Liquid-Liquid Phase Transition in Modified Jagla Model for Water

Jiayuan Luo

Boston University

Advisor: **H. Eugene Stanley**

Collaborators: C. Austen Angell, Sergey V. Buldyrev, Limei Xu

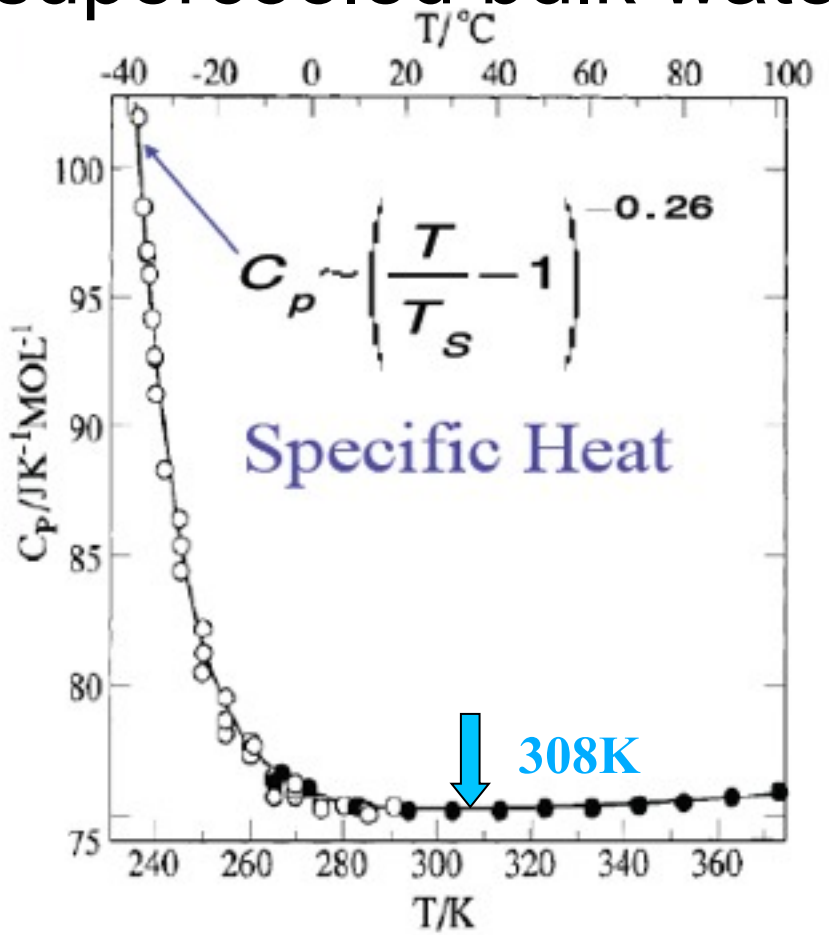
1, **J. Luo**, L. Xu, S. V. Buldyrev, C. A. Angell, H. E. Stanley, *Liquid-Liquid Phase Transition in Modified Jagla Models*, in preparation.

2, **J. Luo**, L. Xu, S. V. Buldyrev, C. A. Angell, H. E. Stanley, *Relationship in Glass Transition and Liquid-Liquid Phase Transition in Modified Jagla Models*, in preparation.

Introduction

- Why do we care about water?
  - Water is the most common but anomalous substance, 67 anomalies so far.
    - Max. density at 4^0C
    - 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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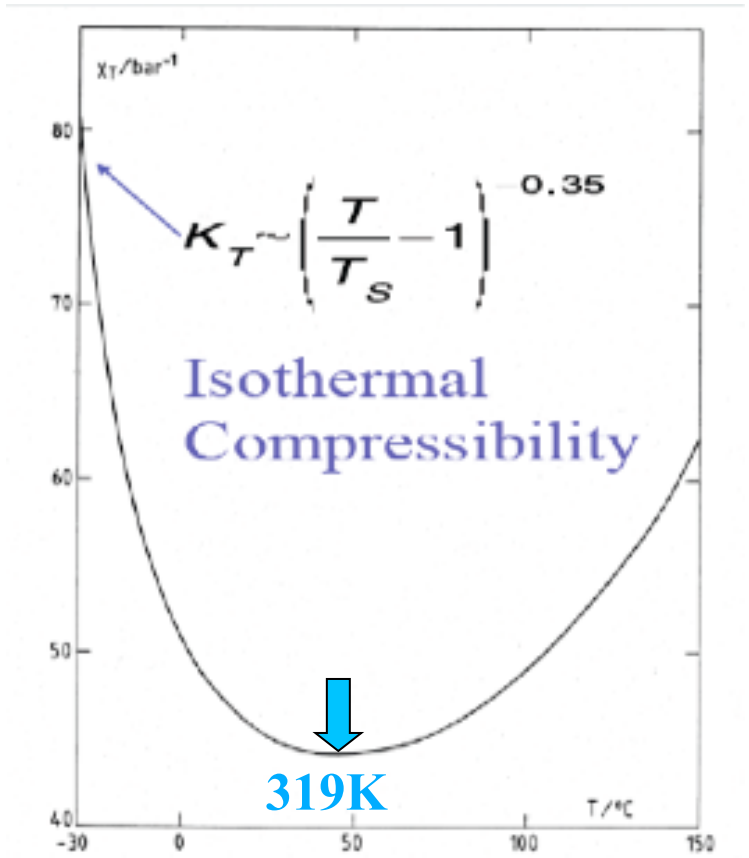

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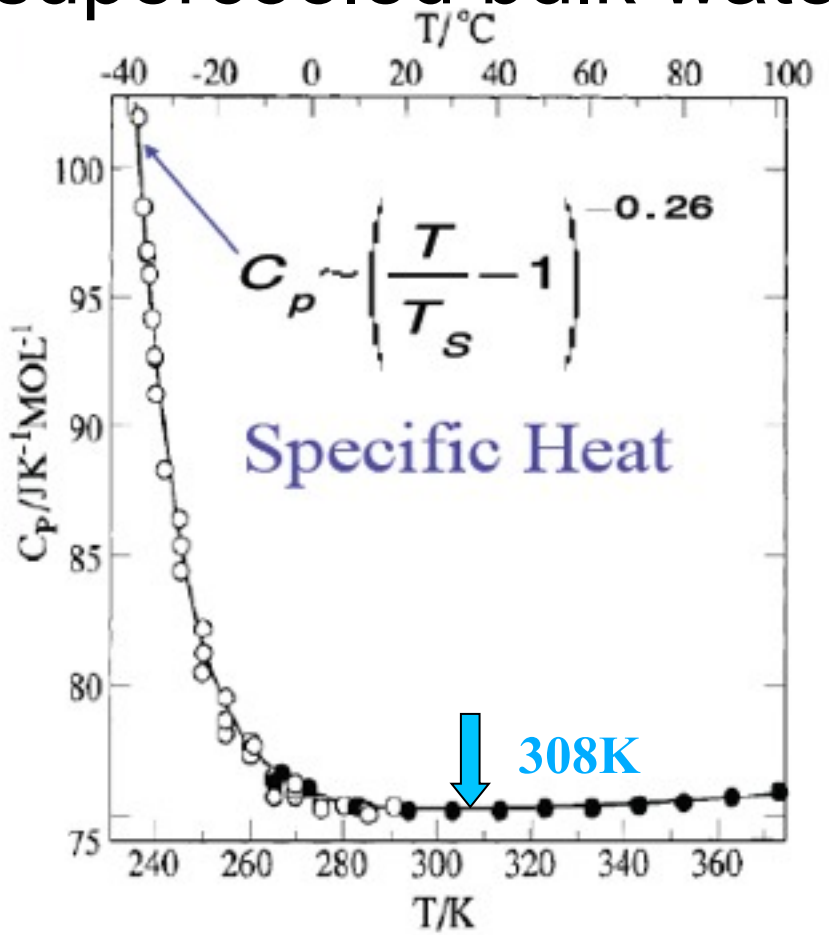
Anomalous thermodynamic properties of supercooled bulk water

T_S=228K



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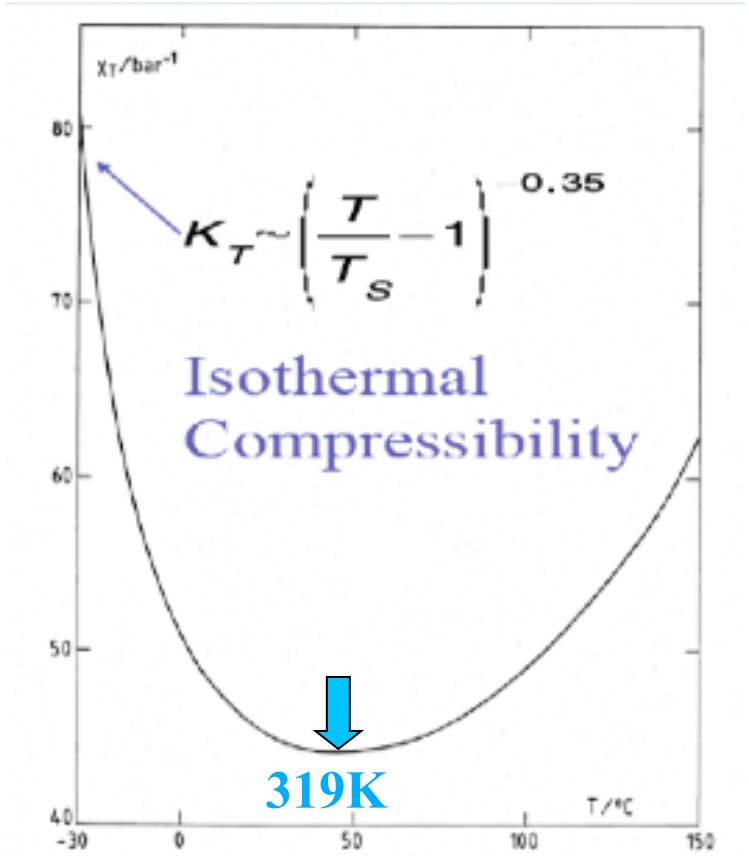

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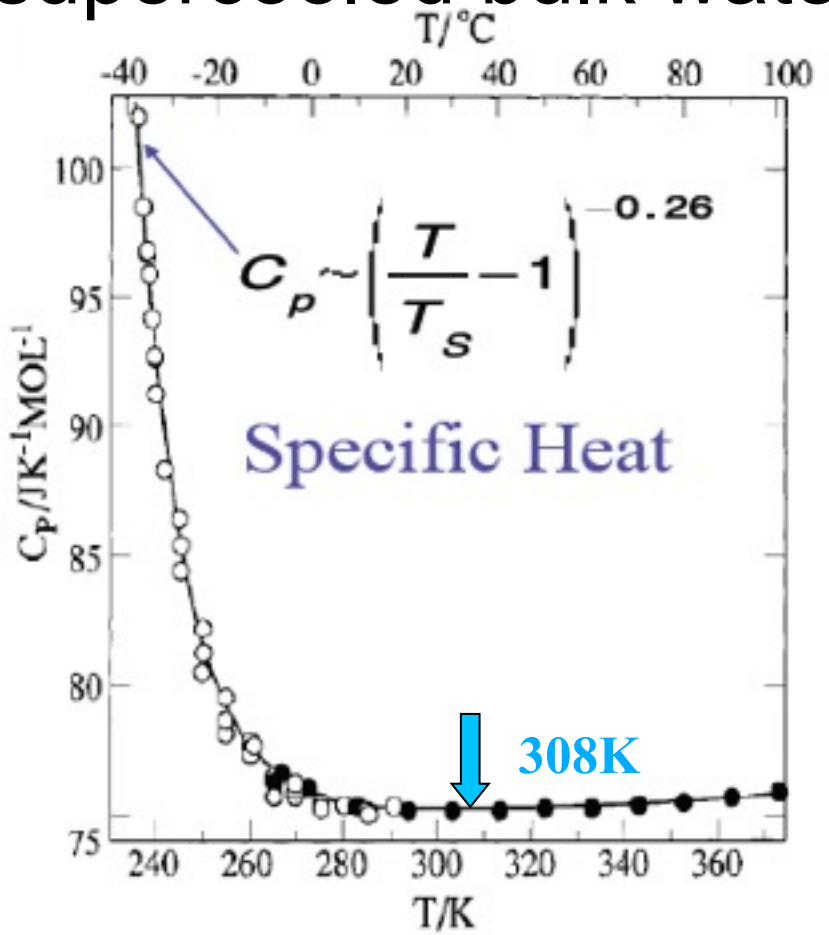

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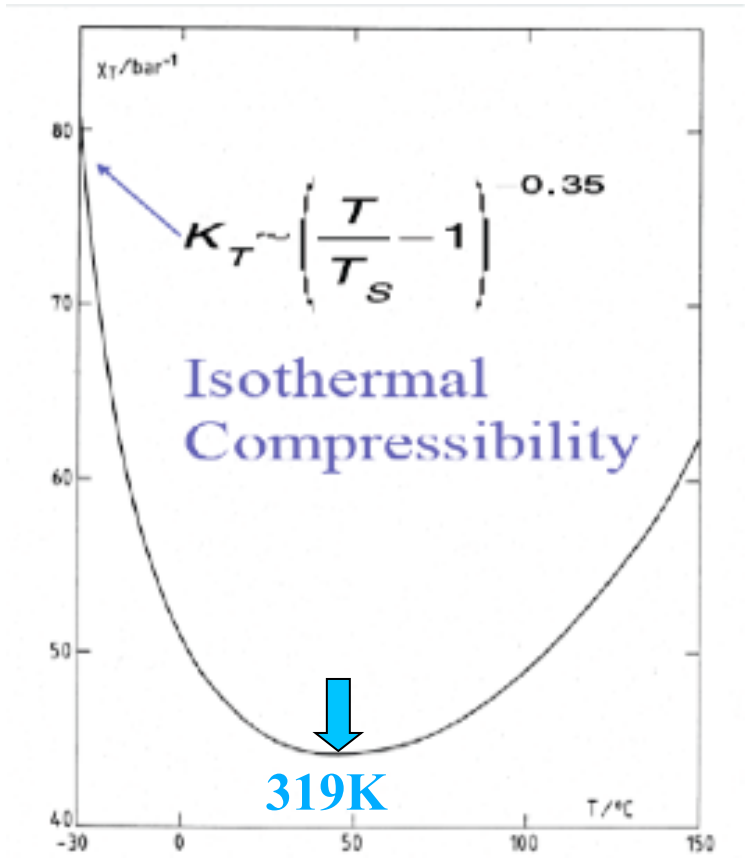

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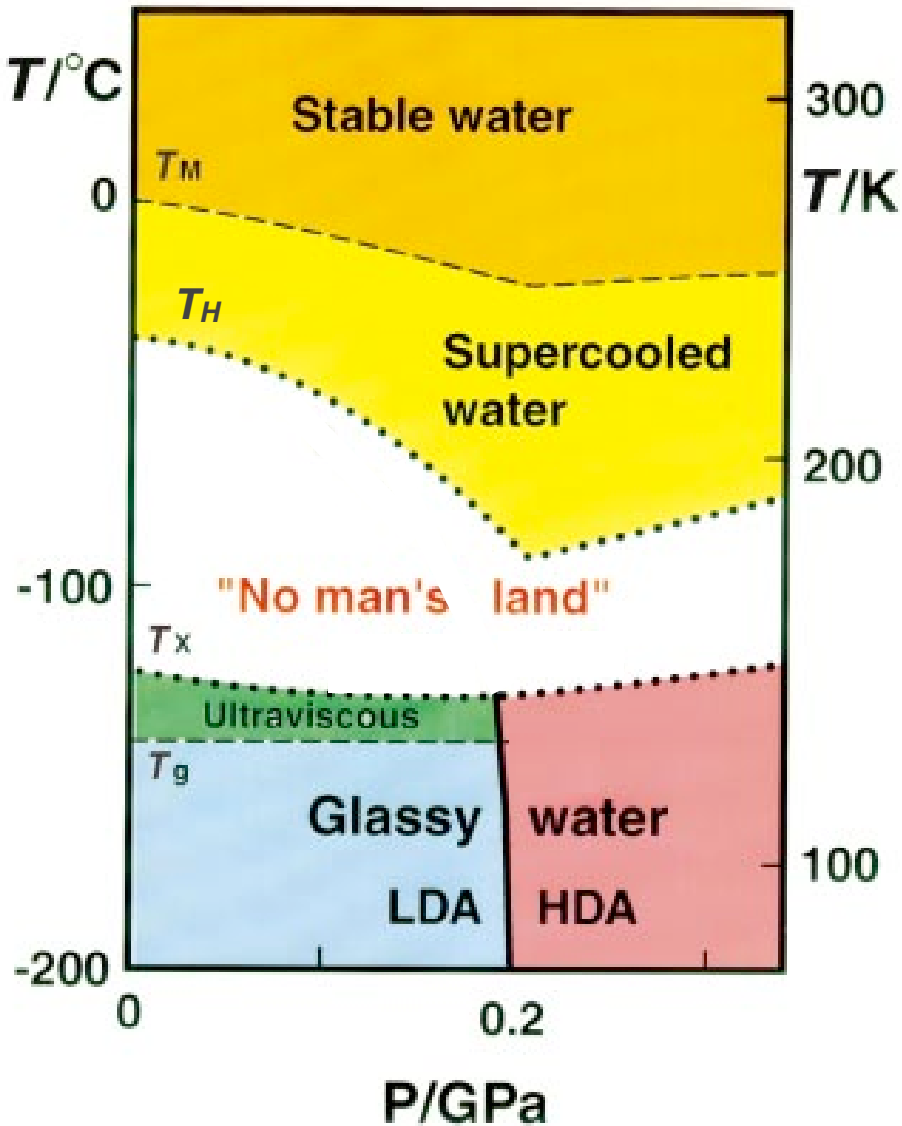
C_p and K_T diverge upon approaching T=228K?

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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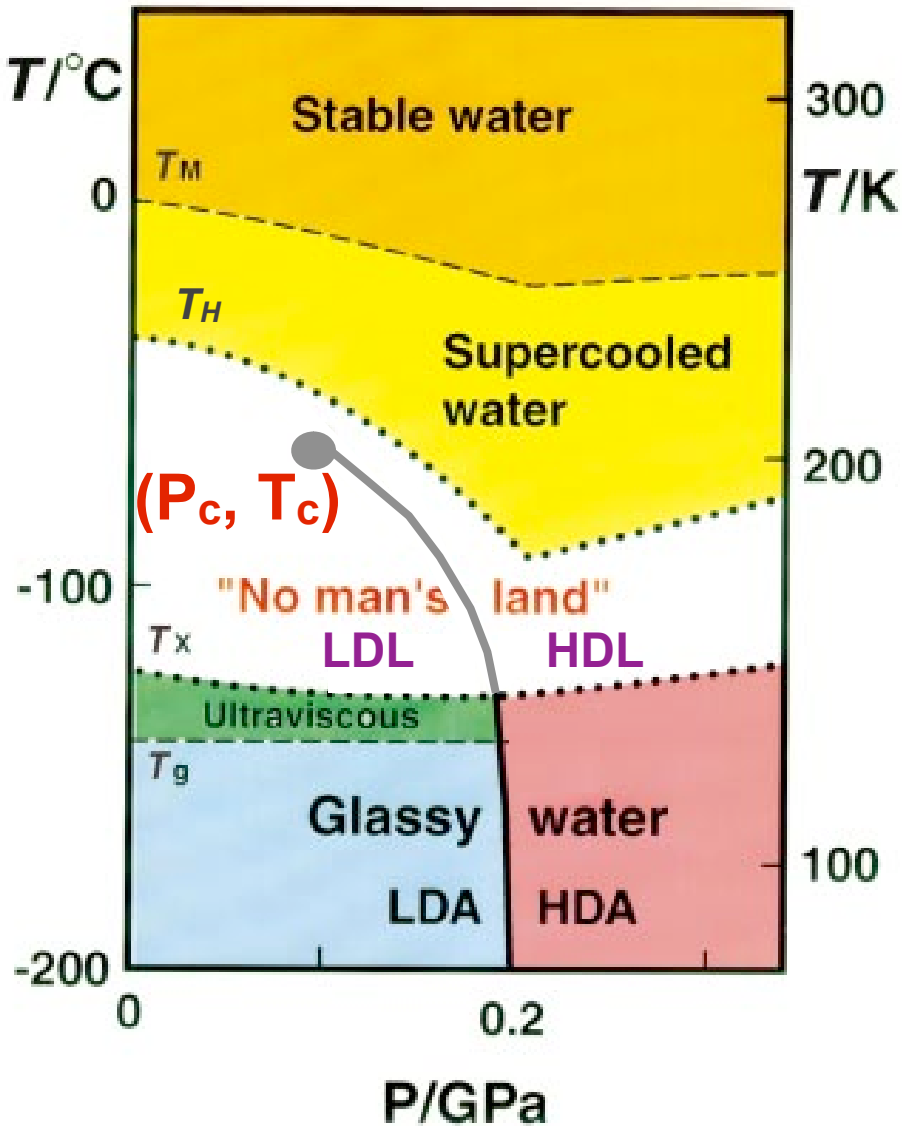

