

On the Statistical Mechanical Treatise of the Wetting Transition of Fluids at an Interface

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A statistical mechanical treatment is applied to the investigation of the density profiles of a fluid by means of a method called *classical density functional theory* (DFT). In particular, the density profiles of fluids are under the influence of a Lennard-Jones potential, exerted by the walls of a container. The consideration of a simple lattice gas (Ising model) which acts as the mean-field approximation to our DFT allows the study of the interfacial properties to build up from homogeneous to inhomogeneous fluids. The resulting bulk phase diagram exhibits the coexistence of gas and liquid by a binodal line within the plotted heatmap. The different configuration of temperature, chemical potential and wall attraction constant is shown to manifest different theoretical observables of wetting behaviour. The emergence of pre-wetting "jump" is also observed, plotted and discussed.

I. INTRODUCTION

Wetting is a ubiquitous phenomenon in our everyday lives, whilst also an ongoing interdisciplinary research endeavours across many industries. At small scales, the idea of wetting have been extended to "electro-wetting" in order to solve microfluidic systems driven by electromagnetic forces.^[1] On a larger scale, the wetting of oil on water has been shown to have a significant influence on several oil-recovery^[2] processes (e.g., oil drainage) and also have an effect on the efficiency of water drainage from highways.^[3] Therefore, the nature of interfacial interactions is paramount to the behaviour and efficiency of a liquid as a lubricant. Since this experiment involves the molecular interactions of fluids on a surface and under the influence of its external potential, its motivation for using a microscopic approach is justified; thus it is consequently subjected to a statistical mechanical point of view. As it can be seen later that due to the external potential of choice by our lattice gas fluid model being that of Lennard-Jones'; it is for these kind of potentials where classical *density functional theory* (DFT) is most suitable as a general framework that allows one to derive any important thermodynamic quantities.

At the heart of this statistical mechanical treatise is the partition function Z from the appropriate canonical ensemble of choice, since the useful thermodynamic quantities such as pressure and chemical potential can be derived as derivatives of the classical partition function with respect to the right thermodynamic variable, as it will be shown later. However, with Z being defined as a sum over all the possible states of the system, its exact evaluation is rare. To compromise, DFT seeks to develop mean-field approximations for the free energy. DFT is based on the result that under an external field $V_{\text{ext}}(\mathbf{r})$, there exists a one-to-one correspondence between each spatially varying potential V_i of the Hamiltonian of the ensemble average density for an inhomogeneous fluid.^[4] As a consequence, it can be shown under the mean-field approximation that the free energy is a *functional* of the fluid density profile $\rho(\mathbf{r})$ and the minimization of the grand potential functional with respect to $\rho(\mathbf{r})$ gives the equilibrium density profile of the inhomogeneous fluid.^[5]

II. STATISTICAL MECHANICAL MODEL OF SIMPLE LIQUIDS.

For the microscopic analysis of a fluid, it is first define as comprising of N atoms/molecules in a system, where each particle has mass m and their own corresponding position and momentum coordinates, $\mathbf{r}^N \equiv \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ and $\mathbf{p}^N \equiv \{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N\}$ respectively. In order to describe their molecular interactions, a Hamiltonian is necessarily defined as such^[6]

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K(\mathbf{p}^N) + E_{\text{int}}(\mathbf{r}^N) + E_{\text{ext}}(\mathbf{r}^N), \quad (1)$$

where K is the sum of each individual particle's kinetic energy, $E(\mathbf{r}^N)$ is the sum of the potential energy due to the particle interactions and any external potential that depends on its positions relative to where the potential is defined. It is then suitable to treat a closed system in a canonical ensemble as there will be a fixed volume V , particle number N and temperature T . It can be shown that the partition function can be obtained to be

$$Z = \Lambda^{-3N} Q, \quad (2)$$

where $\Lambda = \sqrt{\beta \hbar^2 / 2m\pi}$ is the thermal de Broglie wavelength and

$$Q = \frac{1}{N!} \int d\mathbf{r}^N e^{-\beta E(\mathbf{r}^N)}, \quad (3)$$

which is just the configuration integral. Changing Λ would just add a linear constant to the Helmholtz free energy per particle later, so taking it as unity removes the constant and simplifies the partition function. The focus then shifts to the evaluation of Q as it could not generally be evaluated without the help of approximations.

