Daiguji and Hsu Lab

T39.00005
Thermodynamic modelling of equilibrium phase transitions in confined fluids

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Session T39: Physics of Liquids I

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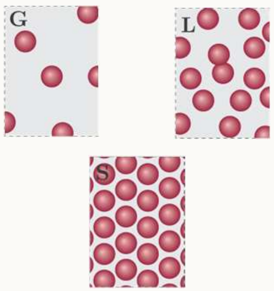
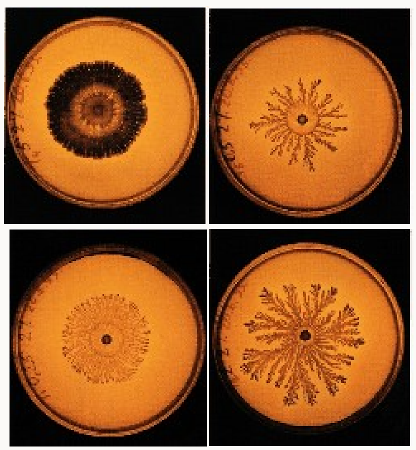
Phase

Phase



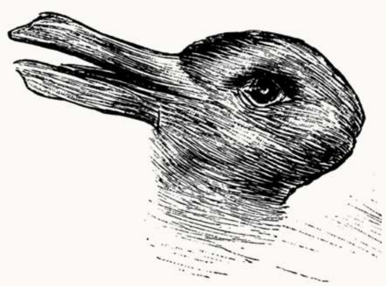
Physical Phases of Matter [1]

Murmuration [2]



Bacterial growth patterns [3]

Fish Schools [2]



Duck or rabbit? [4]

Transitions between **alternate states** have been defined in several contexts ranging from physical properties, ecological processes, and even our thoughts! [3]

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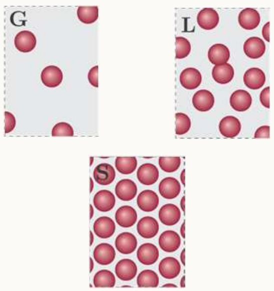

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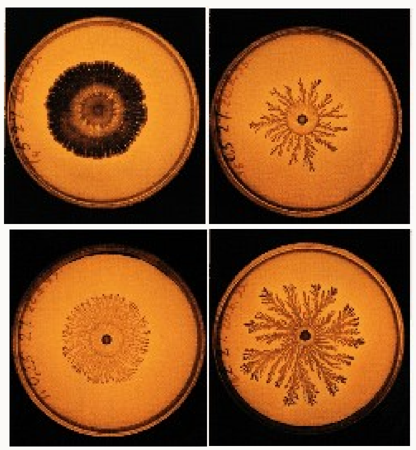

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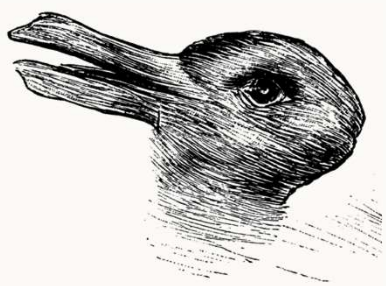

Duck or rabbit? [4]

Transitions between **alternate states** have been defined in several contexts ranging from physical properties, ecological processes, and even our thoughts! [3]

Collective patterns of organization are referred to as ***phases*** and the transitions as ***phase transitions***

G. Nicolis and I. Prigogine. Exploring complexity an Introduction. (1989)

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Orderliness of the system defines the phase of the system

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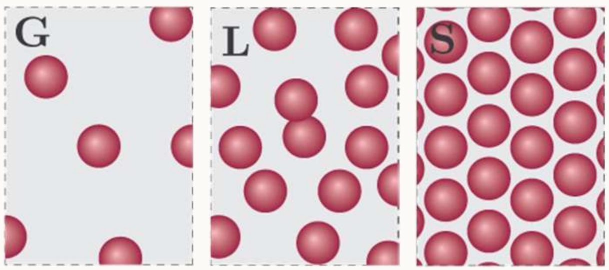
Homogenous phase



Highly disordered | **Disordered** | **Highly ordered**

Orderliness → Entropy (S)
(Disorder)

$$S = -k_B \, ln(\omega)$$

Number of possible microstates

At a given temperature T for a closed system,

$$S_G > S_L > S_S$$

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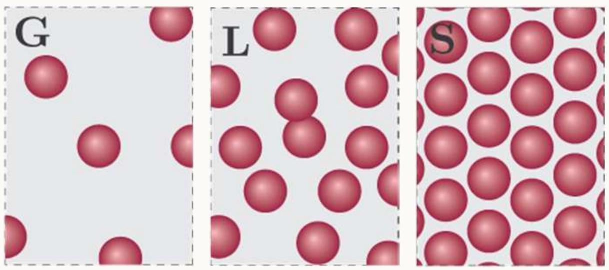

