Thermodynamics I: Introduction

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- Molecular pairwise interactions

Thermodynamic Properties

Extensive

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  - E.g., Volume, Potentials $(U, H, G, \ldots)$

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  - E.g., Volume, Potentials $(U, H, G, \dots)$

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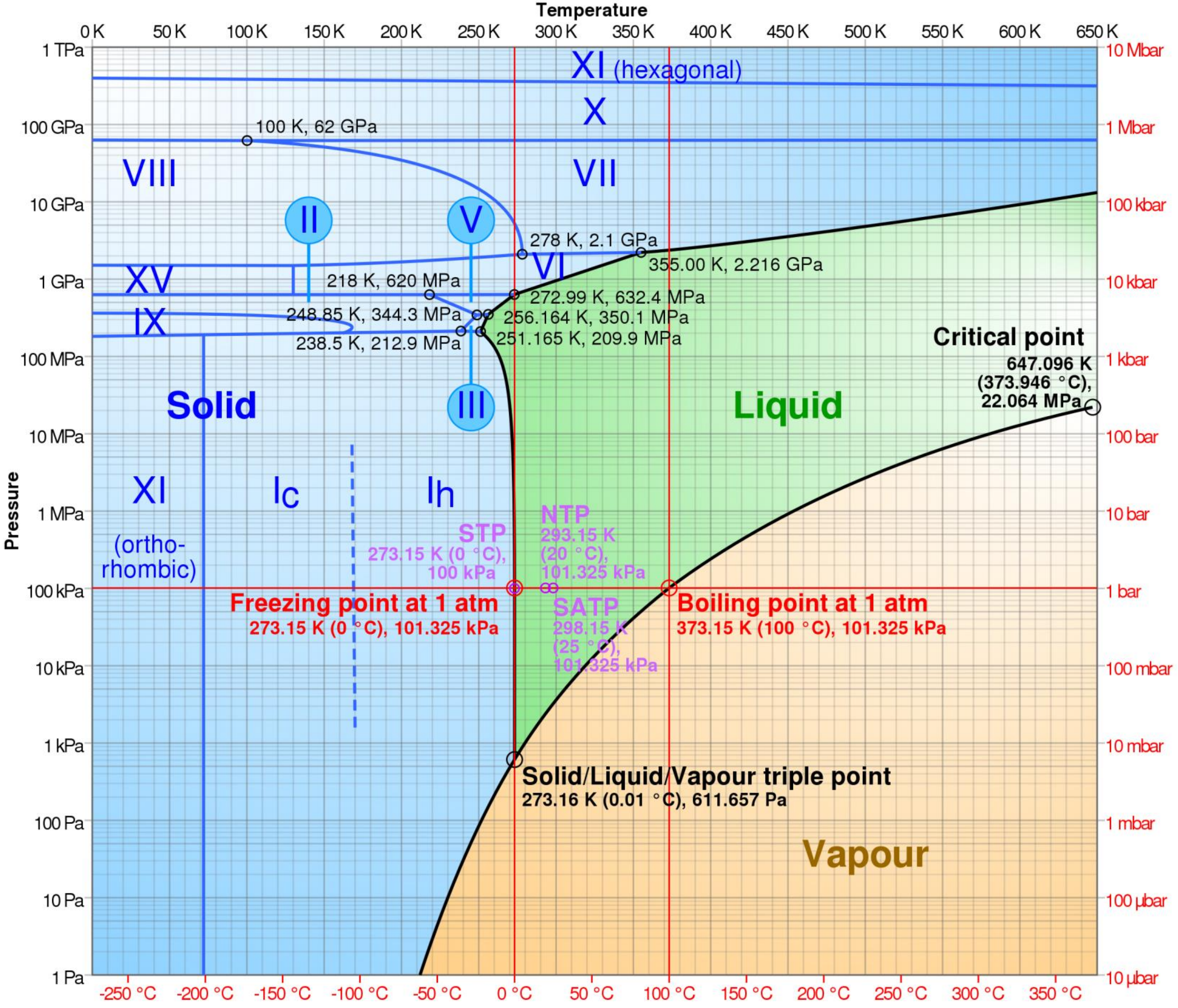
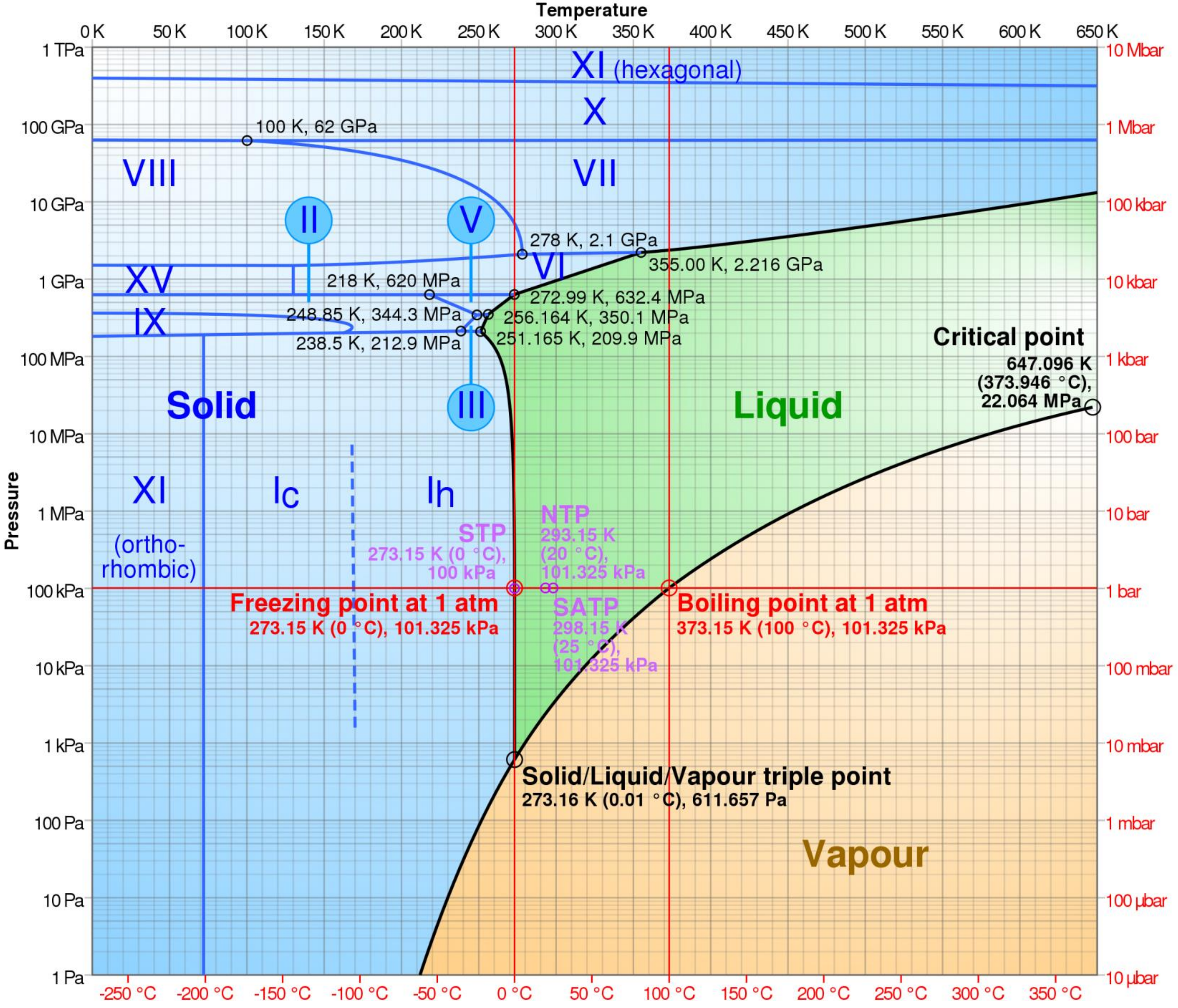
- Size independent
  - E.g., Temperature (T), Pressure (P)
- **Specific**
  - Normalized properties
  - E.g., Molar Volume, Mass Density

Phase Diagram (Water)



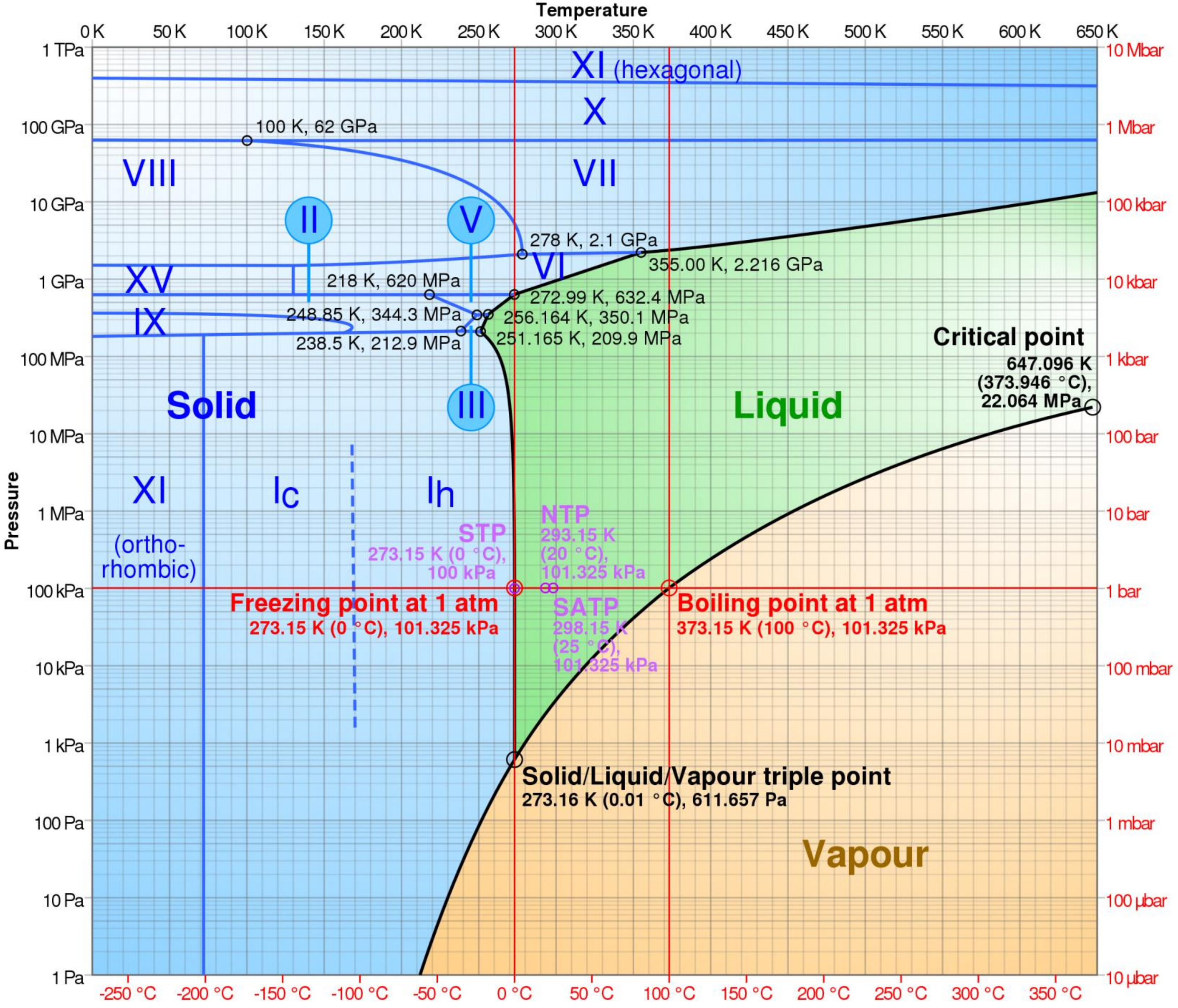
Phase Diagram (Water)

- Isobars (horizontal)



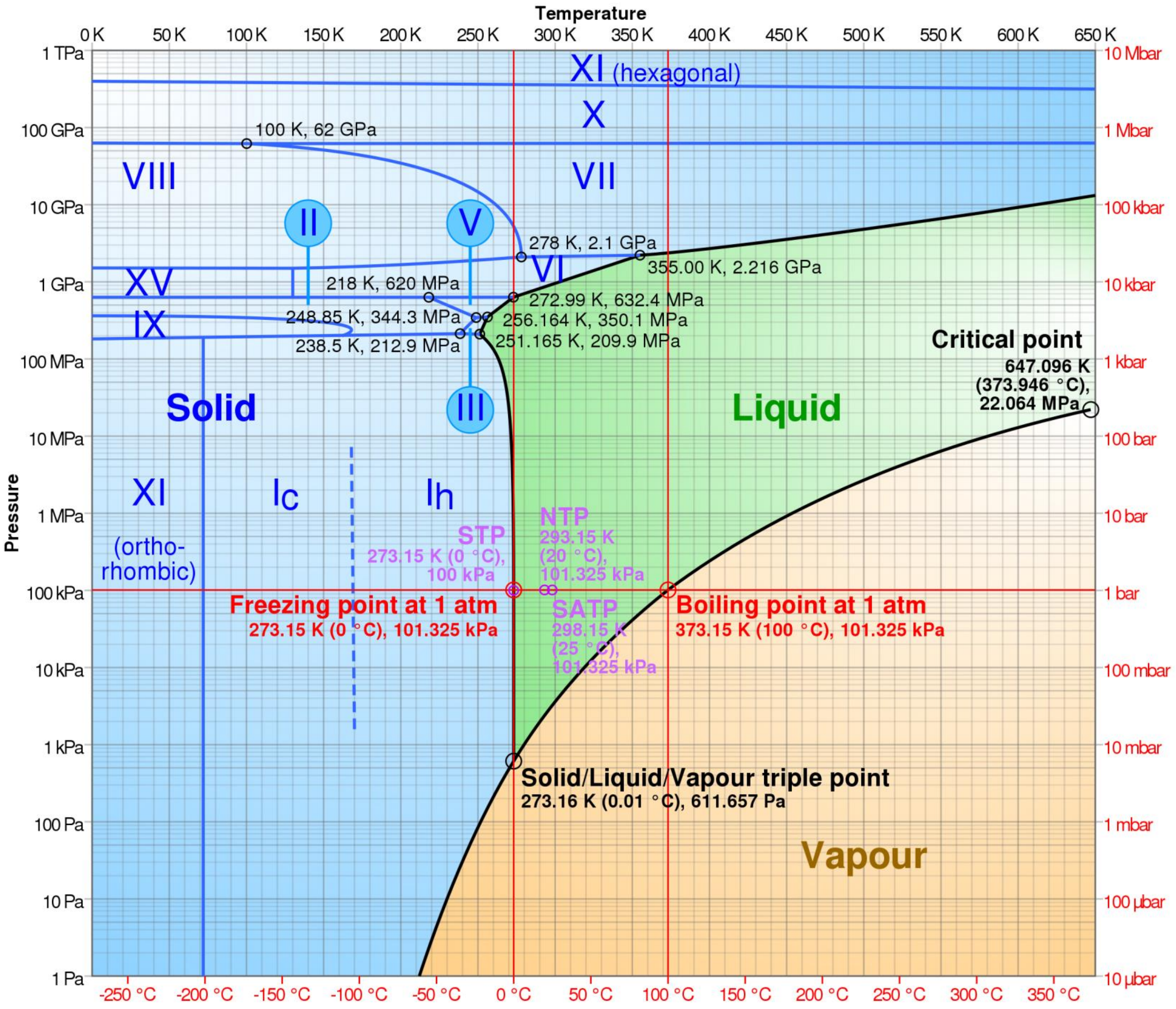
Phase Diagram (Water)

- Isobars (horizontal)
- Isotherms (vertical)



Phase Diagram (Water)

- Isobars (horizontal)
- Isotherms (vertical)
- Single component, single phase →



Phase Diagram (Water)

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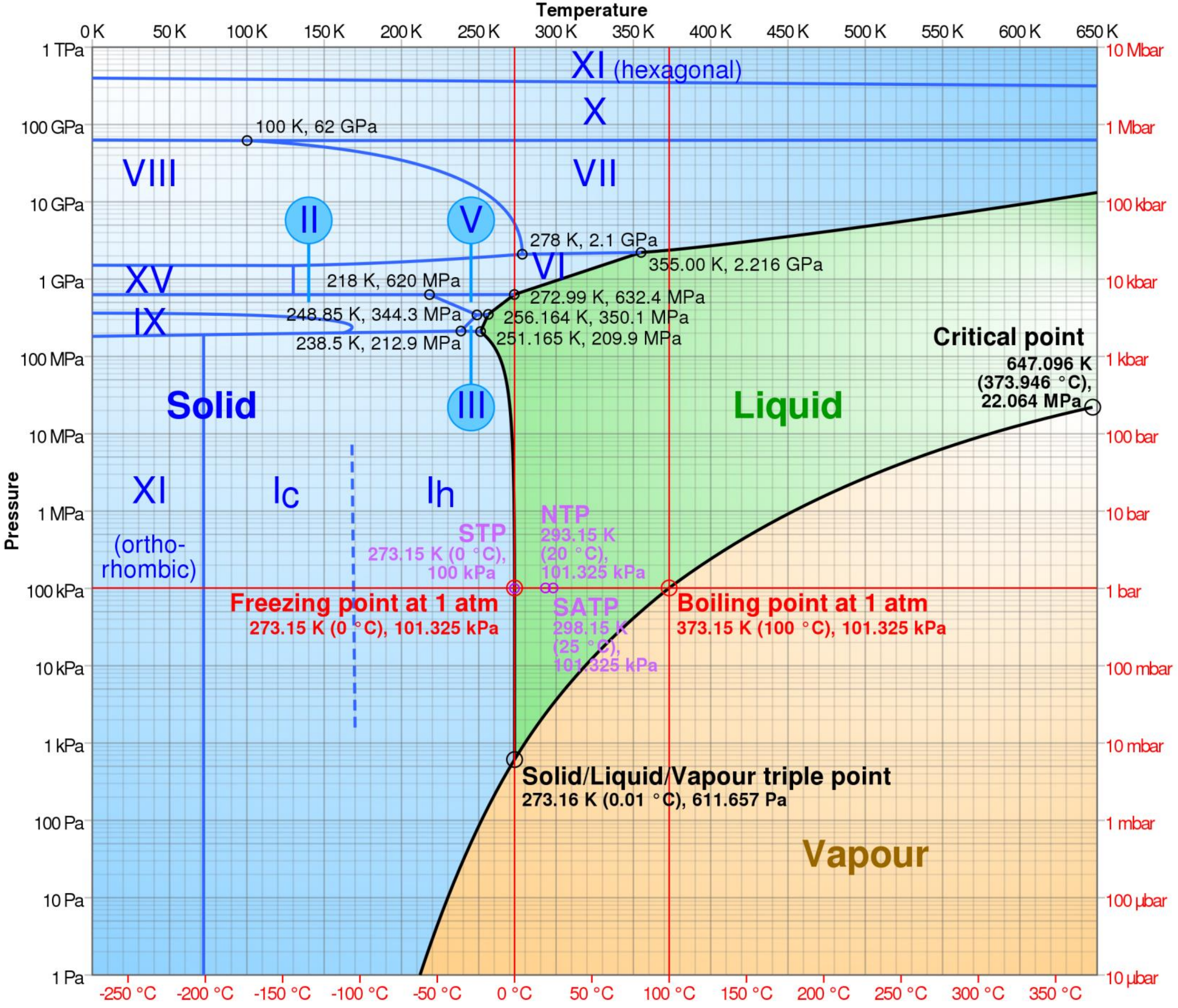
  - $(T, P) \to V$



Phase Diagram (Water)

- Isobars (horizontal)
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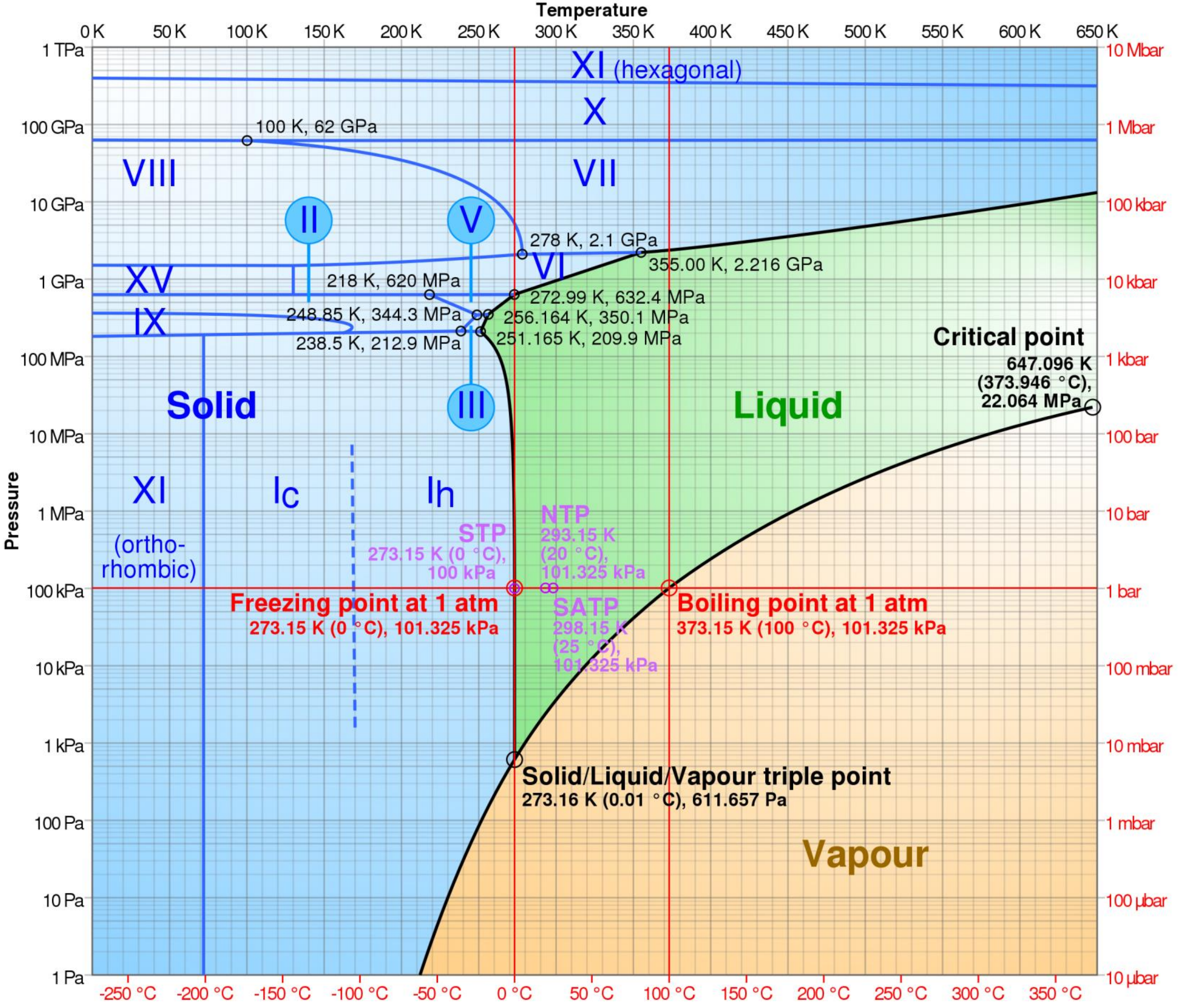
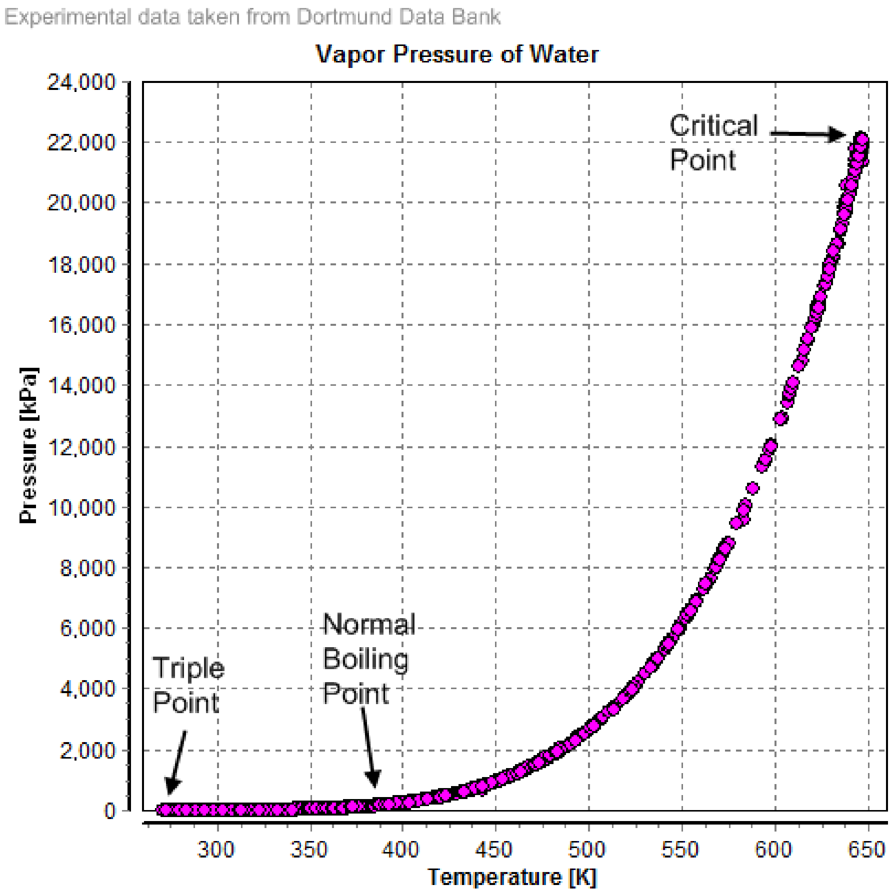
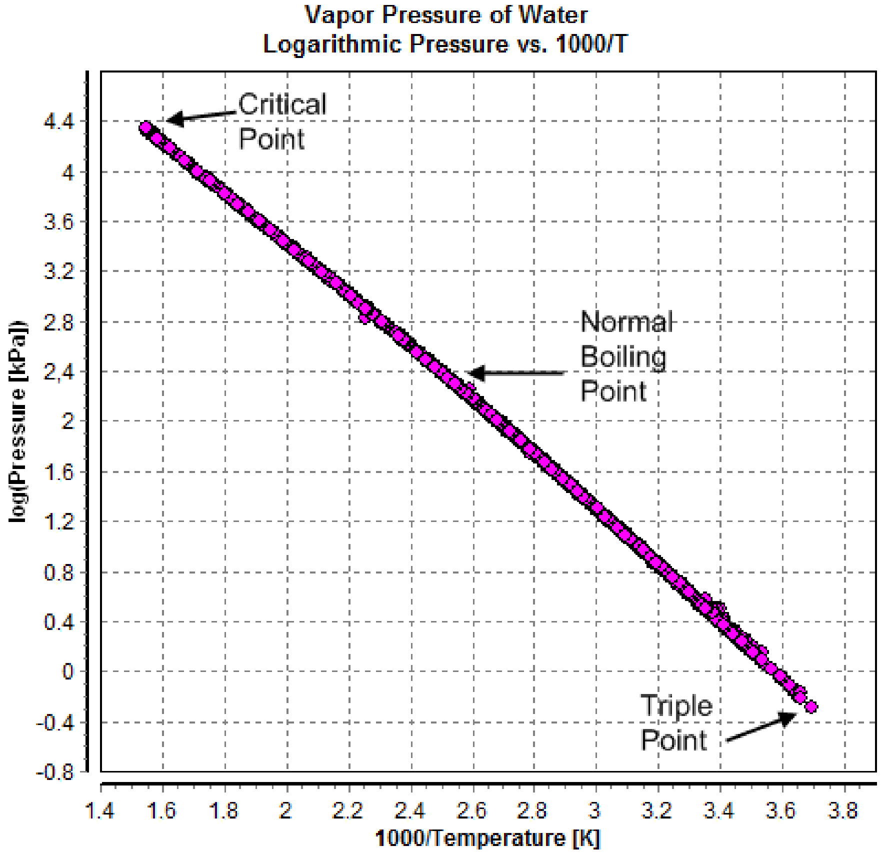
- Single component, single phase →
  - $(T, P) \rightarrow V$
- Two phases?