III. DISCRETE LATTICE MODEL AND THE MEAN-FIELD APPROXIMATION

The lattice model separates the space into lattices so that each lattice can be described as filled or unfilled. The total N particles can be described by a configurations of M filled and unfilled lattices sites. The assumption made on the particles

being spherical provides a symmetry in all direction such that any of their orientations are identical. For a grand canonical ensemble with fixed V and T with variable N within a reservoir, the probability of being in a particular configuration, n_i can be defined as

$$P(\{n_i\}) = \frac{e^{-\beta(E-\mu N)}}{\Xi}, \quad (4)$$

with the normalization factor, the grand partition function defined as

$$\Xi = \text{Tr} e^{-\beta(E-\mu N)}, \quad (5)$$

where it is a sum of all the occupancy of the M lattice. The potential energy equation within the Hamiltonian in Eq. (1) must first be defined, with the assumption where

$$E = \sum_{i=1}^M n_i V_i - \frac{1}{2} \sum_{i,j} \epsilon_{ij} n_i n_j, \quad (6)$$

where the first term is the yet determined external potential V_i and the second term is the sum of potential energy as a result of pair interactions between neighbouring particles, with the pair interactions double counting taken care of. The Helmholtz free energy is then related to the partition function by

$$F = -k_B T \ln Z. \quad (7)$$

For a system with no external field and pair particle interactions, i.e. $V_i = 0$ and $\epsilon_{ij} = 0$, the Helmholtz free energy can be simplified and related to the uniform density of the homogeneous fluid by using Stirling's approximation so that

$$F = M k_B T [\rho \ln \rho + (1 - \rho) \ln (1 - \rho)]. \quad (8)$$

for a large system where M and N are large. For an inhomogeneous fluid, the potential V_i will vary across different lattices and that will have an effect on the density in space. The mean-field approximation is then applied onto the free energy, by defining that the average density at each lattice point i is defined as the average value of the occupation number at site i , over all possible configurations

IV. MINIMIZATION OF GRAND POTENTIAL

For a homogeneous fluid without the presence of an external potential, the density is identical everywhere and $V_i = 0$ for all sites i . Minimizing the free energy $\hat{\Omega}$ gives the equilibrium density profile which is then solved as a function of the inverse temperature β and chemical potential μ . There are two different scenarios of solved function, shown in Fig. 1. The density of the solution being a low density gas ($\rho \ll 1$) or a high density liquid ($\rho \approx 1$) is solely based on the values of β and μ .

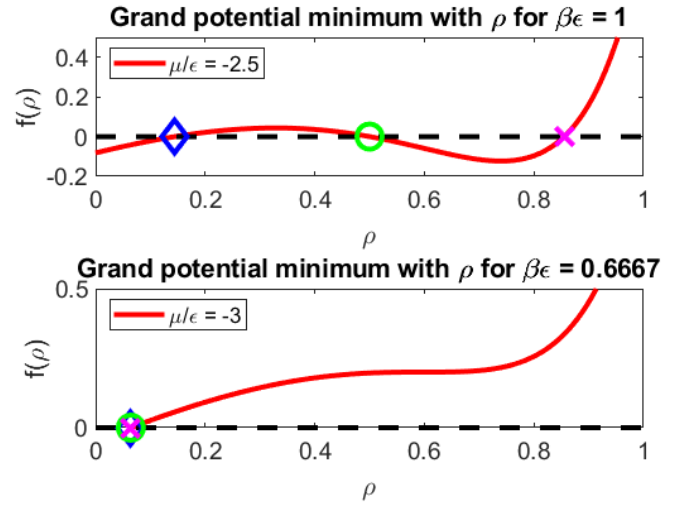


FIG. 1. The bulk phase diagram solved for $\beta\epsilon = 1$, $\mu/\epsilon = -2.5$ and $\beta\epsilon = 0.6667$, $\mu/\epsilon = -3$, showing three and one solutions respectively.

