.



**FIGURE 1.** (a) A typical density profile [ $(\mu - \mu_{\text{coex}})/k_B T = 0.11$ ,  $\mu_{\text{coex}}/k_B T = -3.01$ ,  $k_B T = 0.83\epsilon$ ]. (b) Cross sections of density profiles for droplets of different radii at  $k_B T = 0.83\epsilon$ . Position and radii are measured in number of lattice cells. Horizontal lines represent bulk densities.



**FIGURE 2.** (a) 2D analog of surface tension (in  $k_B T$ /lattice cell size) for different temperatures and droplet radii. (b) Dependence of chemical potential (in  $k_B T$ ) on droplet radii, where  $\mu_{\text{coex}}/k_B T = -2.50\epsilon/k_B T$ , and horizontal lines represent these  $\mu_{\text{coex}}$  values for corresponding temperatures. Radii are measured in the number of lattice cells.

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