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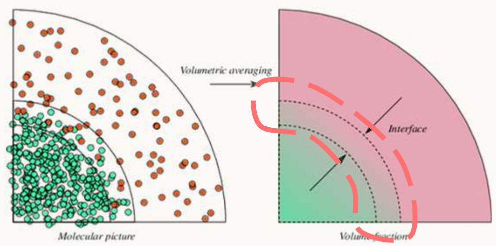
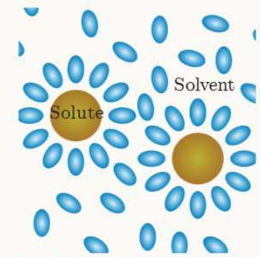
Heterogeneity creates anisotropy



S. Jain, J. Comput. Phys., 418 (2020)



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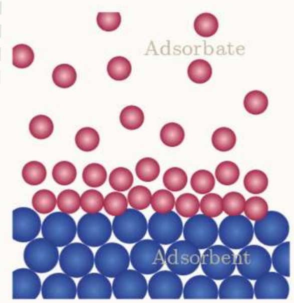

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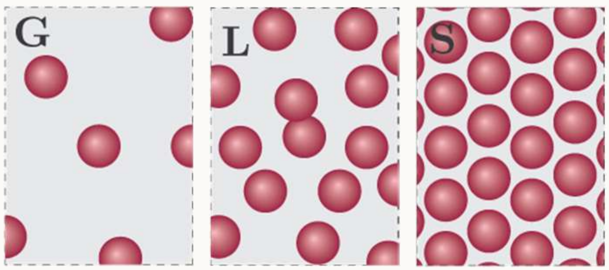

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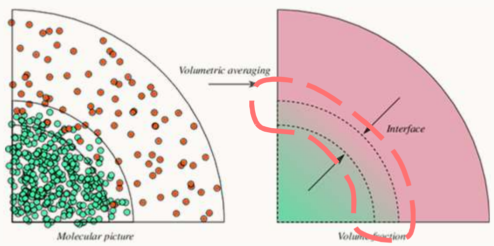

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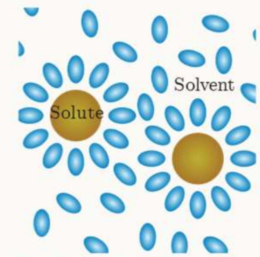

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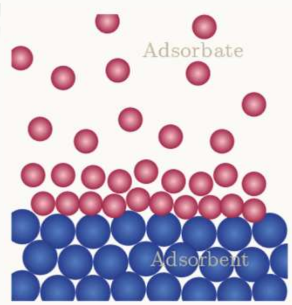

*"Local order in a region of **nonuniform composition** will depend both on the **local composition** and on the **composition of the immediate environment**"*

J. Cahn and J. Hilliard, J. Chem. Phys, 28, (1958)

The cubic MOF model

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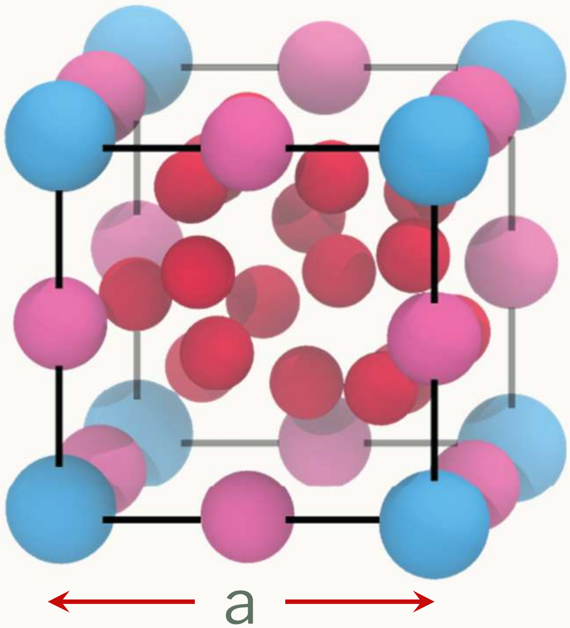