Vapor Pressure (Antoine's Equation)





What is Temperature?

Kinetic Theory of Gases

Equilibrium (Entropy)

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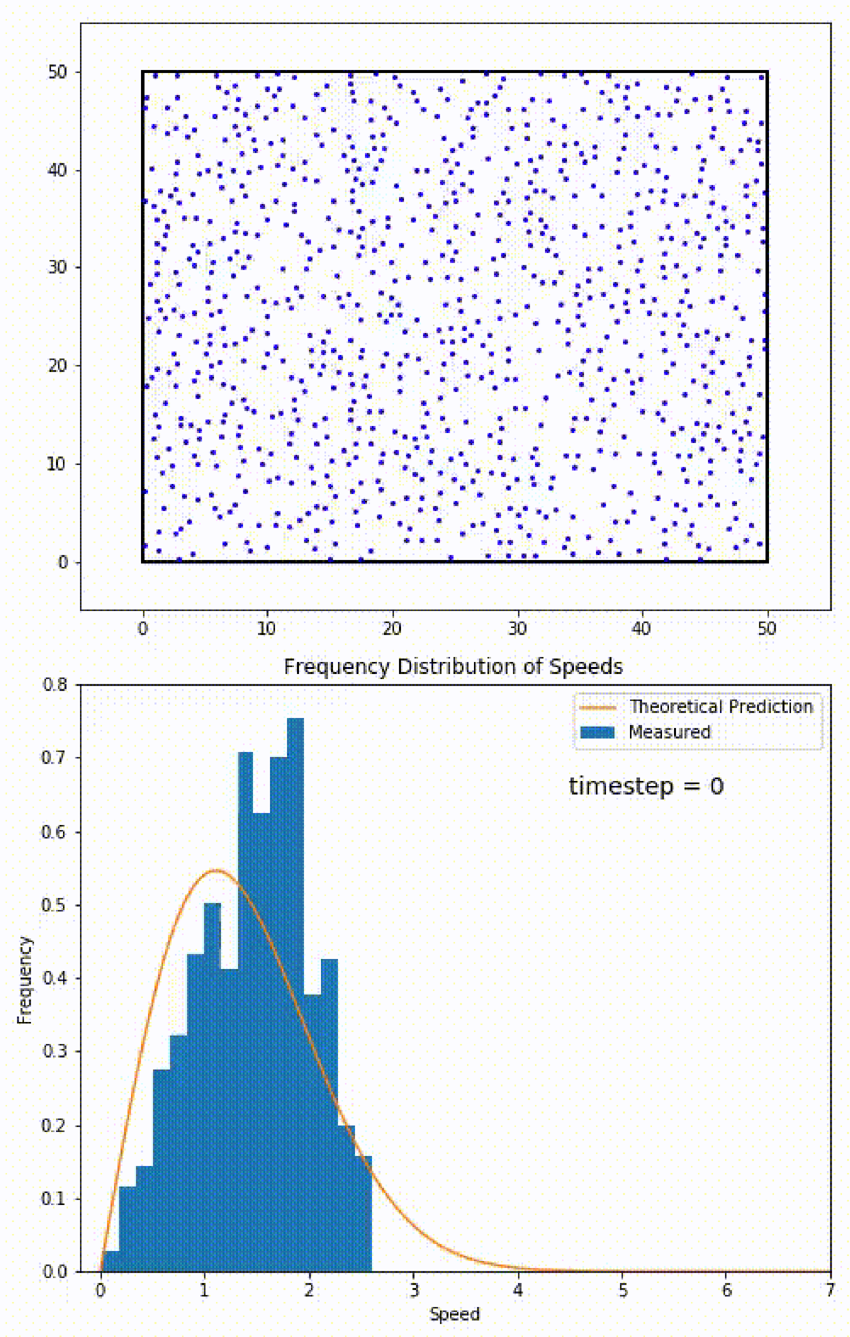
Equilibrium (Entropy)

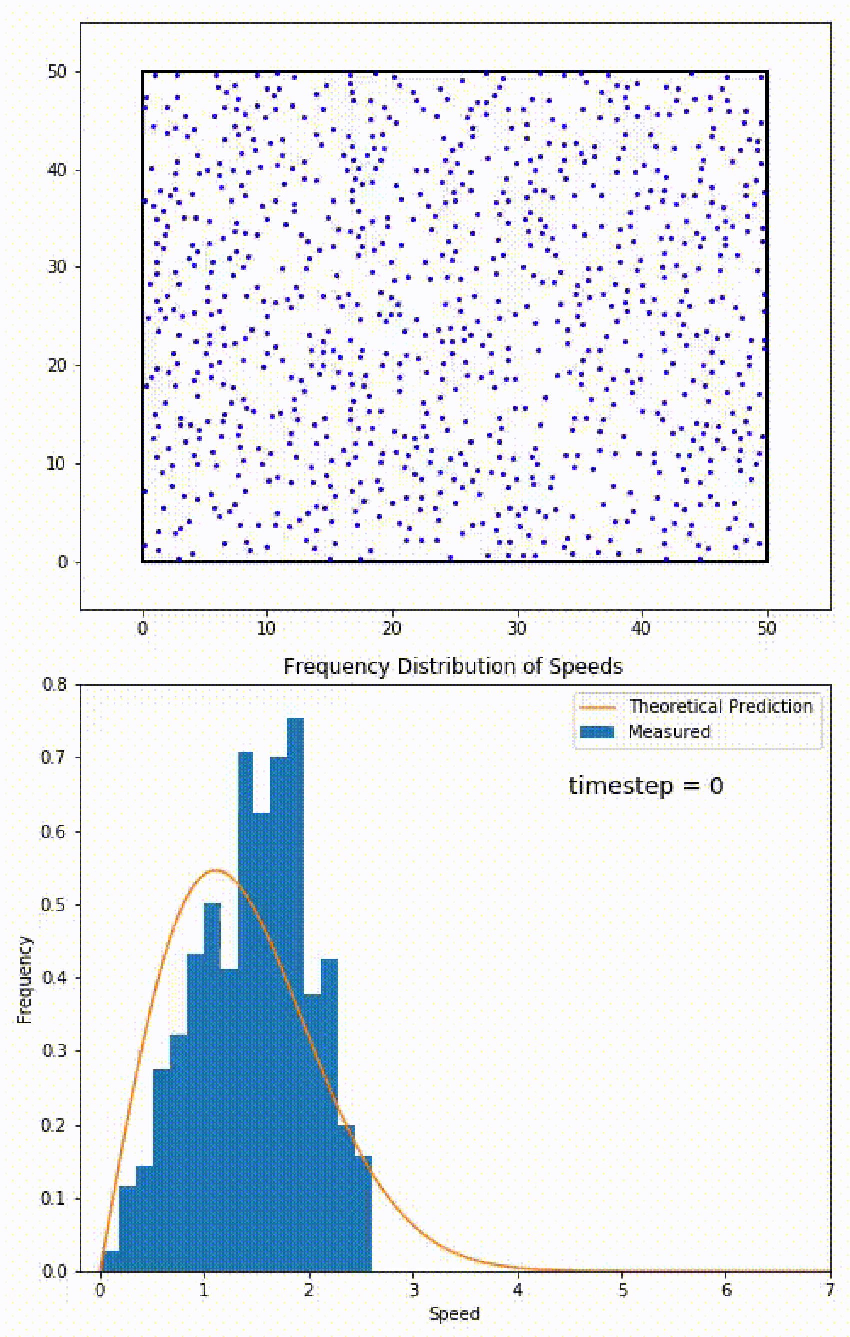
- $T = \frac{dU}{dS}$
    - To be continued (chapter 4)

Velocity Distribution



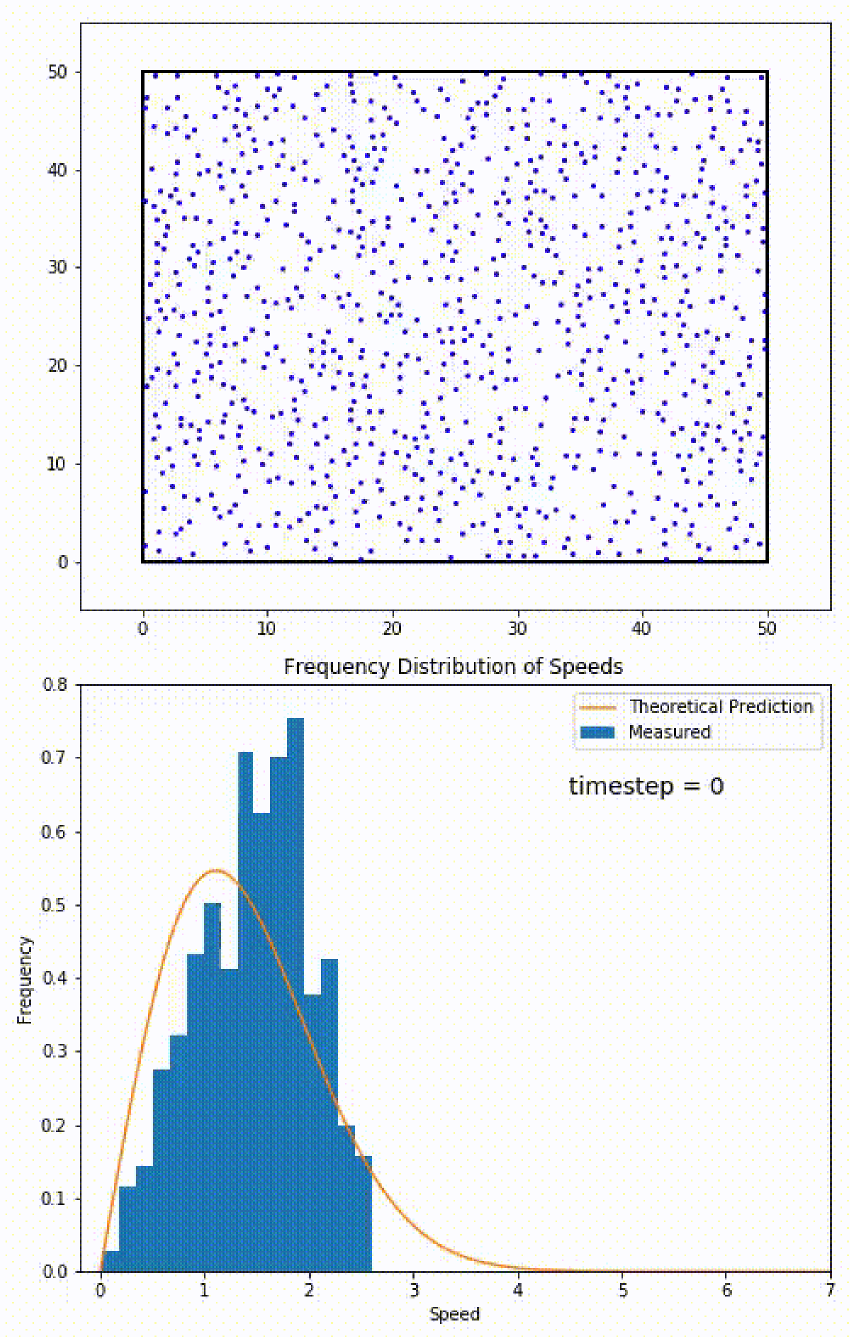
Velocity Distribution

- Hard Spheres: inelastic collisions →
  - Maxwell-Boltzmann distribution

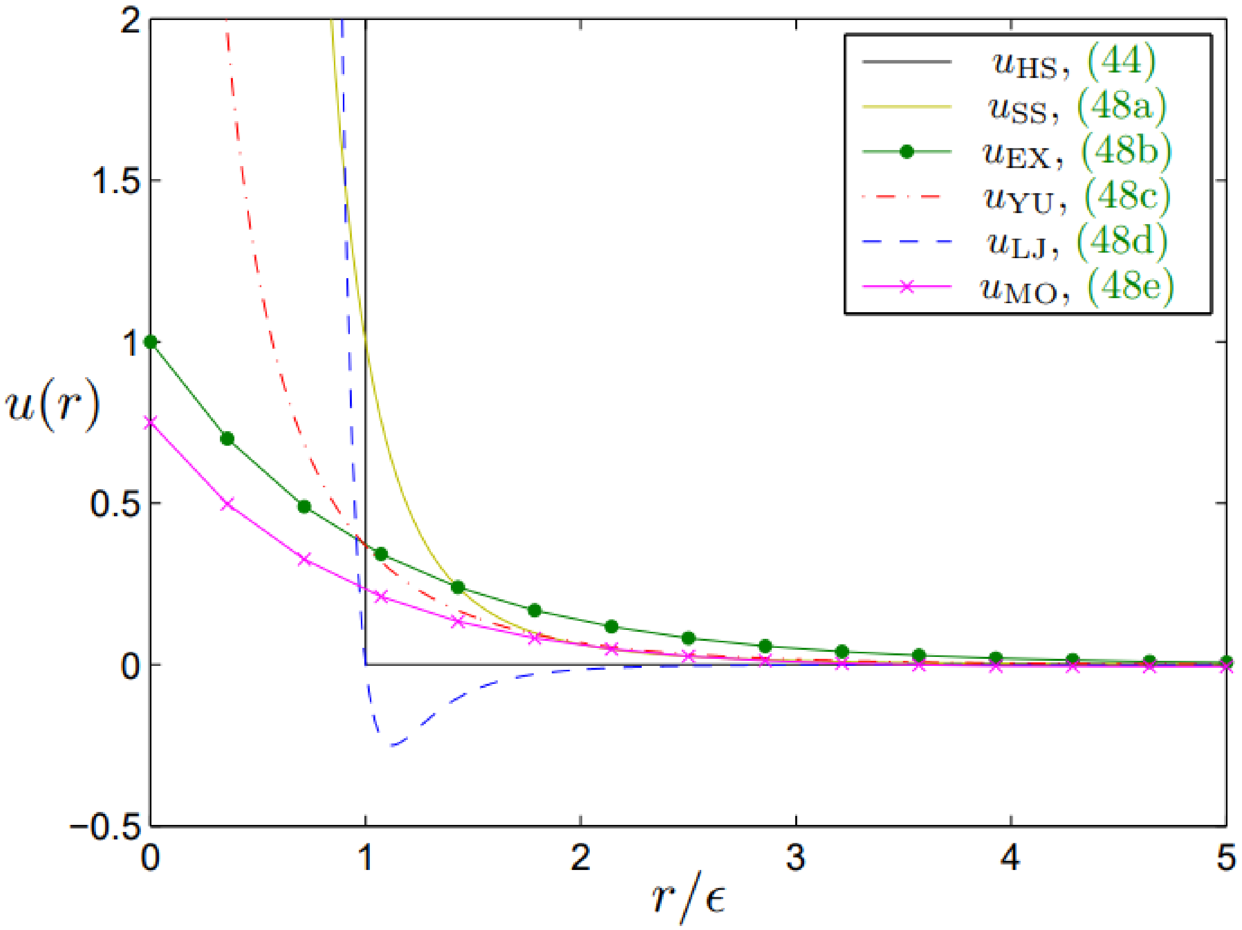


Velocity Distribution

- Hard Spheres: inelastic collisions →
  - Maxwell-Boltzmann distribution
- $v_p \approx 0.886\bar{v} < \bar{v} < 1.085\ \bar{v} \approx v_{rms} = \sqrt{\overline{v^2}}$



Intermolecular Pair Potentials



Bruna, Maria & Chapman, Stephen & Robinson, Martin. (2017). Diffusion of Particles with Short-Range Interactions. SIAM Journal on Applied Mathematics. 77. 10.1137/17M1118543.

Intermolecular Pair Potentials

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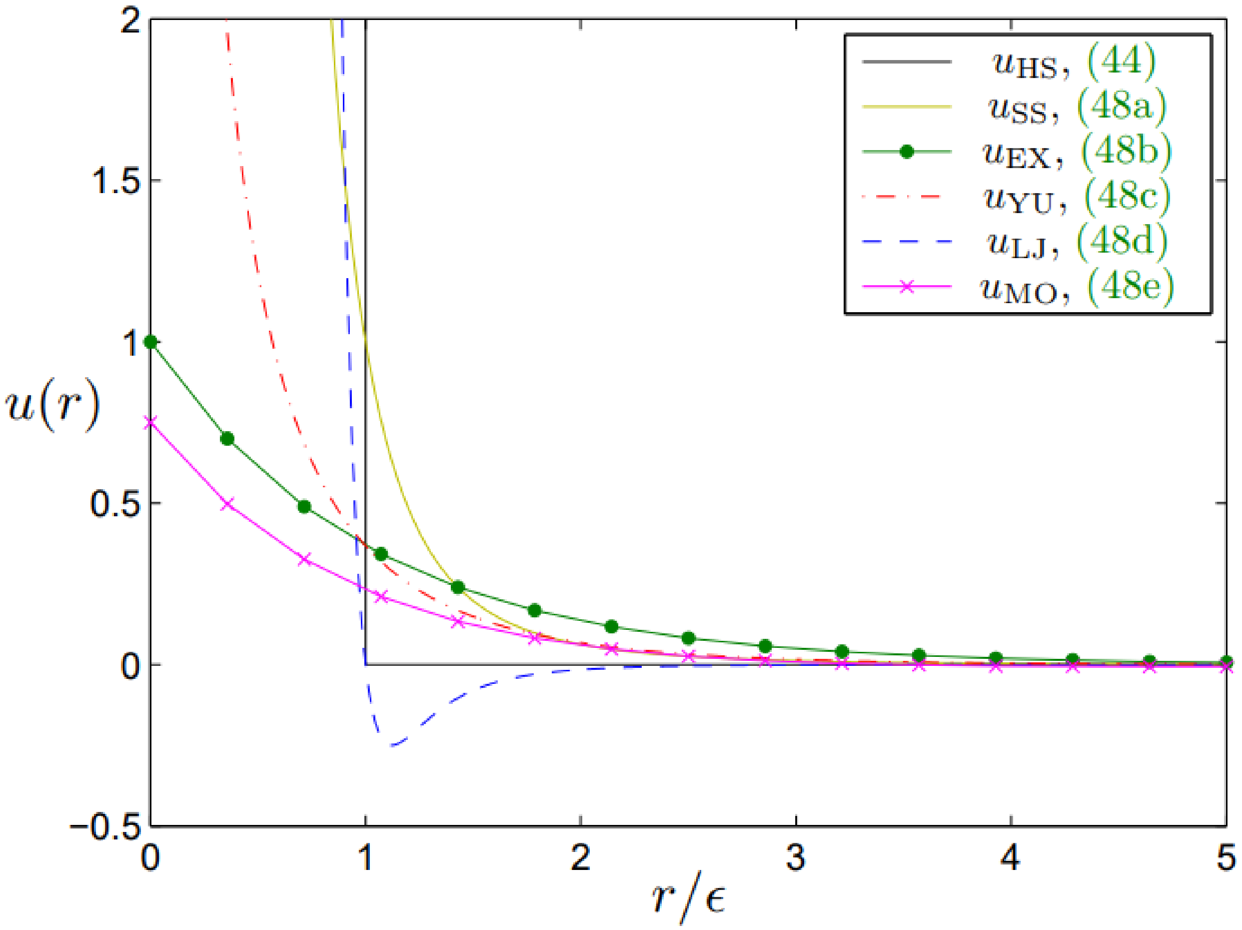