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P_C=0.1GPa=1000atm

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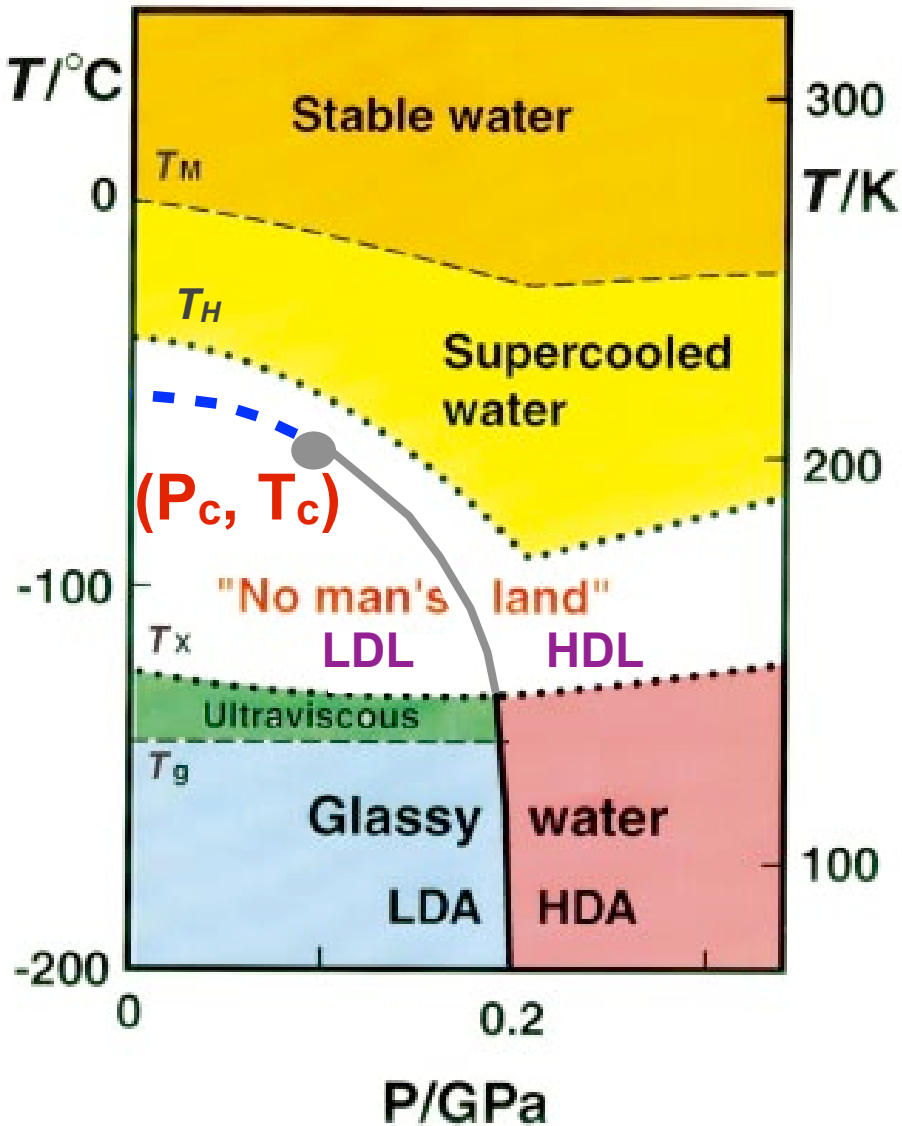

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Widom Line: Locus of Max. Correlation Length, where C_P and K_T show maximum

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Simulation Approach

- Model must have:
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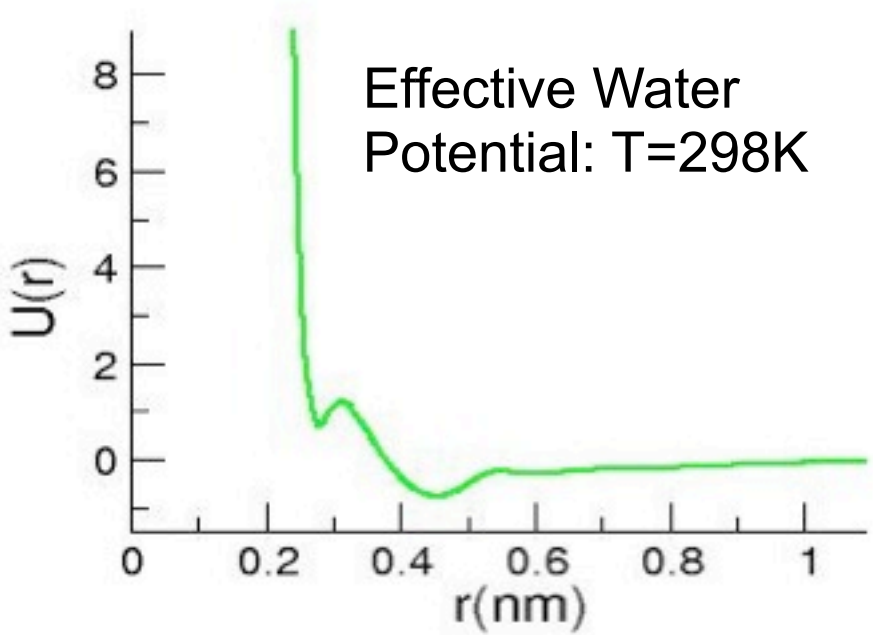
Two-Scale Spherically Symmetric

Jagla Ramp Potential

Two-Scale Spherically Symmetric Jagla Ramp Potential Model



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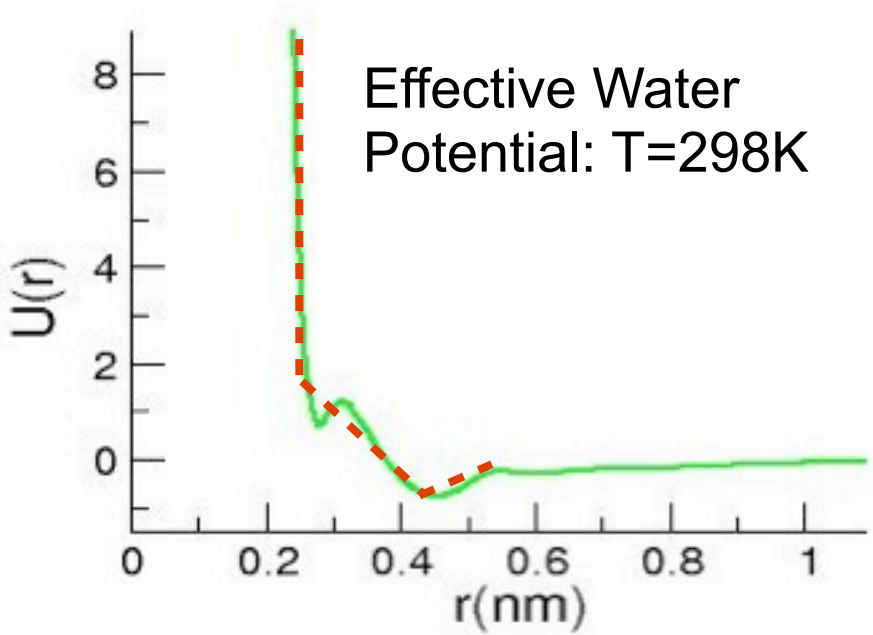

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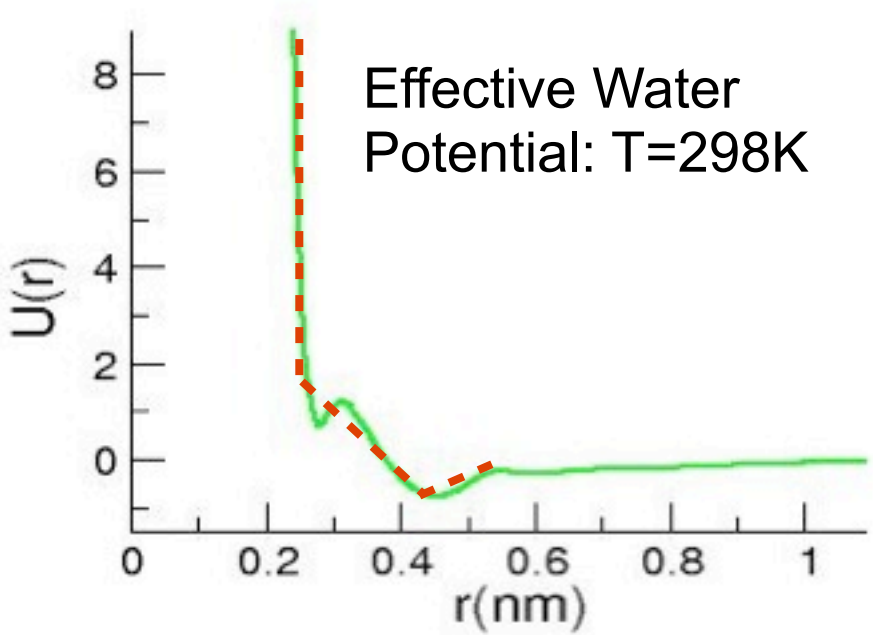

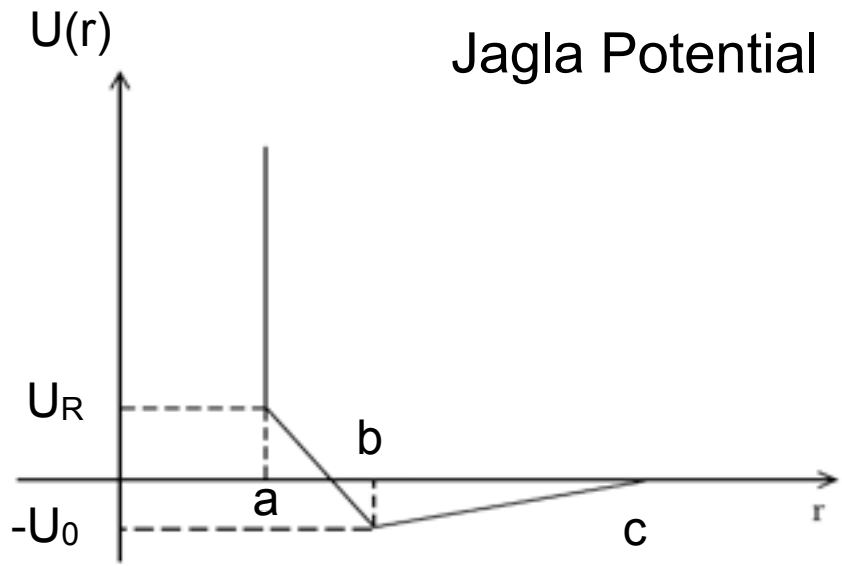

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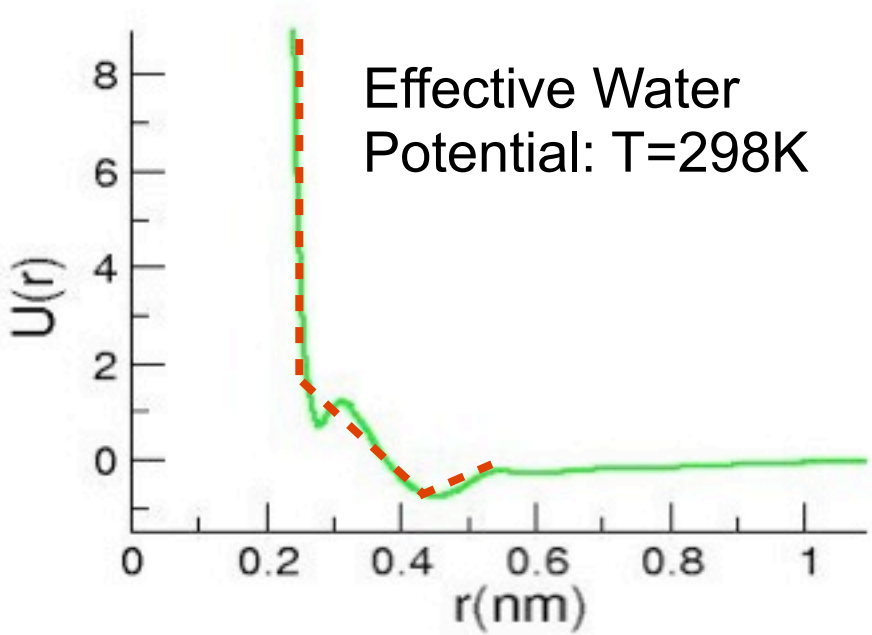

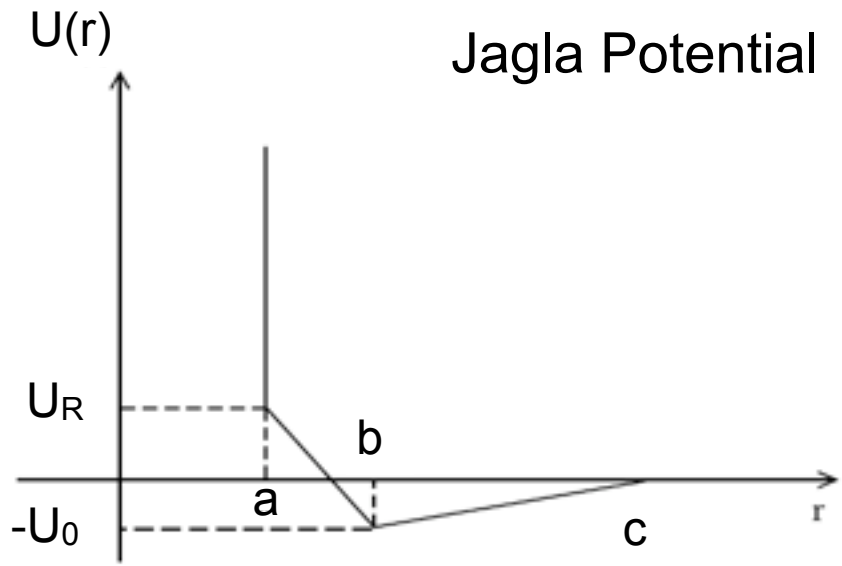

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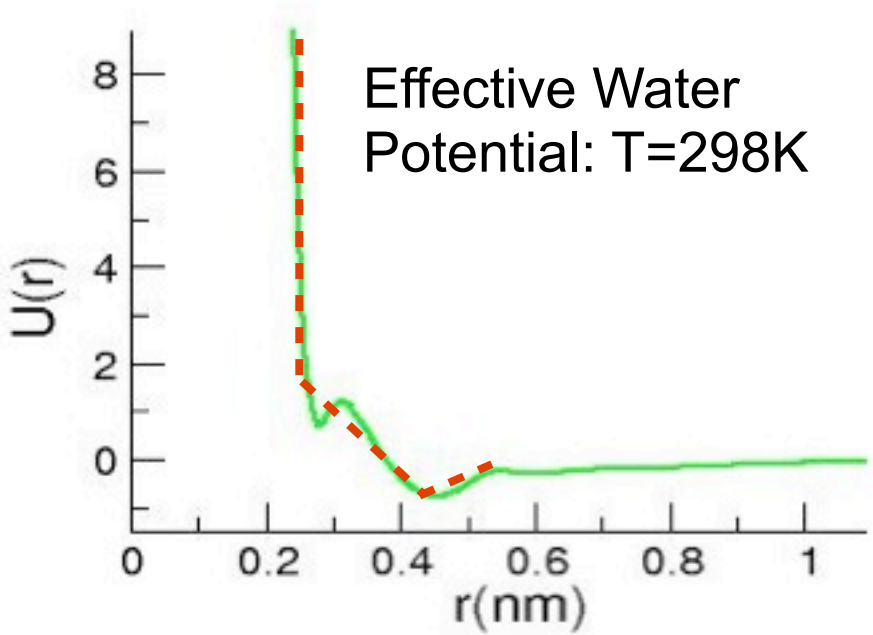

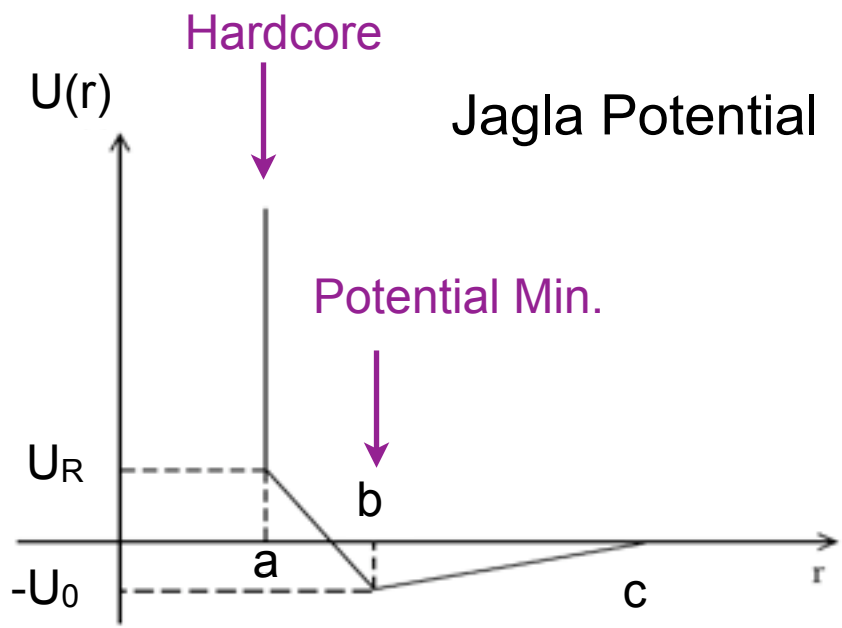

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Jagla Model for Water

- Pros:
  - Have accessible LL phase transition and LL critical point.
  - Show water-like anomalies.
- Cons:
  - Positive sign of the coexistence line slope.

L. Xu, et al. *Proc Natl Acad Sci USA* **102**, 16558 (2005)

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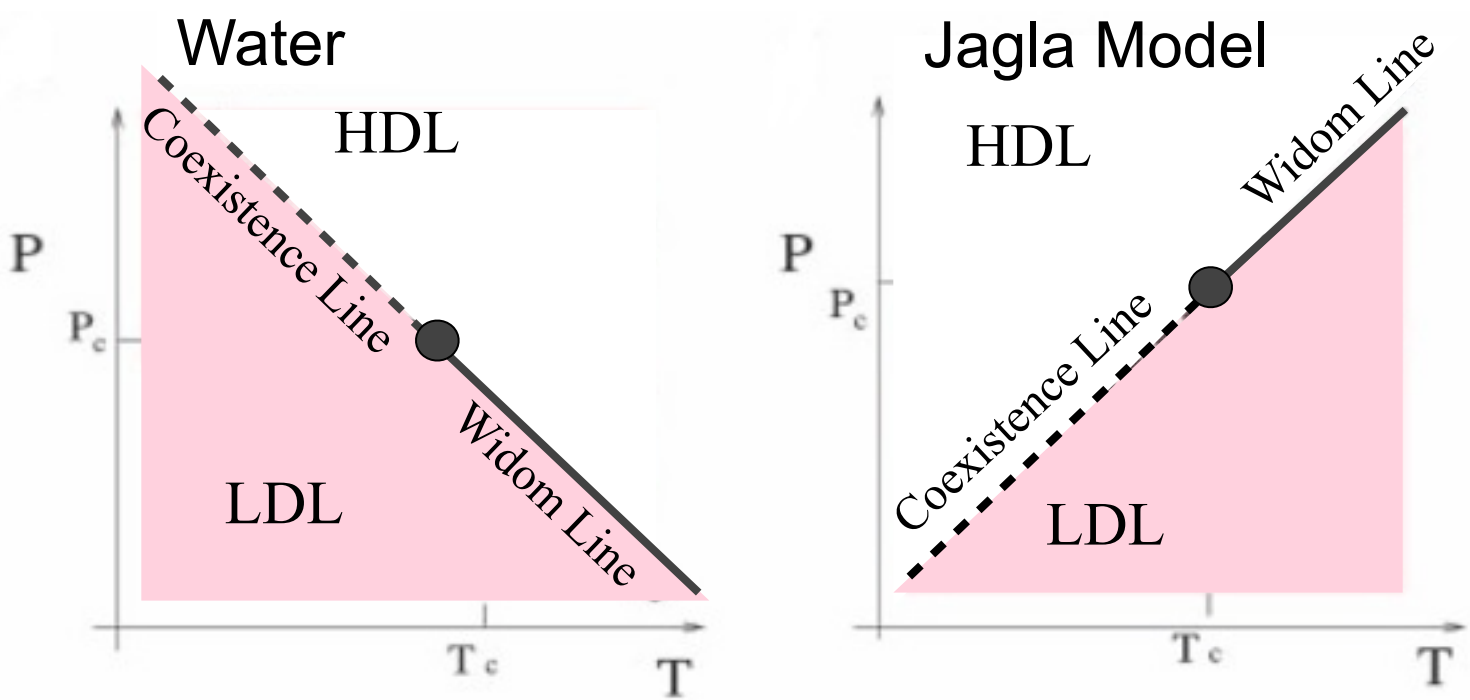