V. BULK PHASE DIAGRAM FOR A HOMOGENEOUS FLUID

The minimization of the free energy is again solved but this time for an interval of values of $1/\beta$ and μ and its corresponding bulk phase diagram is shown in Fig. 2. The binodal line

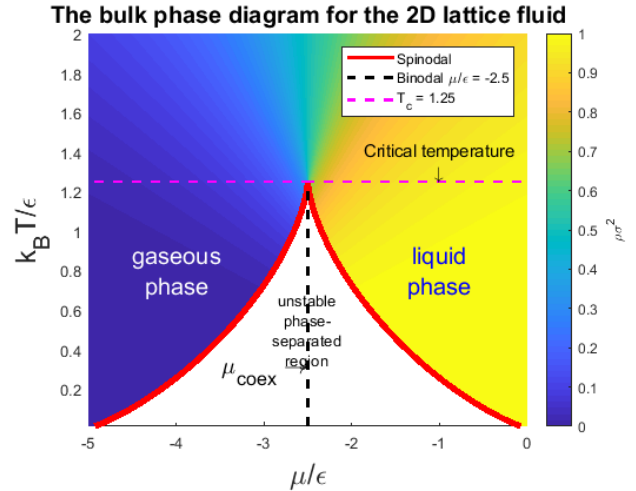


FIG. 2. The bulk phase diagram for a homogeneous fluid is solved across the dimensionless β - μ plane between $-5 \leq \mu/\epsilon \leq 0$ and $0 \leq 1/\beta\epsilon \leq 2$

is defined as the point where the pressure and the chemical potential of both liquid and gas phases are equal due to the coexistence of both phases, hence it has to lie on the value of $\mu/\epsilon = \mu_{coex} = -2.5$. The binodal line equation can be found by equating the pressure of the gas and liquid, namely $P(\rho_l) = -(\partial F/\partial V)_{T,N} = P(1 - \rho_g)$. The maximum on the binodal corresponds to the critical point, above which there is no gas-liquid phase separation. The spinodal line is defined by the point where the double derivative of Helmholtz free energy per lattice site w.r.t the density is zero. The spinodal

equation can then be found by solving what's left of the double derivative $(d\mu(\rho)/d\rho) = (\partial/\partial\rho)(\partial F/\partial N)_{T,V}$, which is a quadratic equation. The region on the left and right above the spinodal line are the regions where the specific choices of inverse temperature and chemical potential result in a single solution that correspond to gaseous and liquid phase of the bulk respectively. On the contrary, the aforementioned definition of the spinodal means that it denotes the boundary for which the compressibility of the fluid is zero. As a consequence, the region within this curve is unstable and spontaneous phase separation occurs due to having negative compressibility. If the low and high single density solutions correspond to gaseous and liquid state respectively, then the fact that having multiple density solutions under the spinodal means that theoretically the fluid cannot physically manifests as a real life observable. It is natural to then confirm if the density solutions would di-

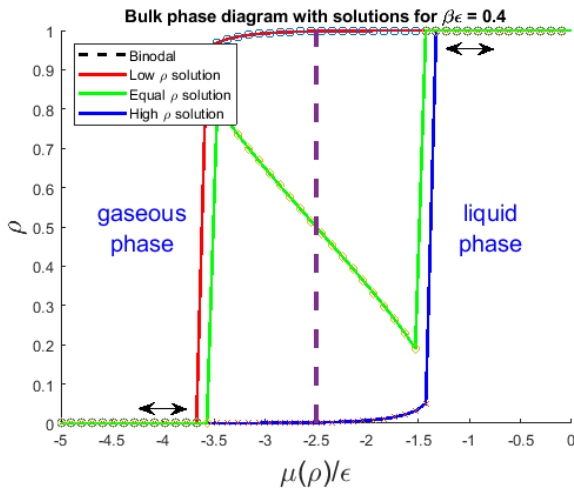


FIG. 3. The bulk phase diagram for a homogeneous fluid with multiple solutions for $\beta\epsilon = 0.4$. The black double-headed arrows denote approximately where the metastable states are found.

verge and then re-converge when plotted against μ for a value of temperature that's lower than the critical temperature, as shown in Fig. 3

Indeed, the solutions start off with being low density gas, diverging into 3 different solutions and the re-converged into a high density liquid. Whilst the binodal remained a line, the spinodal however can only be defined for the starting and ending value of μ that encapsulates the region between the gaseous and liquid phase. The metastable curves are region where the metastable states exist, defined mathematically^[6] by $(\partial\mu/\partial\rho)_T > 0$. But to be exact, they are the region lying in between the binodal and spinodal curve when the temperature is plotted against density, as shown in Fig. 4^[7].