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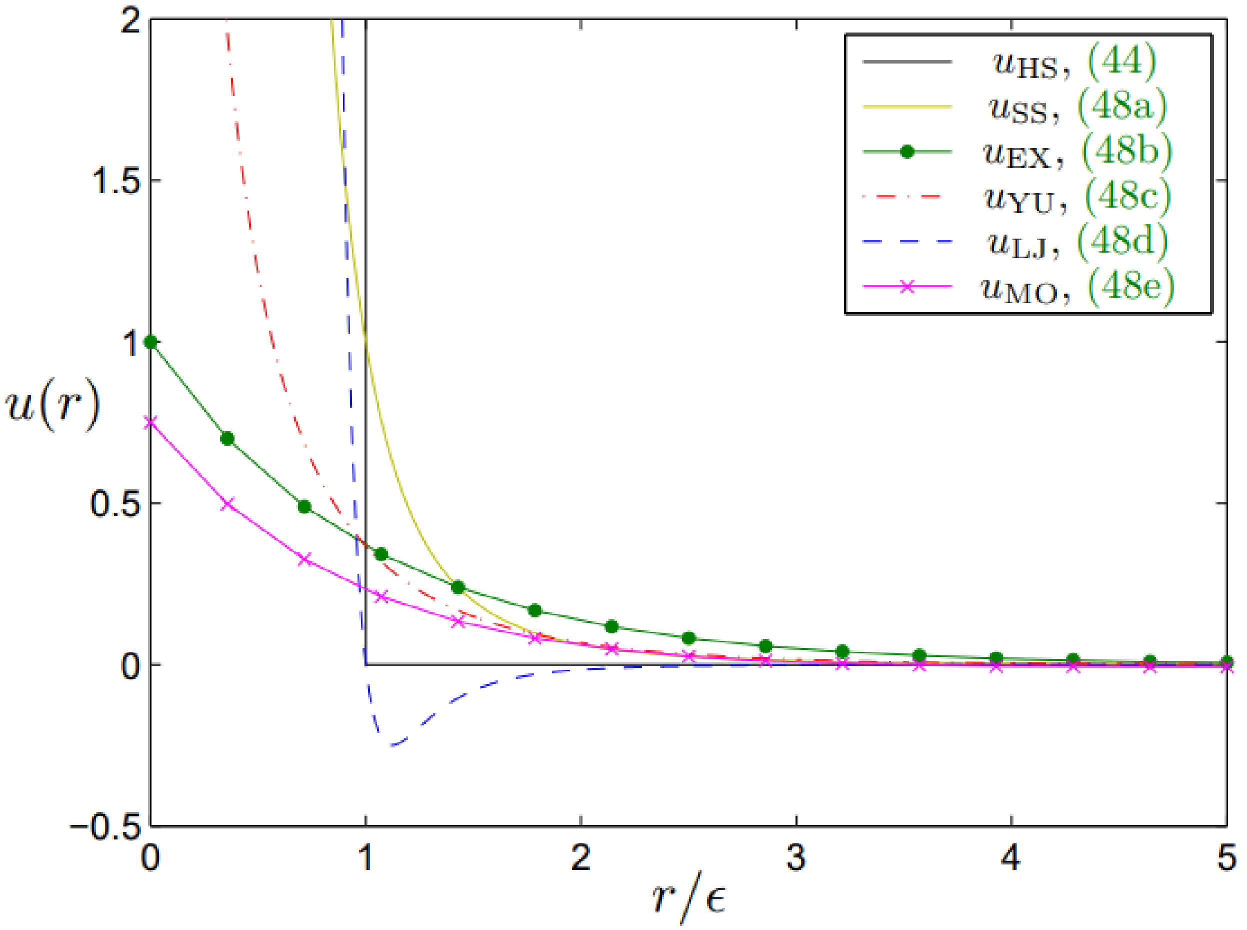

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Intermolecular Pair Potentials

- Hard-Sphere
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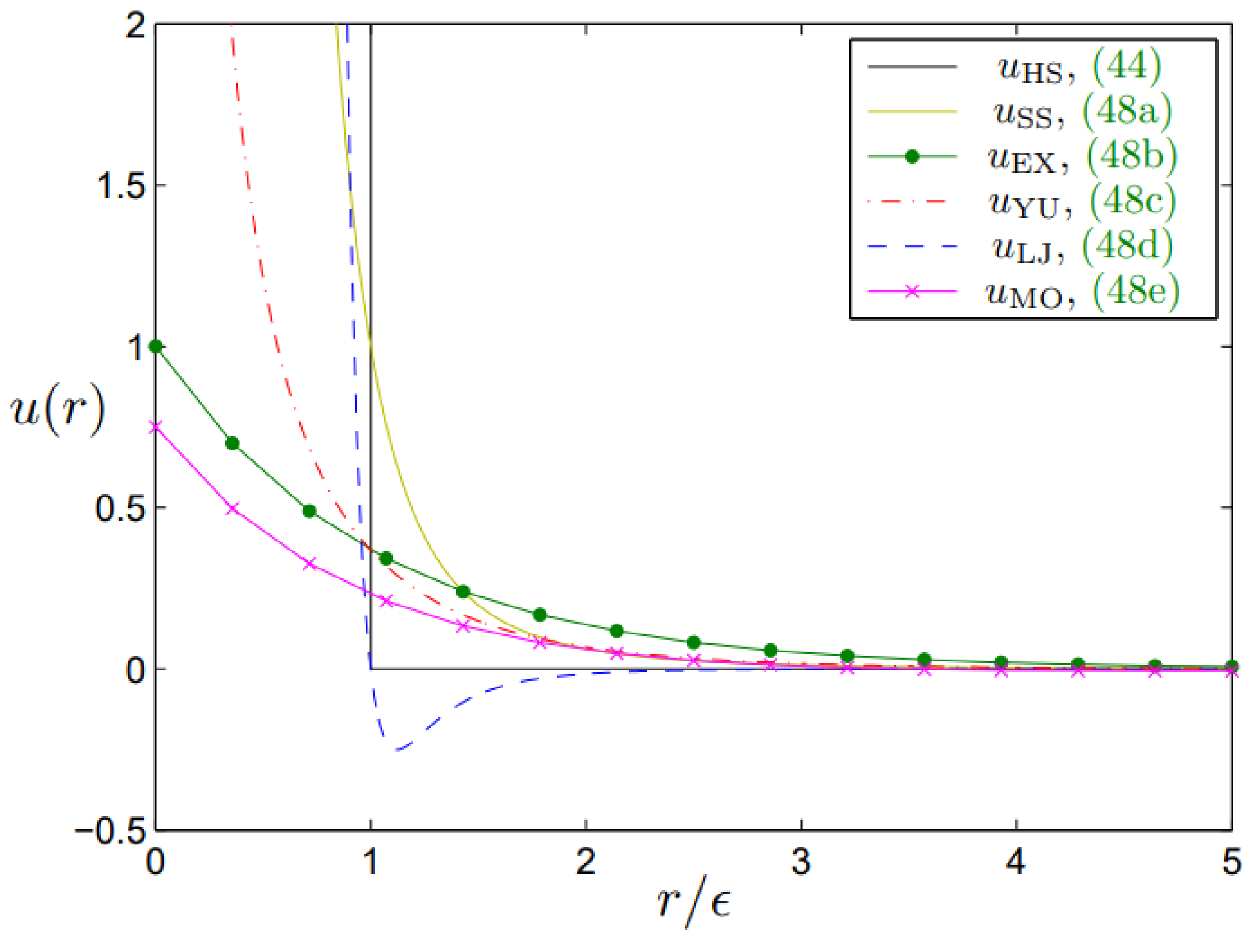
  - $u(r) \propto r^{-12}$
- Lennard-Jones
  - Repulsion r^{-12}
  - Attraction r^{-6}



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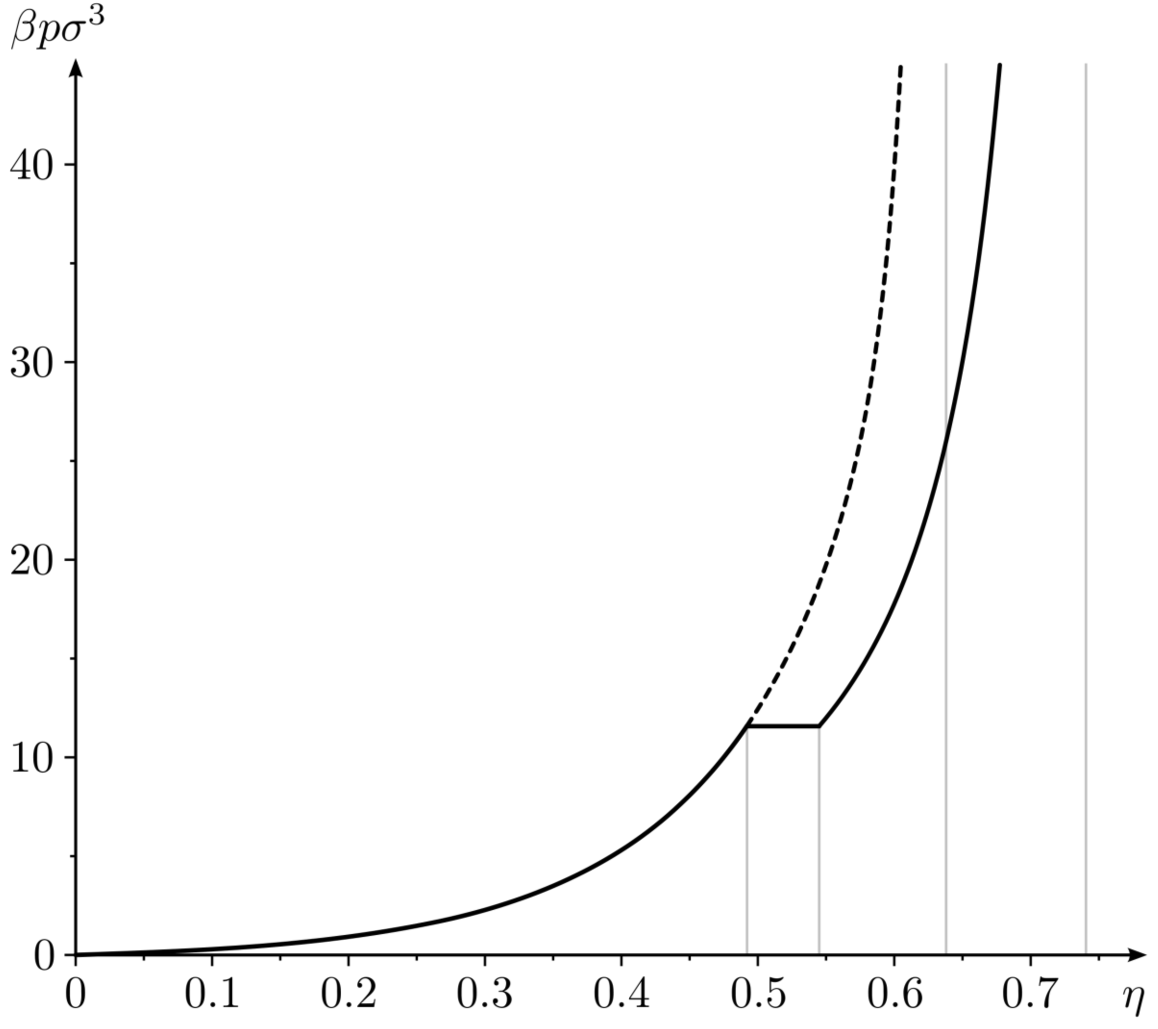
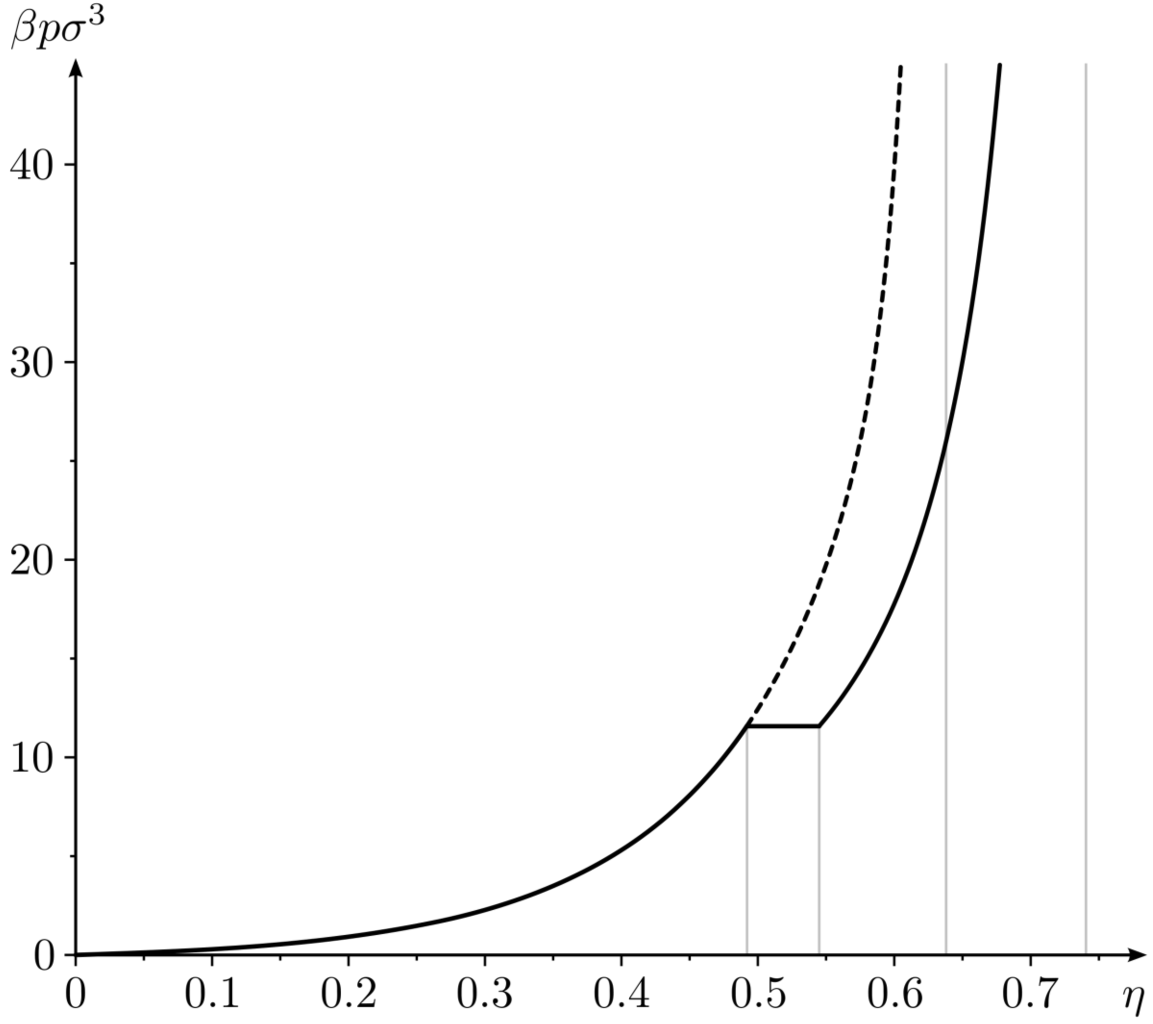
Hard Sphere Phase Diagram



Hard Sphere Phase Diagram

- Volume fraction η



Hard Sphere Phase Diagram

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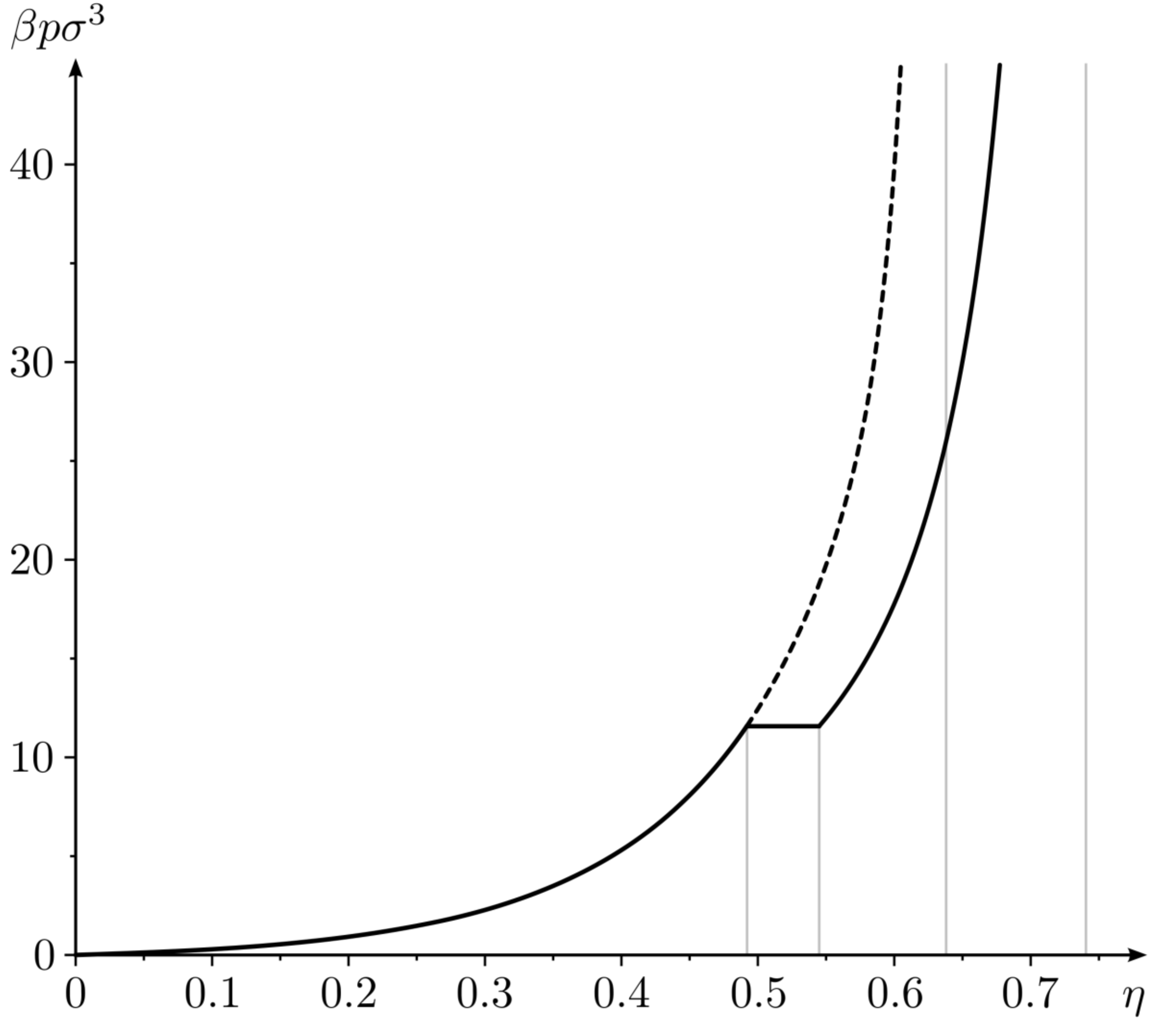
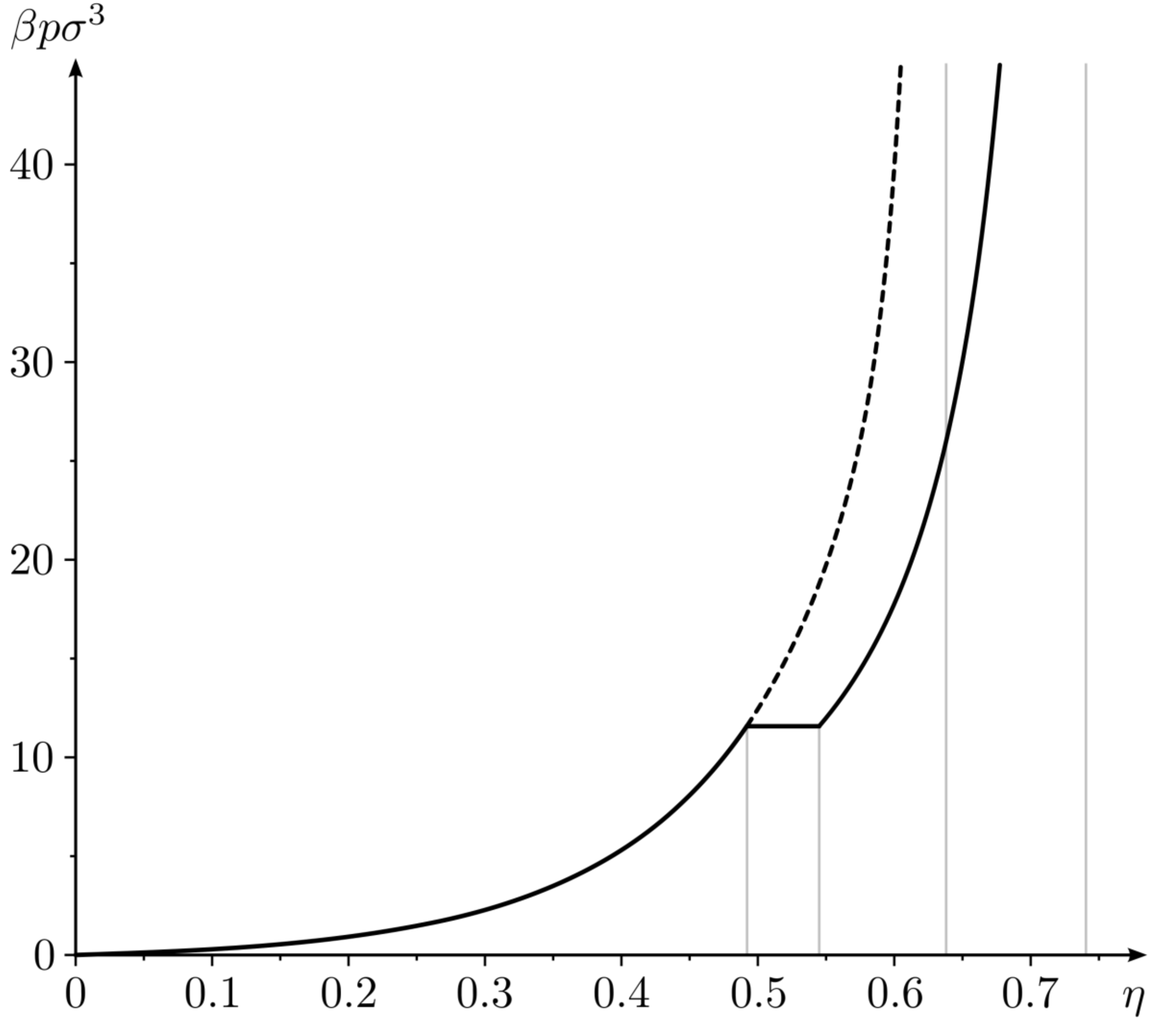
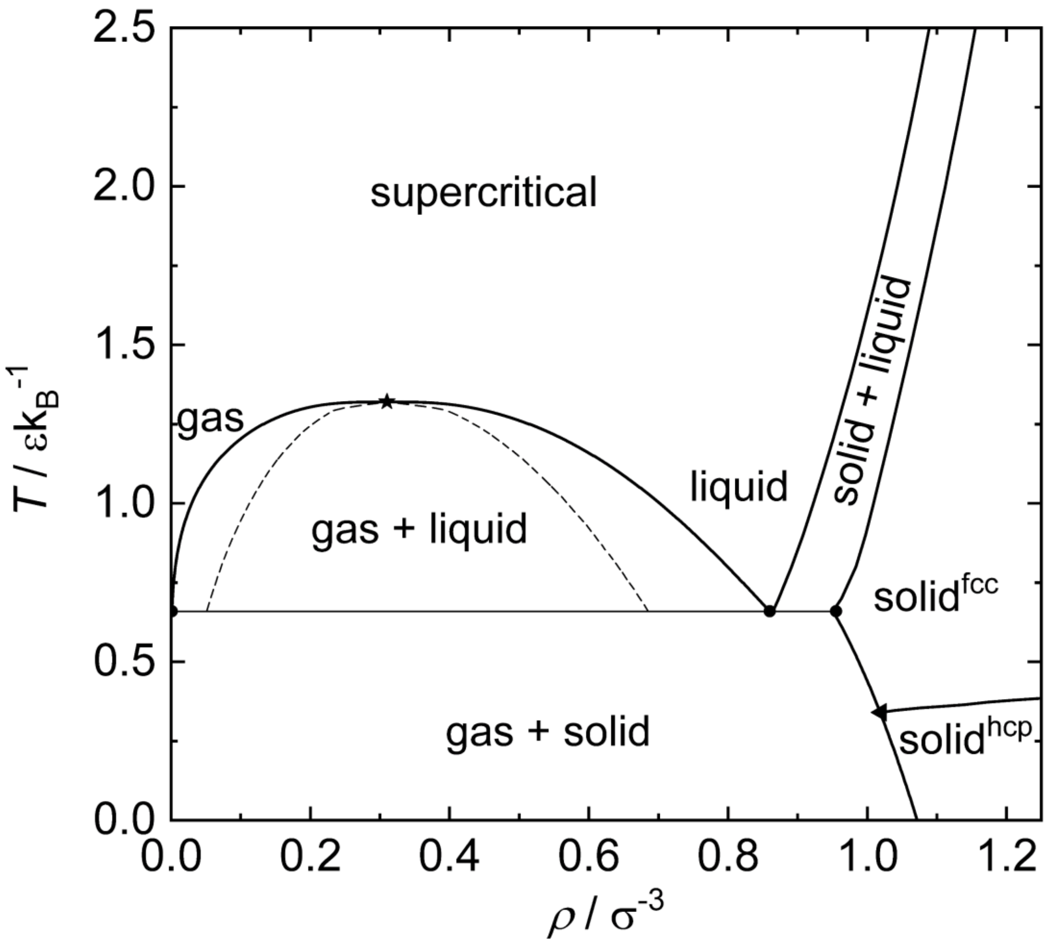