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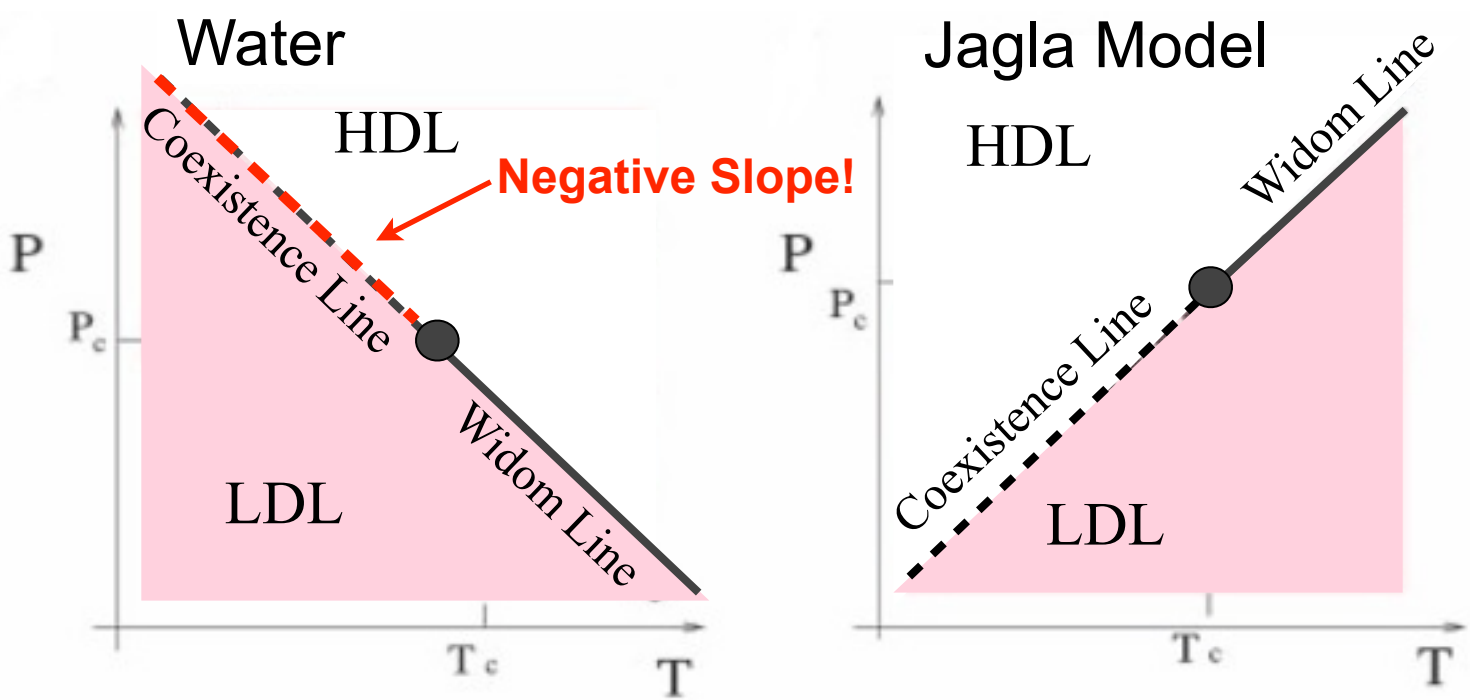

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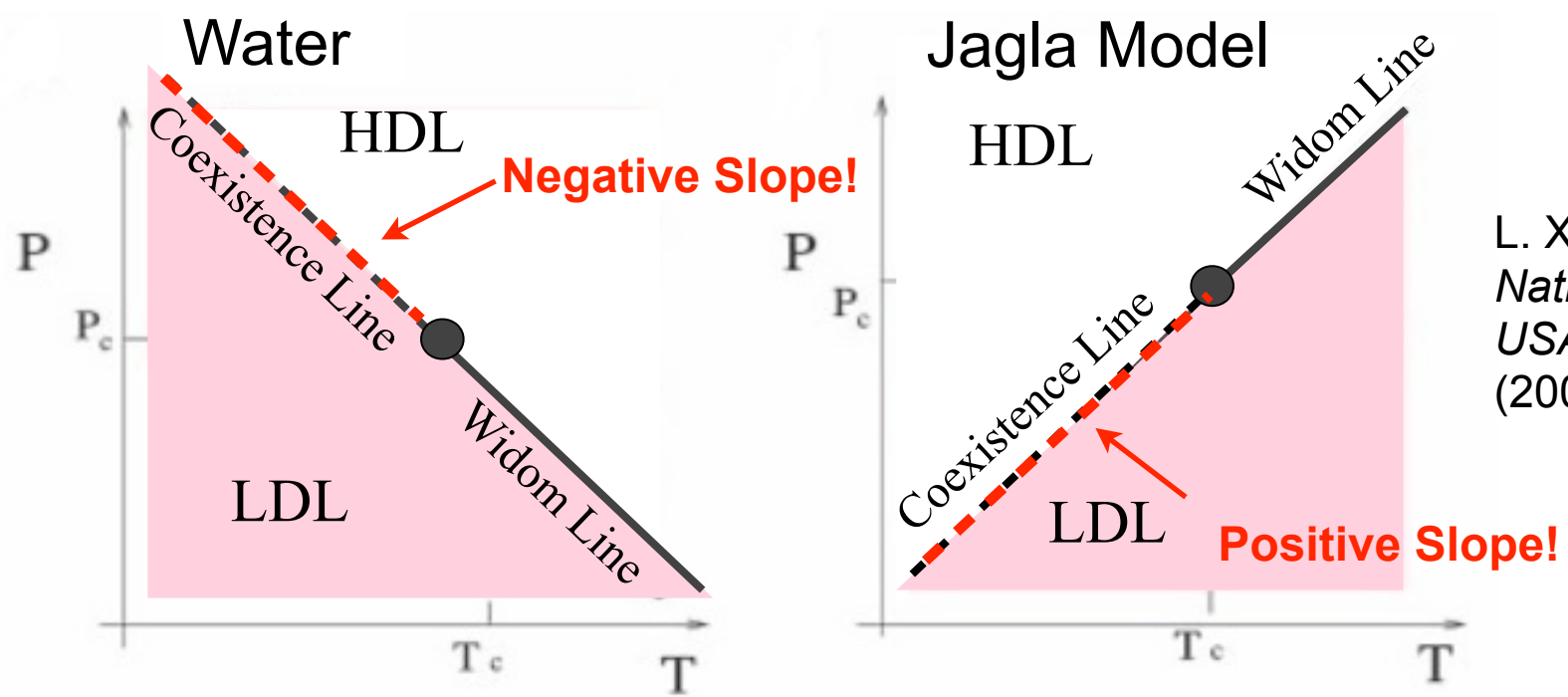

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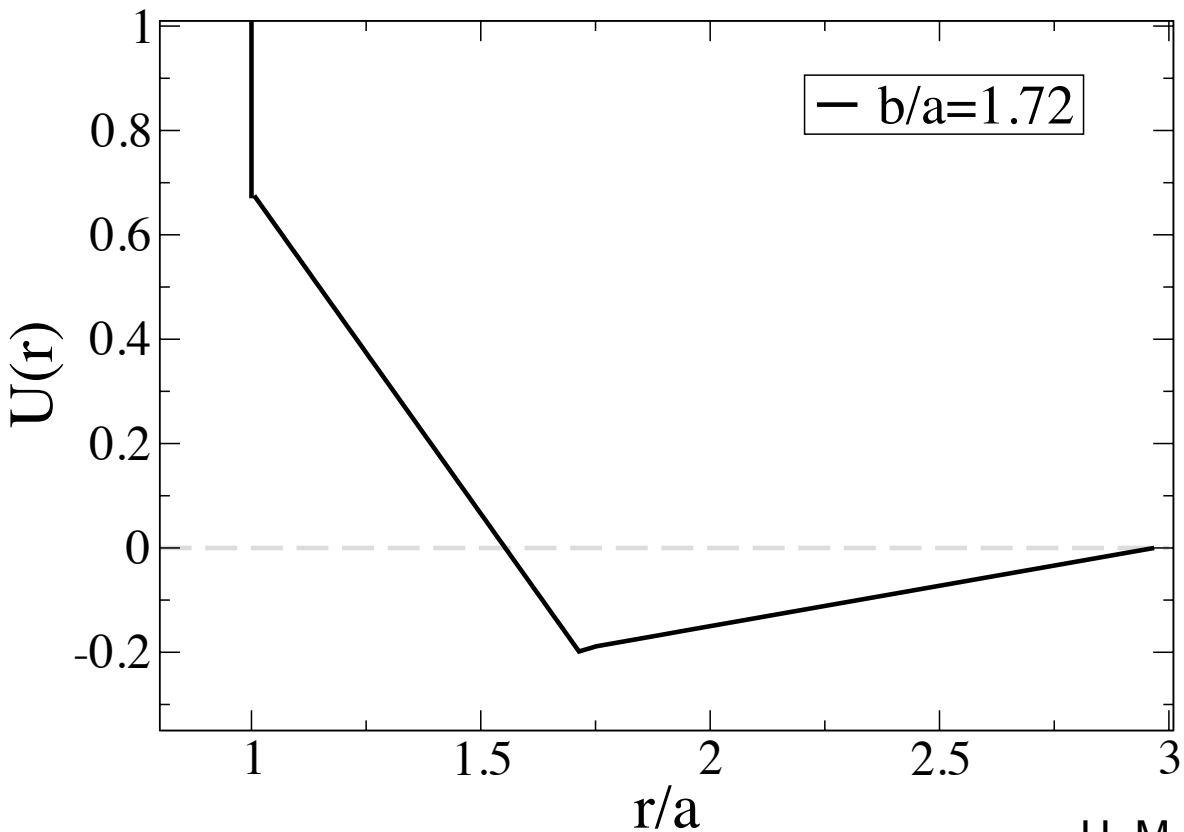
Question:

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

Model: Modified Jagla Potential



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

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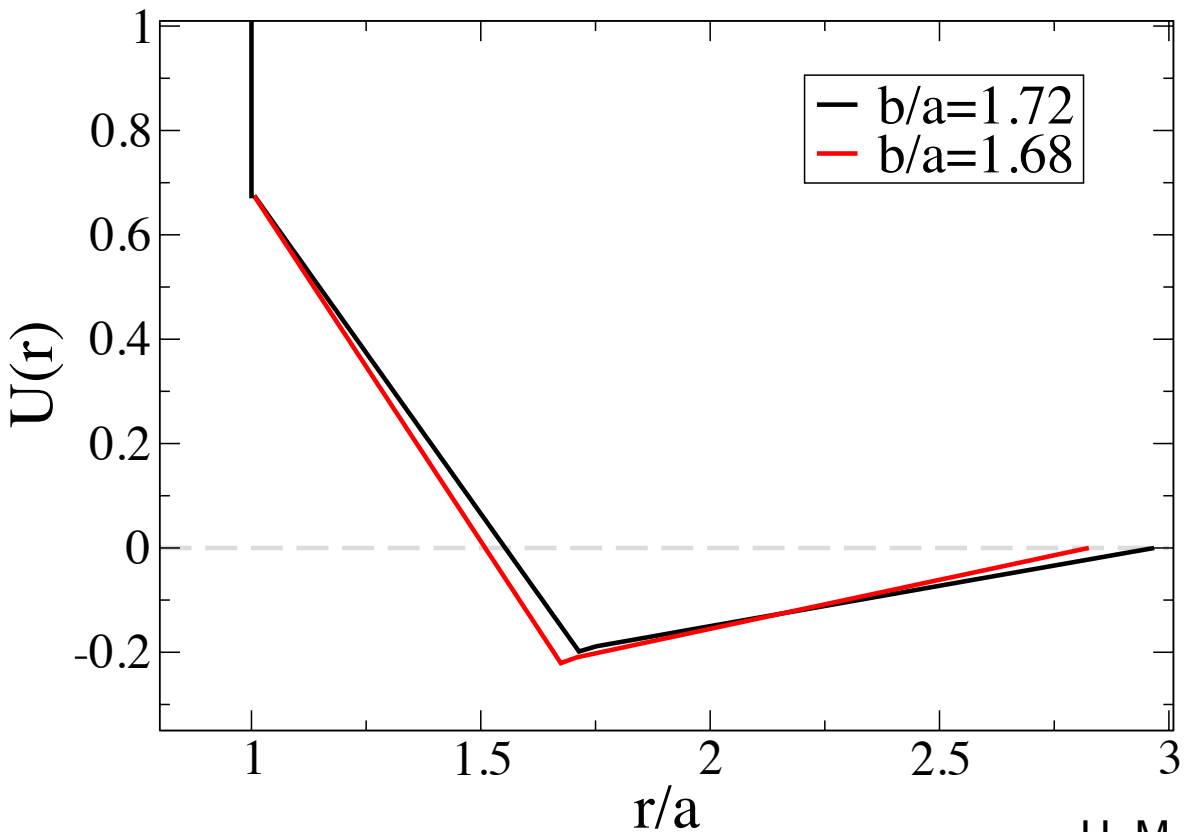

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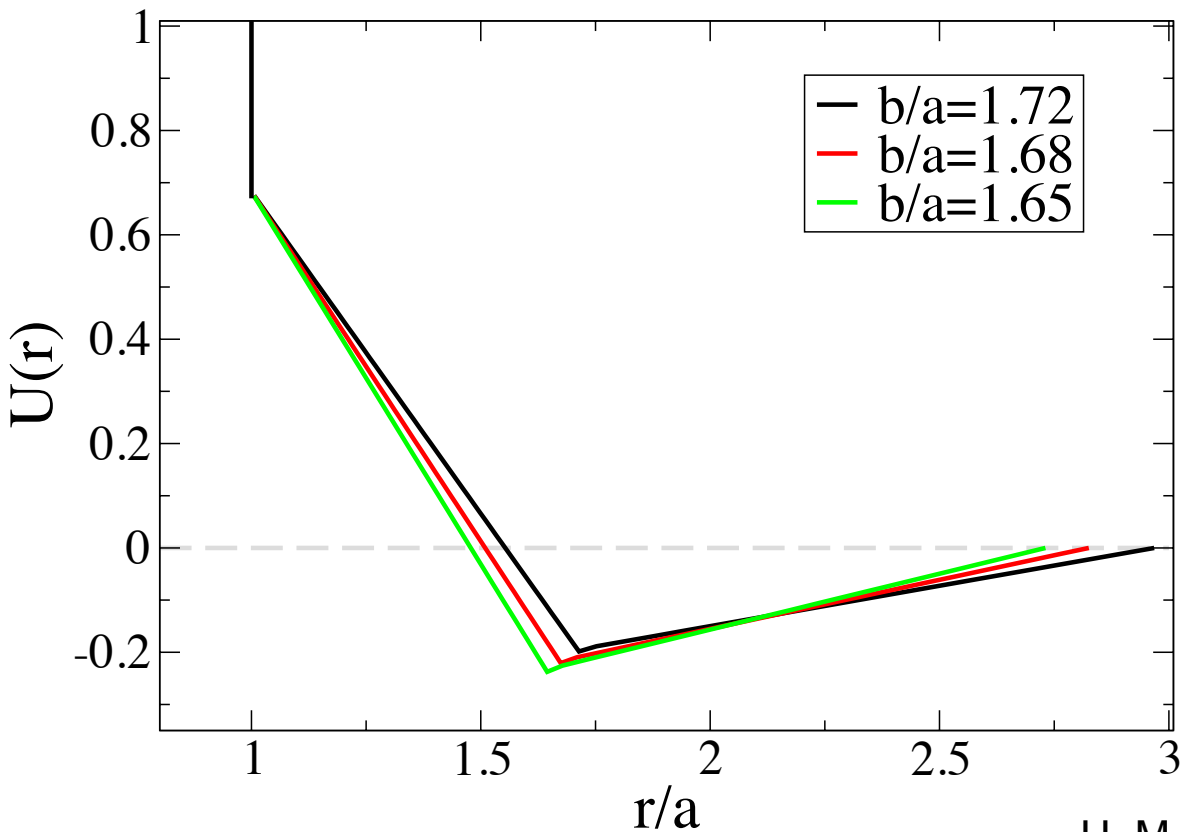

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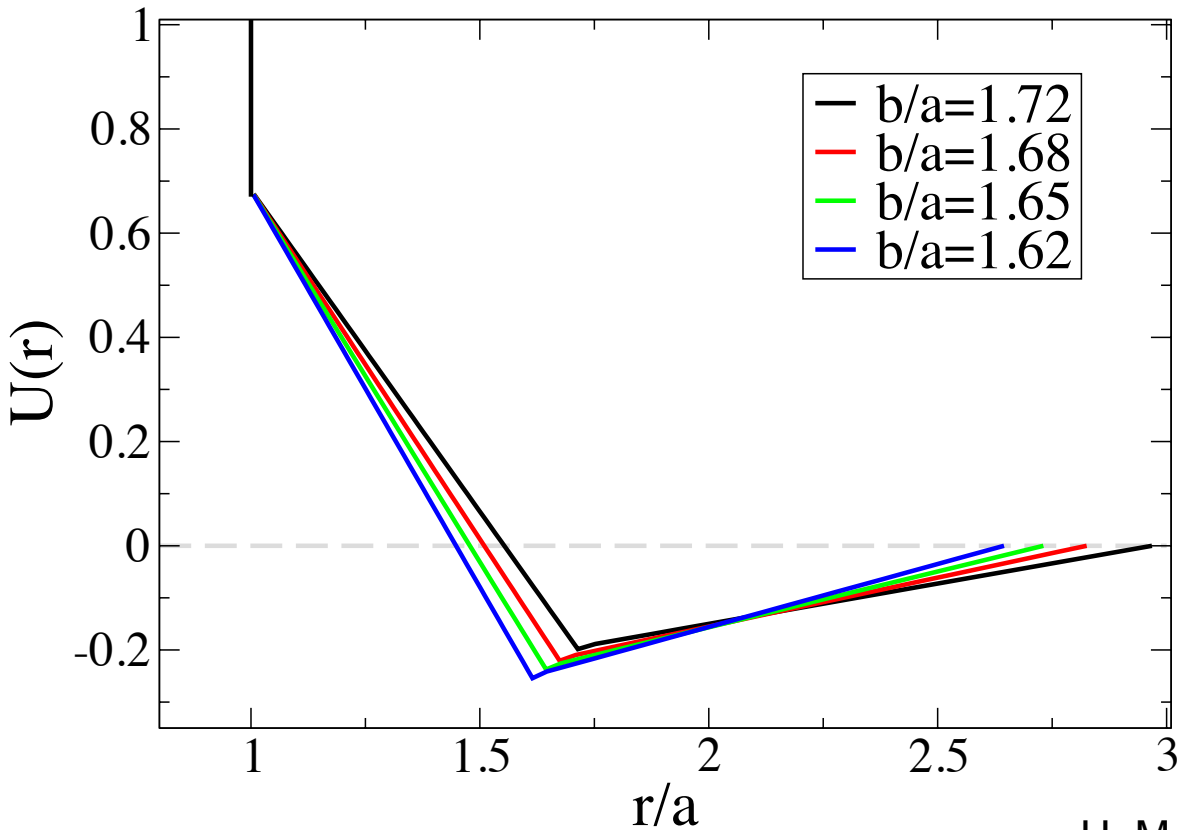

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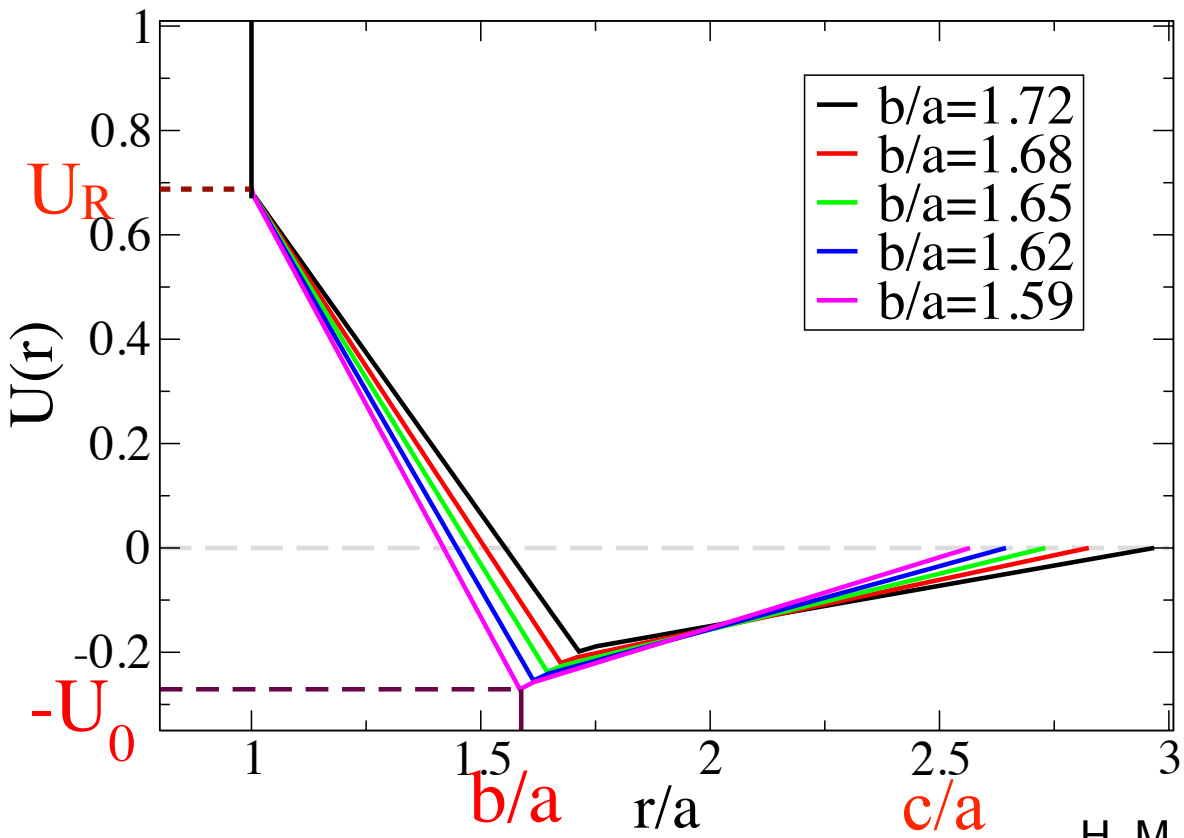