Metal Ligand Argon

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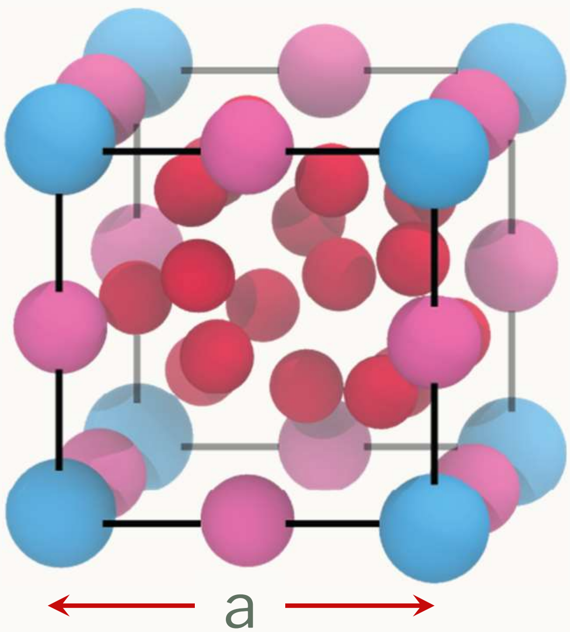

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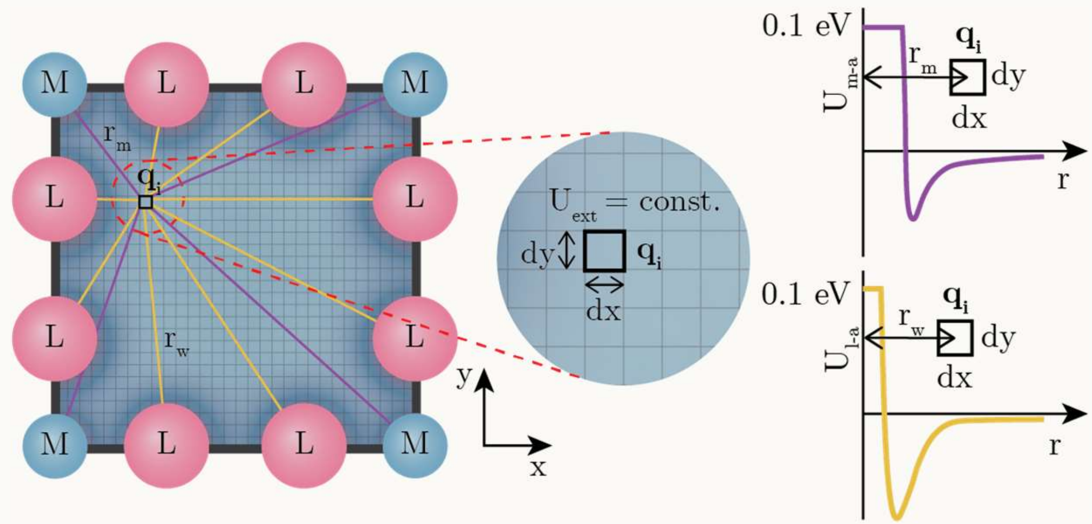


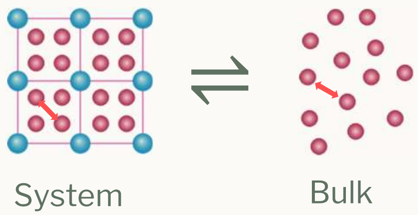
Assumptions

- Only Van-der Waals interactions
- Coarse grained model for the ligands
- Potential due to different sources are additive

Statistical Model

Statistical Model

Assumption



$$\mu_{ads} = \mu_{bulk}$$ [1-4]

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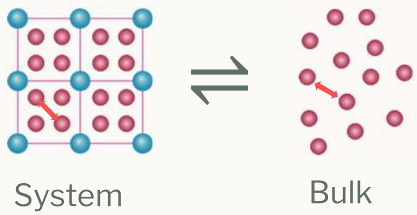

$$\mu_{ads} = \mu_{bulk}$$ [1-4]

Grand Canonical Ensemble ($\mu_{ads} VT$)

$$\mathcal{Z}_{ads} = \sum_{N=0}^{\infty} (\mathbb{Z}_{k,N} \cdot \mathbb{Z}_{u,N})\, e^{\mu_{ads} N/k_B T}$$

Grand partition function

Canonical partition function

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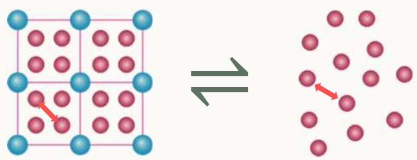

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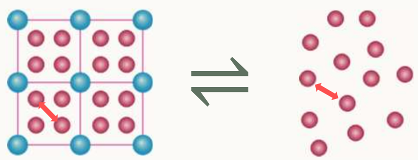

System Bulk

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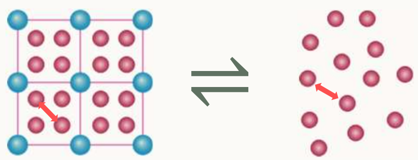