Hard Sphere Phase Diagram

- Volume fraction η
- Reduced pressure $\beta p \sigma^3$
- Two phases:
  - Solid
  - Fluid

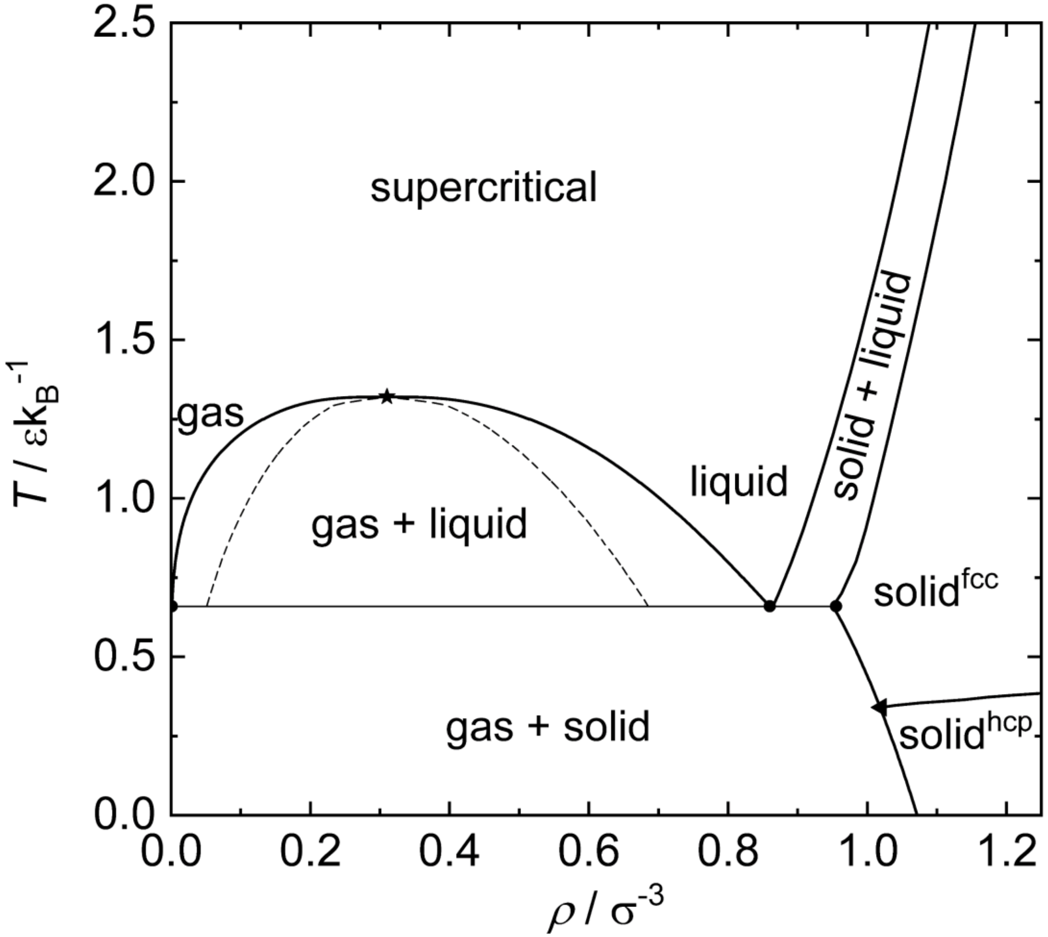


Lennard-Jones Phase Diagram



Lennard-Jones Phase Diagram

- $u(r) \propto \epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$



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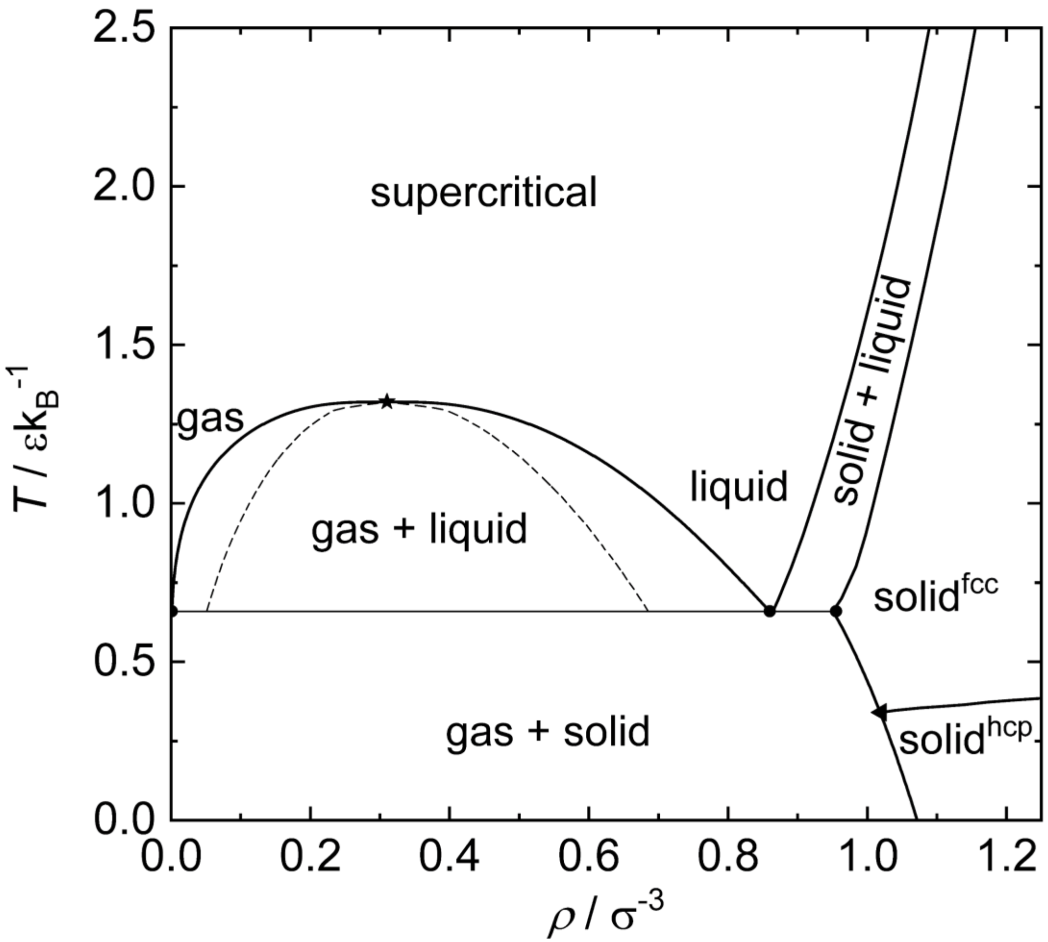

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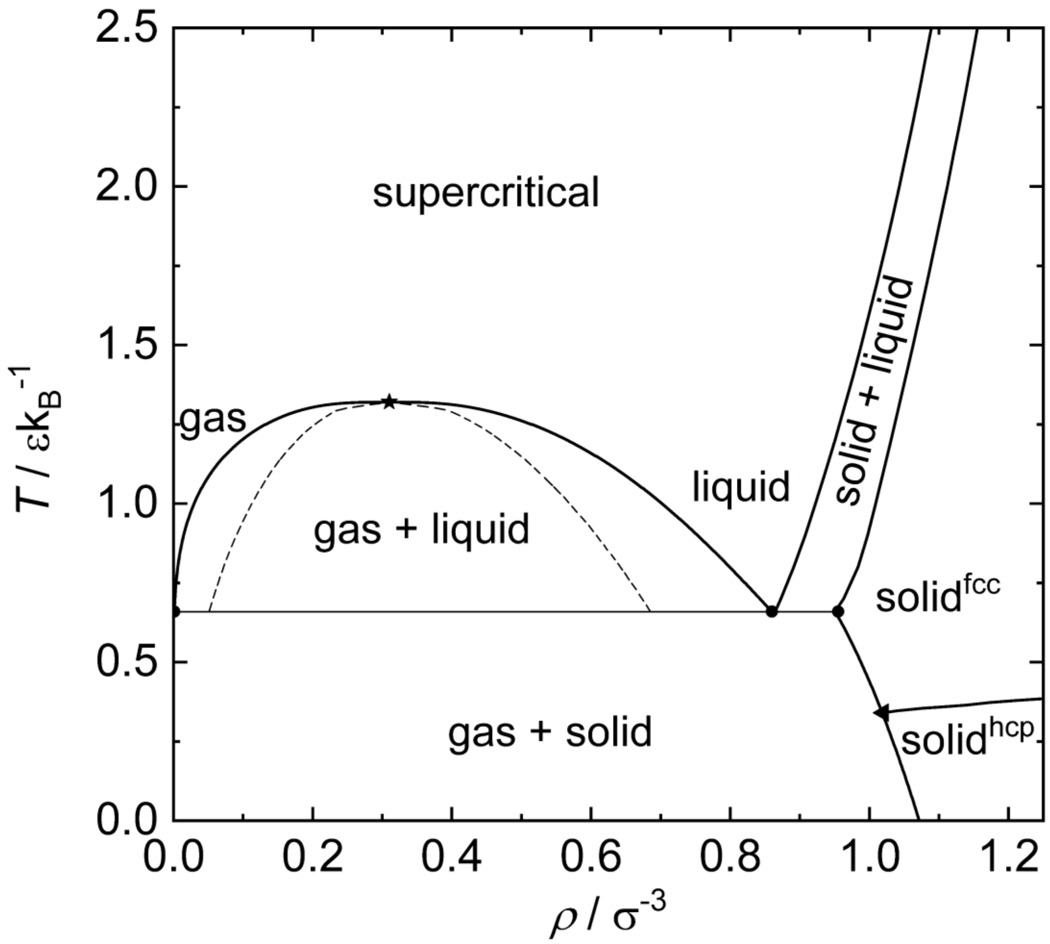
  - $\sigma = 0.34$ nm
  - $\frac{\epsilon}{k_B} = 120$ K



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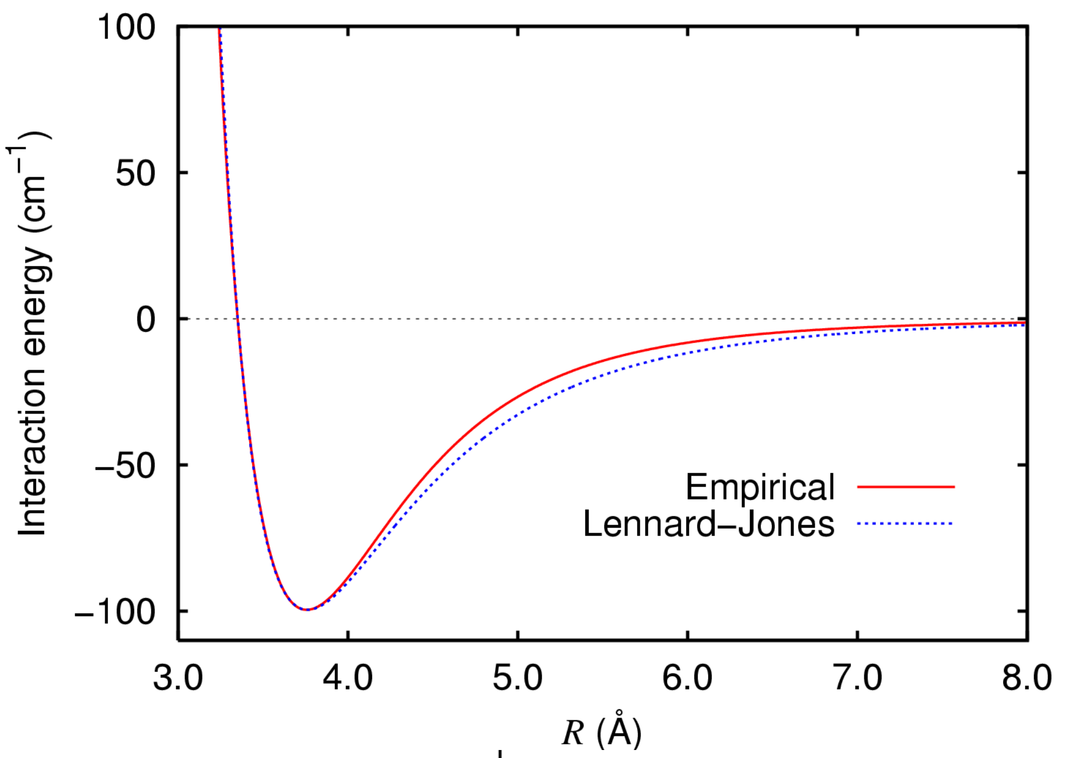

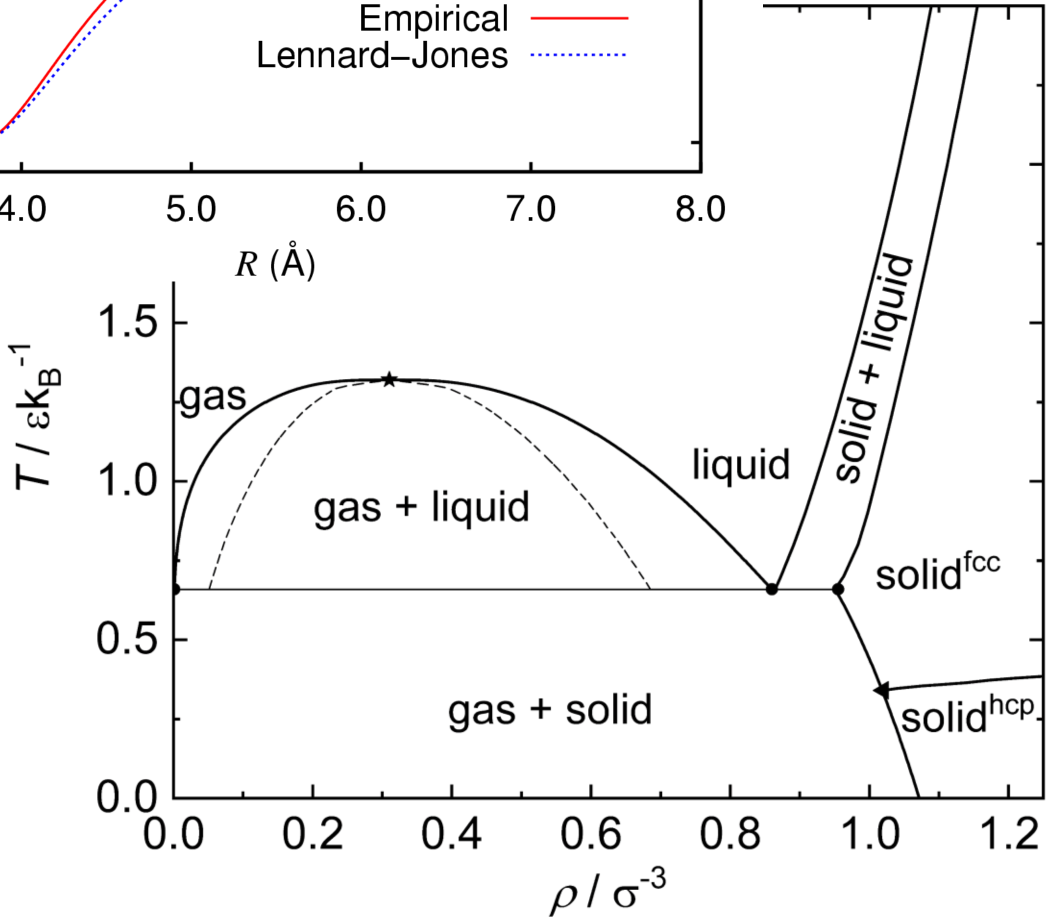

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- Ideal gas: $T \propto E_k \propto \overline{v^2}$
- Particle attraction and repulsion alone leads to familiar, realistic solid/liquid/vapor behavior

Thursday, August 25

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  - Thermodynamic state variables (T, P)

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  - Latent Heat

Equilibrium

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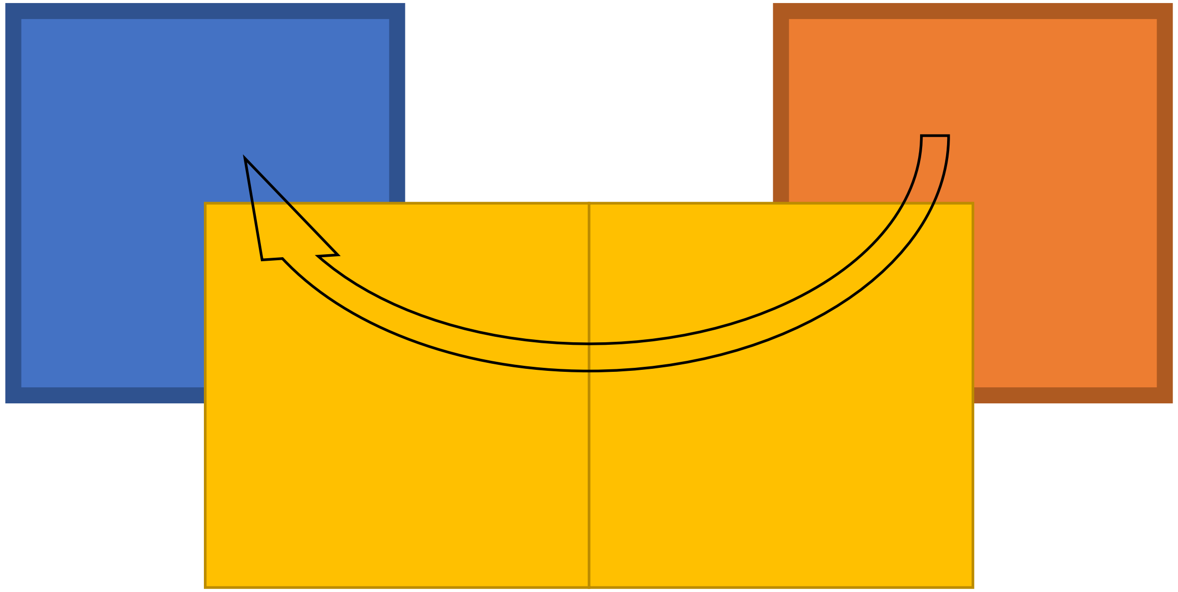
- $E_{orange} > E_{blue}$

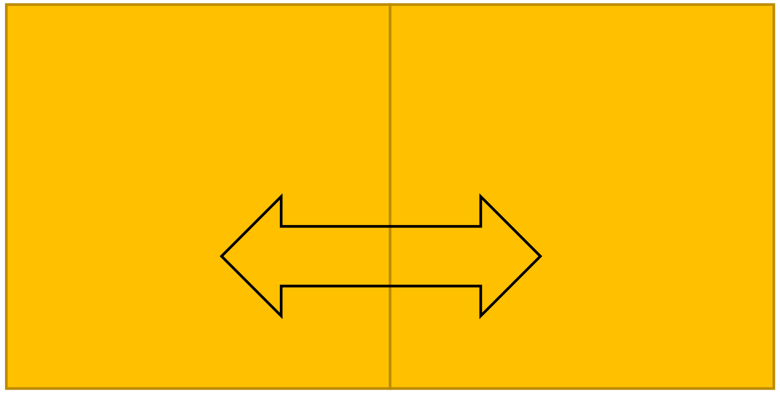
Equilibrium

- $E_{orange} > E_{blue}$



Equilibrium

- $$E_1 = E_2$$



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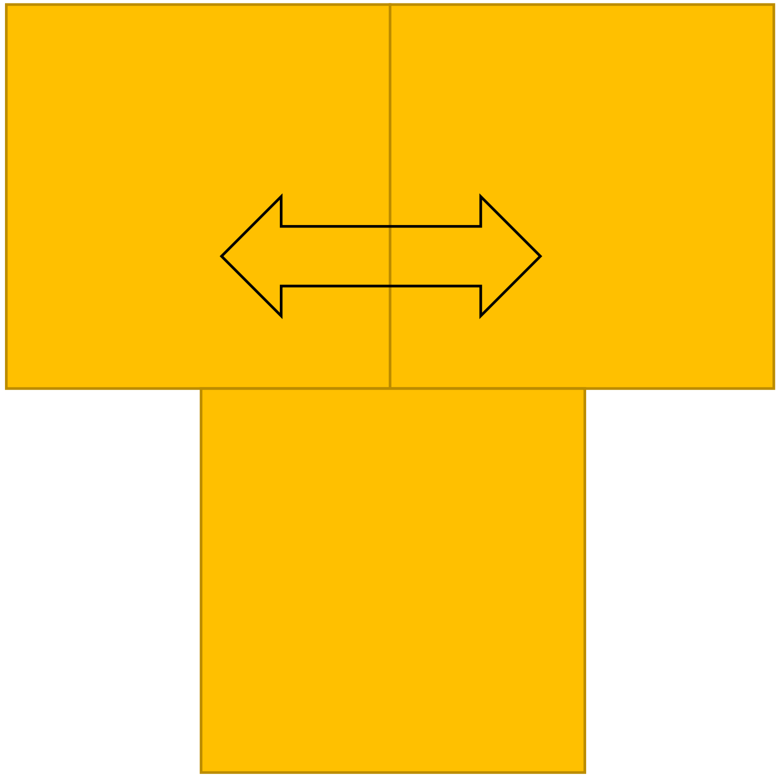

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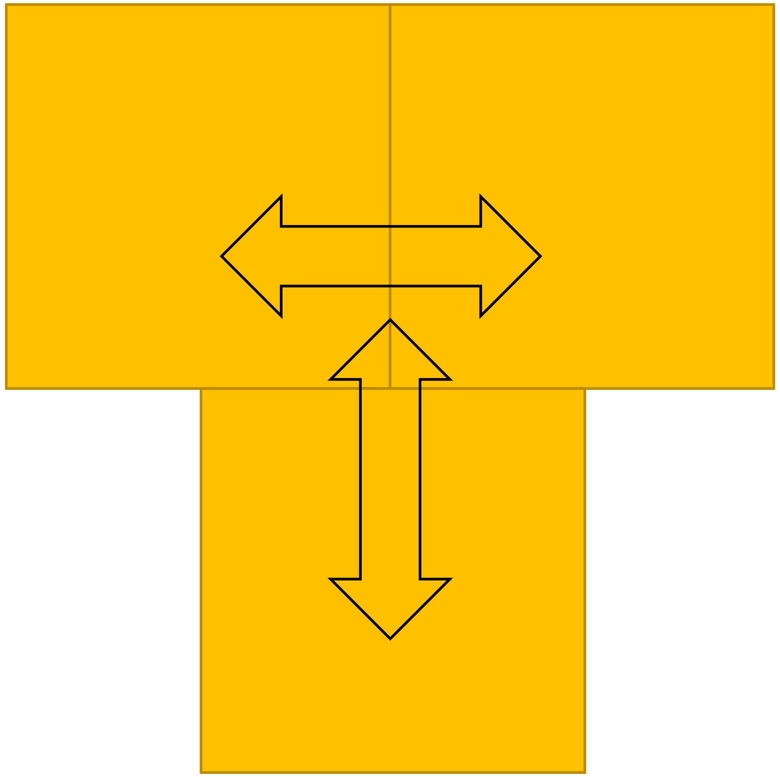
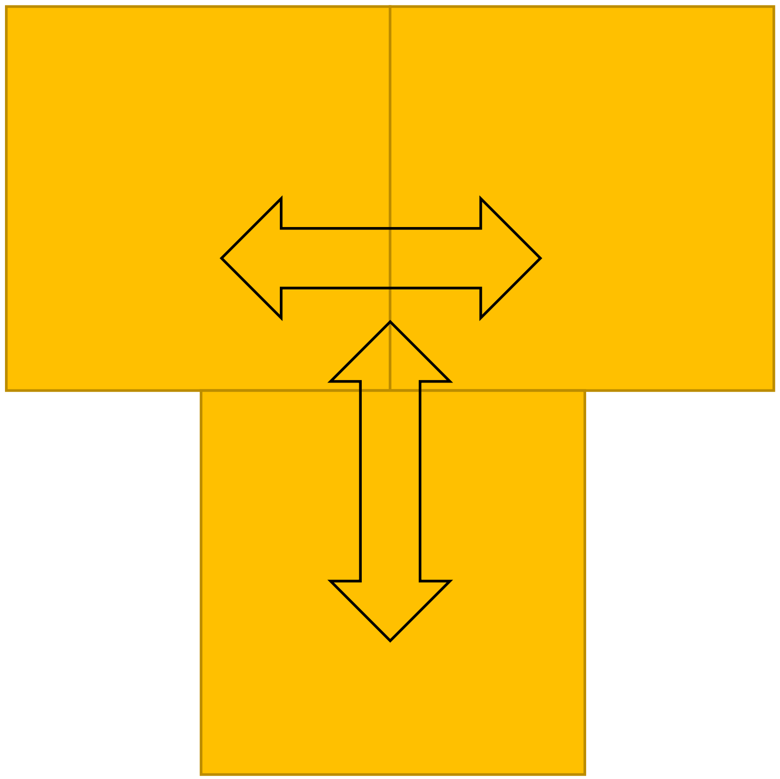