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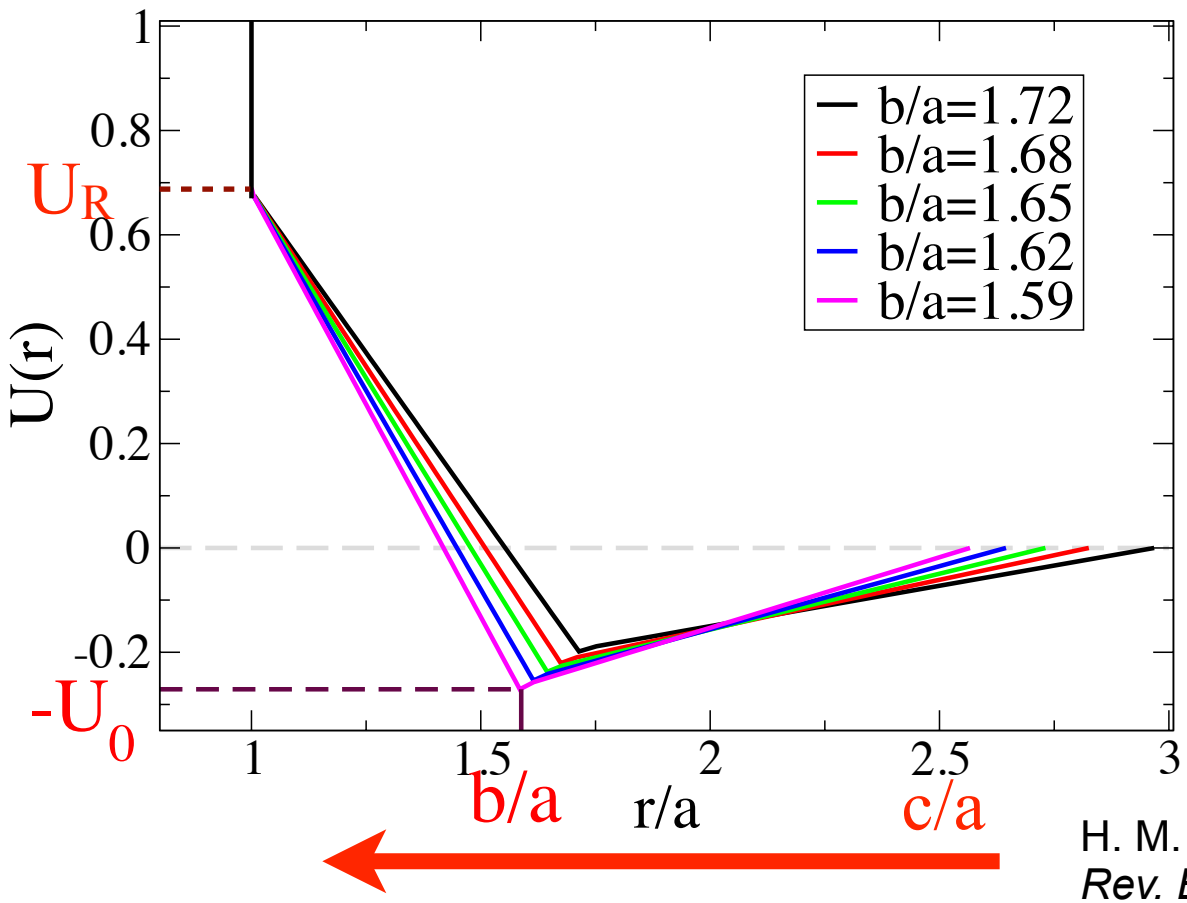

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Modified Jagla:

- Decrease b/a and c/a
- Increase magnitude of U_0
- Keeping U_R and a=1 constant

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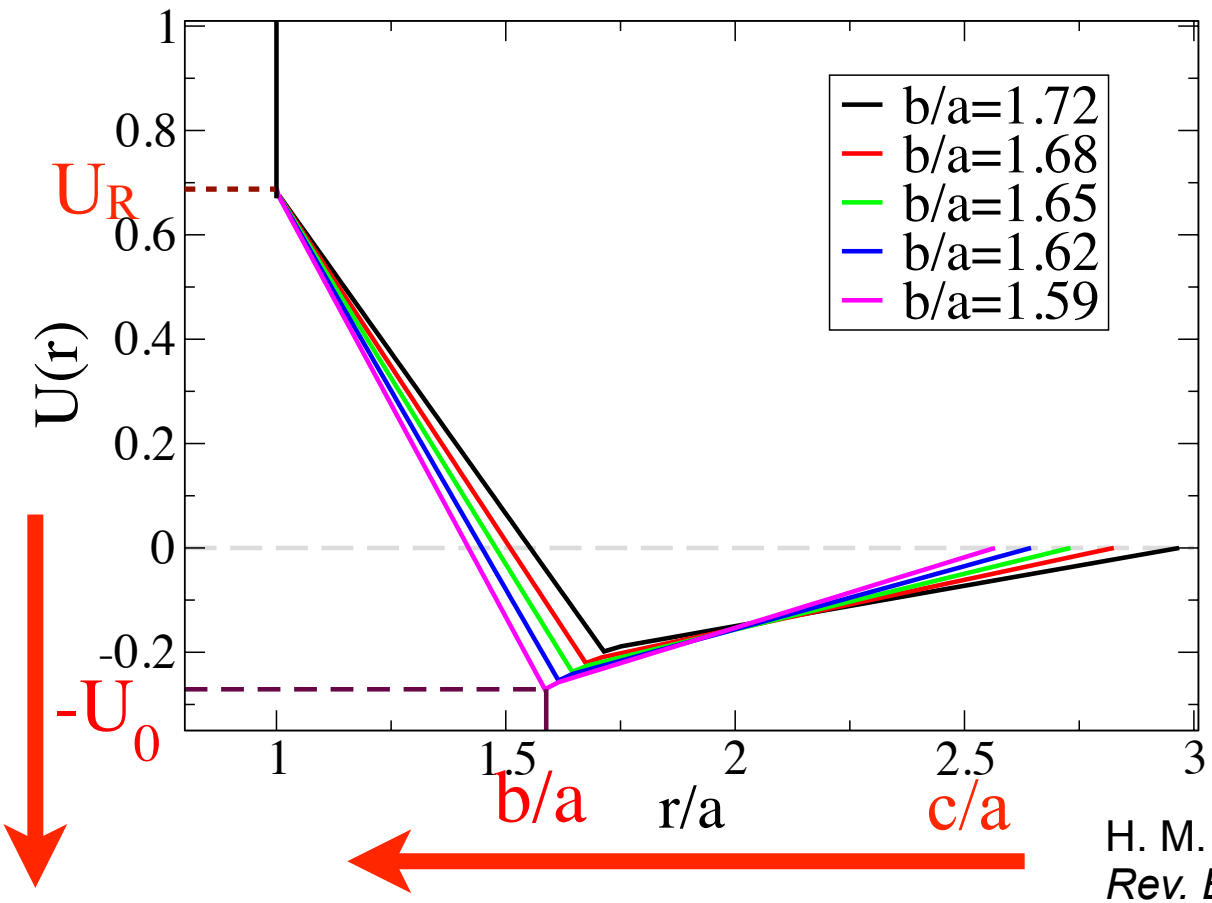

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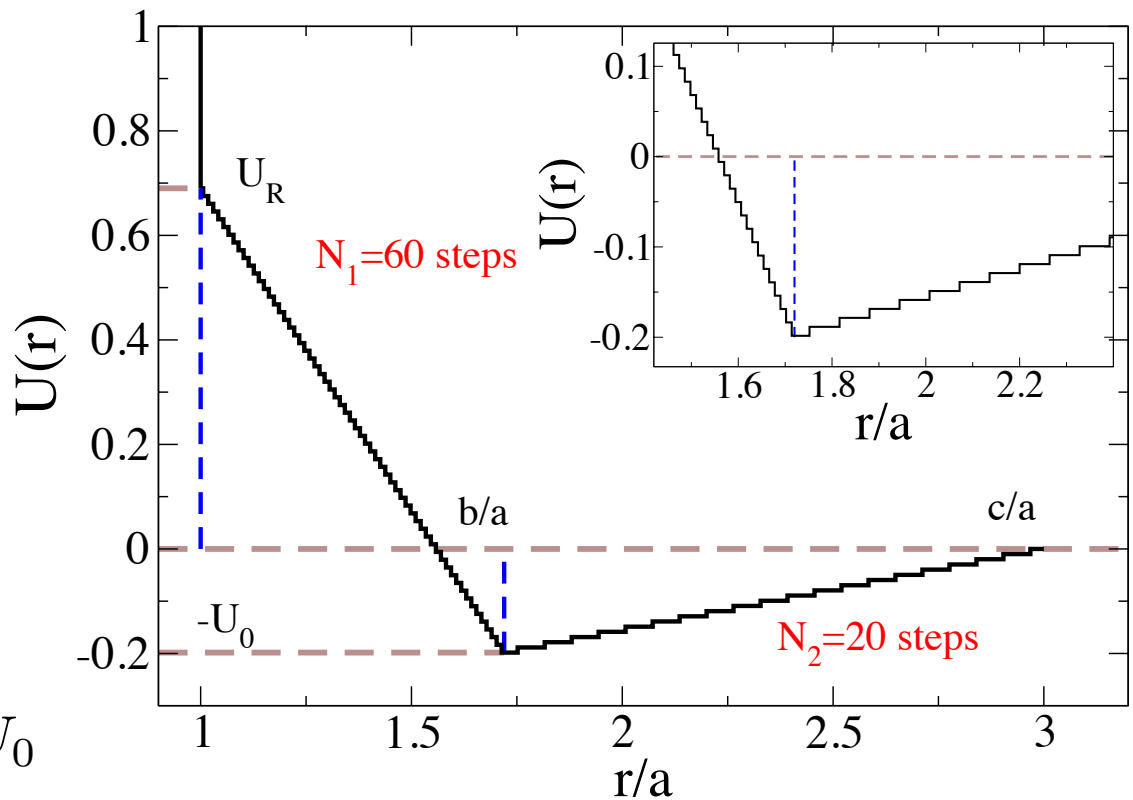
Method: Discrete Molecular Dynamics (DMD)

- 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:

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

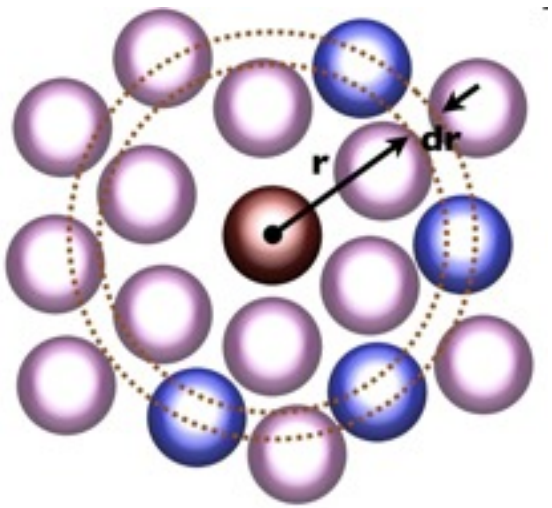
Does the system have two liquid phases?

g(r)=radial distribution function

g(r) is the probability of finding particles at a given distance r from another particle

Normalization:

g(r)=1 for r=∞



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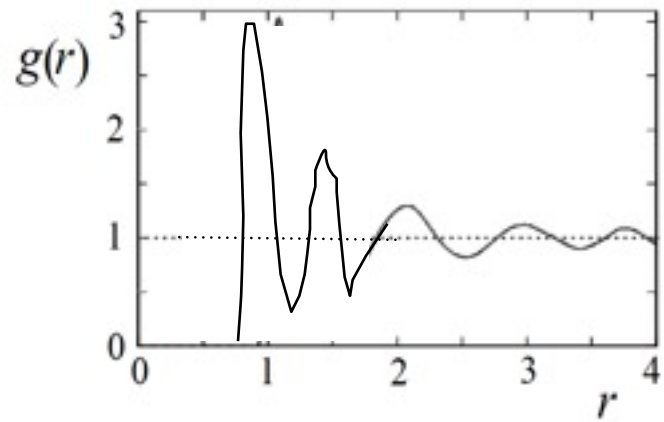

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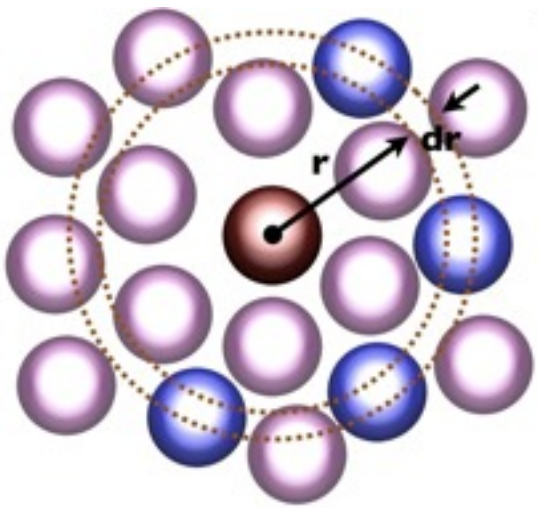

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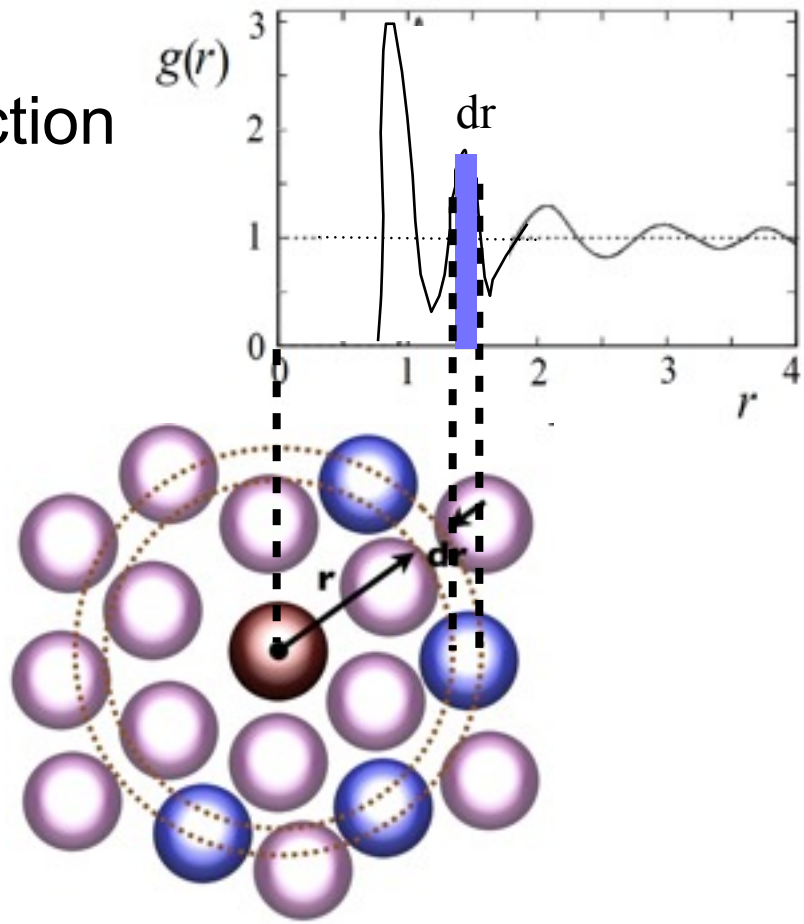

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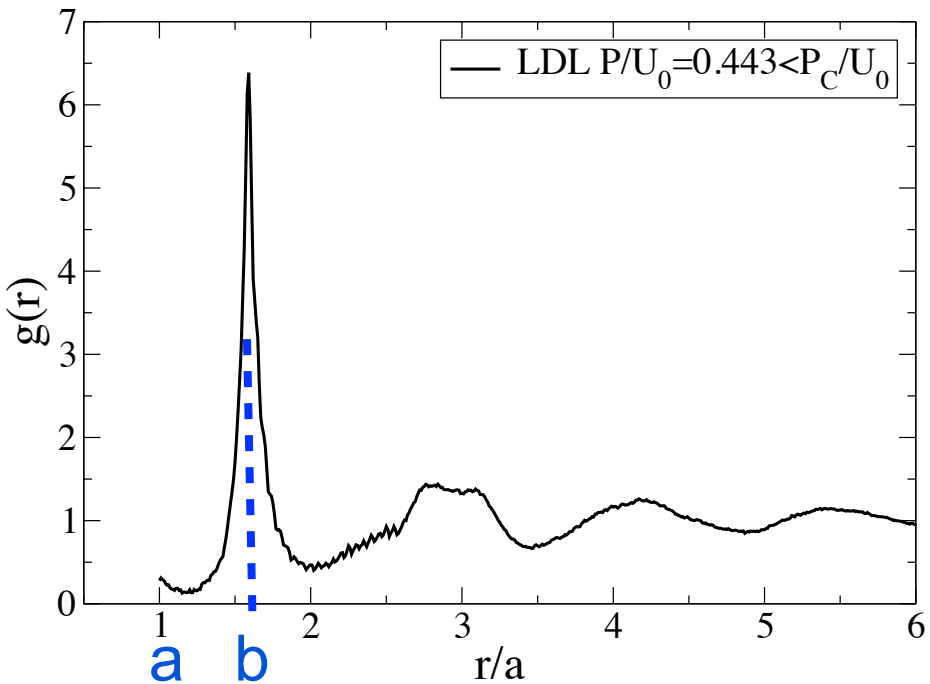
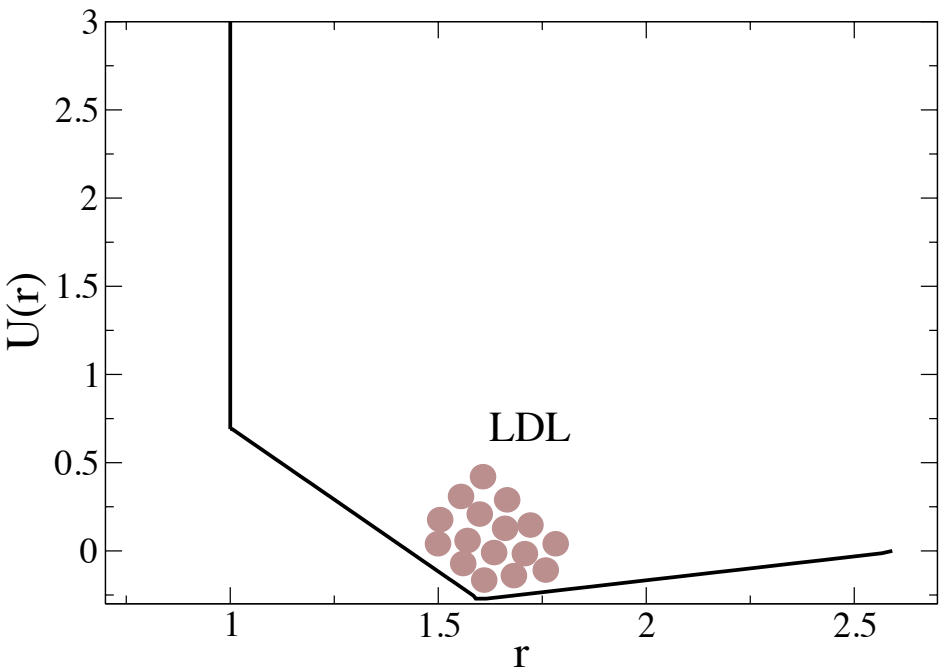
Two Liquid Phases: LDL vs. HDL