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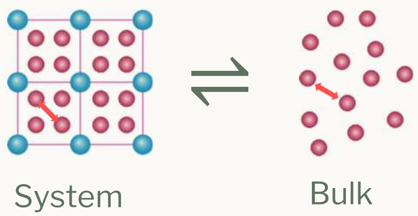

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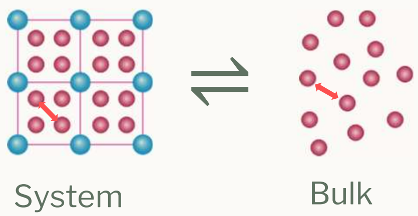

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Mean-field approximation

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Adsorption isotherms (**Benchmarking**)

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T = 100 K

T= 110 K

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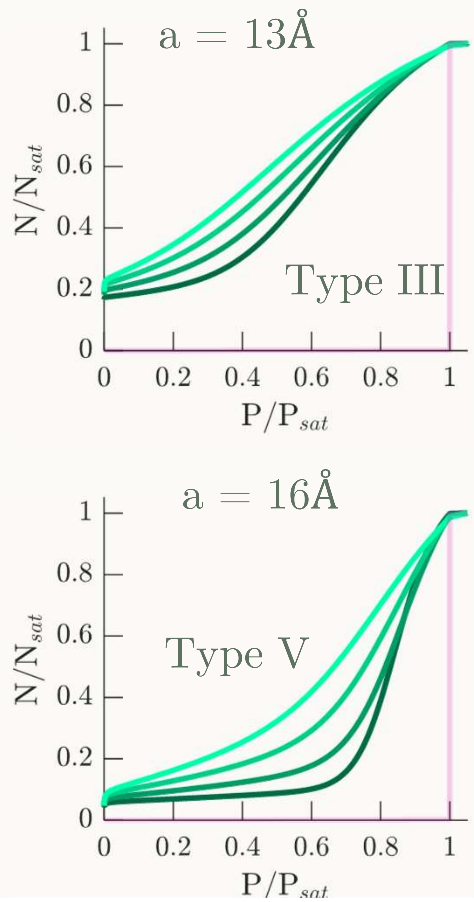

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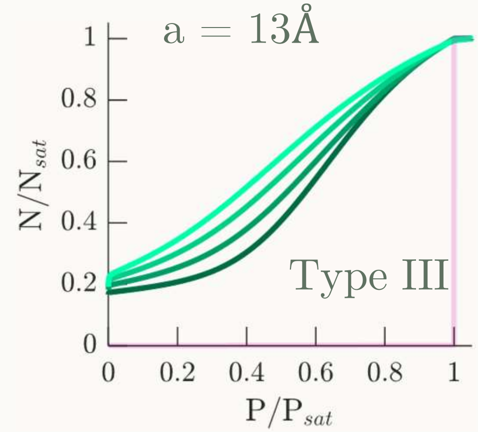
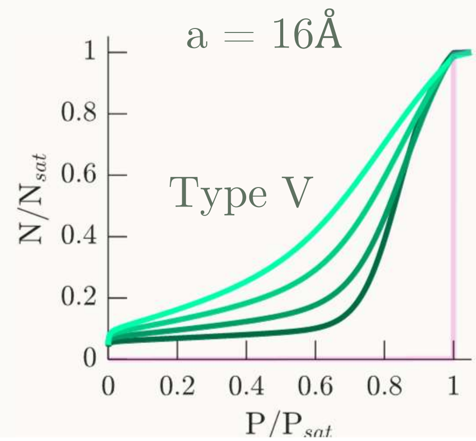
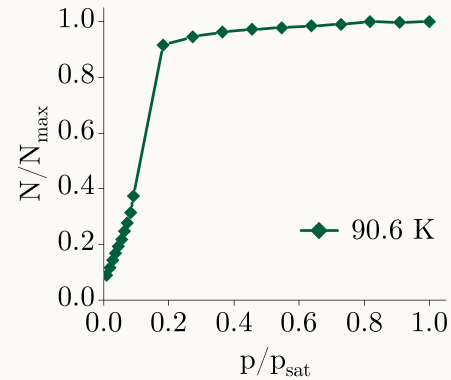
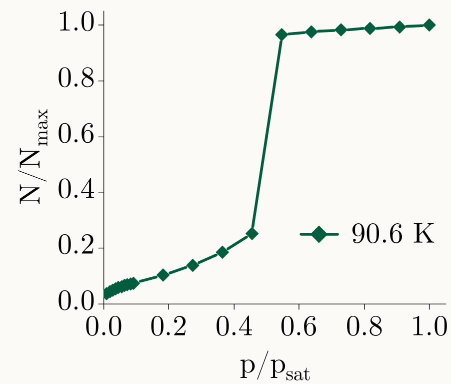