Equilibrium

- $$E_1 = E_2$$
- Zeroth law of thermodynamics



Equilibrium

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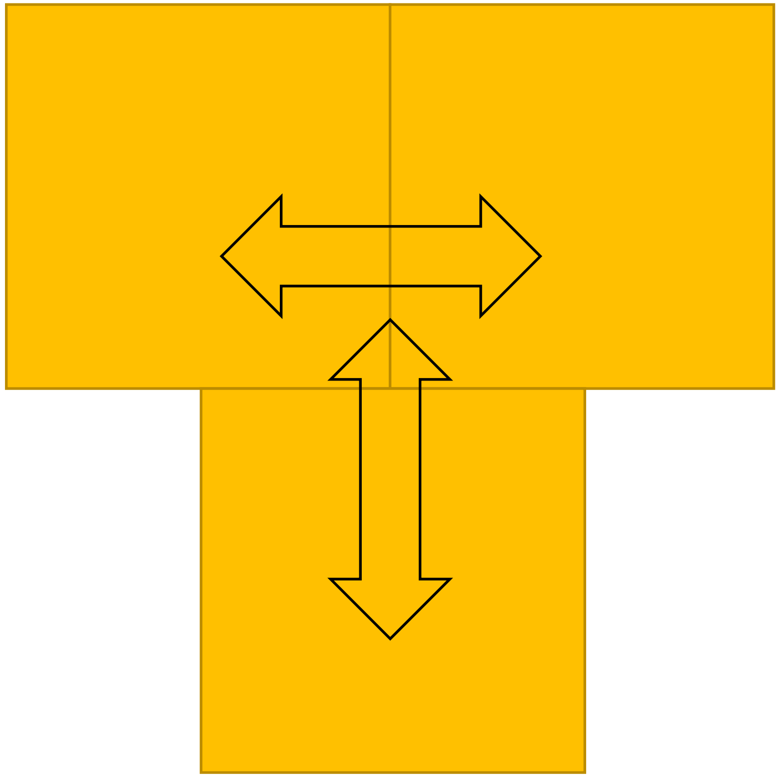
- $E_1 = E_2 = E_3$



Equilibrium

- $E_1 = E_2$
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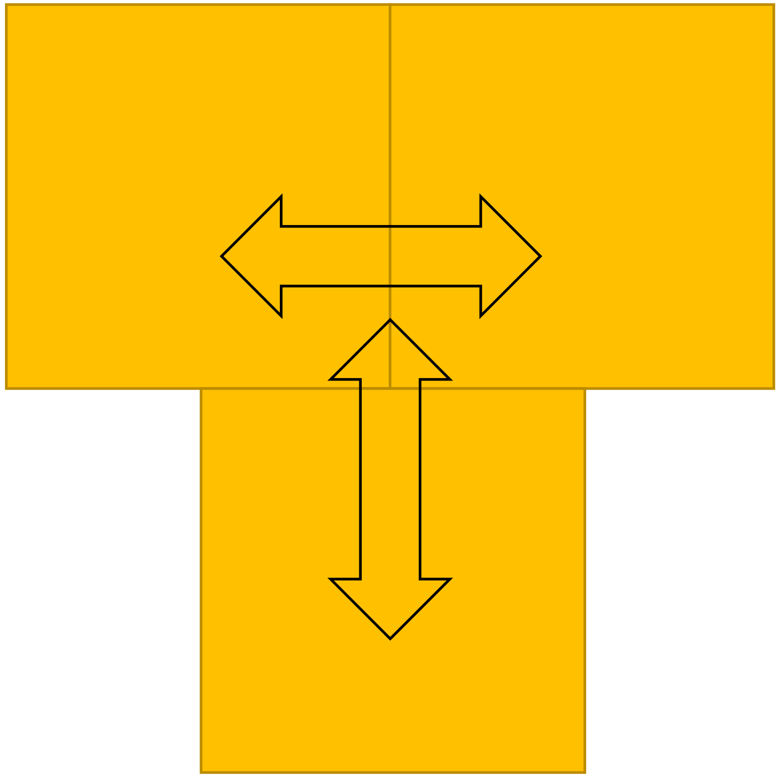
- $E_1 = E_2 = E_3$
  - $E_k \propto T$



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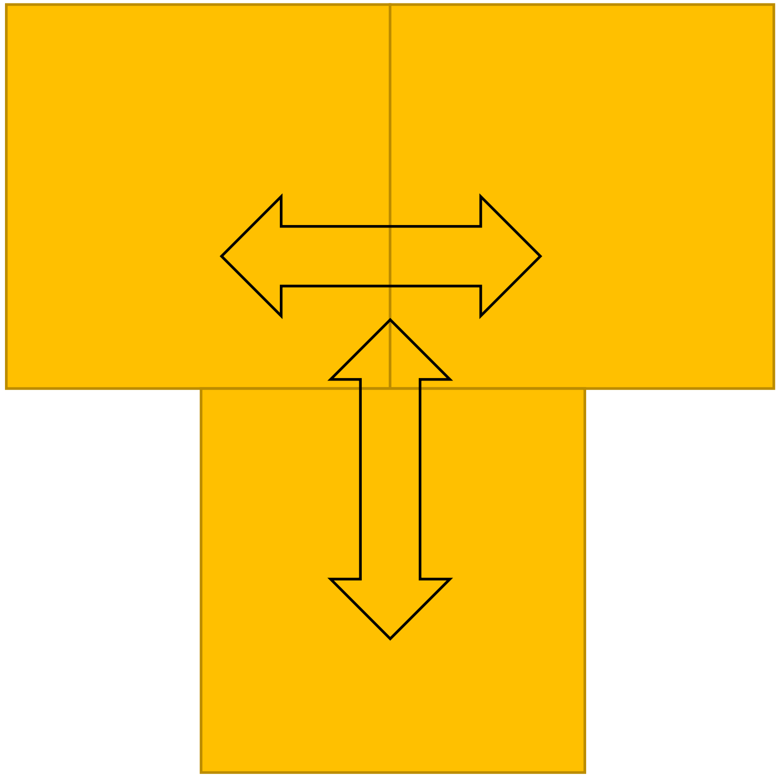

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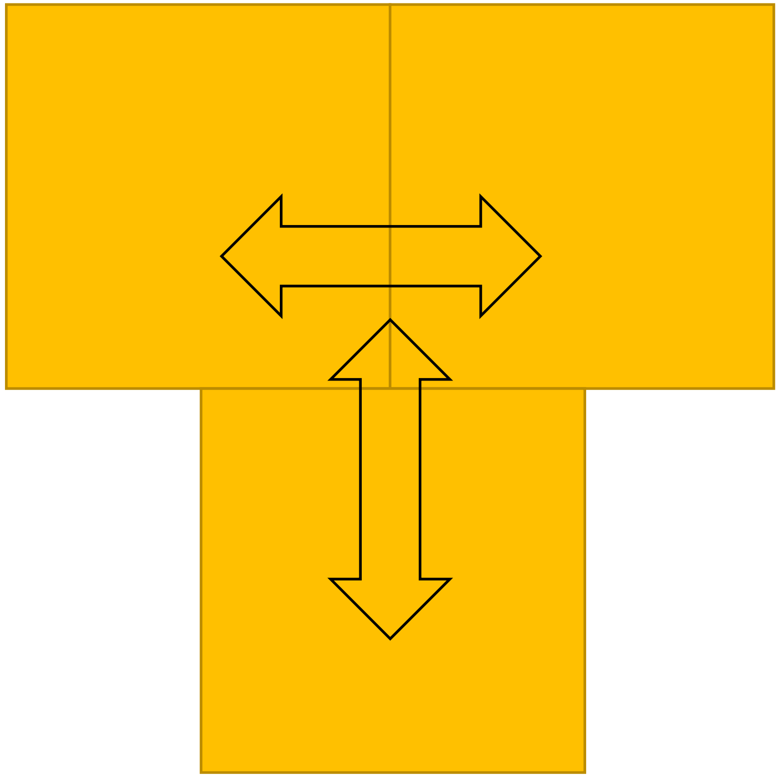
    - Kelvin (Rankine)



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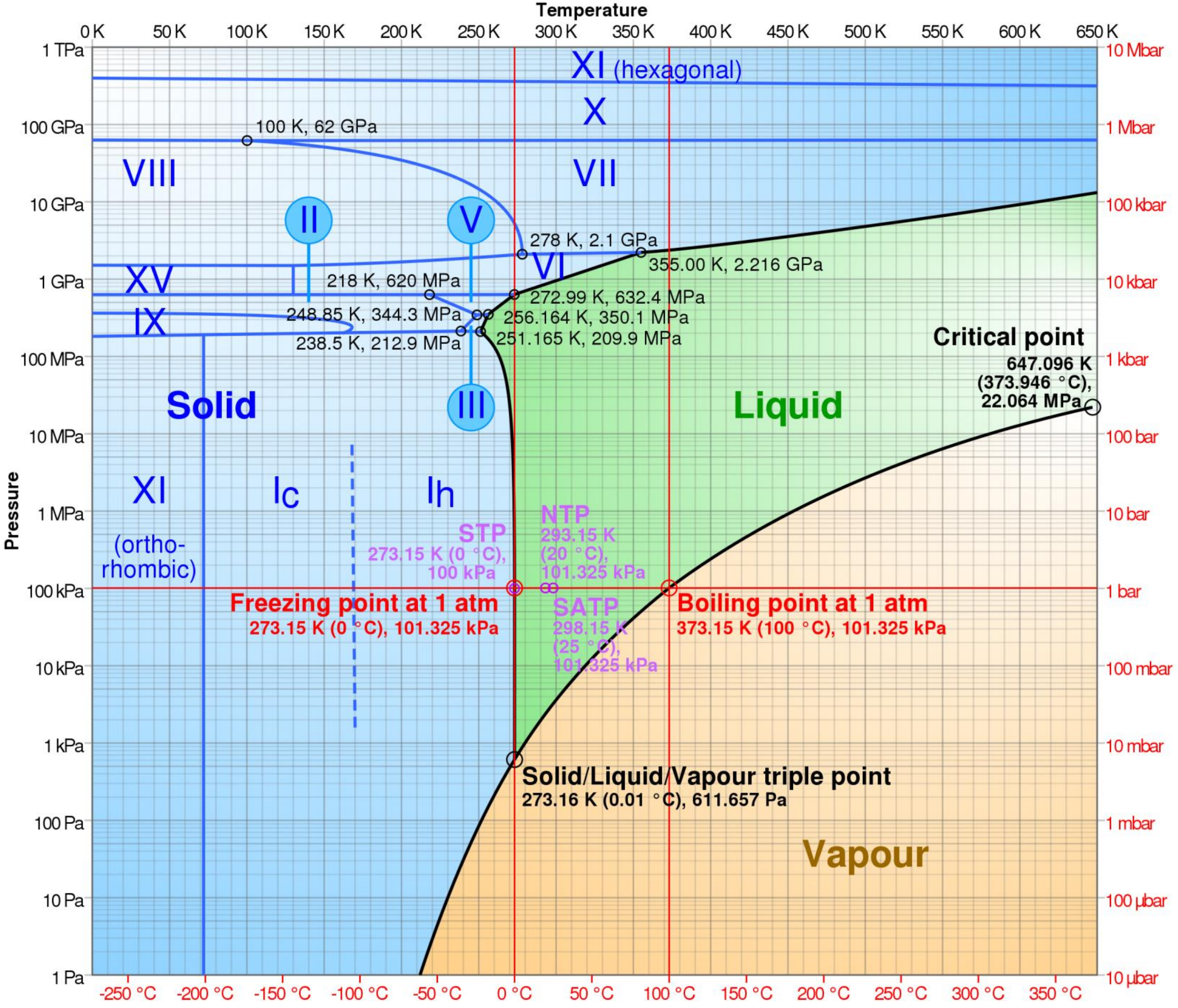

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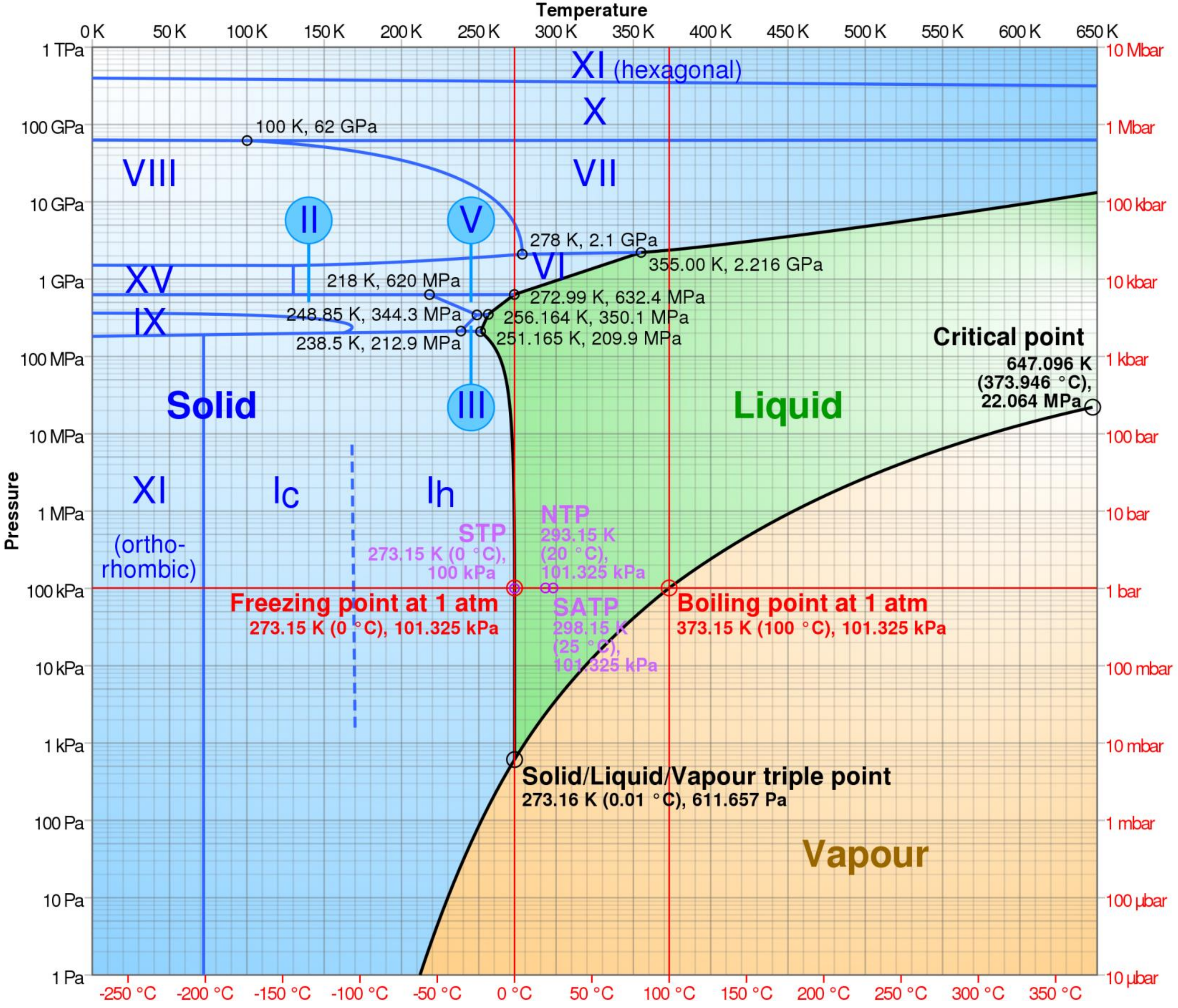

Phase Diagram (Water)

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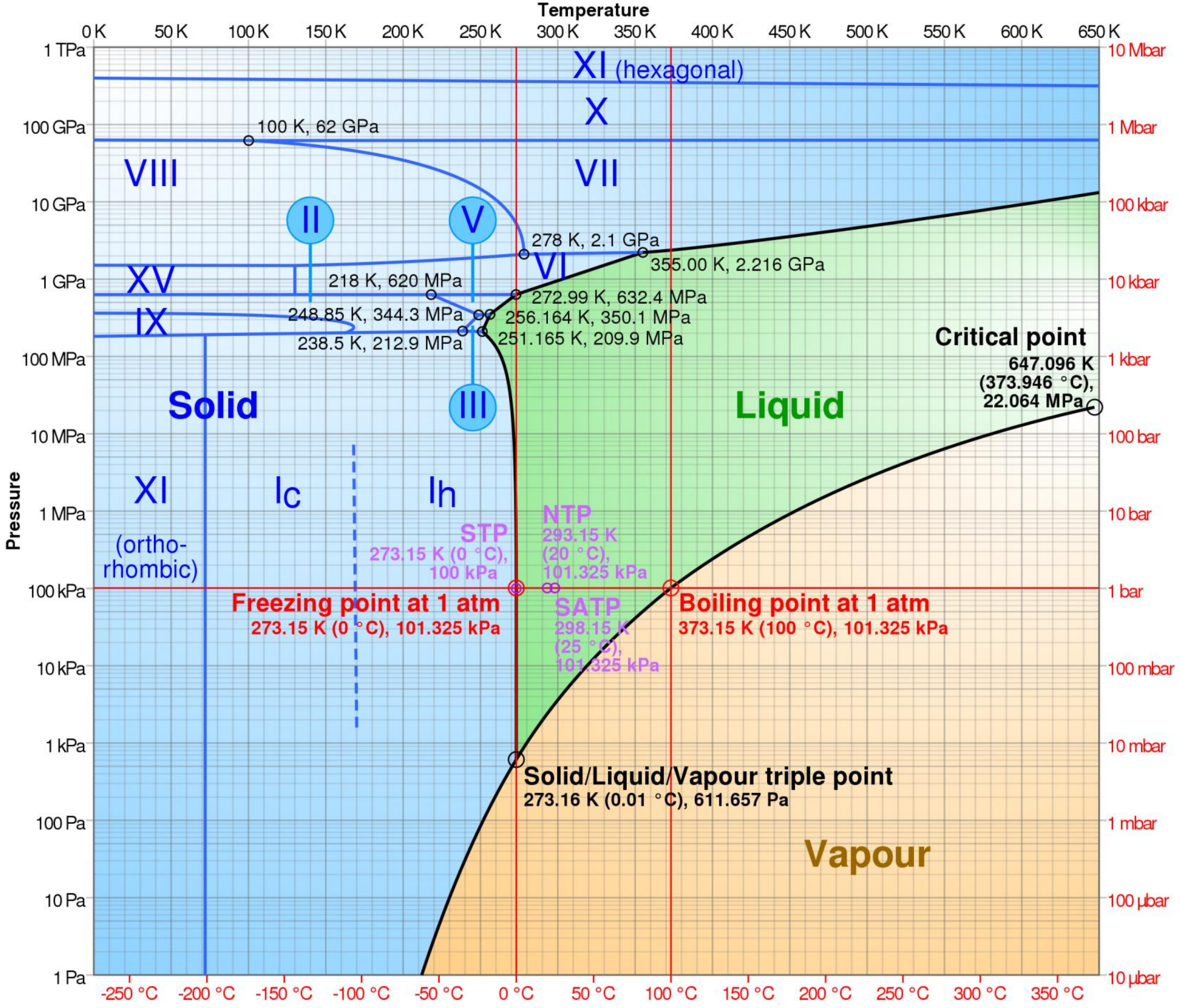

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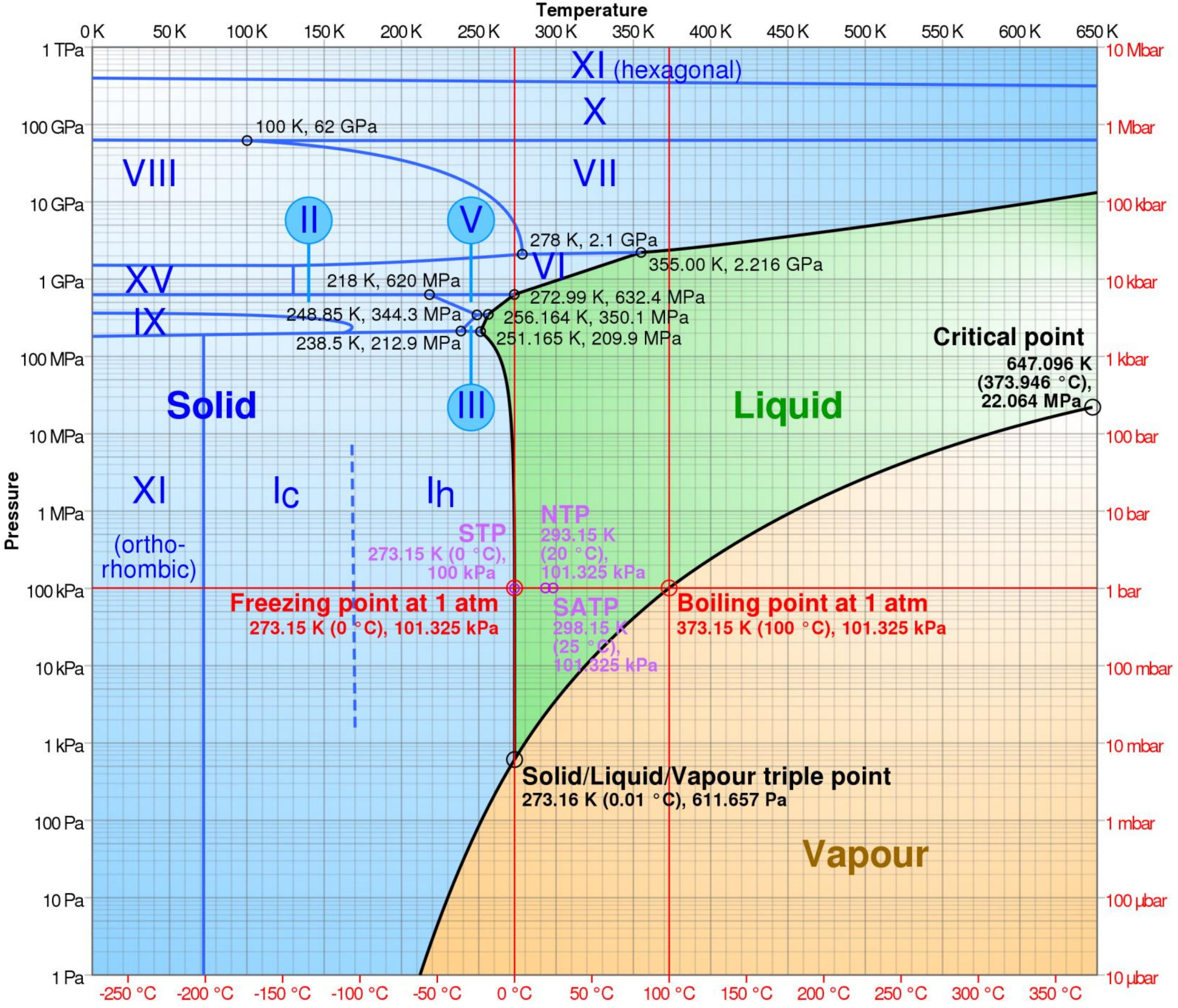

