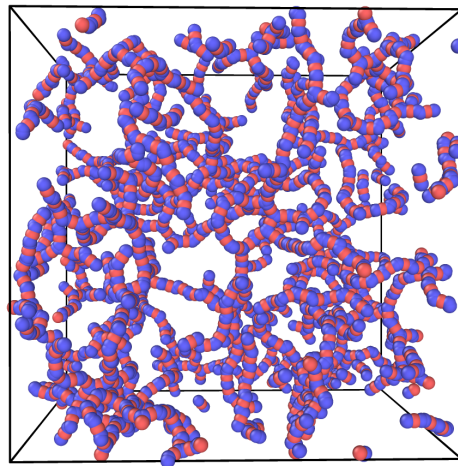


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Brownian Dynamics Simulation  
Project- III

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# 1 Liquid-Vapor Critical Point of a Lennard-Jones Fluid in the Presence of Contamination

This project focuses on the calculation of **liquid-vapor coexistence densities** and the estimation of the **critical point** of a Lennard–Jones (LJ) fluid using Brownian Dynamics simulations. The study is extended to investigate the effect of **contamination** in the form of a secondary particle species on phase coexistence and critical behavior.

Understanding how impurities or contaminants modify phase behavior is crucial in real fluids, colloidal suspensions, and industrial processes, where ideal single-component systems are rarely realized.

## 1.1 Introduction

Phase coexistence between liquid and vapor phases is a hallmark of intermolecular attractions in simple fluids. Below a critical temperature, the system separates into dense and dilute phases, while above the critical point the distinction between liquid and vapor disappears.

Molecular simulations provide a direct route to studying phase coexistence by resolving microscopic density fluctuations and interfacial structure. In particular, slab-based coexistence simulations allow the simultaneous observation of both phases in a single simulation box.

In realistic systems, the presence of contaminants or impurities can shift coexistence densities, alter surface tension, and modify the location of the critical point. In this project, students will explore these effects by introducing a small concentration of contaminant particles interacting with the LJ fluid.

## 1.2 Model and Brownian Dynamics Description

Particle motion is governed by the overdamped Langevin equation:

$$\gamma \frac{d\mathbf{r}_i}{dt} = \mathbf{F}_i + \boldsymbol{\xi}_i(t), \quad (1)$$

where  $\gamma$  is the friction coefficient,  $\mathbf{F}_i$  is the total deterministic force due to interparticle interactions, and  $\boldsymbol{\xi}_i(t)$  is a Gaussian random force satisfying

$$\langle \xi_{i\alpha}(t) \xi_{j\beta}(t') \rangle = 2k_B T \gamma \delta_{ij} \delta_{\alpha\beta} \delta(t - t'). \quad (2)$$

This framework neglects inertia and is appropriate for highly damped systems such as colloidal fluids.

## 1.3 Interaction Potentials and Contamination

The primary fluid particles interact via the Lennard–Jones potential:

$$U_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (3)$$

A small fraction of contaminant particles is introduced, which may interact with the fluid particles using modified LJ parameters ( $\epsilon_c, \sigma_c$ ). By tuning these parameters, students can model weakly repulsive or weakly attractive impurities.

The concentration of contaminants serves as a control parameter influencing phase stability and critical behavior.

## 1.4 System Geometry and Coexistence Setup

The simulation box is elongated along the  $z$ -direction to allow the formation of a liquid slab coexisting with vapor regions on both sides. Periodic boundary conditions are applied along  $x$  and  $y$ , while non-periodic boundaries are imposed along  $z$  during the coexistence simulation.

The liquid phase is first prepared at high density and later merged with low-density vapor regions to create a stable liquid–vapor interface.

## 1.5 Symbols

Symbol	Meaning
$\rho_l$	liquid density
$\rho_g$	vapor density
$T$	temperature
$T_c$	critical temperature
$\rho_c$	critical density
$x_c$	contaminant concentration
$N$	number of fluid particles
$N_c$	number of contaminant particles

Table 1: List of symbols used in the project.

## 1.6 Project Tasks

- Generate a high-density liquid configuration using NpT compression
- Remove periodicity along the coexistence direction
- Merge liquid and vapor phases in an elongated simulation box
- Introduce contaminant particles at controlled concentrations
- Compute density profiles along the  $z$ -direction
- Extract coexistence densities using profile fitting
- Estimate the critical point from temperature-dependent data

## 1.7 Simulation Studies

Measure the steady-state density profile  $\rho(z)$  and extract liquid and vapor densities using a hyperbolic tangent fit.

### Study 1: Temperature Dependence of Liquid-Vapor Coexistence

In this study, you will determine the gas–liquid coexistence curve (binodal) of a simple fluid by analyzing liquid–vapor interfaces at different temperatures. The coexistence densities obtained from simulations are used to construct the binodal and estimate the critical point. In addition, you will compute the surface tension using the pressure-tensor method and discuss the physical basis of the formula used.