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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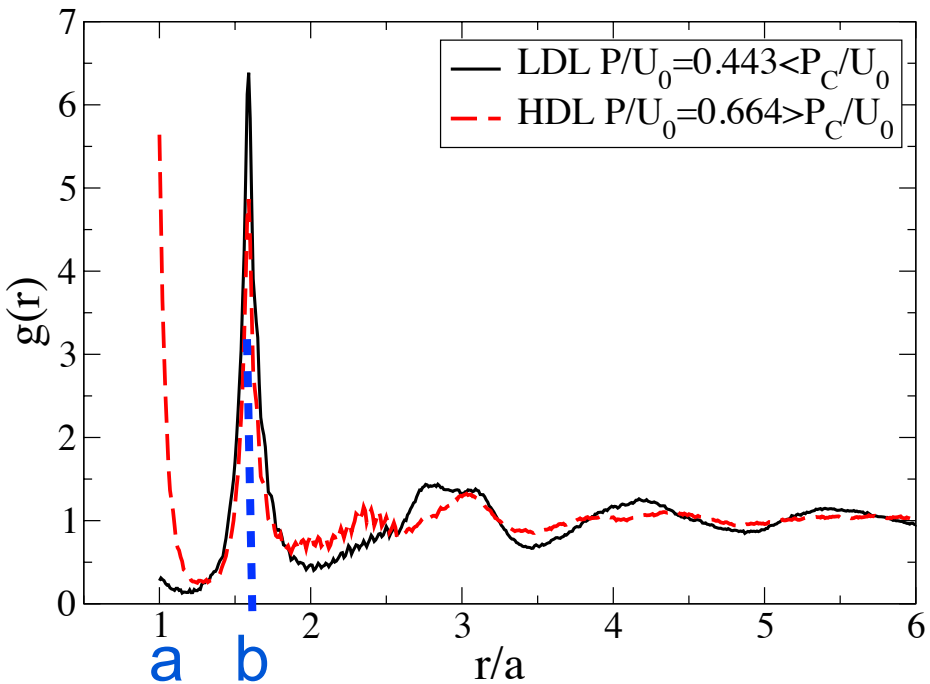

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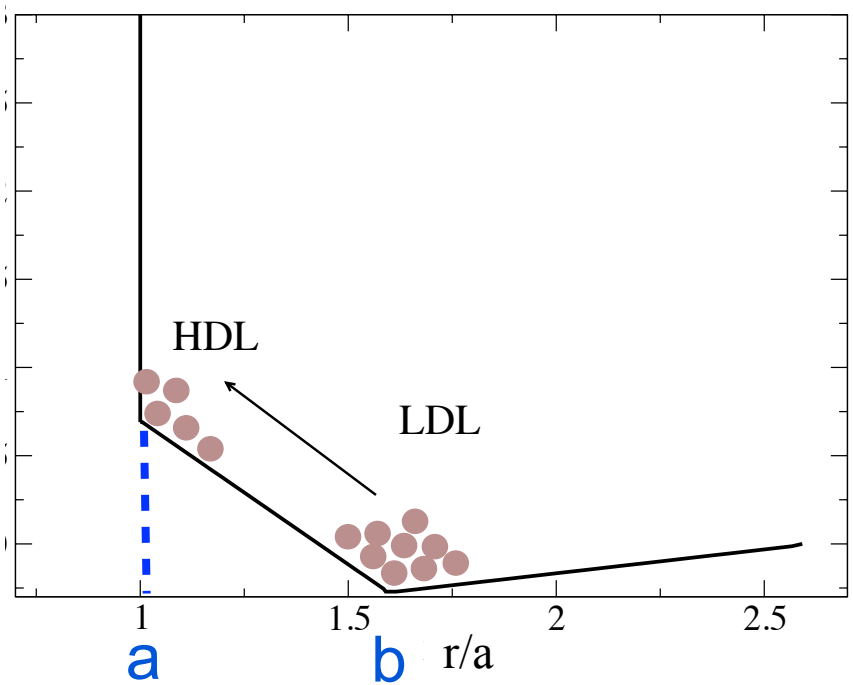

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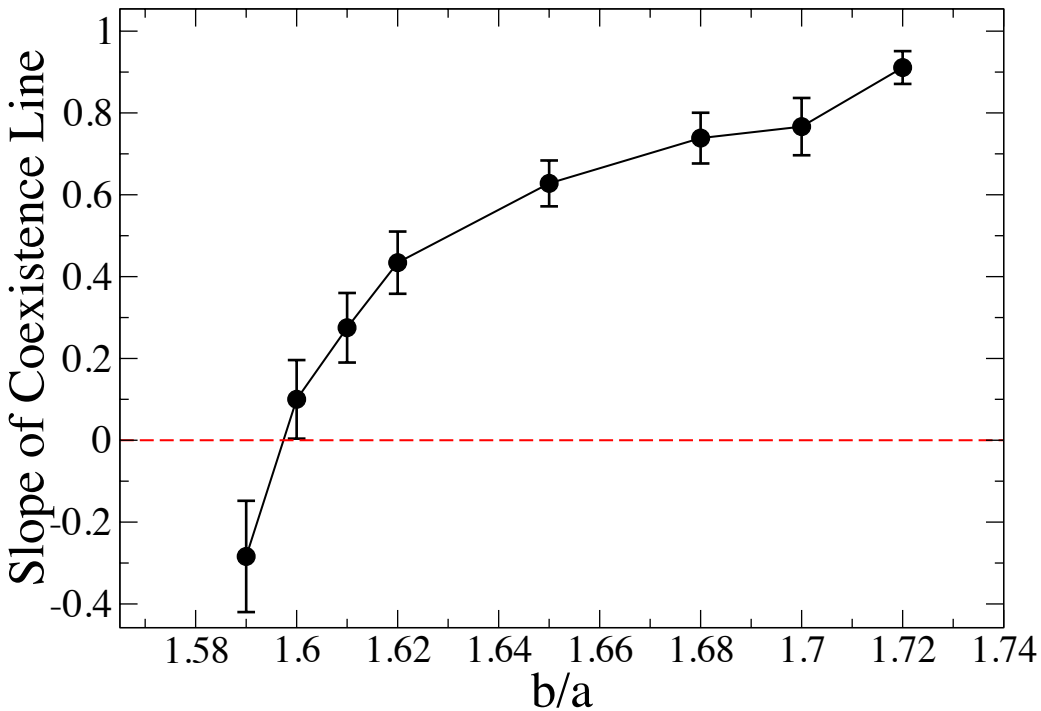

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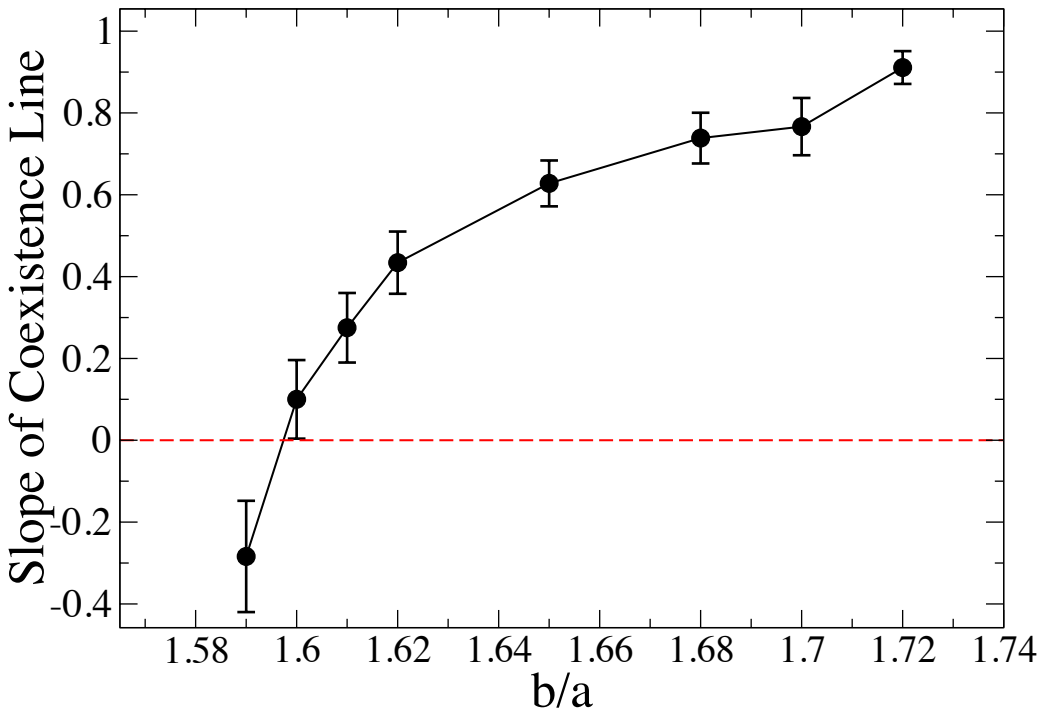

The slope of the coexistence line changes from positive to negative, as we decrease the value of b/a to 1.59.

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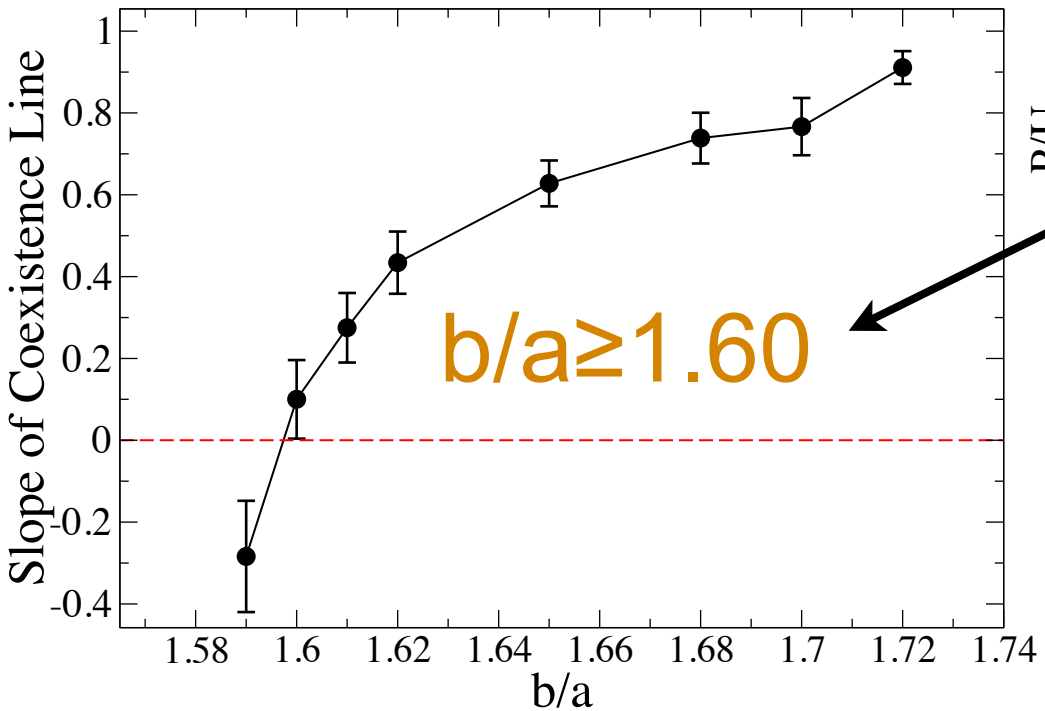

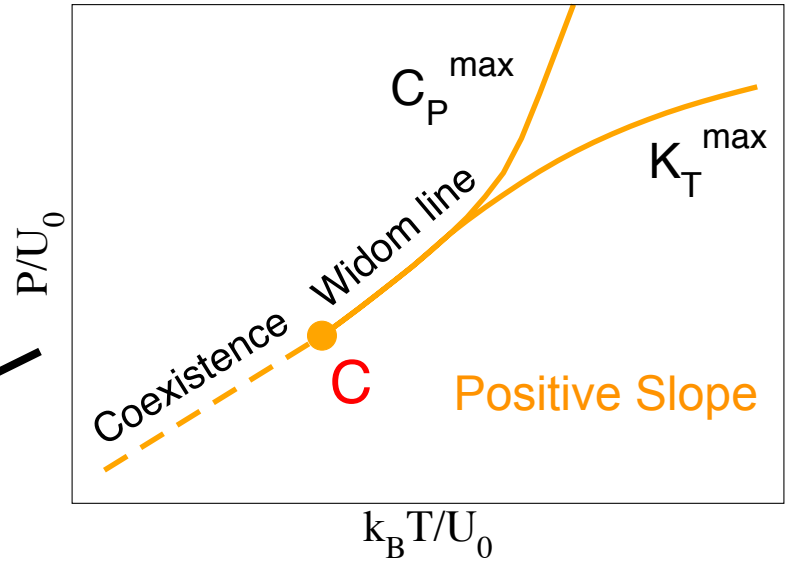

The slope of the coexistence line changes from positive to negative, as we decrease the value of b/a to 1.59.

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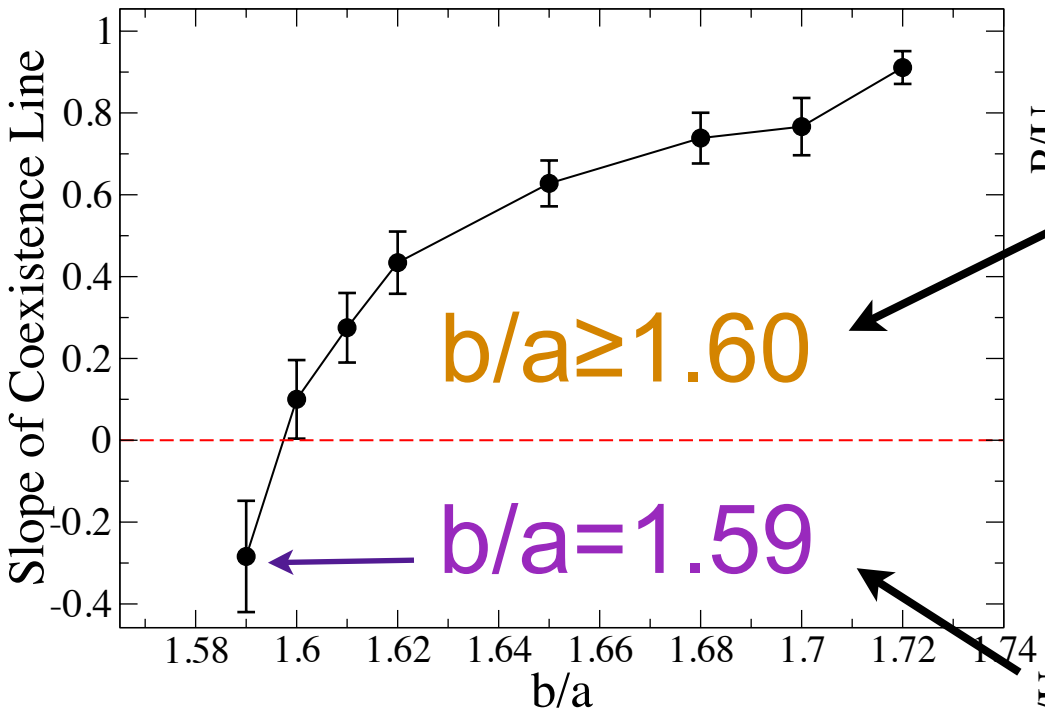

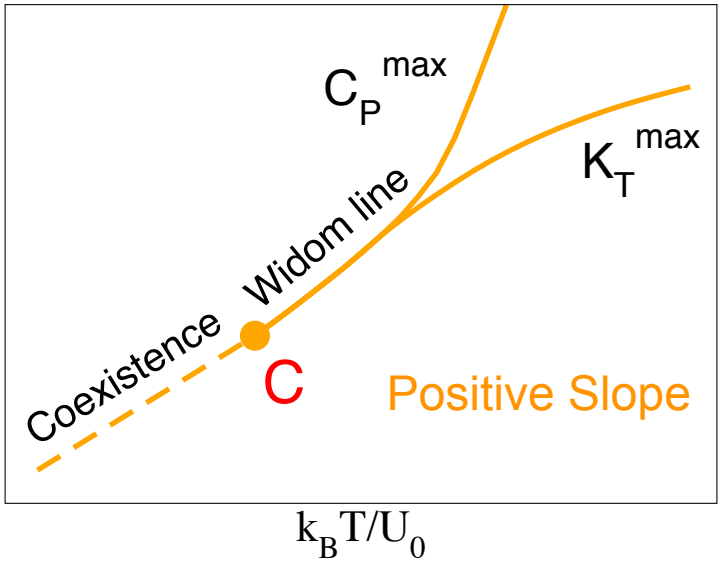

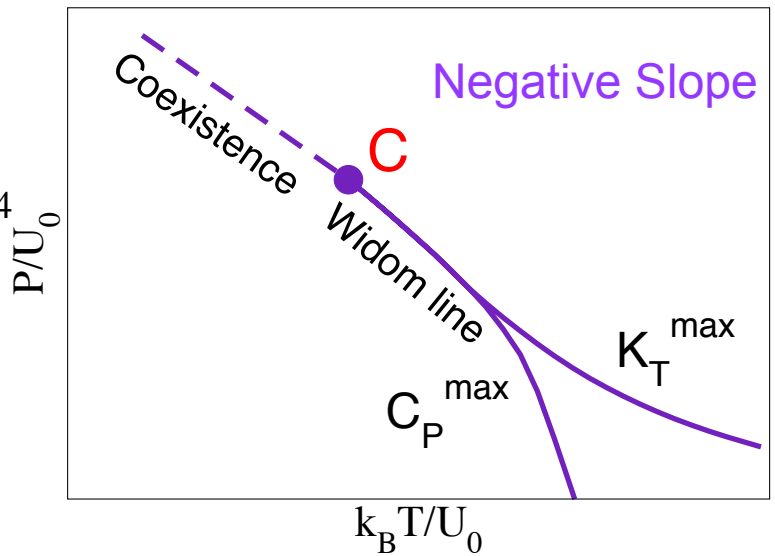

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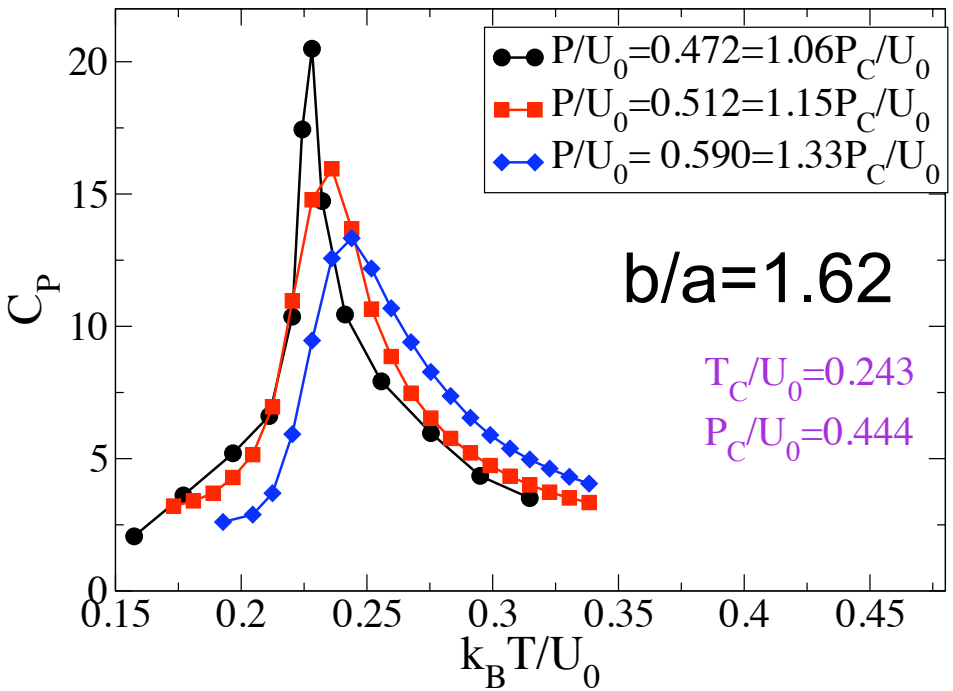
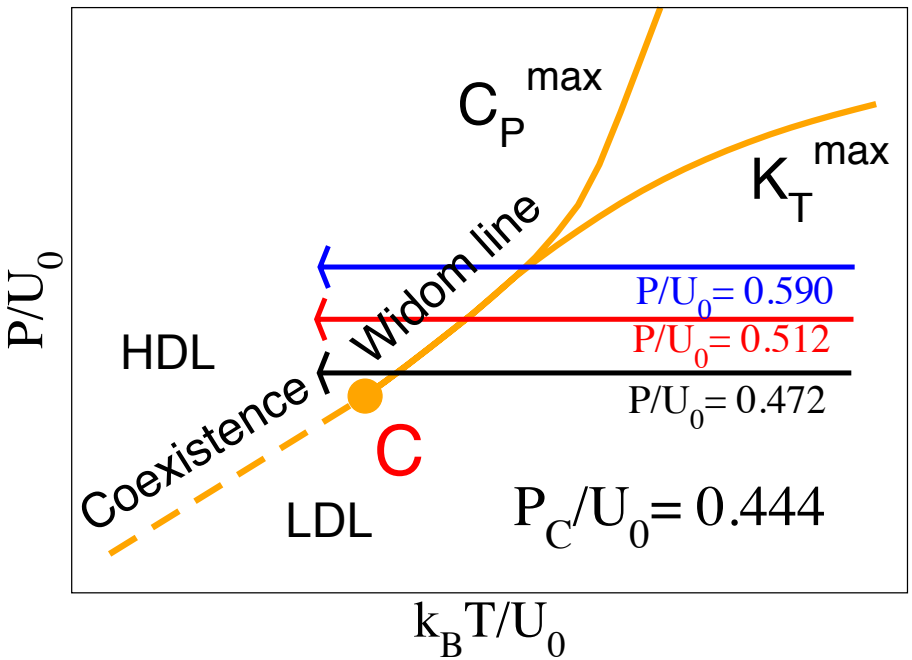
b/a≥1.60: Specific Heat C_P Max.