GCMC Simulations





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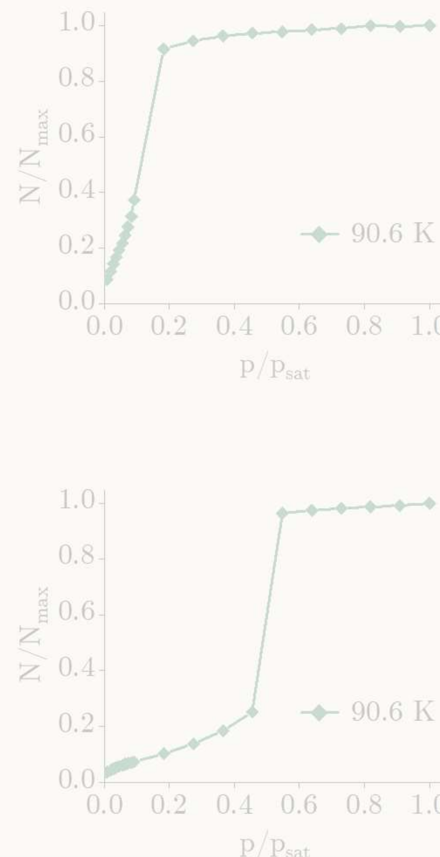

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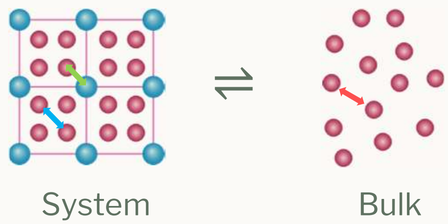
Corrected assumption



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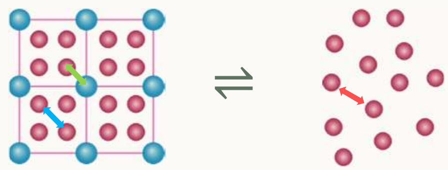

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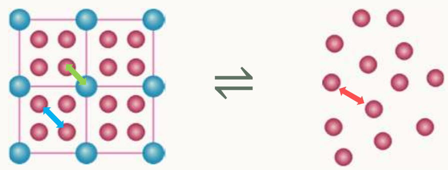

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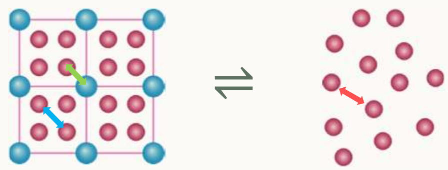