#	$T$
1	0.6
2	0.7
3	0.8
4	0.9
5	1.0
6	1.1
7	1.2
8	1.3

Table 2: Temperatures used to compute liquid-vapor coexistence.

### Study 1: Effect of Contaminant Concentration on the Liquid–Vapor Binodal

In this study, you will compute the liquid–vapor coexistence curve (binodal) for different contaminant concentrations. From the binodal, you will estimate the critical temperature and critical density and analyze how these quantities shift with increasing contamination.

#	$x_c$
1	0.00
2	0.02
3	0.05
4	0.10

Table 3: Contaminant mole fractions used for binodal calculations.

### Step 1: Folder structure and setup

1. Navigate to the main directory:

`Project_3/Binodal/Coexistence_densities/0.00, 0.02, 0.05, 0.10/`

2. For each contaminant concentration listed in Table 1, modify the contaminant mole fraction  $x_c$  in the LAMMPS input scripts.

3. For a given  $x_c$ , perform simulations at multiple temperatures to obtain coexistence data for binodal construction.

## Step 2: Liquid–vapor interface simulations

1. Generate a high-density liquid configuration by running:

```
liquid_box_creator.in
```

2. Remove periodicity along the  $z$ -direction using:

```
intermediate.in
```

3. Extend the simulation box symmetrically along the  $z$ -axis to create vapor regions.
4. Equilibrate the liquid–vapor interface by running:

```
coexistence_simulator.in
```

5. The spatial particle distribution is stored in:

```
bin_particles.LAMMPSstrj
```

## Step 3: Extracting coexistence densities

1. Run:

```
data_rectifier.py
```

to obtain the time-averaged density profile:

```
averaged_density_profile.txt
```

2. Identify the coexisting gas density  $\rho_g$  and liquid density  $\rho_l$  from the flat regions of the profile.
3. For each temperature, append the data to:

```
density_vs_temperature.txt
```

using the format:

$$T \quad \rho_g \quad \rho_l$$

## Step 4: Binodal construction and critical point estimation

1. After collecting coexistence data for all temperatures, run:

```
binodal_plotter.py
```

to construct the liquid–vapor binodal.

2. The script estimates the critical temperature  $T_c$  and critical density  $\rho_c$  for the given contaminant concentration.
3. Record  $T_c$  and  $\rho_c$  for each value of  $x_c$ .

### Step 5: Analysis

1. Plot the binodal curves for different contaminant concentrations on the same graph.
2. Analyze how increasing  $x_c$  shifts the critical temperature and critical density.
3. Provide physical explanations based on changes in effective interactions and mixing entropy.

## Study 2: Effect of Contaminant Concentration on Surface Tension

In this study, you will compute the liquid–vapor surface tension as a function of contaminant concentration at a fixed temperature  $T = 0.5$ . The surface tension is calculated using the mechanical (pressure-tensor) definition.

### Step 1: Simulation setup

1. Use the same directory:

`Project_3/Surface_tension/0.00, 0.02, 0.05, 0.10/`

2. Fix the temperature at:

$$T = 0.5$$

3. Vary the contaminant mole fraction  $x_c$  according to Table 1.
4. Ensure that all other simulation parameters remain unchanged.

### Step 2: Interface equilibration

1. Generate and equilibrate the liquid–vapor interface following the same procedure described in **Study 1**.
2. Confirm that the interface is stable before collecting pressure data.

### Step 3: Surface tension calculation

1. Run the Python script:

`surface_tension_calculator.py`

2. The surface tension  $\gamma$  is computed using:

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} [P_N(z) - P_T(z)] dz$$

where  $P_N$  is the normal pressure component and  $P_T$  is the tangential pressure component.

3. Record the surface tension values for each contaminant concentration.

#### **Step 4: Physical interpretation**

1. Explain the physical origin of the pressure anisotropy at a liquid–vapor interface.
2. Describe why the surface tension decreases as the system approaches the critical point.
3. Discuss how contaminant concentration modifies interfacial structure and surface tension.

#### **Study 4: Critical Point Estimation**

Using the coexistence curve, estimate the critical temperature  $T_c$  and critical density  $\rho_c$  by fitting the binodal envelope and analyzing the disappearance of phase separation.

### **1.8 Presentation and Project Report**

- **Introduction (1 page):** Liquid-vapor phase transitions and critical phenomena.
- **Model and Simulation Details (1 page):** Chemical properties e.g, fugacity in the binary system. Phase behavior of multi-component system.
- **Results and Discussion (6–10 pages):** Phase diagram, binodal curves, critical points and the effect of contamination on the same.
- **Conclusion (1 page):** Physical interpretation, limitations, and finite-size effects.