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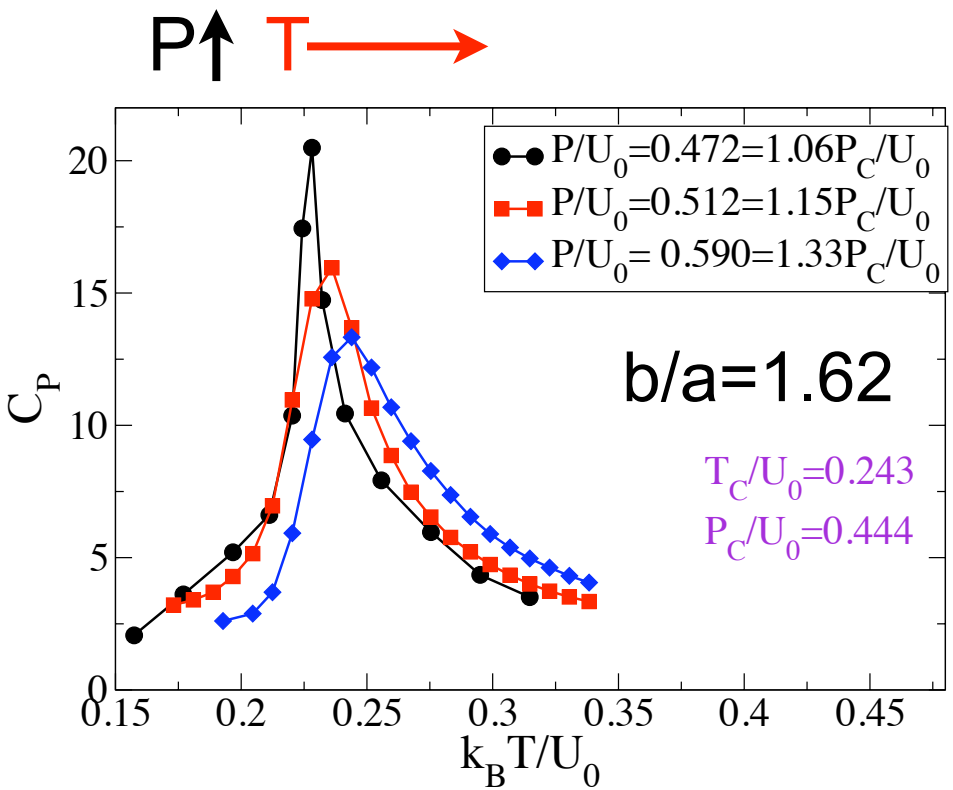

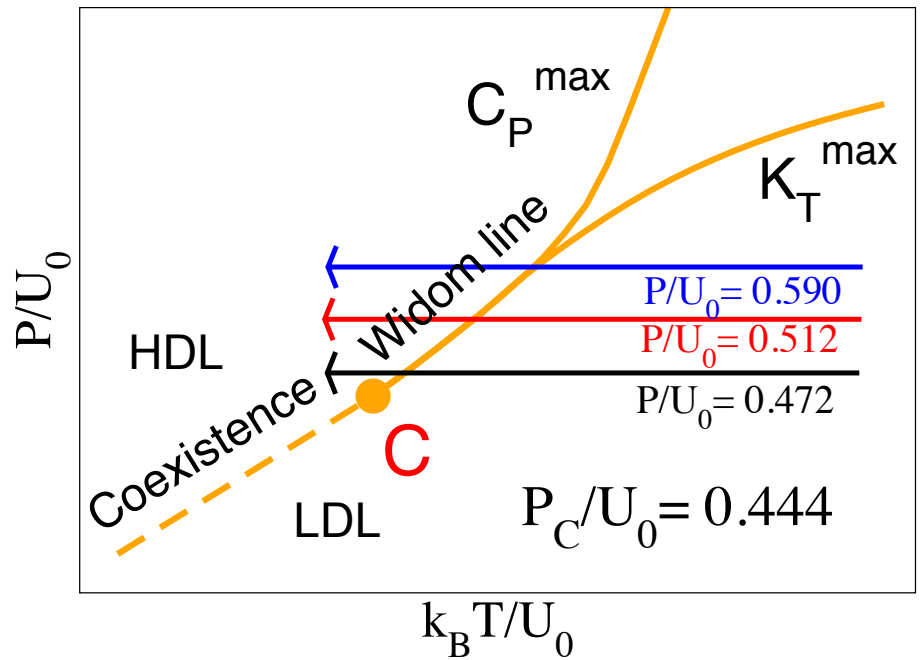

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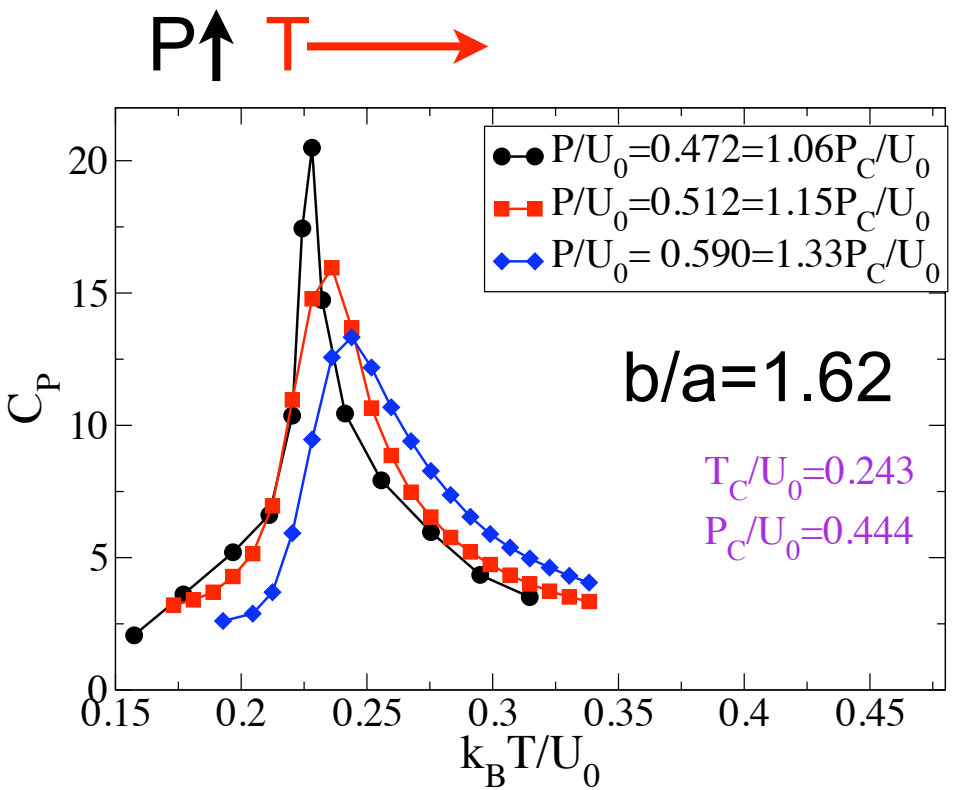

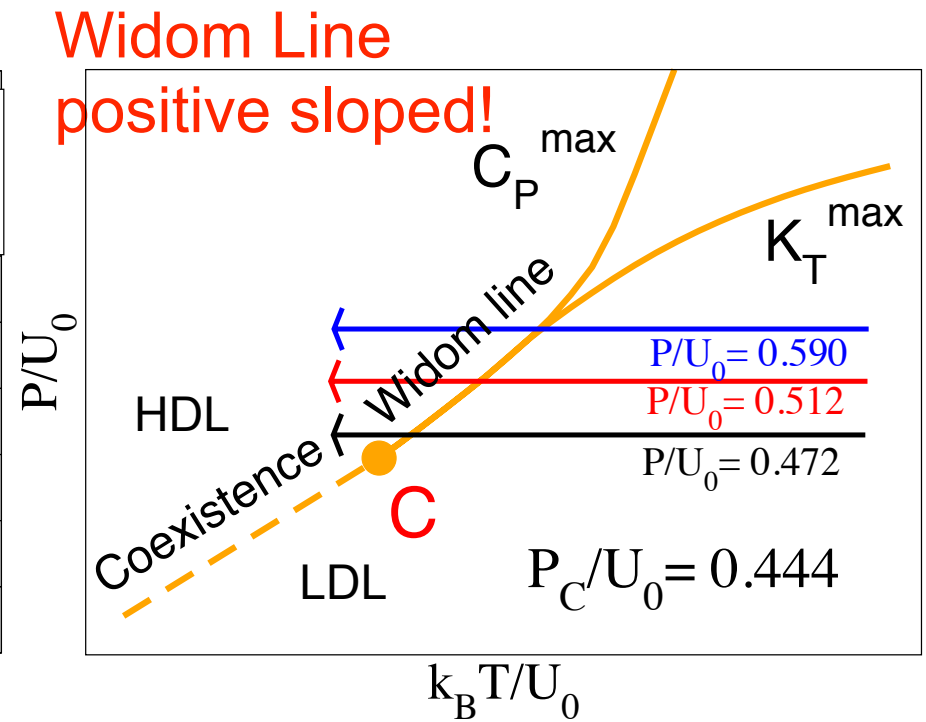

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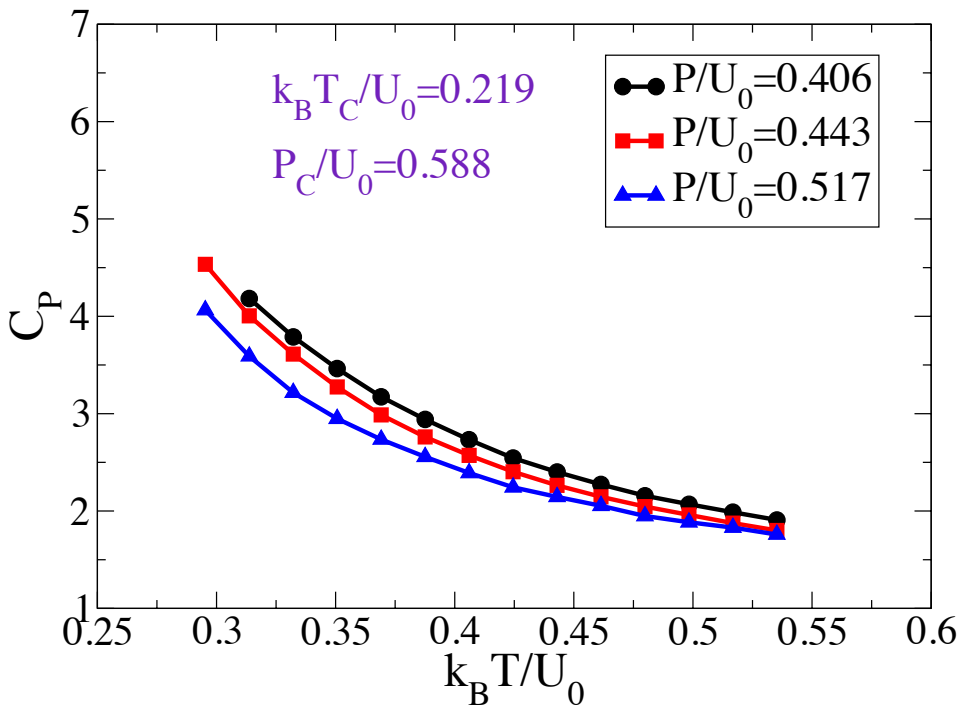

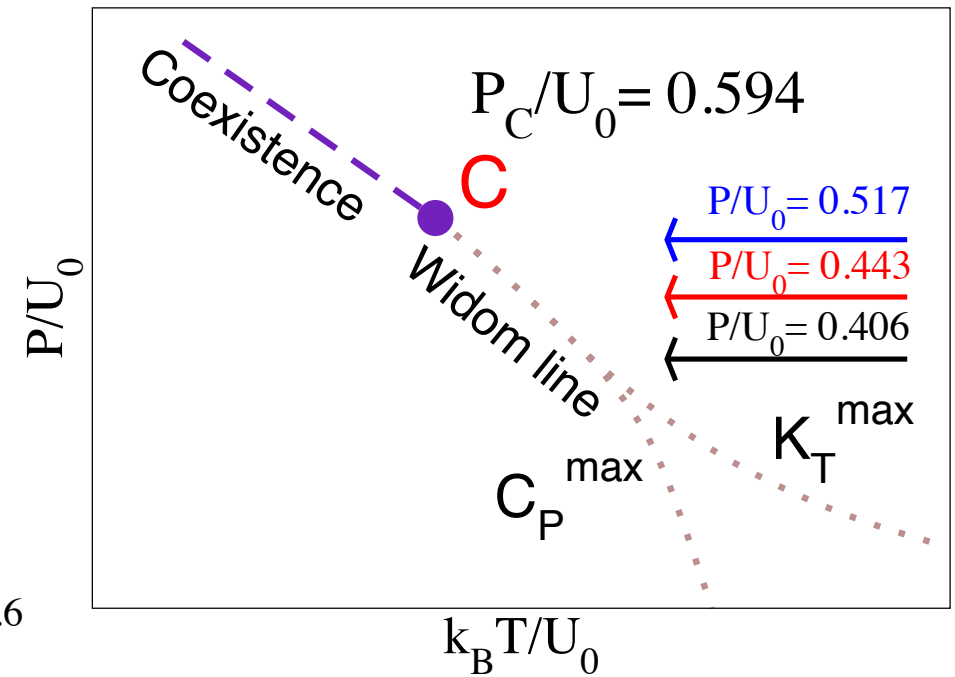

System crystallizes before reaching Cp maximum.

What can we do?

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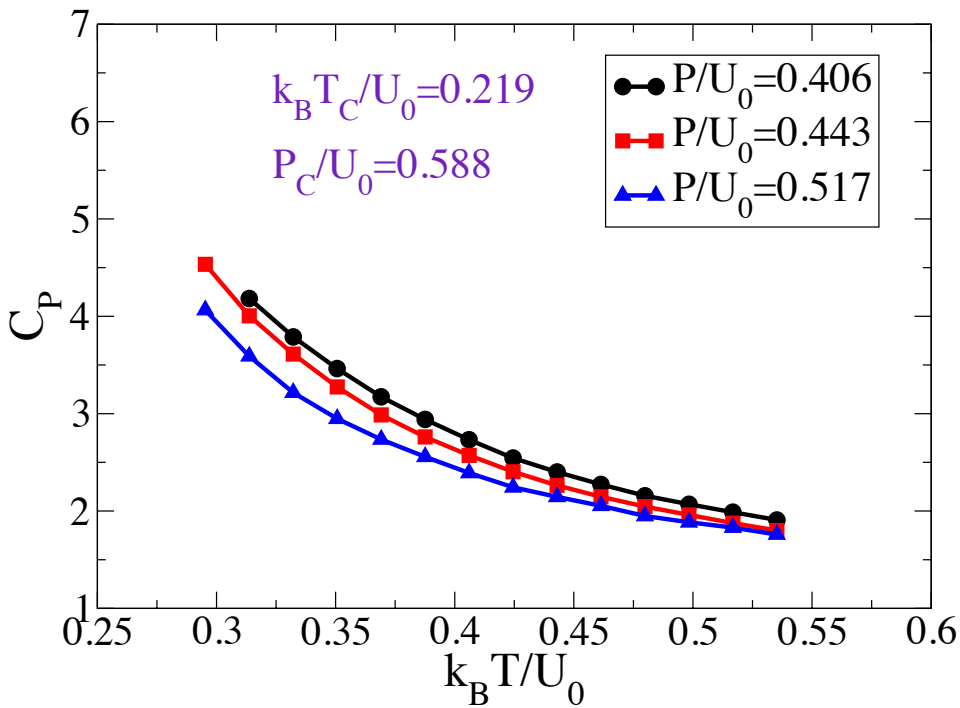

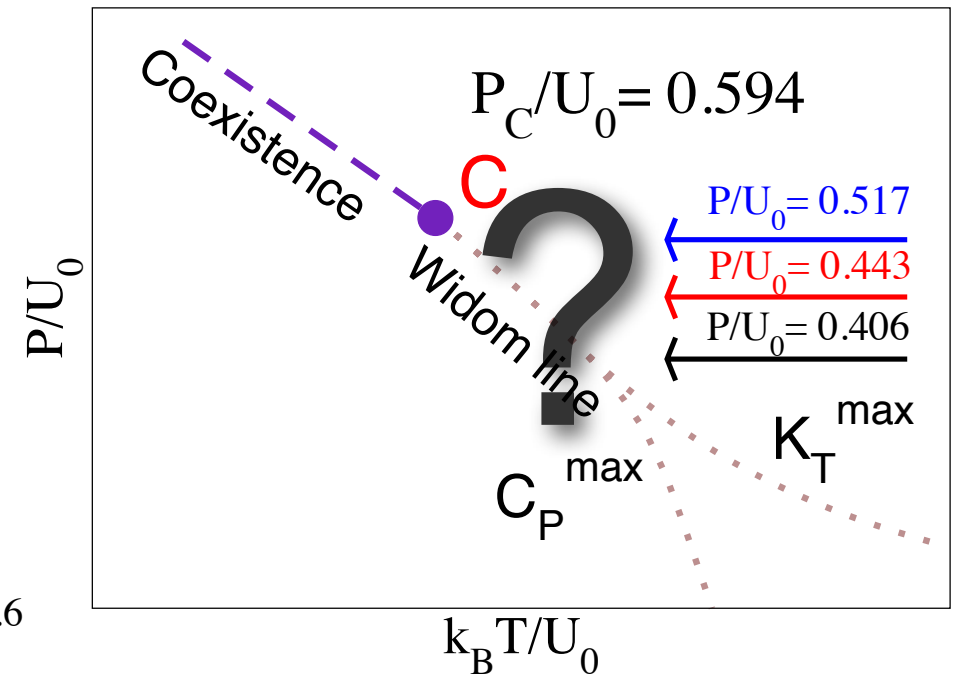

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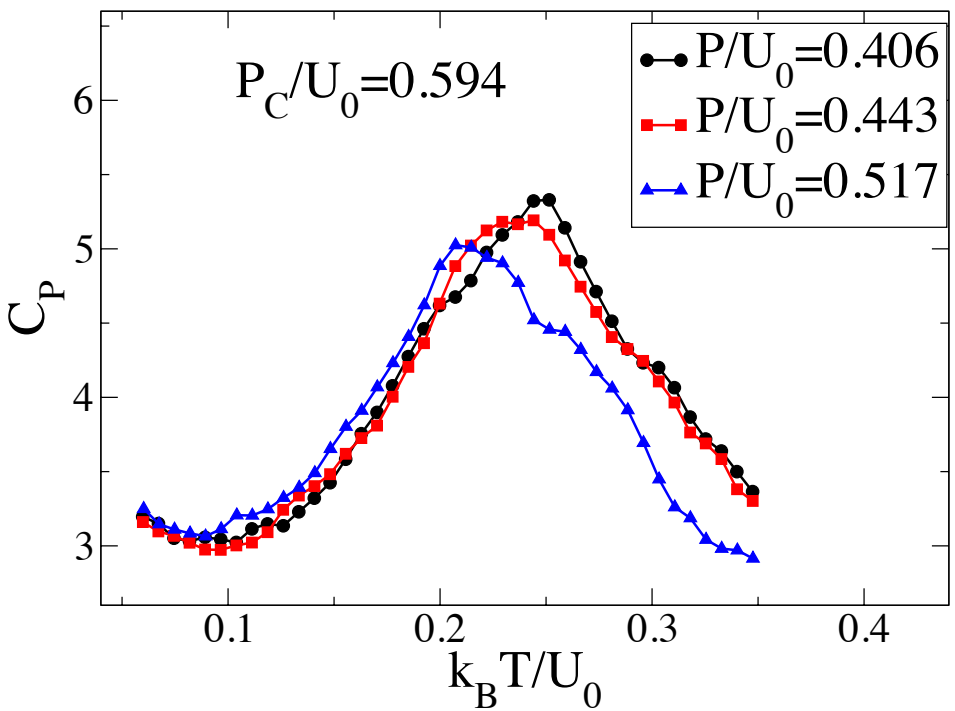
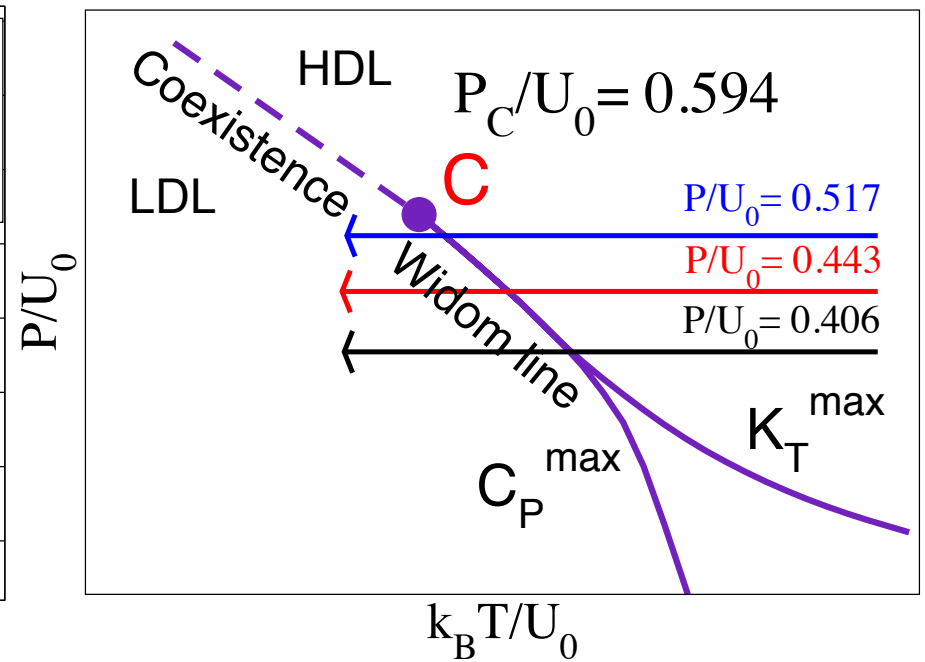
b/a=1.59: Specific Heat C_P Max. w/ fast cooling





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

Results are average of 10 independent runs.