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Benchmarking

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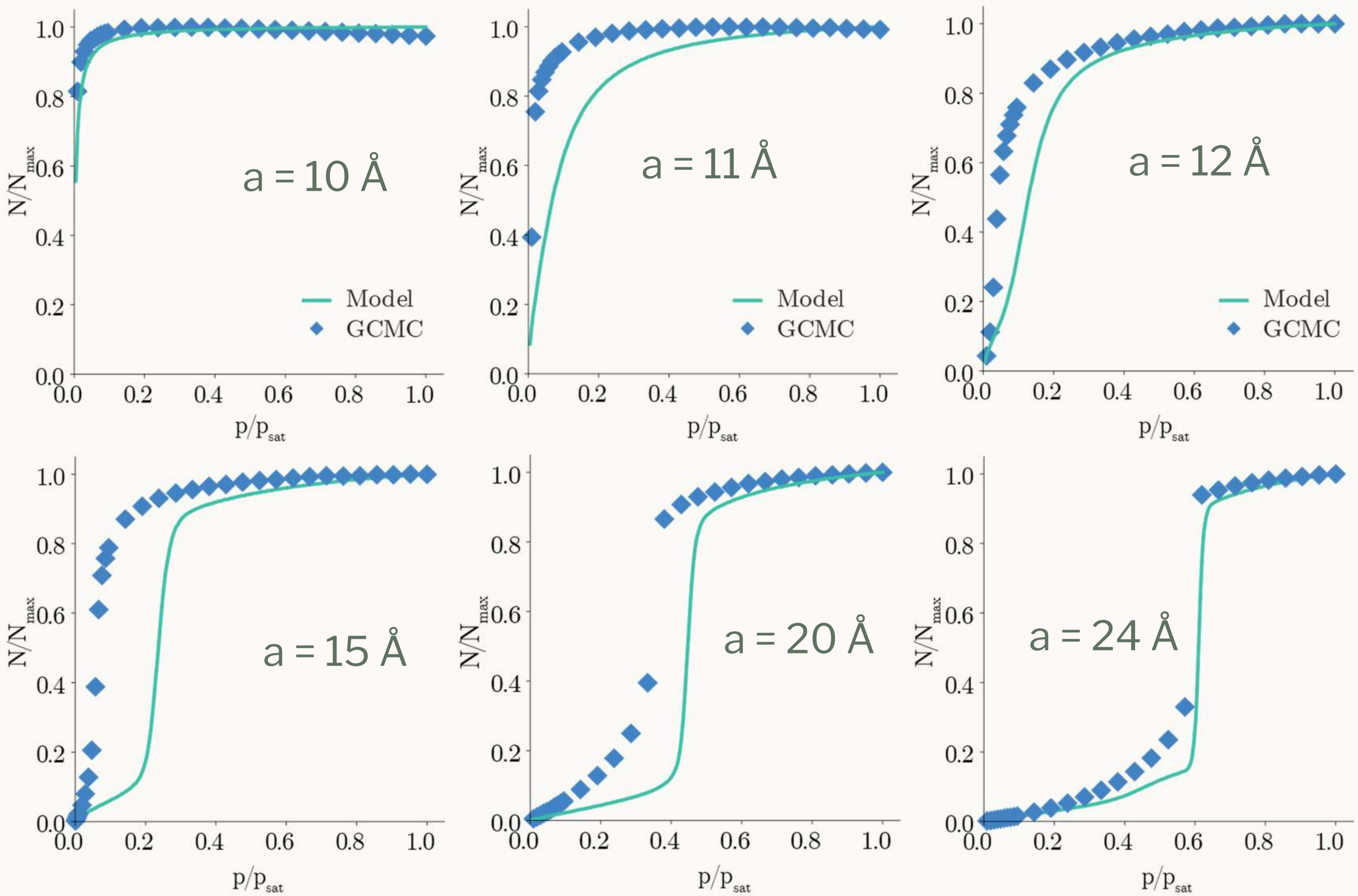
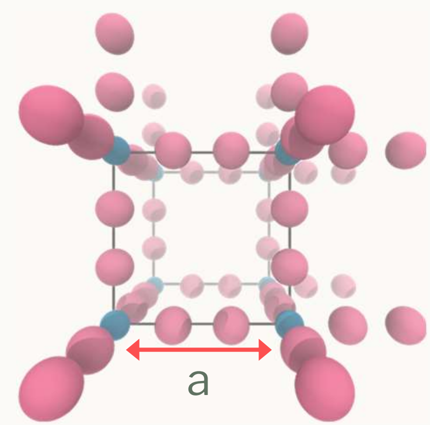




Thermodynamic Functions

$$\emptyset = \left(\frac{\partial E}{\partial N}\right)$$

Reference: [1] T. Hill, Thermodynamics of small systems

Thermodynamic Functions

Energy, $(F, \Omega, \mathcal{E})$

Intensive thermodynamic function $\quad \emptyset = \left(\frac{\partial E}{\partial N}\right) \quad$ Extensive thermodynamic function

For example,

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \quad p = \left(\frac{\partial F}{\partial V}\right)_{N,T}$$

Reference: [1] T. Hill, Thermodynamics of small systems

Thermodynamic Functions

Energy, $(F, \Omega, \mathcal{E})$

$$\phi = \left(\frac{\partial E}{\partial N}\right)$$

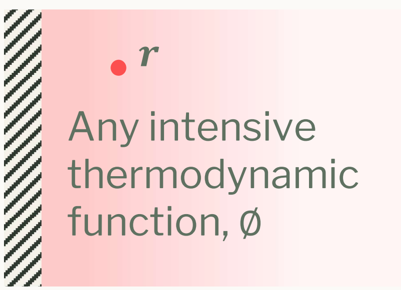
Intensive thermodynamic function

Extensive thermodynamic function

For example,

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \quad p = \left(\frac{\partial F}{\partial V}\right)_{N,T}$$

Differential Thermodynamic Functions



$$E = E(\boldsymbol{r})$$

$$\phi = \left(\frac{\partial E(\boldsymbol{r})}{\partial N}\right)$$

$$\mu(\boldsymbol{r}) = \left(\frac{\partial F(\boldsymbol{r})}{\partial N}\right)_{V,T}$$

Chemical potential distribution

$$p(\boldsymbol{r}) = \left(\frac{\partial F(\boldsymbol{r})}{\partial V}\right)_{N,T}$$