### **1.9 Future Aspects**

Discuss possible extensions including multi-component mixtures, surfactant-like contaminants, surface tension measurements, finite-size scaling analysis of the critical point, and comparison with molecular dynamics simulations.



## 2 Project Report Guidelines

### 1. Introduction to the Problem

This section should be approximately one page long (or slightly more) and must include at least five (minimum three) scientific references from peer-reviewed literature.

The introduction should explain the physical concept of liquid–gas coexistence in simple fluids and its description within statistical mechanics. In particular, students should:

- Introduce phase coexistence and first-order phase transitions.
- Explain the concept of liquid–vapor equilibrium and binodal curves.
- Define the critical point and its thermodynamic significance.
- Briefly describe the role of fluctuations near criticality.

Students should then motivate the inclusion of a contaminant species and discuss:

- How impurities or additives modify intermolecular interactions.
- Physical examples such as gas mixtures, atmospheric aerosols, and impurities in fluids.
- Why contamination can shift coexistence curves and critical parameters.

The goal of the project should be clearly stated:

*To quantify how contaminant concentration affects liquid–gas coexistence, the critical point, and interfacial properties.*

### 2. Technical Description of the Simulations

This section should describe the simulation methodology used to compute phase coexistence and surface tension.

Students must describe:

- The interaction potential used for the base fluid (e.g., Lennard–Jones).
- The contaminant species and how its concentration  $x_c$  is defined.
- Simulation geometry used to create a liquid–vapor interface.
- The ensemble employed (e.g.,  $NVT$  or  $NVE$  with thermostats).

Details of the interface construction should include:

- Preparation of a high-density liquid slab.
- Creation of vapor regions by extending the simulation box.
- Removal of periodicity along the interface normal.

Students should clearly state the range of temperatures and contaminant concentrations explored.

### 3. Study 1: Binodal Construction and Critical Point Estimation

In this study, students will compute coexistence densities for different temperatures and contaminant concentrations.

#### Procedure

- For each contaminant mole fraction  $x_c$ , perform simulations over a range of temperatures.
- Extract gas and liquid densities from the flat regions of the density profile  $\rho(z)$ .
- Store the data in:

`density_vs_temperature.txt`

using the format:

$$T \quad \rho_g \quad \rho_l$$

Students should then:

- Use `binodal_plotter.py` to construct the coexistence curve.
- Identify the binodal envelope for each value of  $x_c$ .
- Extract the critical temperature  $T_c$  and critical density  $\rho_c$ .

#### Analysis

Students must:

- Plot binodals for different contaminant concentrations on the same graph.
- Analyze how  $T_c$  and  $\rho_c$  shift with increasing  $x_c$ .
- Discuss whether contamination stabilizes or destabilizes the liquid phase.

### 4. Study 2: Surface Tension at Fixed Temperature

In this study, students will compute the surface tension at a fixed temperature (e.g.,  $T = 0.5$ ) for different contaminant concentrations.

#### Procedure

- Perform liquid–vapor interface simulations at fixed temperature.
- Record the spatially resolved pressure tensor components:

$$P_N(z), \quad P_T(z)$$

- Use the script:

`surface_tension_calculator.py`

to compute the surface tension.

The surface tension is calculated using the mechanical definition:

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} [P_N(z) - P_T(z)] dz$$

## Analysis

Students should:

- Plot surface tension  $\gamma$  as a function of contaminant concentration  $x_c$ .
- Discuss why surface tension decreases as the critical point is approached.
- Explain how contamination alters interfacial free energy.

## 5. Main Findings and Discussion

This section should form the core of the report and be approximately 5–10 pages long (or 3–6 pages for a shorter report).

Students should integrate results from both studies and discuss:

- The relationship between binodal narrowing and surface tension reduction.
- The physical meaning of critical point shifts.
- The role of microscopic interactions in determining macroscopic phase behavior.

Connections to classical theories (e.g., van der Waals theory, capillarity theory) should be made wherever appropriate.

## 6. Conclusion

This section should be approximately half a page to one page long.

The conclusion should:

- Summarize the impact of contamination on phase coexistence and interfacial properties.
- Highlight the consistency (or deviation) from theoretical expectations.
- Reflect on the importance of molecular simulations in studying multicomponent phase behavior.
- Suggest possible extensions, such as varying contaminant interaction strength or studying finite-size effects.

## References

- [1] Malhotra, Isha, and Hartmut Löwen. "**Double Mpemba effect in the cooling of trapped colloids.**" *The Journal of Chemical Physics* 161.16 (2024): 164903.
- [2] **Theory of Simple liquids** by Hansen and McDonald.
- [3] **Nonequilibrium Statistical Mechanics** by Robert Zwanzig