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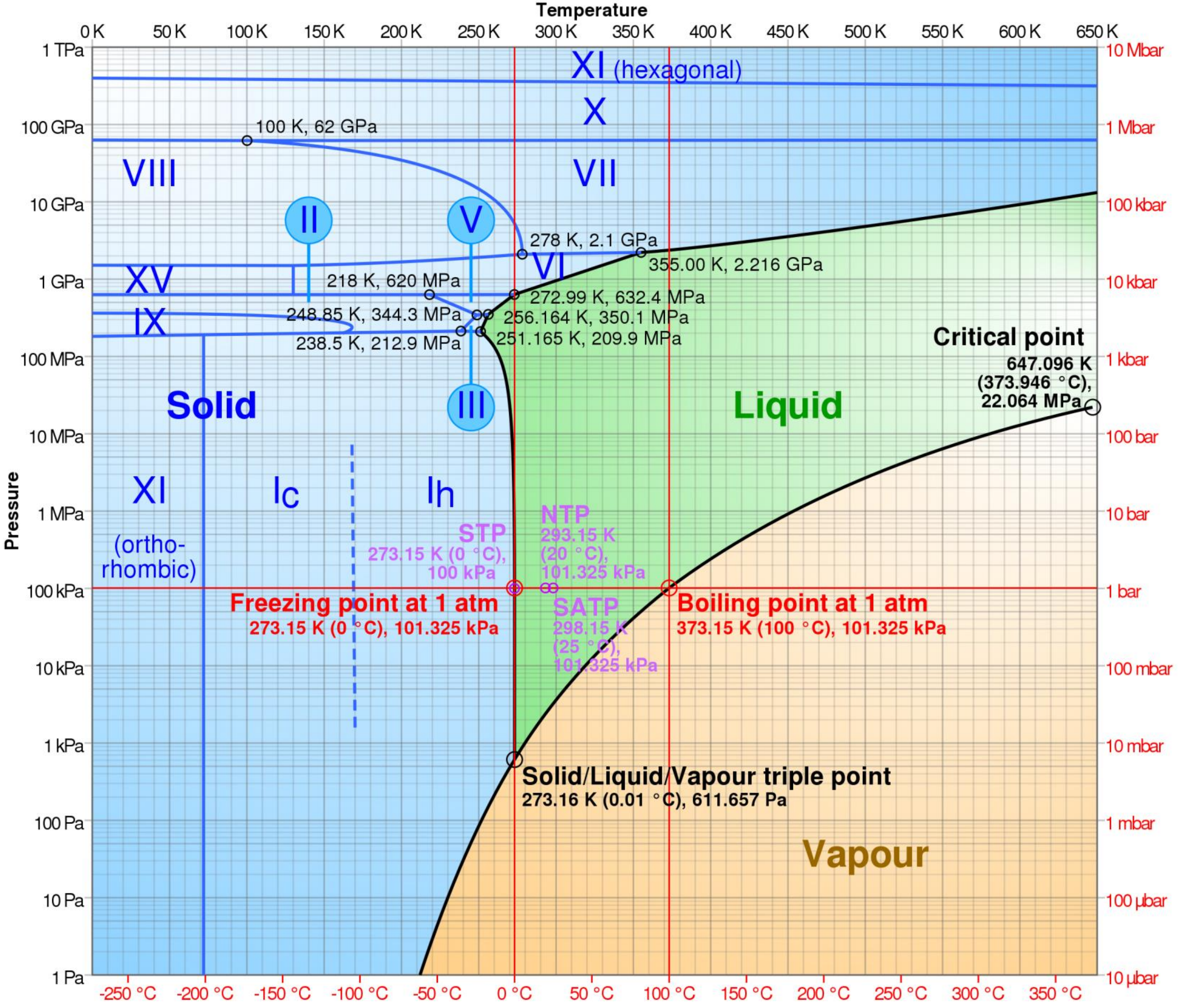

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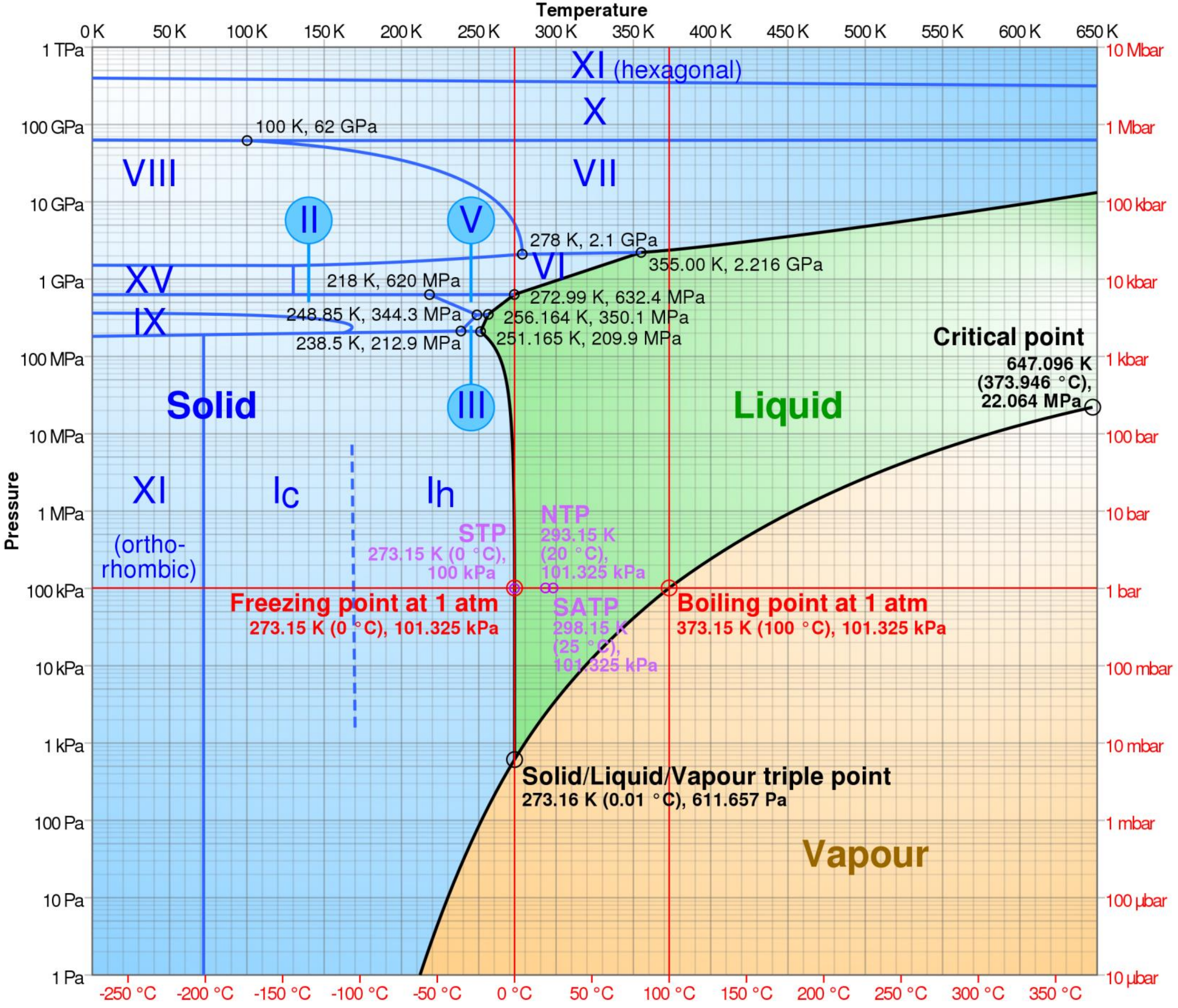

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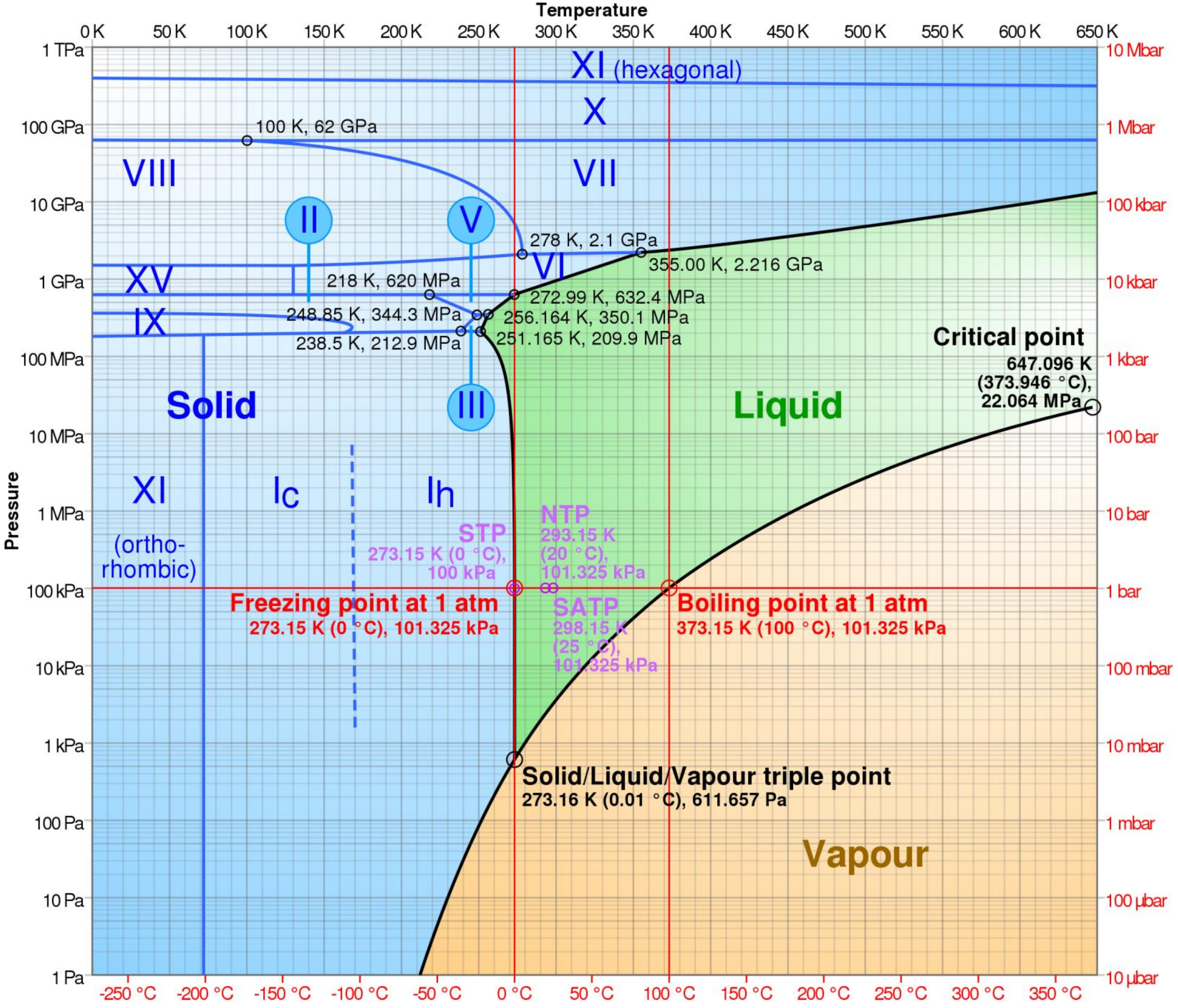

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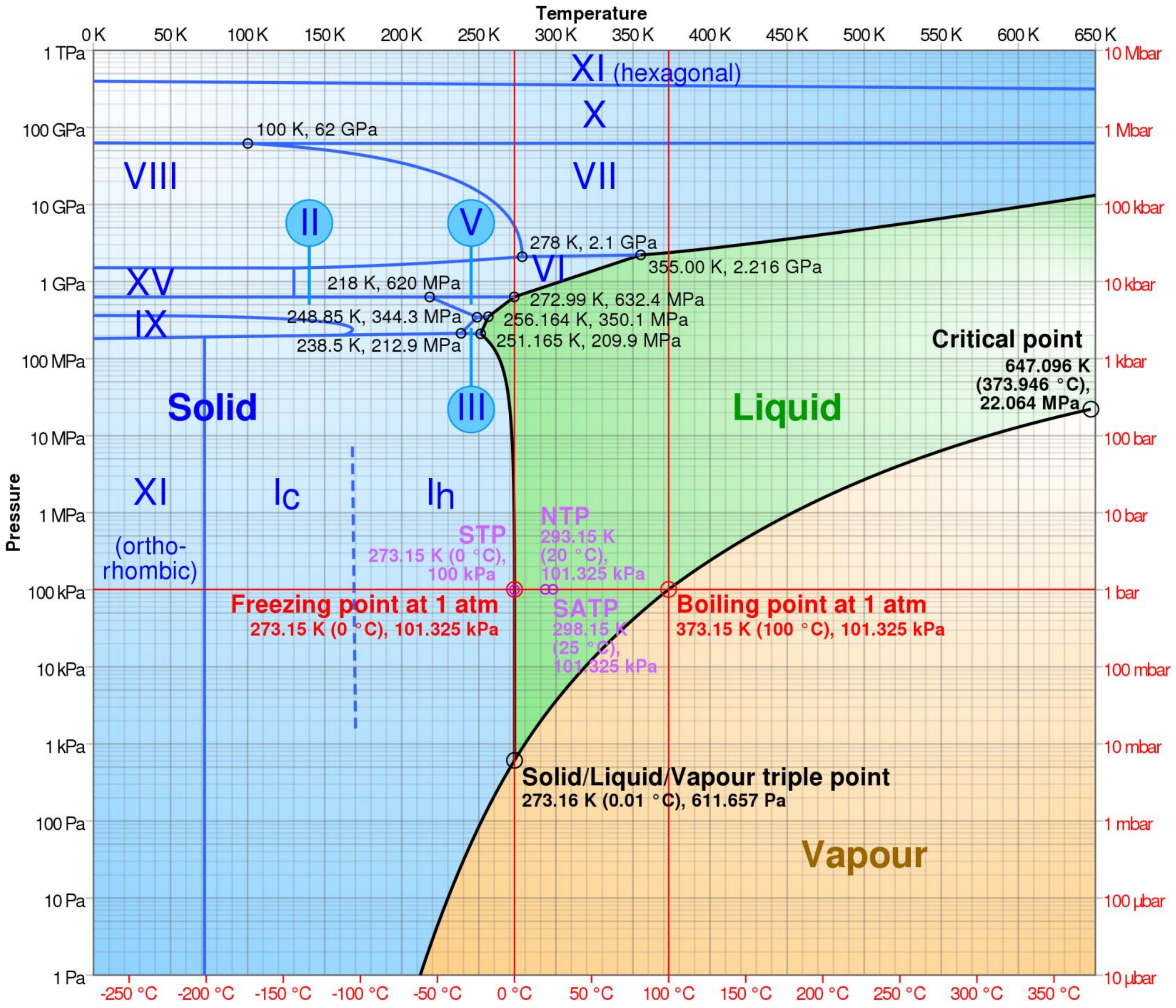

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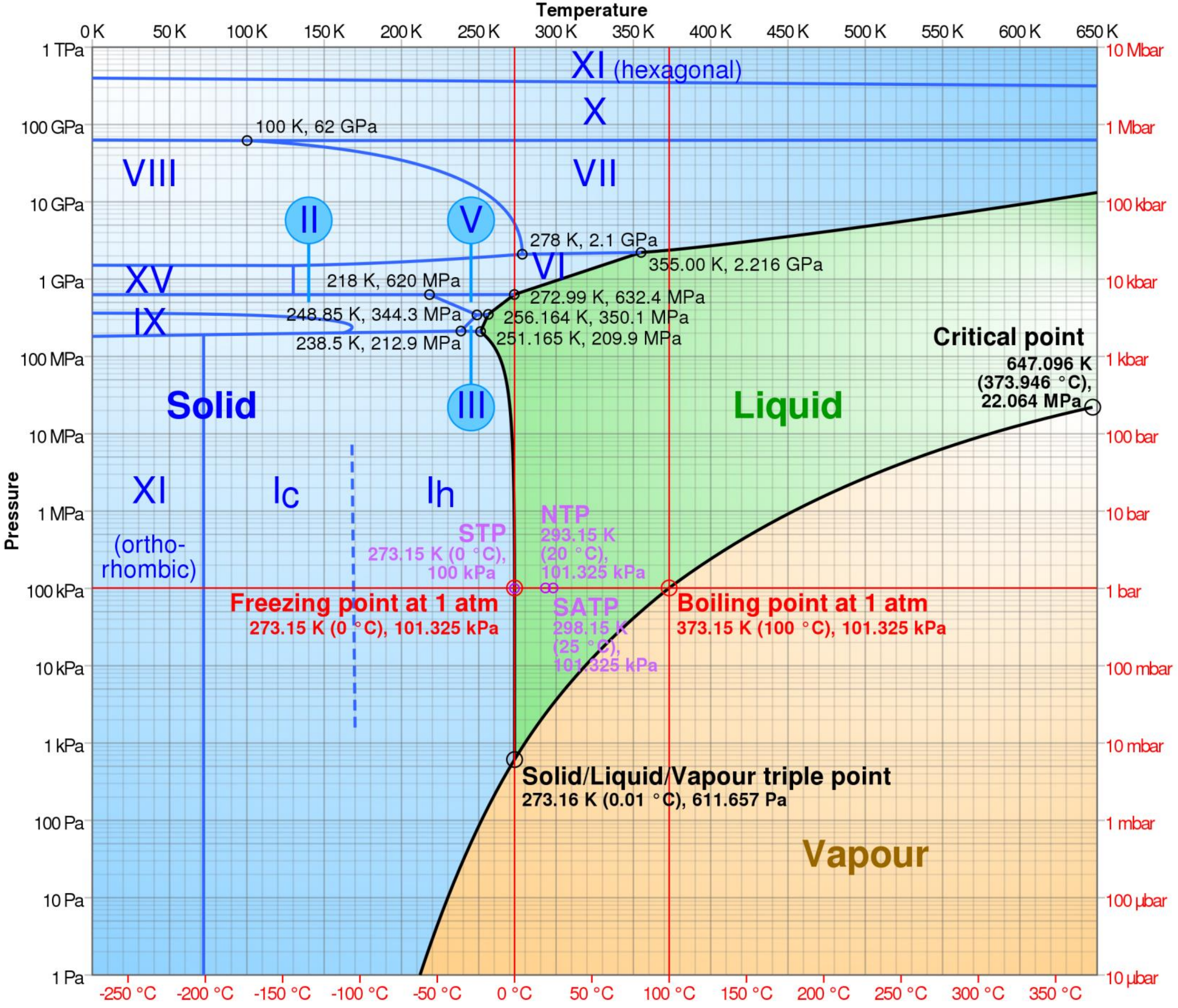
  - $P(V)$



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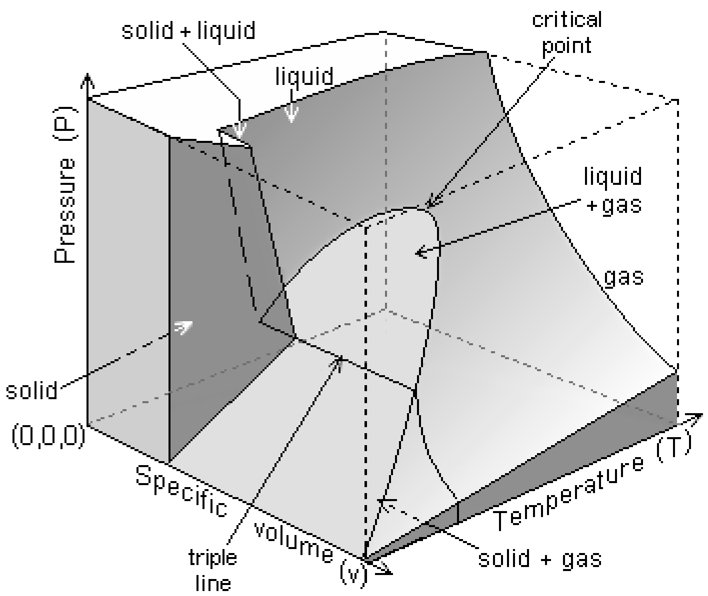
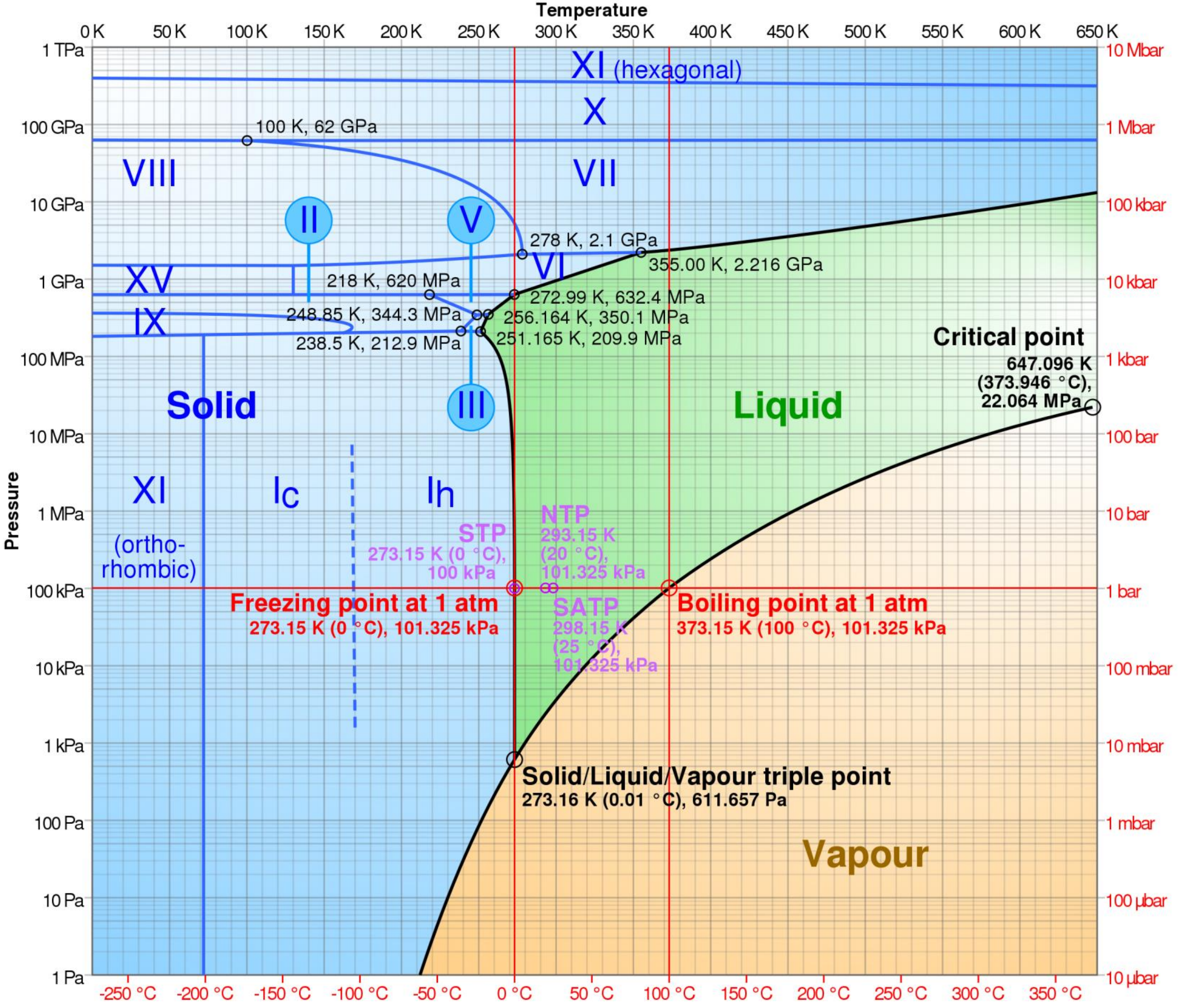
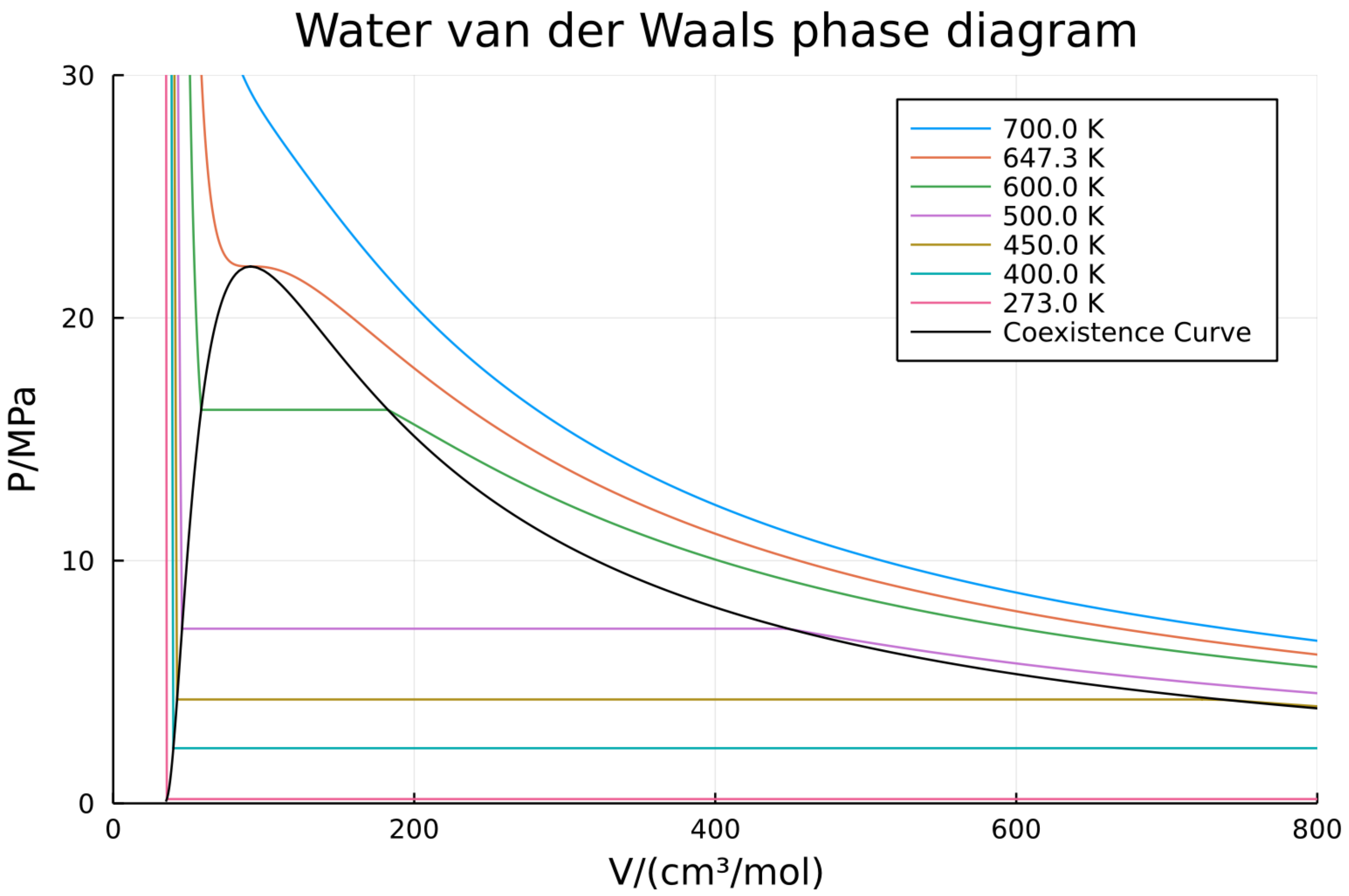