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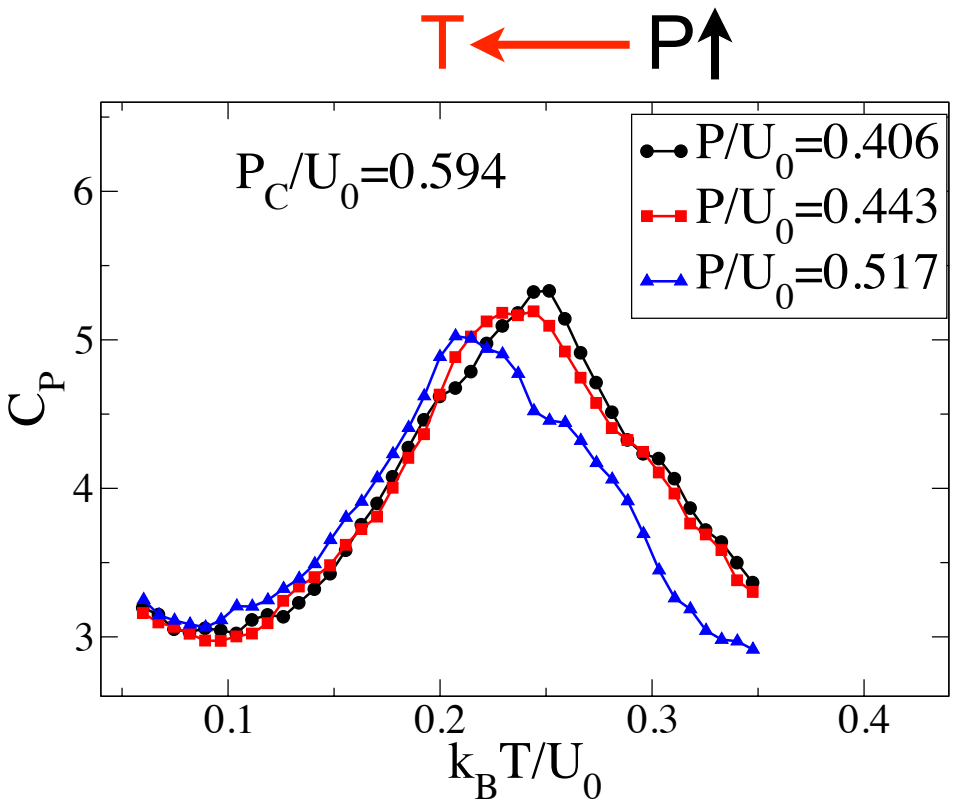

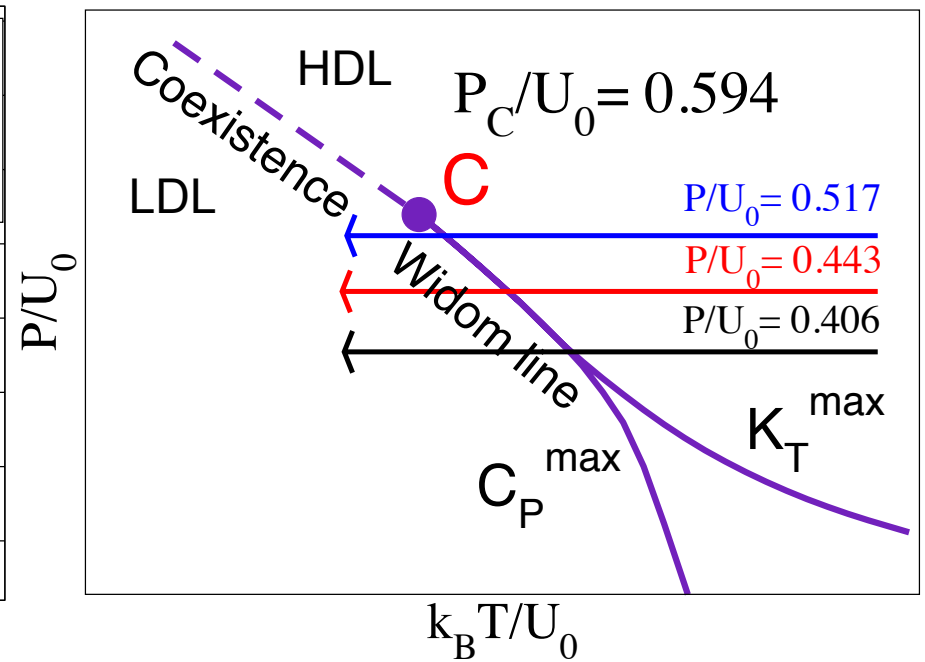

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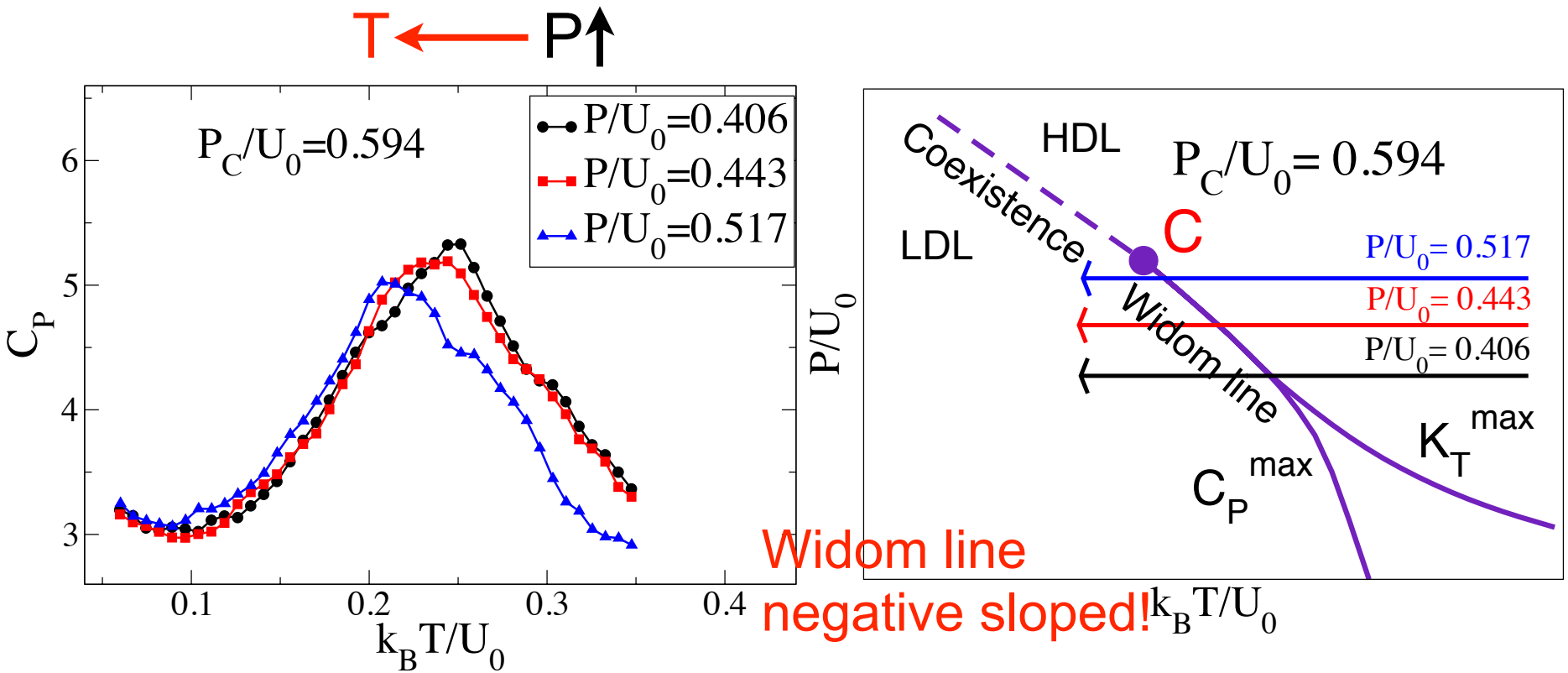

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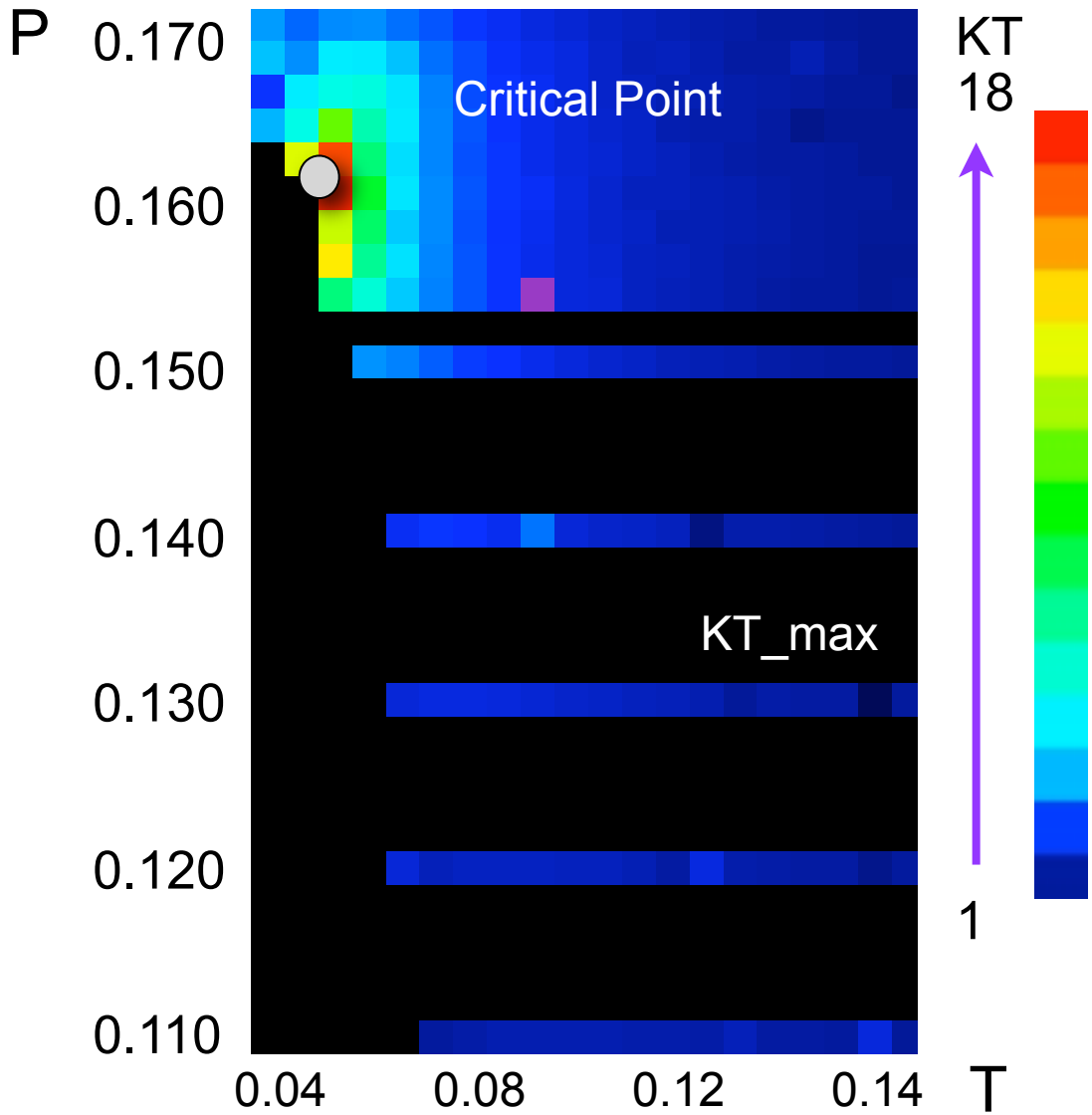

Color map shows KT max with negative slope.

20

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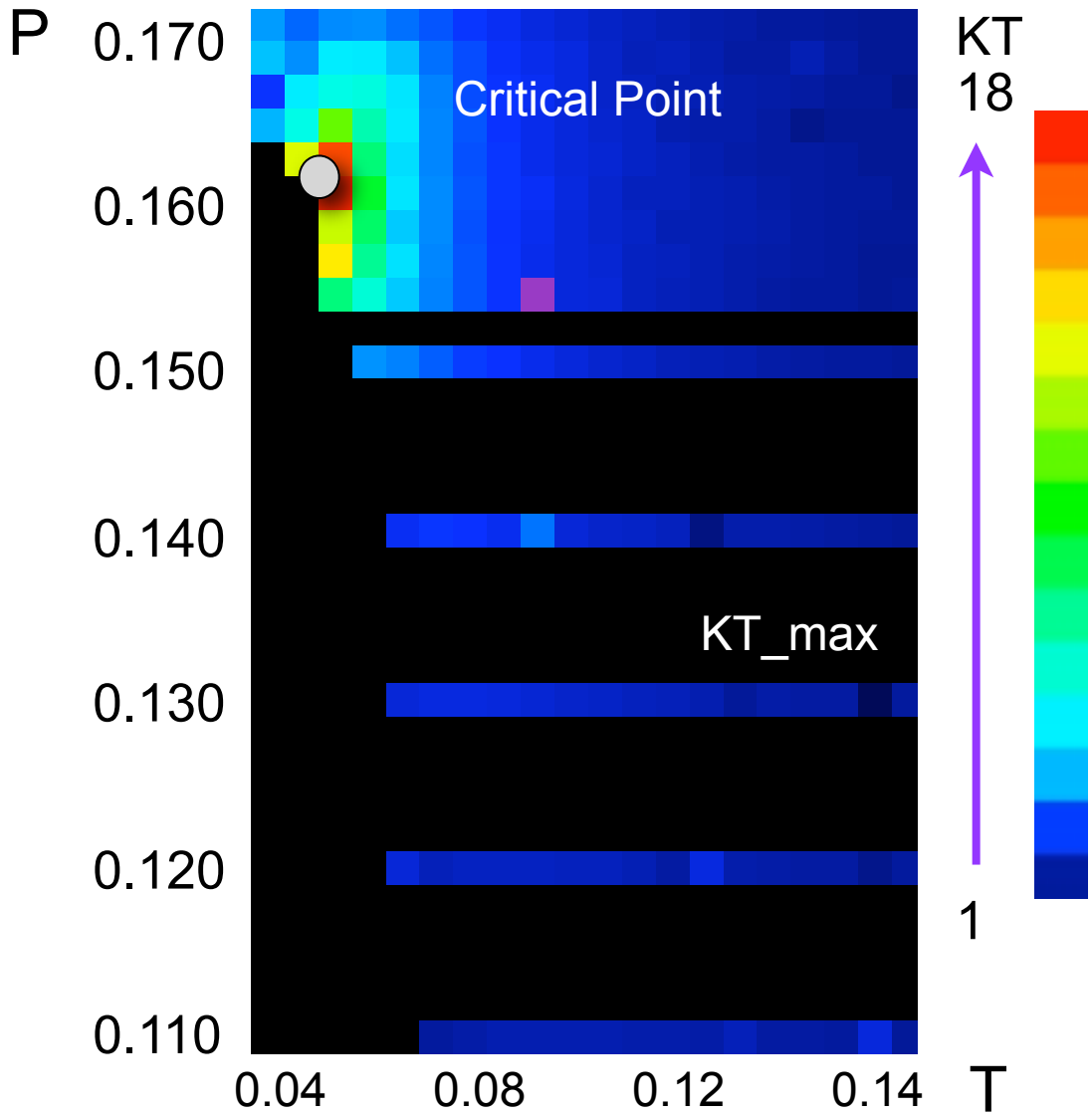

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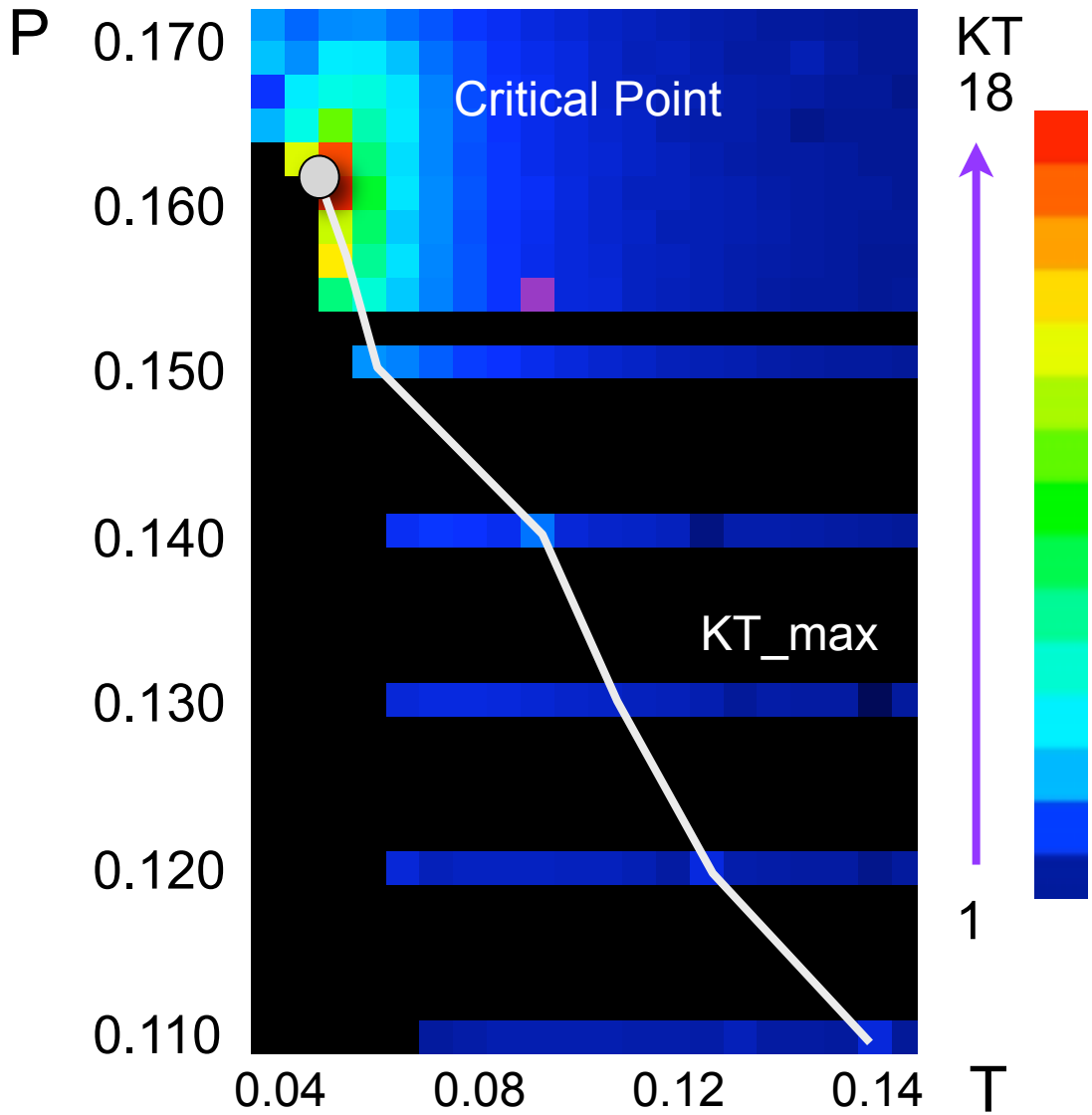

