Liquid-Liquid Phase Transition in Modified Jagla Model for Water

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Introduction

- Why do we care about water?
  - Water is the most common but anomalous substance, 67 anomalies so far.
    - Max. density at 4°C
    - Ice floats on top of water
    - Unusually high specific heat
    - Unusually high surface tension
    - Unusually low compressibility
    - Variety of solid structure
Anomalous thermodynamic properties of supercooled bulk water

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\[ T_s = 228 \text{K} \]

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Anomalous thermodynamic properties of supercooled bulk water \( T_s = 228 \text{K} \)

\[ C_p \sim \left( \frac{T}{T_s} - 1 \right)^{-0.26} \]

\[ K_T \sim \left( \frac{T}{T_s} - 1 \right)^{0.35} \]

\[ T/K: 308 \text{K}, 319 \text{K} \]


\( C_p \) and \( K_T \) diverge upon approaching \( T = 228 \text{K} \)?
Liquid-Liquid Critical Point Hypothesis

- \( T_M \): Melting Temperature
- \( T_H \): Homogeneous Nucleation Temp.
- \( T_g \): Glass Transition Temperature
- LDA: Low Density Amorphous
- HDA: High Density Amorphous


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LDA: Low Density Amorphous
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LDL: Low Density Liquid
HDL: High Density Liquid

$T_C=215K=-58^0C,$
$P_C=0.1GPa=1000atm$


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- LDL: Low Density Liquid
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$T_C = 215 K = -58^0C$, $P_C = 0.1 GPa = 1000 atm$

Widom Line: Locus of Max. Correlation Length, where $C_P$ and $K_T$ show maximum


Simulation Approach

Model must have:
- Accessible Liquid-Liquid phase transition and critical point
- Water-like anomalies
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Two-Scale Spherically Symmetric Jagla Ramp Potential
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Jagla Model for Water

Pros:
- Have accessible LL phase transition and LL critical point.
- Show water-like anomalies.

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Question:

What can we do to reproduce the correct slope of coexistence line and Widom line for Jagla model?
Model: Modified Jagla Potential


Legend:
- a: Hardcore
- b: Potential Min.
- c: Cut off
- $U_0$: Potential well depth
- $b/a=1.72$: Original Jagla

Graph showing the potential $U(r)$ as a function of $r/a$.
Model: Modified Jagla Potential


- **a**: Hardcore
- **b**: Potential Min.
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Graph showing the modified Jagla potential for two values of b/a: 1.72 and 1.68.
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- b/a=1.72
- b/a=1.68
- b/a=1.65
- b/a=1.62
- b/a=1.59

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- Decrease $b/a$ and $c/a$
- Increase magnitude of $U_0$
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Modified Jagla Potential

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Method: Discrete Molecular Dynamics (DMD)

- Potential ramps are treated as sum of steps.
- Particles interact when distance jumps steps.
- Number of particles: 1728
- Discrete steps: $N_1=60$, $N_2=20$
- Quantity:
  - Temperature: $k_B T/U_0$
  - Pressure: $Pa^3/U_0$
  - time: $t\sqrt{\frac{U_0}{ma^2}}$
Results:

- Does the system have two liquid phases in the supercooled region?
- What does the coexistence line look like?
- How about Widom line?
- Does the system have water-like anomalies?
- How can we interpret the result?
Does the system have two liquid phases?

\[ g(r) = \text{radial distribution function} \]

\[ g(r) \text{ is the probability of finding particles at a given distance } r \text{ from another particle} \]

Normalization:
\[ g(r) = 1 \text{ for } r = \infty \]

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Two Liquid Phases: LDL vs. HDL

LDL vs. HDL phase for $b/a=1.59$

Two characteristic length scales of phases.

Note: We have two distinct phases, LDL and HDL, and two characteristic length scales - hardcore distance and potential minimum, respectively.
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Change of Coexistence Line Slope

![Graph showing the change of coexistence line slope over b/a values ranging from 1.58 to 1.74.](image-url)
The slope of the coexistence line changes from positive to negative, as we decrease the value of $b/a$ to 1.59.
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b/a ≥ 1.60: Specific Heat $C_P$ Max.