Pressure distribution

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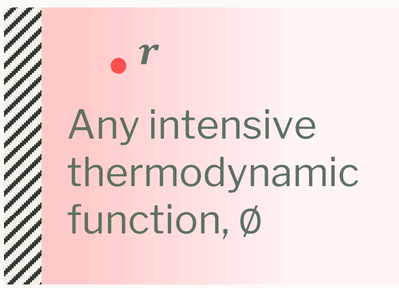

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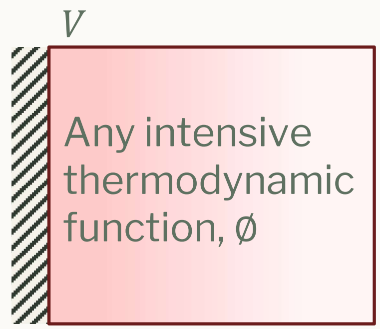
Integral Thermodynamic Functions



$$\bar{E} = \frac{1}{V}\int_V E(\boldsymbol{r})dV$$

$$\hat{\phi} = \left(\frac{\partial \bar{E}}{\partial N}\right) = \frac{\bar{E}}{N}$$

$$\hat{\mu} = \left(\frac{\partial \bar{F}}{\partial N}\right)_{V,T} = \frac{\bar{F}}{N}$$

Integral chemical potential

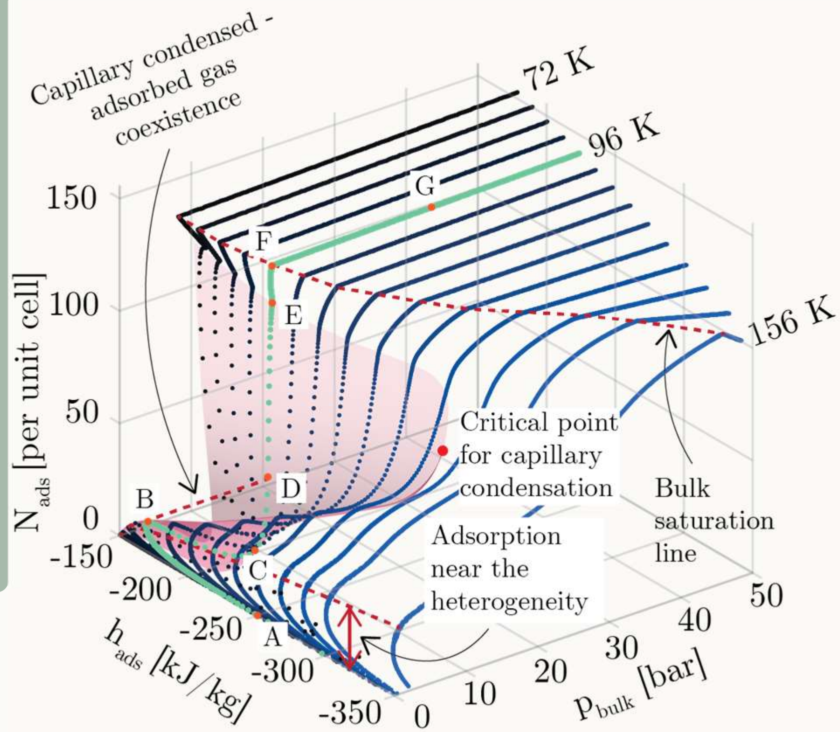
$$\hat{p} = \left(\frac{\partial \bar{F}}{\partial V}\right)_{N,T} = \frac{\bar{F}}{V}$$