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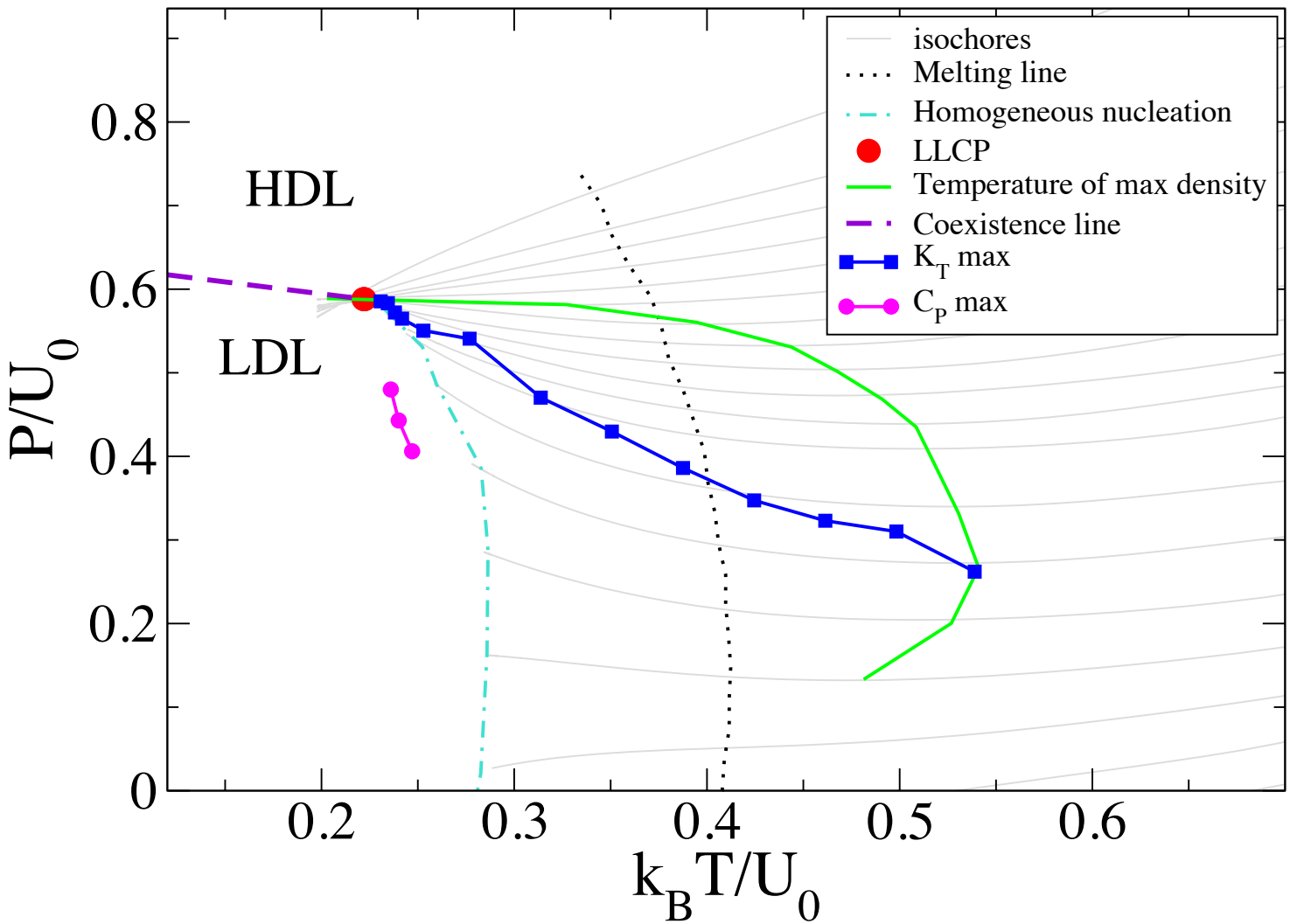
b/a=1.59: Phase Diagram and Anomalies



21

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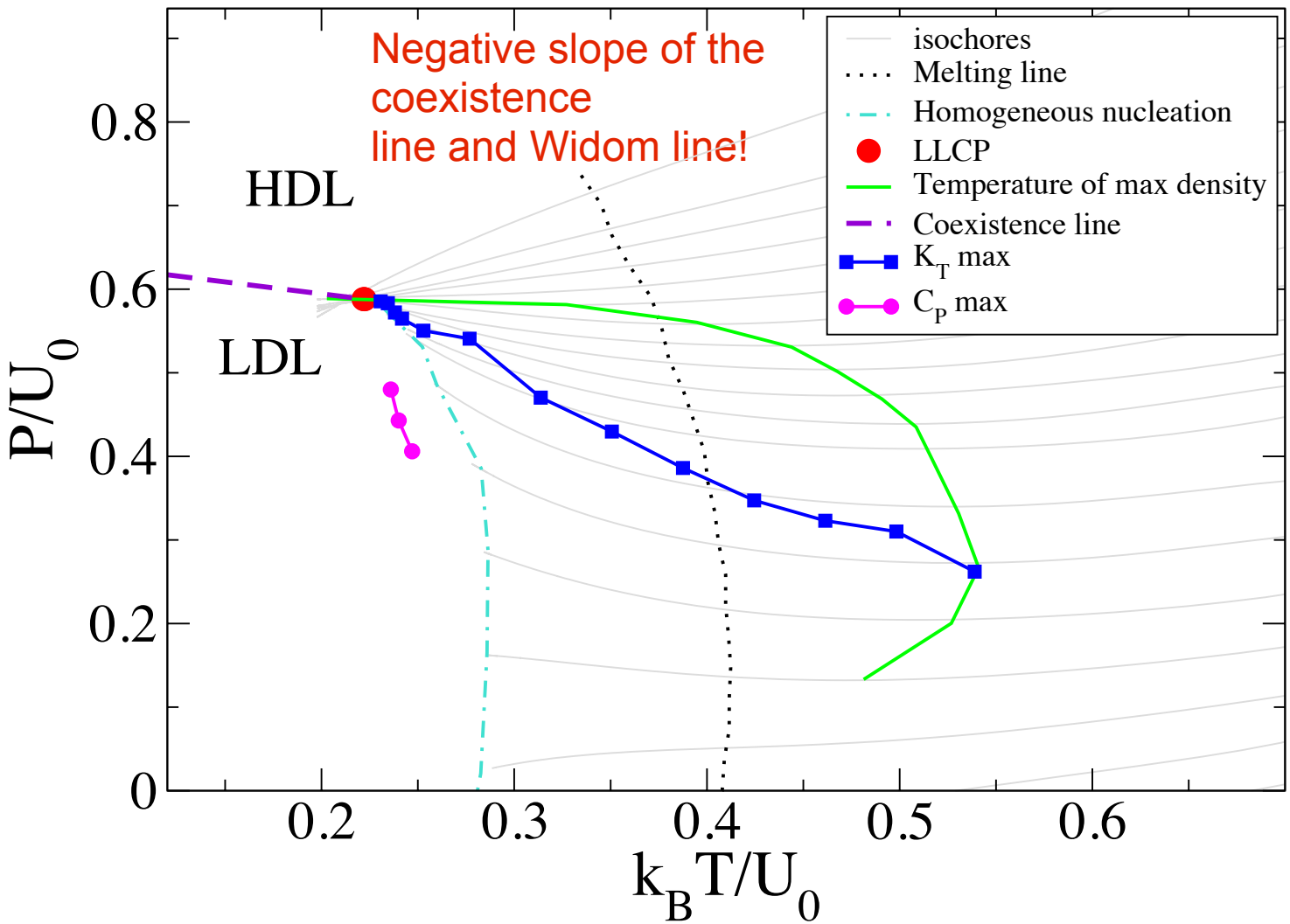

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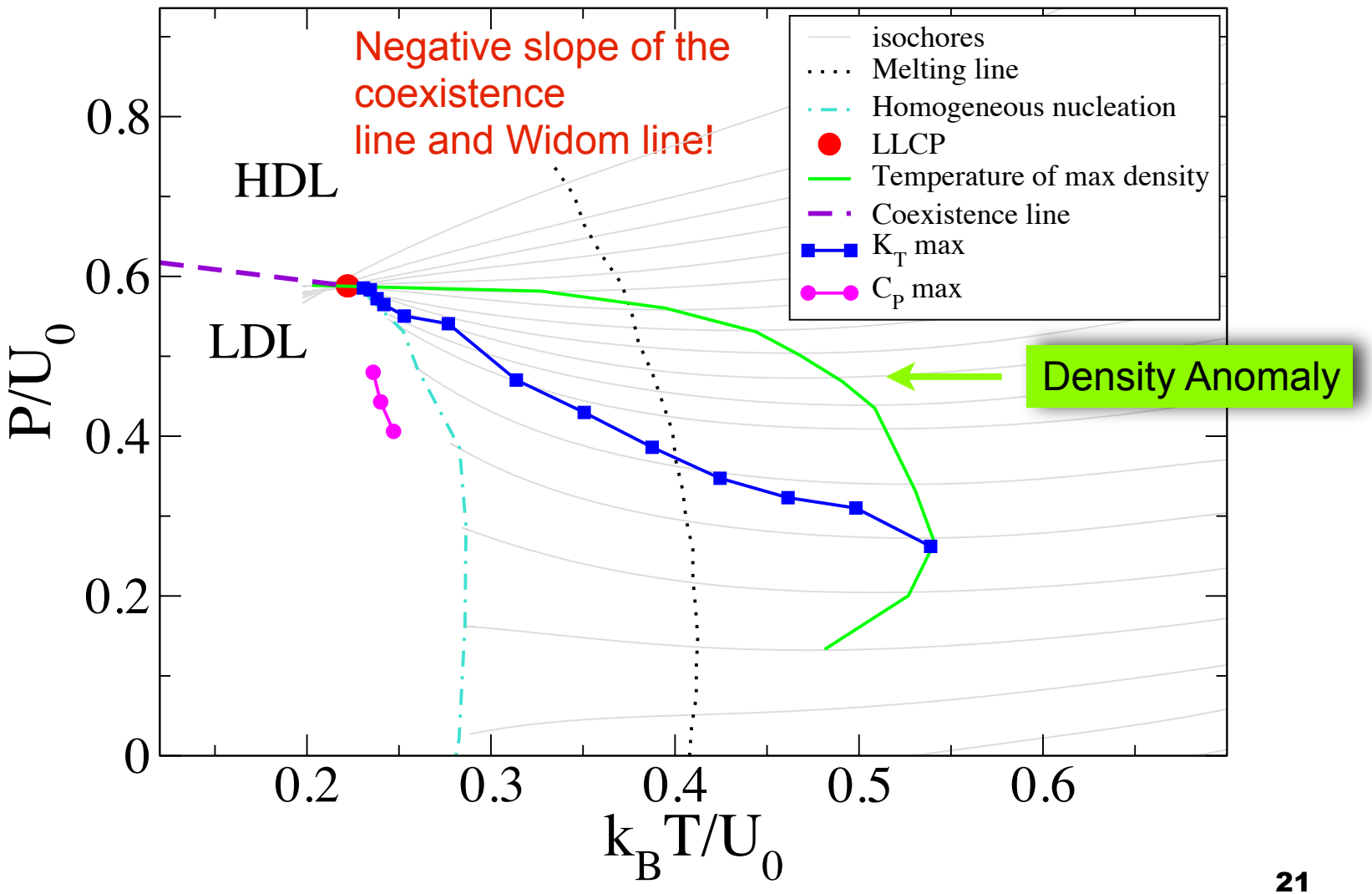

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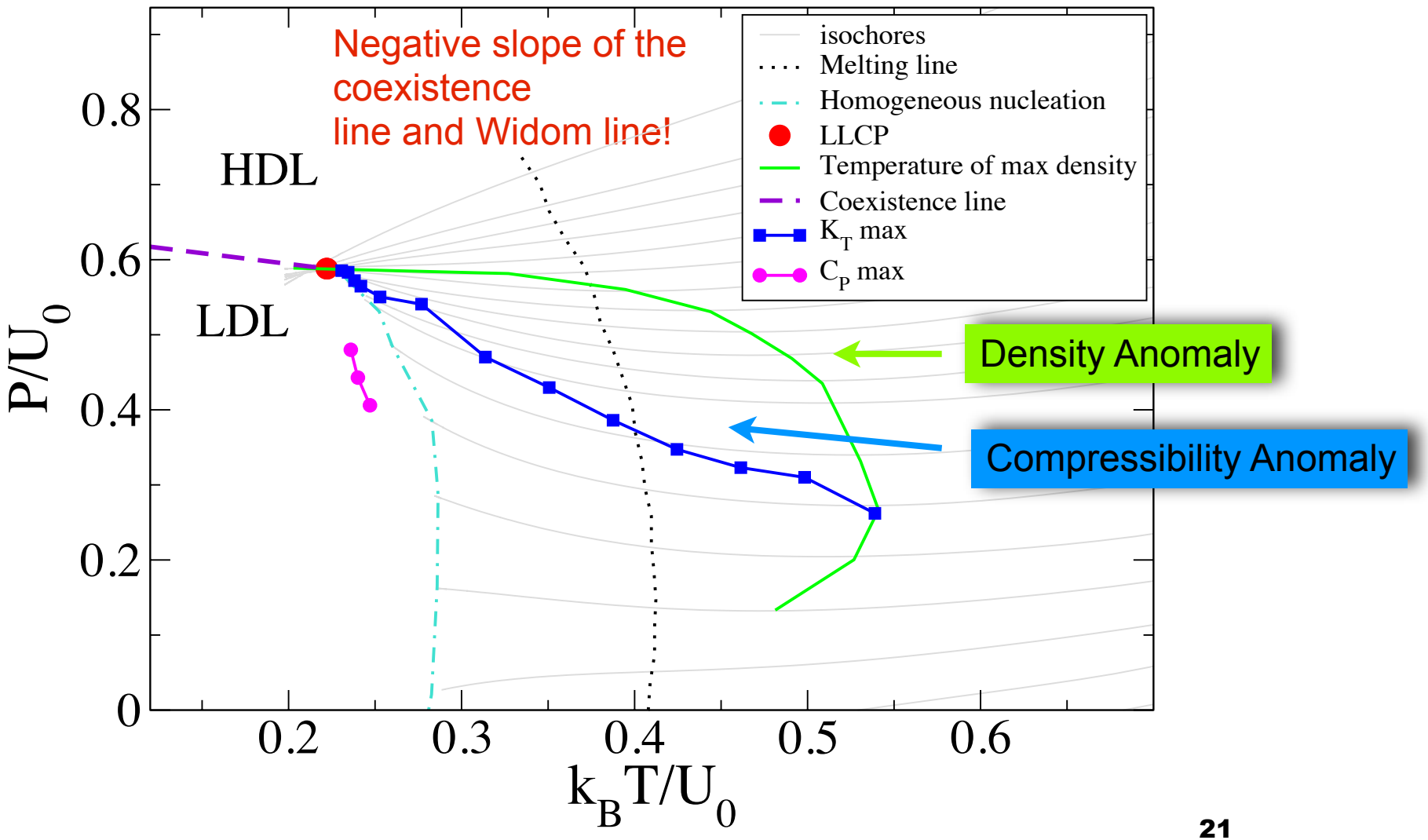

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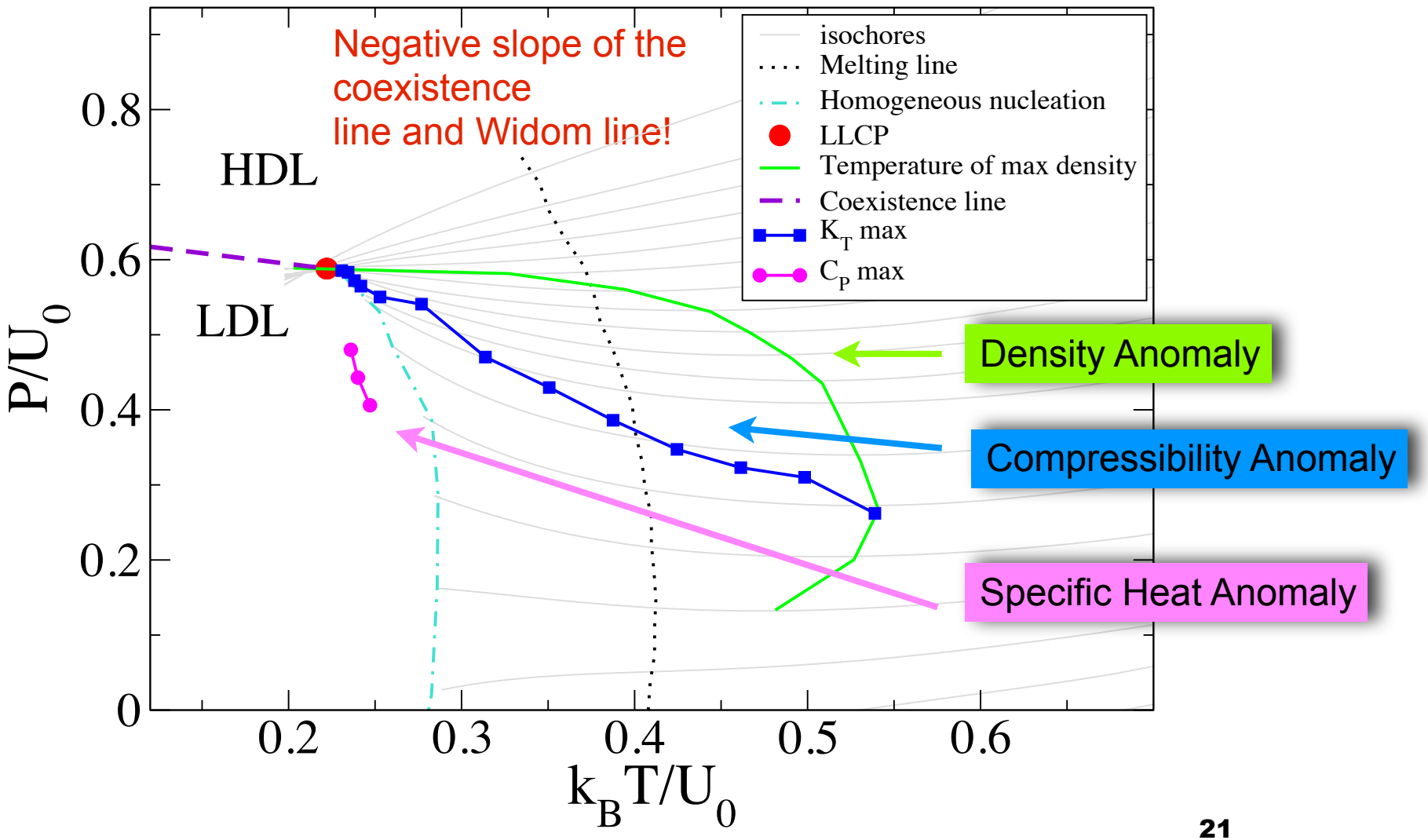

21

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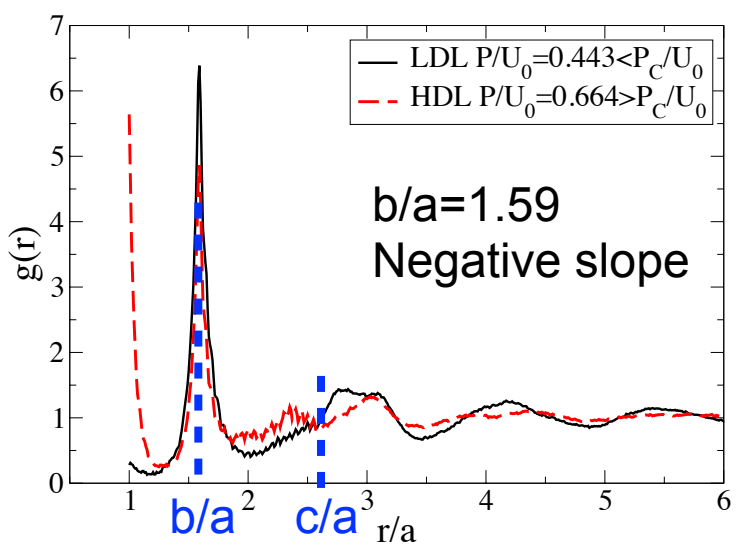
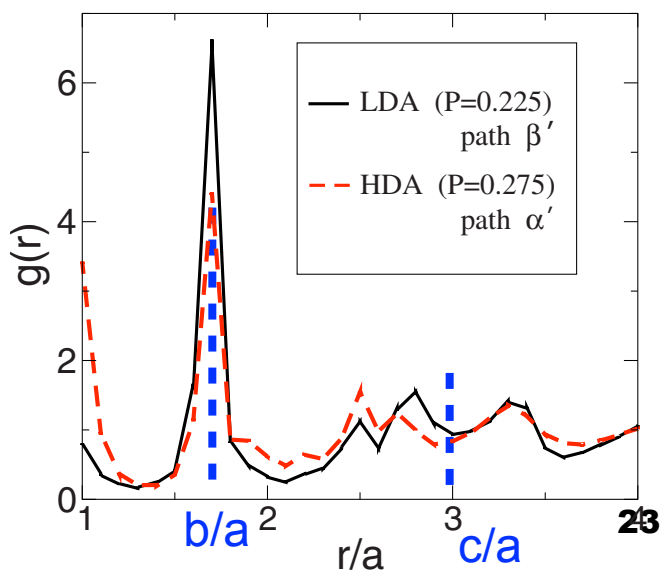
Insights on how we can get this:

- Slope: $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$
- Negative Slope: $\frac{dP}{dT} < 0 \Rightarrow \frac{\Delta S}{\Delta V} < 0$
- LDL -> HDL: $\Delta V < 0$

$$\Rightarrow \Delta S = S_{HDL} - S_{LDL} > 0 \quad \Rightarrow \quad S_{HDL} > S_{LDL}$$

- LDL is more ordered than HDL.





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Modified Jagla can be a good model for water!

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Modified Jagla can be a good model for water!

- 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!