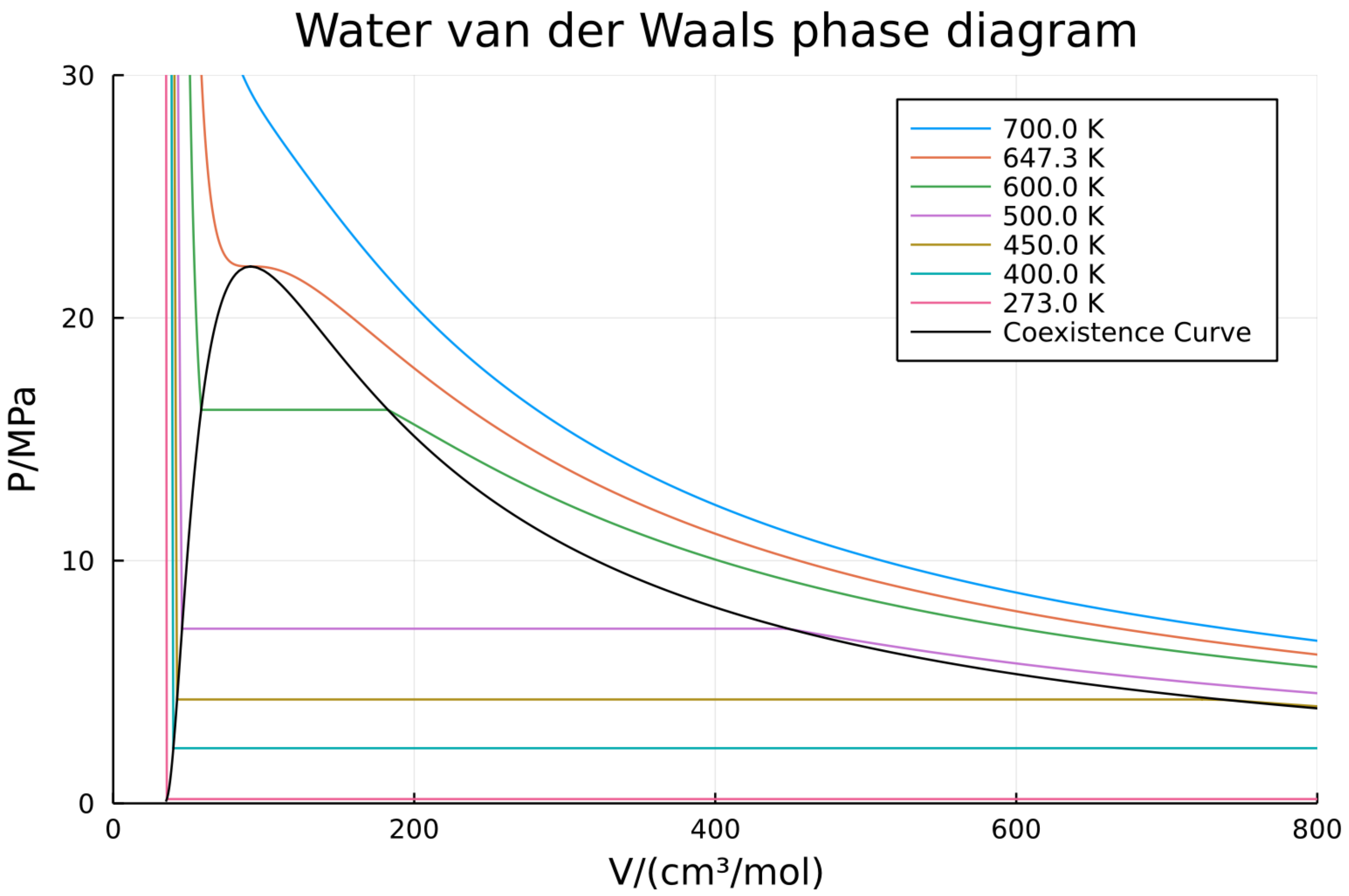


$$P(V,T)$$


Water van der Waals phase diagram
P/MPa
V/(cm³/mol)
0
10
20
30
0
200
400
600
800
700.0 K
647.3 K
600.0 K
500.0 K
450.0 K
400.0 K
273.0 K
Coexistence Curve

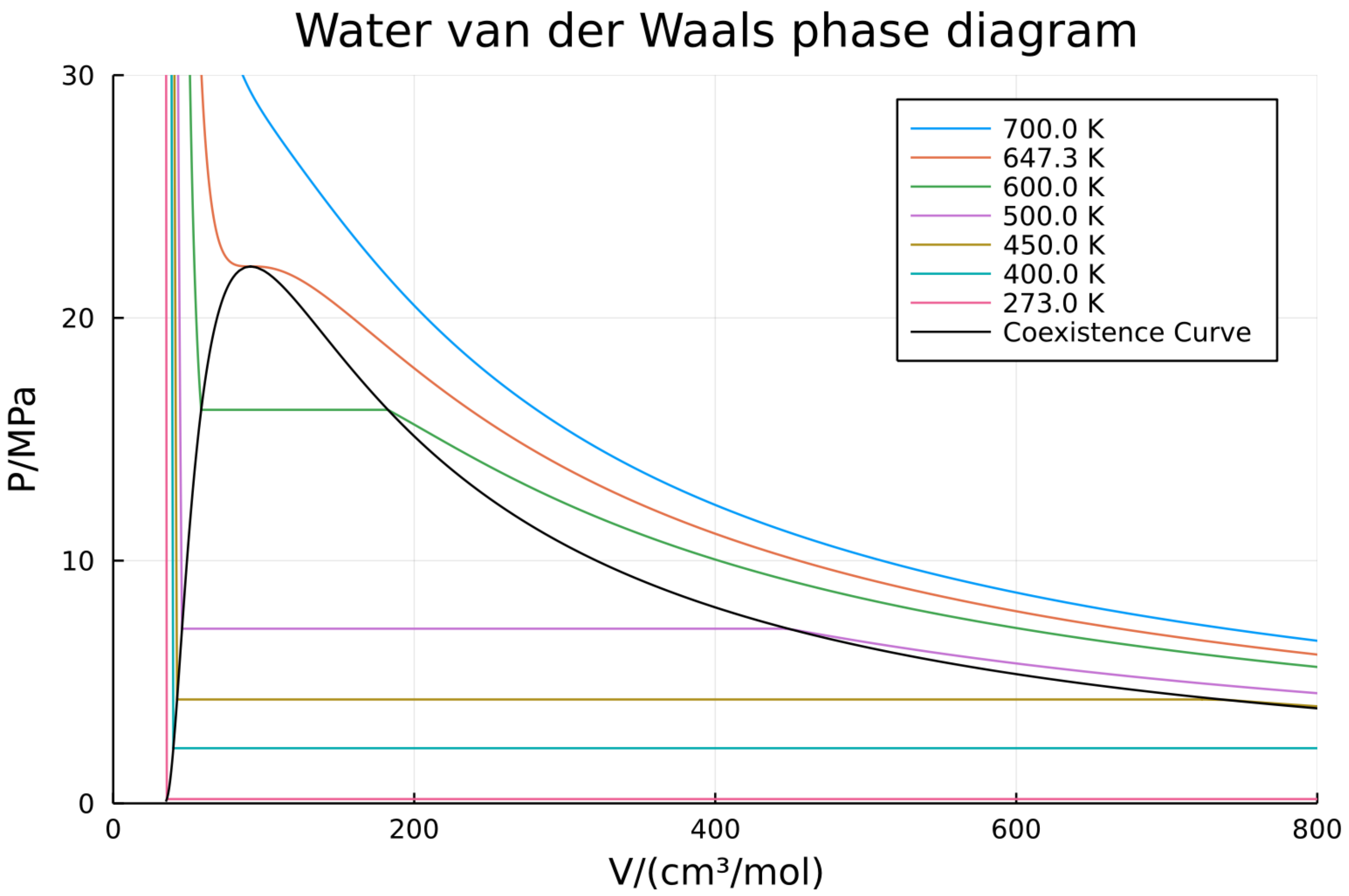
$$P(V,T)$$

- Horizontal lines → “tie lines”



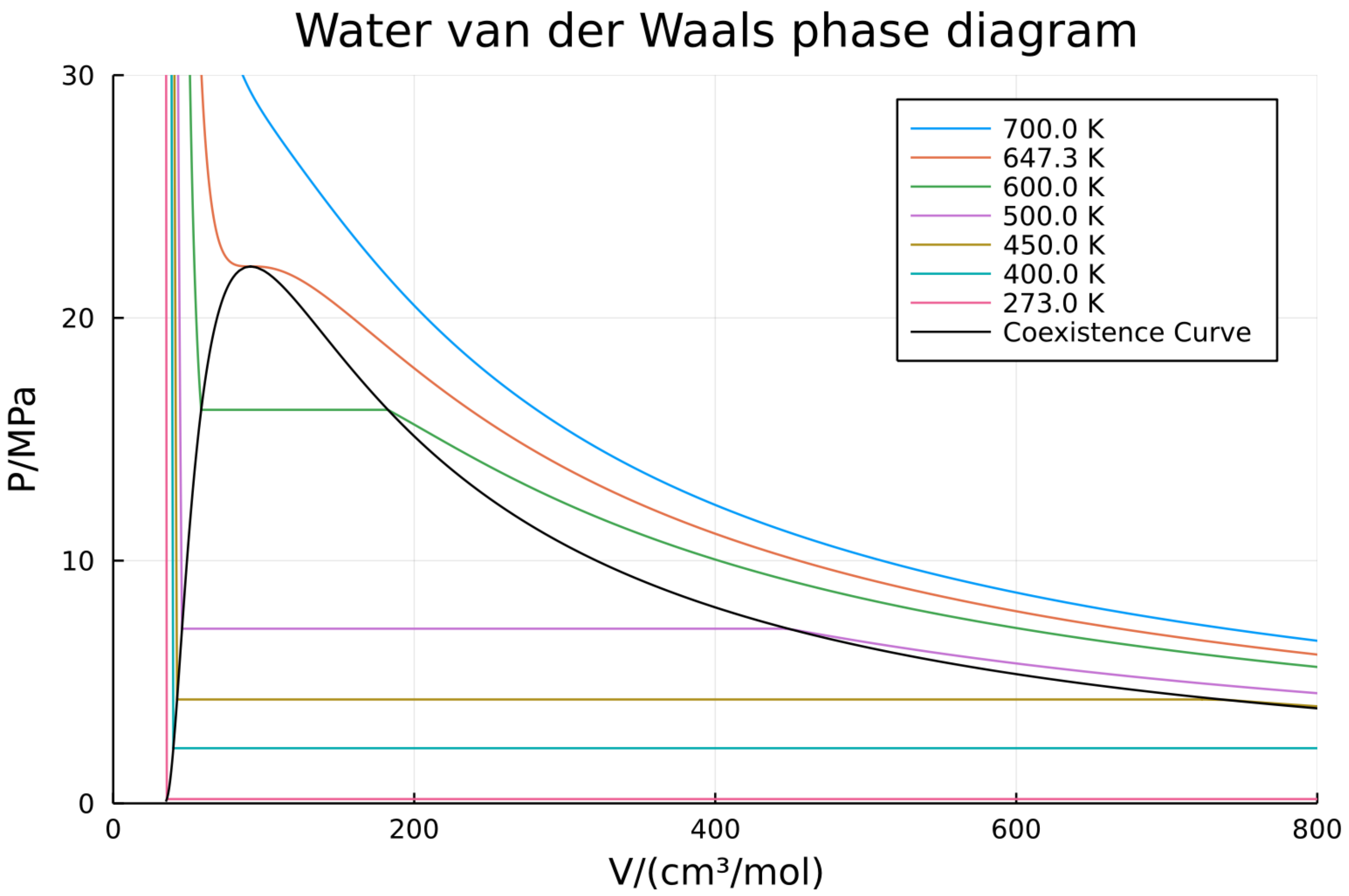
$P(V,T)$

- Horizontal lines → "tie lines"
  - $\left(T = 600\ K, V \approx 400 \frac{cm^3}{mol}\right) \rightarrow P_{sat} \approx 16.2\ MPa$

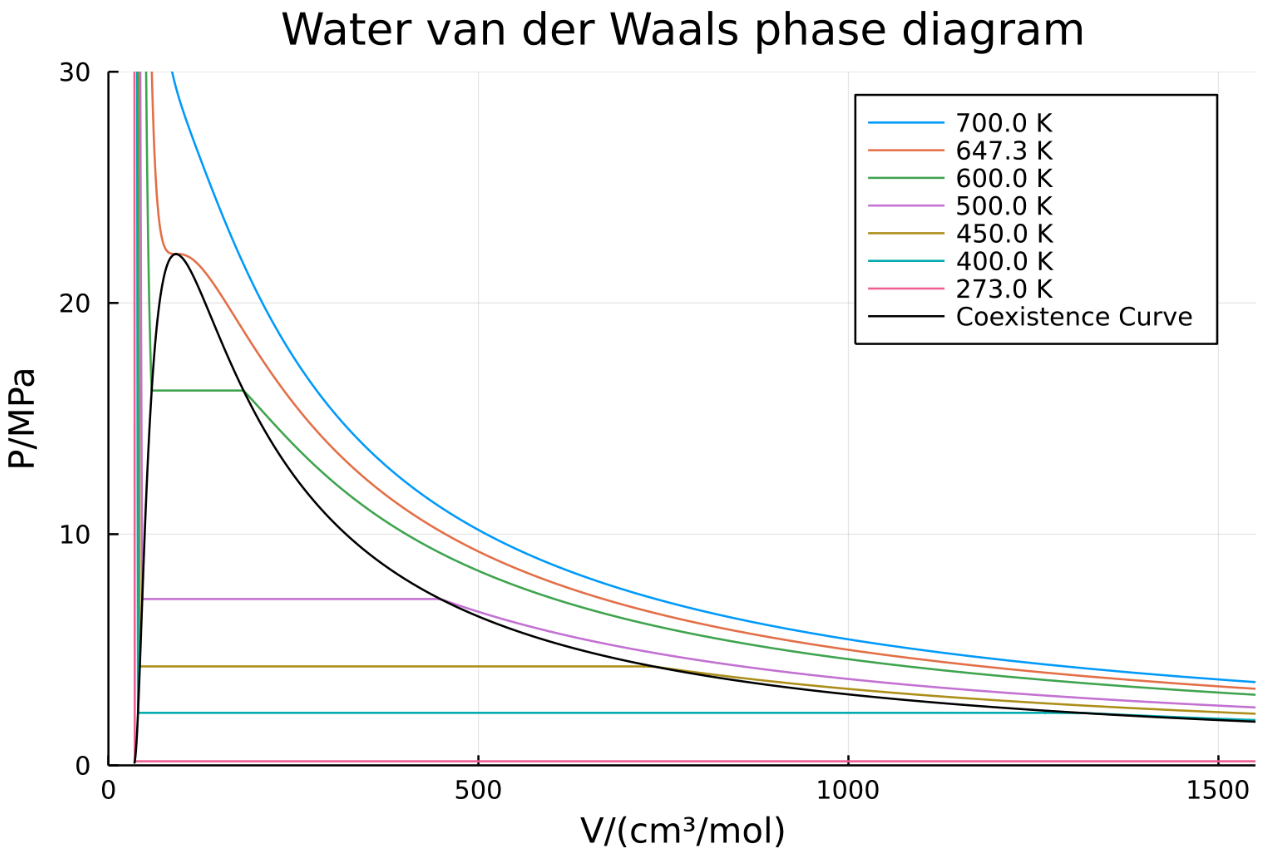


$$P(V,T)$$

- Horizontal lines → "tie lines"
  - $\left(T = 600\ K, V \approx 400 \frac{cm^3}{mol}\right) \rightarrow$ $P_{sat} \approx 16.2\ MPa$
- $V_{vapor}(T = 400\ K, P \approx 2.3\ MPa)$?