VI. LIQUIDS AT INTERFACE WITH BOUNDARY CONDITIONS AND ADSORPTIONS

How does one choose the specific type of potential for this wall problem, in which the pair potential these molecules interact with has both a sharp repulsive part that dominates at

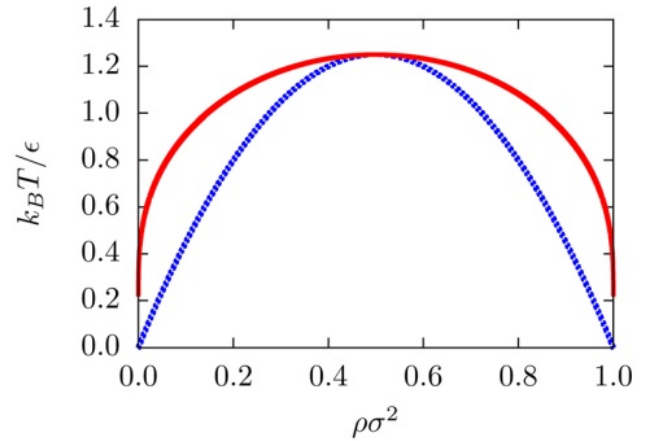


FIG. 4. The bulk phase diagram displayed in the dimensionless temperature $k_B T/\epsilon$ against density plane. The red and blue lines denote the binodal and spinodal respectively.^{4[7]}

its closest range, and a longer ranged attractive part that dominates at large r ? The particles at the wall are assumed to be only interacting with the nearest and next nearest neighbouring particles, so it is for such system with these assumptions that one might expect Lennard-Jones' potential to be most ideal. For the case of inhomogeneous fluid in the presence of an external potential, again minimising $\hat{\Omega}$ still returns the equilibrium density profile, except this time because of the pair interactions and the potential of the wall, at each lattice the density of each particle will be subjected by a different V_i and affected by its neighbouring particles such that a set of coupled equations are required to solve the density profiles iteratively. The boundary conditions set the density to be zero "within" the wall. Opposite and being away from the wall, the fluid is assumed to be uniform with a specified fixed density being the density profiles solved for that of the bulk gas earlier.

It turns out that there exists a translational invariance along the x-axis such that going along the transverse direction simply obtains the same density profiles. This is due to the external potential being defined only unidimensionally in the y-direction, and since the density profile is defined as an average over all possible configurations, this must mean that the density profiles have the same translational invariance too. Therefore simplifying this system into 1D is just as trivial as extending it into 3D. The density profiles of the lattices in the transverse density can therefore be linearly added and renormalized such that an on-site interaction is also introduced.

As μ approaches its coexistence value, the density profiles close to the wall increases to a value that is expected of a liquid, shown in Fig. 5. This signifies the moment just before the wall becomes "wet". To quantitatively study the wetting phenomenon, one can define the adsorption as the sum of the difference between each individual density and the bulk density in the y direction (normal to the wall), as shown in Fig. 6. For $\beta\epsilon_w = 1.6$, one can see the emergence of the discontinuous "jump" in adsorption as a result of crossing the pre-wetting line. This jump will also be reflected correspondingly in a plot of the density profiles for a selection of $\beta(\mu - \mu_{coex})$ values

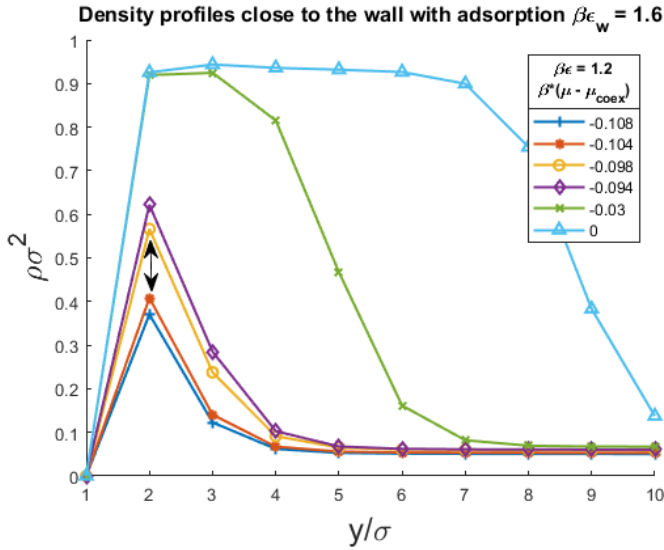


FIG. 5. The density profiles close to the wall with adsorption plotted for 6 different values of $\beta(\mu - \mu_{coex})$ for a single value of wall attraction strength parameter, $\beta\epsilon_w$. The double headed black line indicates the discontinuous jump in Γ .