If $b/a \geq 1.60$, coexistence line and Widom line both show positive slope.
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**b/a ≥ 1.60**: Specific Heat $C_P$ Max.

![Diagram](image)

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**FIG. 3**: The heat capacity $C_P$ at equilibrium for different values of $b/a$. We can see it is universal that the closer we approach the critical pressure from above, the more pronounced the $C_P$ peak is, and the lower the maximum $C_P$ temperature is. In other words, it is all positively sloped in P-T diagram.

- If $b/a = 1.62$, $T_C/U_0 = 0.243$ and $P_C/U_0 = 0.444$.
- Widom Line positive sloped!
$b/a=1.59$: Specific Heat $C_P$ Max.

System crystallizes before reaching $C_p$ maximum.

What can we do?
$b/a=1.59$: Specific Heat $C_P$ Max.

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What can we do?
b/a=1.59: Specific Heat $C_P$ Max. w/ fast cooling

$$\frac{k_B T}{U_0} = 0.594$$

Cooling Rate: $q = \frac{\delta T}{\delta t} = 0.002 \frac{U_0^3}{200 m k_B^2} = 10^{-5} q_0$

Results are average of 10 independent runs.
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Results are average of 10 independent runs.

- Specific Heat \( C_P \) Max. w/ fast cooling
- \( b/a = 1.59 \)
- Coexistence
- HDL
- LDL

Temperature \( T \) vs. Pressure \( P \):

- \( P_{C}/U_0 = 0.594 \)
- \( P/U_0 = 0.406 \)
- \( P/U_0 = 0.443 \)
- \( P/U_0 = 0.517 \)
b/a=1.59: Specific Heat $C_P$ Max. w/ fast cooling

$$q = \frac{\delta T}{\delta t} = \frac{0.002}{200} \sqrt{\frac{U_0^3}{mk_B^2}} = 10^{-5} q_0$$

Results are average of 10 independent runs.
b/a=1.59: Compressibility $K_T$ Max.

The diagram shows a color map for the compressibility $K_T$ in equilibrium for the system with $b/a=1.59$. The color map indicates a negative-sloped maximum line below the critical point, consistent with the finding of the negative-sloped coexistence line, which is water-like.

The color map shows $K_T$ max with a negative slope, with warmer colors like red indicating larger values and cooler colors like blue indicating smaller values. The critical point is marked on the map, and the color bar on the right indicates the range of $K_T$ values.
**b/a=1.59**: Compressibility $K_T$ Max.

The color map shows $K_T$ max with a negative slope. Widom line negative sloped!
$b/a=1.59$: Compressibility $K_T$ Max.

Color map shows $K_T$ max with negative slope.

Widom line negative sloped!
$b/a=1.59$: Phase Diagram and Anomalies

![Phase diagram](image)

- **Isochores**
- **Melting line**
- **Homogeneous nucleation**
- **LLCP**
- **Temperature of max density**
- **K_T max**
- **C_P max**

**Diagram Labels**:
- HDL
- LDL
- $P/U_0$
- $k_B T/U_0$
b/a=1.59: Phase Diagram and Anomalies

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Insights on how we can get this:

- **Slope:**
  \[
  \frac{dP}{dT} = \frac{\Delta S}{\Delta V}
  \]

- **Negative Slope:**
  \[
  \frac{dP}{dT} < 0 \Rightarrow \frac{\Delta S}{\Delta V} < 0
  \]

- **LDL -> HDL:**
  \[
  \Delta V < 0
  \]

\[
\Rightarrow \Delta S = S_{HDL} - S_{LDL} > 0 \Rightarrow S_{HDL} > S_{LDL}
\]

- **LDL is more ordered than HDL.**
Conclusion:
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Modified Jagla can be a good model for water!
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- For b/a=1.59 model, we have:
  - **Water anomalies**: Density, compressibility and specific heat anomalies;
  - **Coexistence line**: Negative slope of the LDL-HDL coexistence line;
  - **Widom line**: Negative slope of Widom line, locus of specific heat $C_P$ and compressibility $K_T$ maximum;
  - **Crystallization**: System easily crystallizes in supercooled region, however accessible to LLPT and LLCP.
Thank you for your attention!