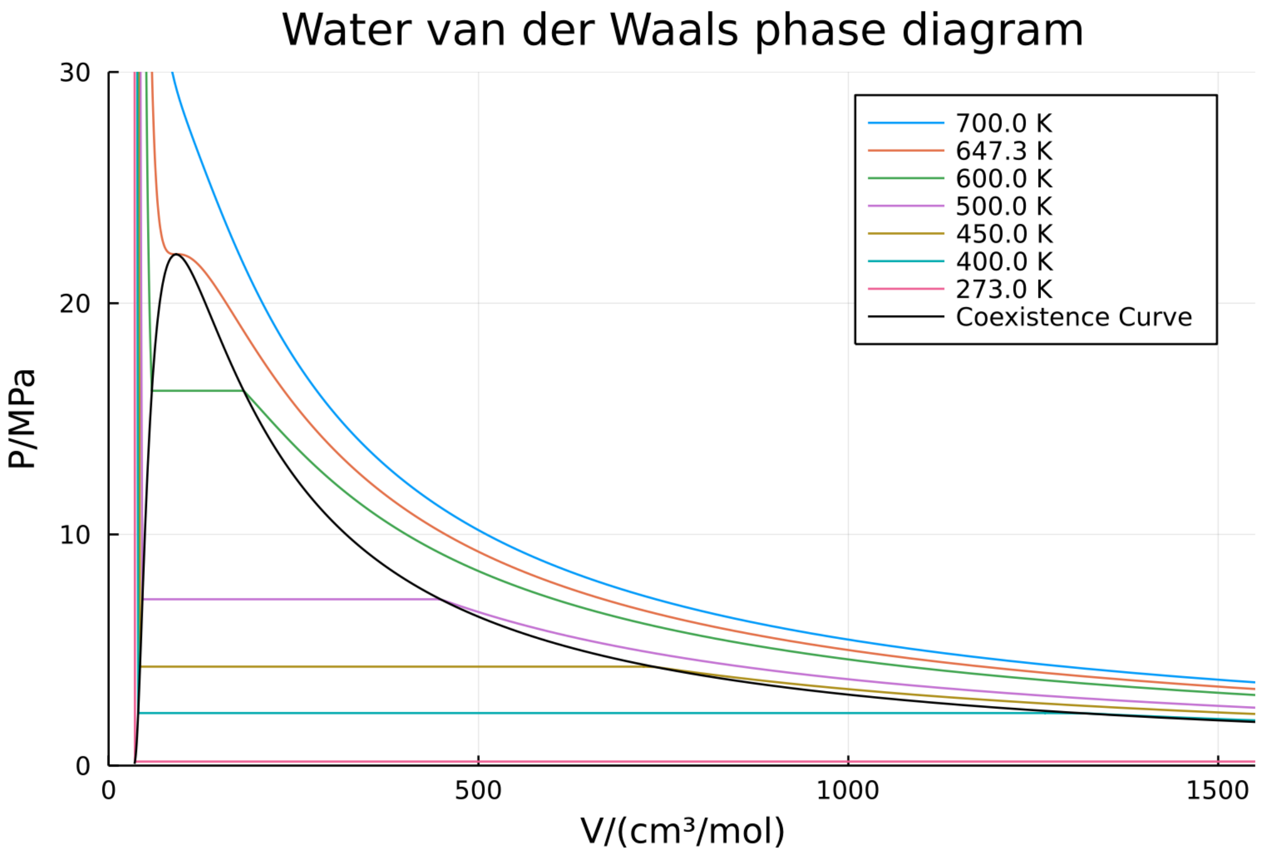


$T = 400\ \mathrm{K}$

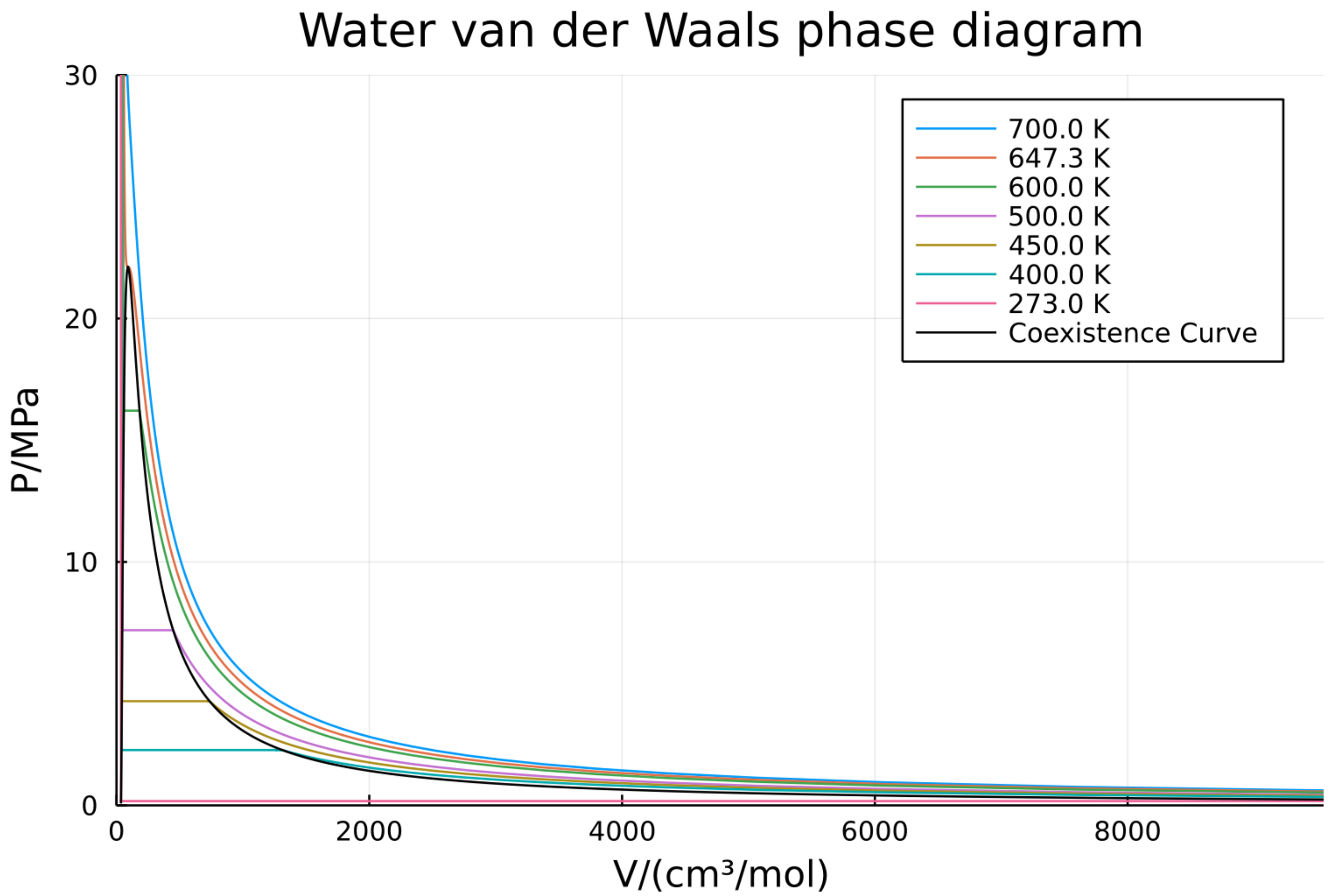


$$T = 400 \text{ K}$$

$$P_{sat}(T = 400\ K) \approx 2.3\ MPa$$

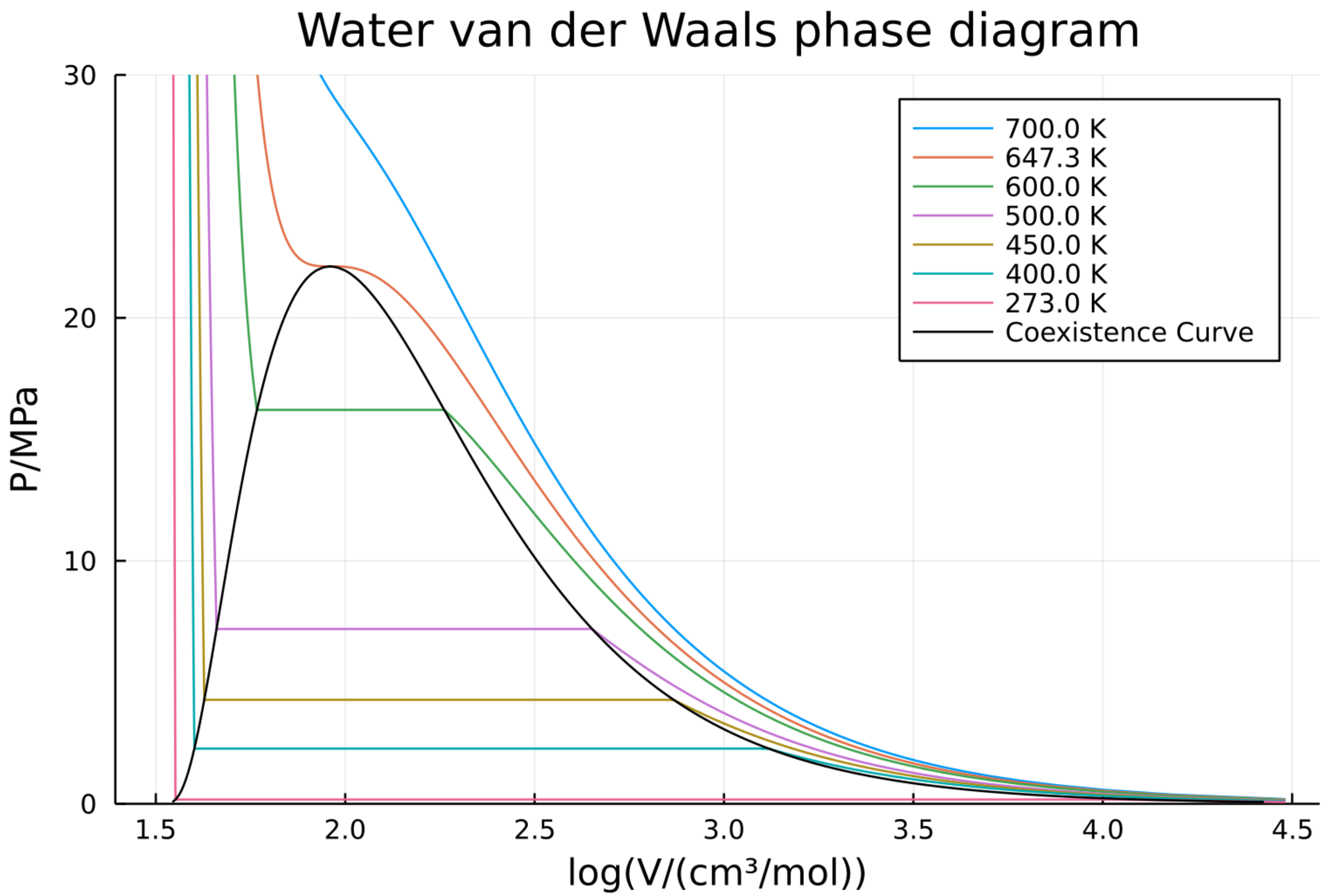


$T = 273$ K?

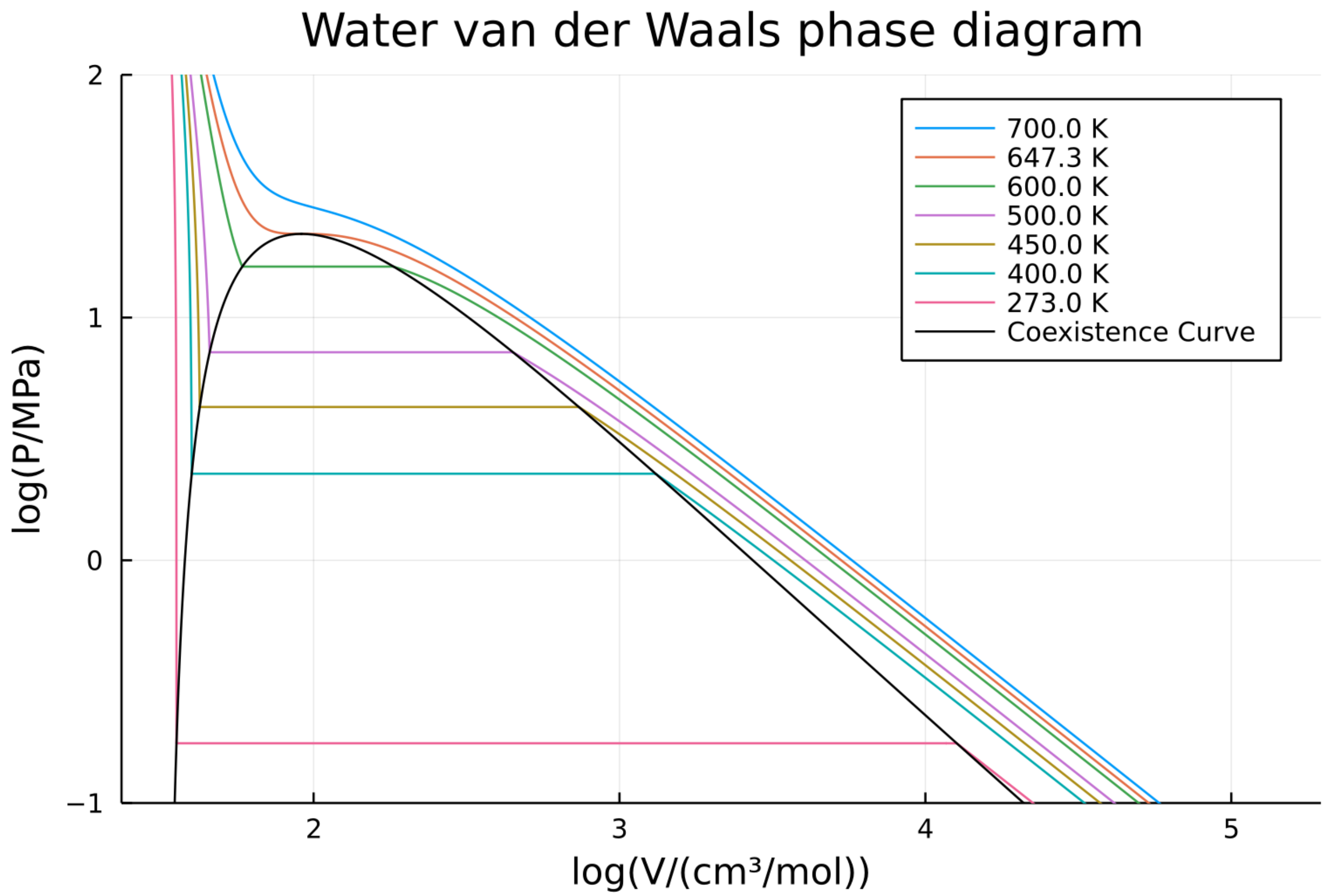


Water van der Waals phase diagram
700.0 K
647.3 K
600.0 K
500.0 K
450.0 K
400.0 K
273.0 K
Coexistence Curve
P/MPa
V/(cm³/mol)
0
10
20
30
0
2000
4000
6000
8000

$P(\log V)$!

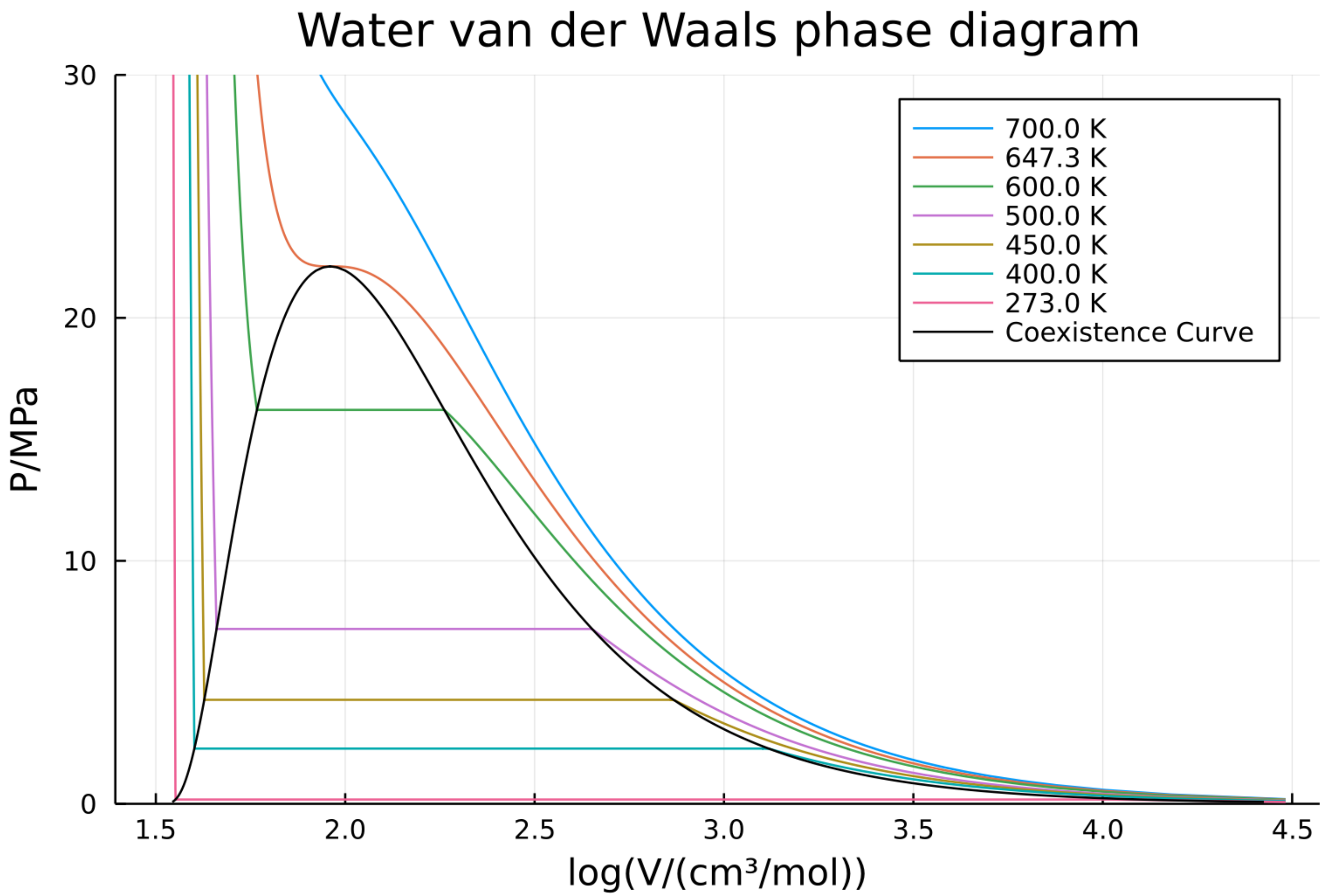

Water van der Waals phase diagram
P/MPa
log(V/(cm³/mol))
700.0 K
647.3 K
600.0 K
500.0 K
450.0 K
400.0 K
273.0 K
Coexistence Curve
0
10
20
30
1.5
2.0
2.5
3.0
3.5
4.0
4.5

$\log P(\log V)$!!



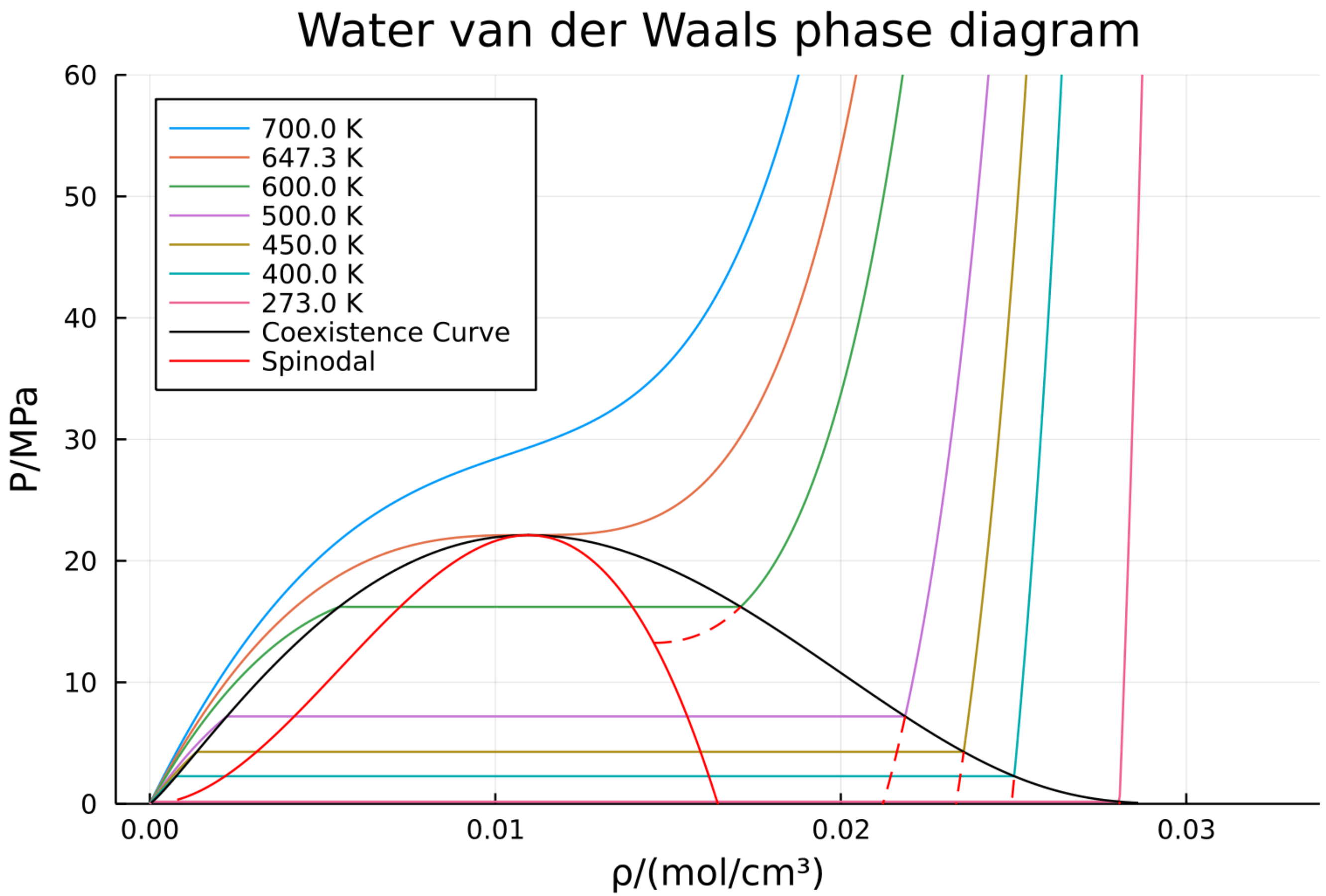
Water van der Waals phase diagram
2
1
0
−1
2
3
4
5
log(P/MPa)
log(V/(cm³/mol))
700.0 K
647.3 K
600.0 K
500.0 K
450.0 K
400.0 K
273.0 K
Coexistence Curve

$$V \to \infty\ ?$$

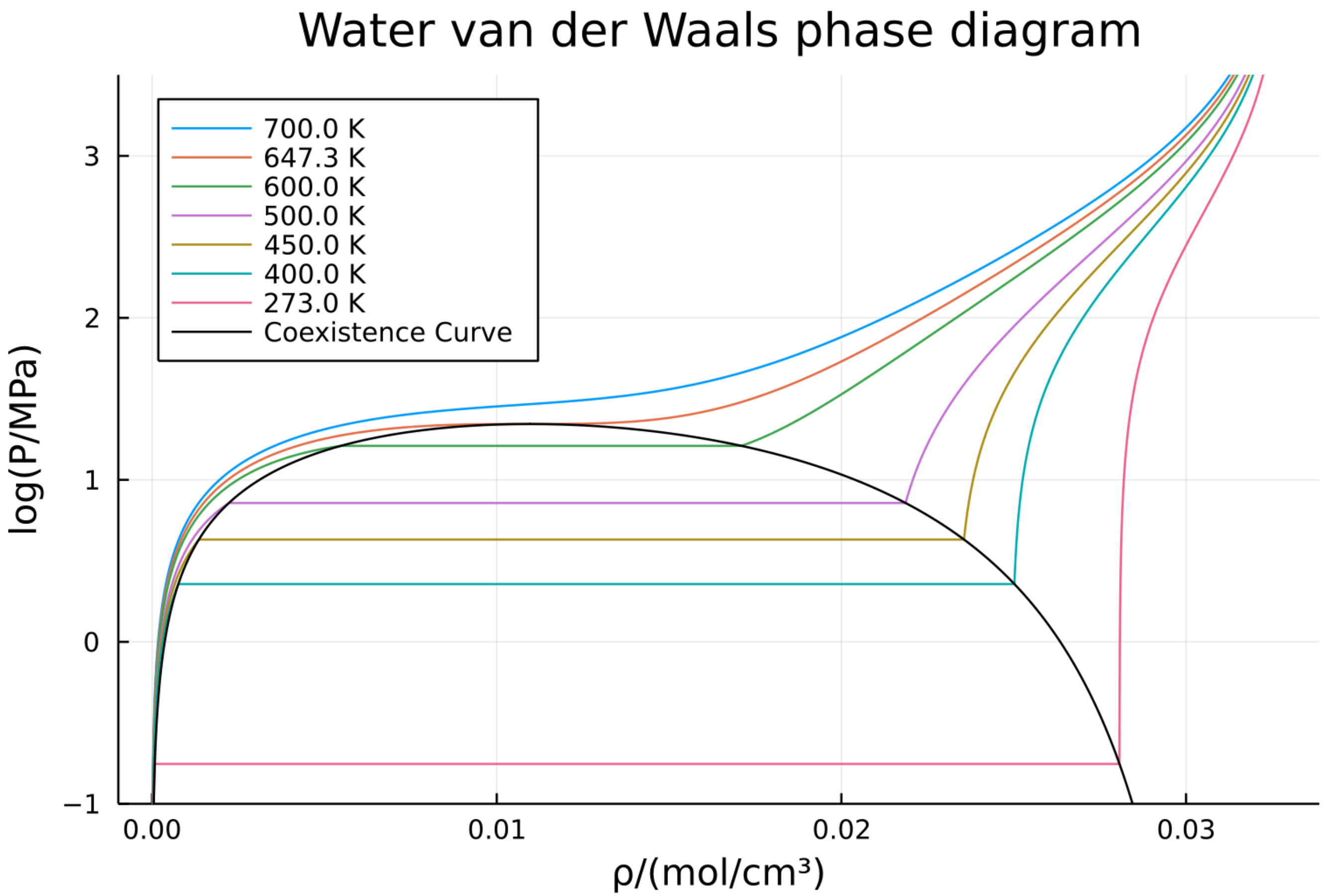


Water van der Waals phase diagram
P/MPa
log(V/(cm³/mol))
700.0 K
647.3 K
600.0 K
500.0 K
450.0 K
400.0 K
273.0 K
Coexistence Curve
0
10
20
30
1.5
2.0
2.5
3.0
3.5
4.0
4.5

$$P\left(\frac{1}{V}\right) = P(\rho)$$



$\log P$ ...



Water van der Waals phase diagram
700.0 K
647.3 K
600.0 K
500.0 K
450.0 K
400.0 K
273.0 K
Coexistence Curve
log(P/MPa)
3
2
1
0
−1
0.00
0.01
0.02
0.03
ρ/(mol/cm³)

Energy Balances

Energy Balances

- Pure, single component:

Energy Balances

- Pure, single component:
  - Two degrees of freedom

Energy Balances

- Pure, single component:
  - Two degrees of freedom
  - $P(T,V)$ or $U(T,V)$ or $H(T,V)$

Energy Balances

- Pure, single component:
  - Two degrees of freedom
  - $P(T,V)$ or $U(T,V)$ or $H(T,V)$
- $\frac{\partial P}{\partial T}$

Energy Balances

- Pure, single component:
  - Two degrees of freedom
  - $P(T,V)$ or $U(T,V)$ or $H(T,V)$
- $\frac{\partial P}{\partial T}$
- $\frac{\partial U}{\partial T} \equiv C_V$

Energy Balances

- Pure, single component:
  - Two degrees of freedom
  - $P(T,V)$ or $U(T,V)$ or $H(T,V)$
- $\frac{\partial P}{\partial T}$
- $\frac{\partial U}{\partial T} \equiv C_V$
- $\frac{\partial H}{\partial T} \equiv C_P$