centred around the jump, as shown in Fig.5 For a surface to

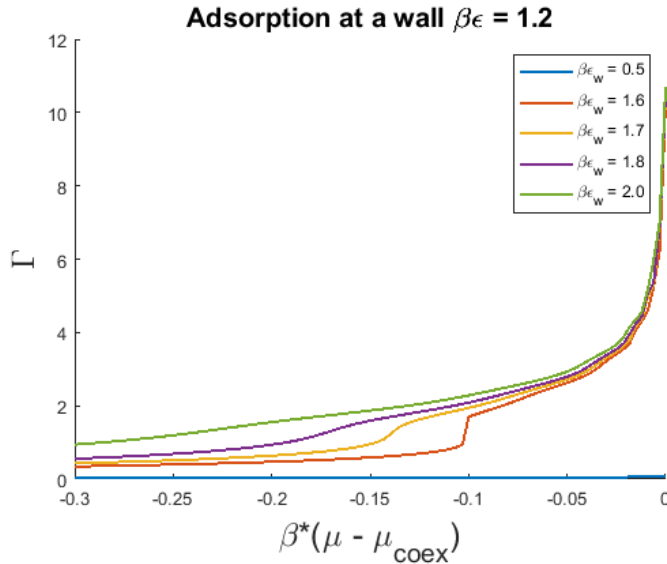


FIG. 6. The adsorption values along y-axis plotted for 4 different values of the wall attraction strength parameter $\beta\epsilon_w$.

be wet, its absorption value must diverge as the chemical potential reaches its coexistence values. The droplet can then be modelled on a surface with a different $\beta\epsilon_w$, as shown in Fig. 77.

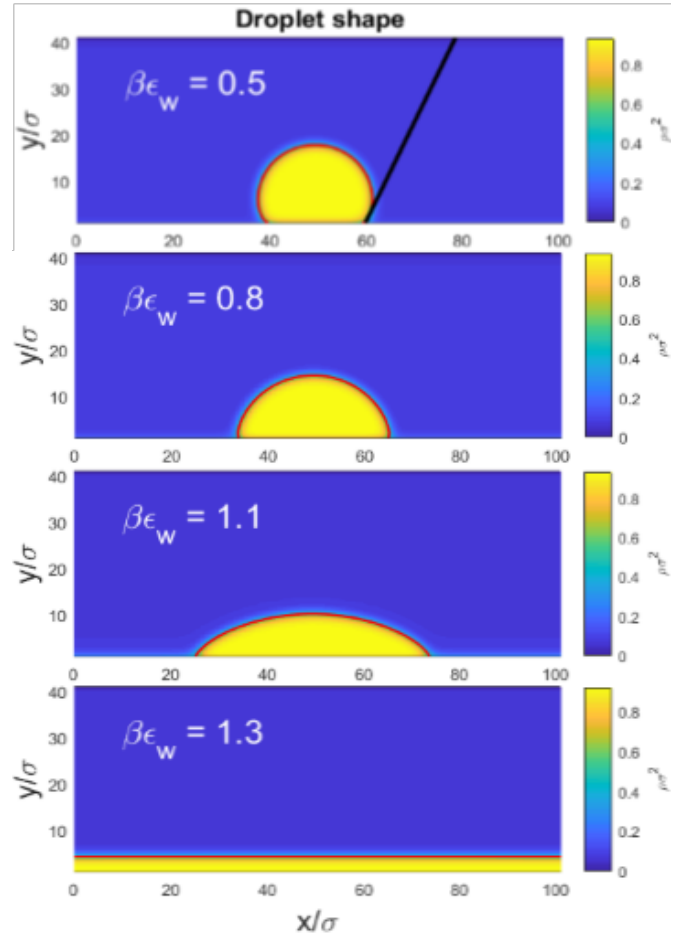


FIG. 7. Droplets with different wall attraction strength parameter modelled on surface.

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VII. REFERENCES

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