Integral pressure

Reference: [1] T. Hill, Thermodynamics of small systems

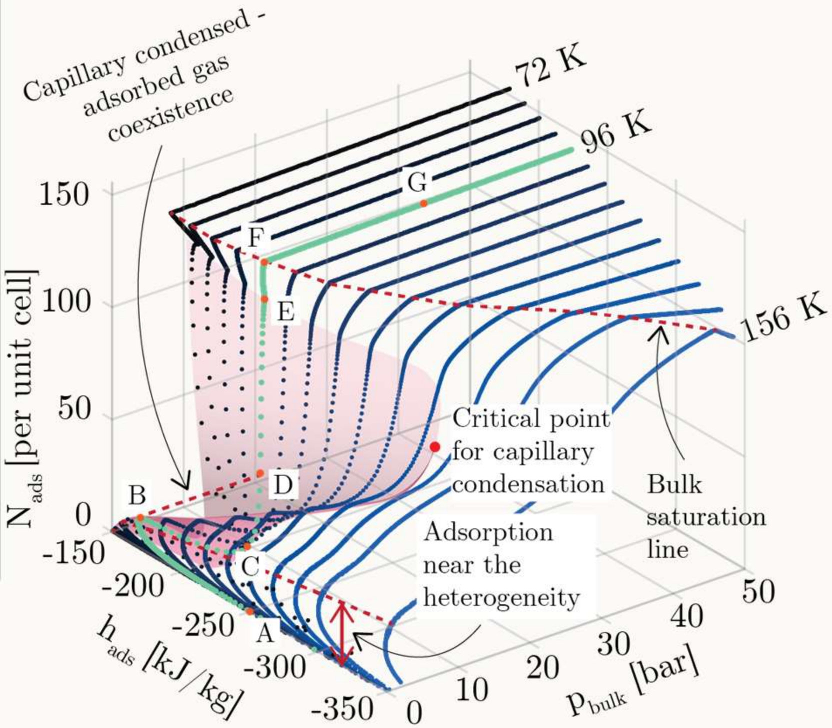
Phase diagram

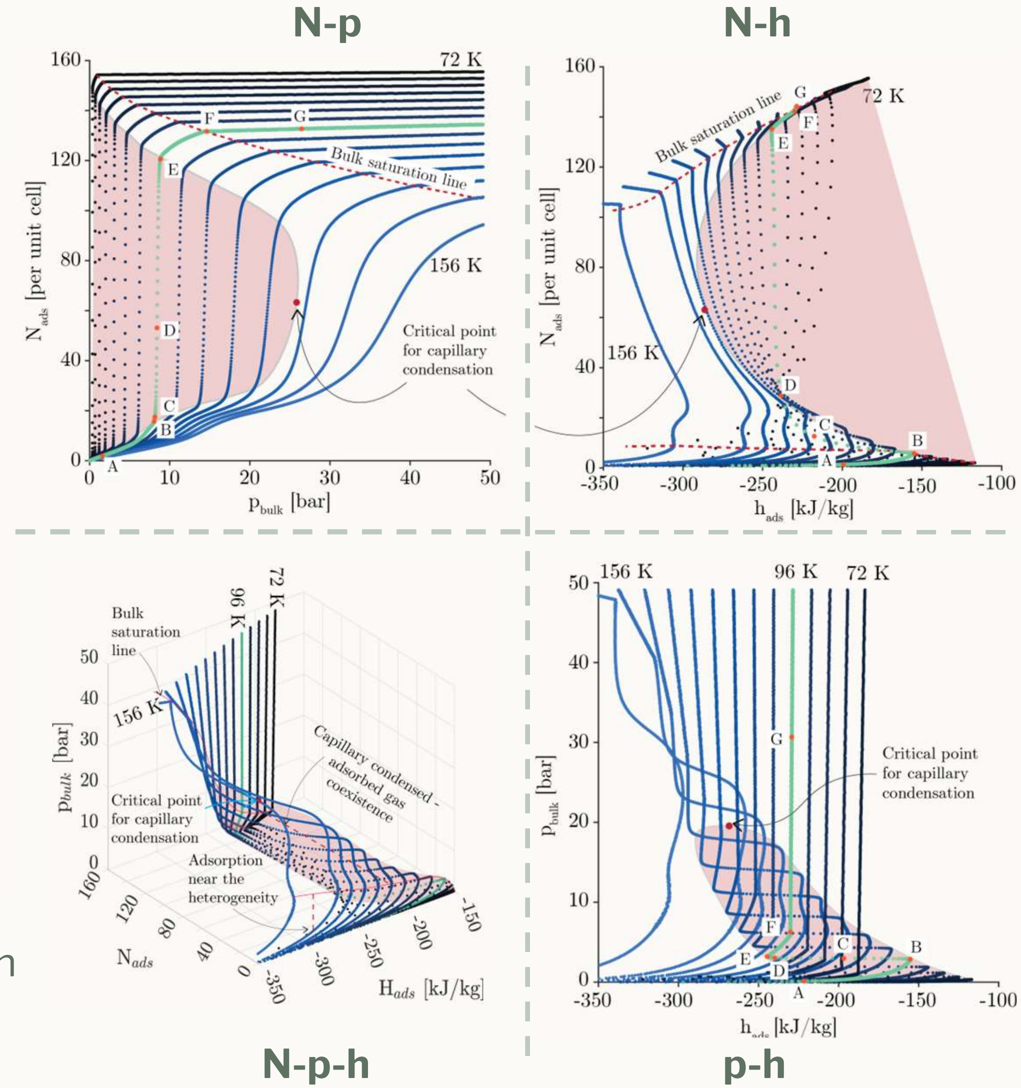
Phase diagram



Phase diagram for argon in a model MOF with
a = 24 Å, σ_m = 5 Å, ε_m = 120 K

Phase diagram





Phase diagram for argon in a model MOF with a = 24 Å, σ_m = 5 Å, ε_m = 120 K

Comparison with the bulk argon

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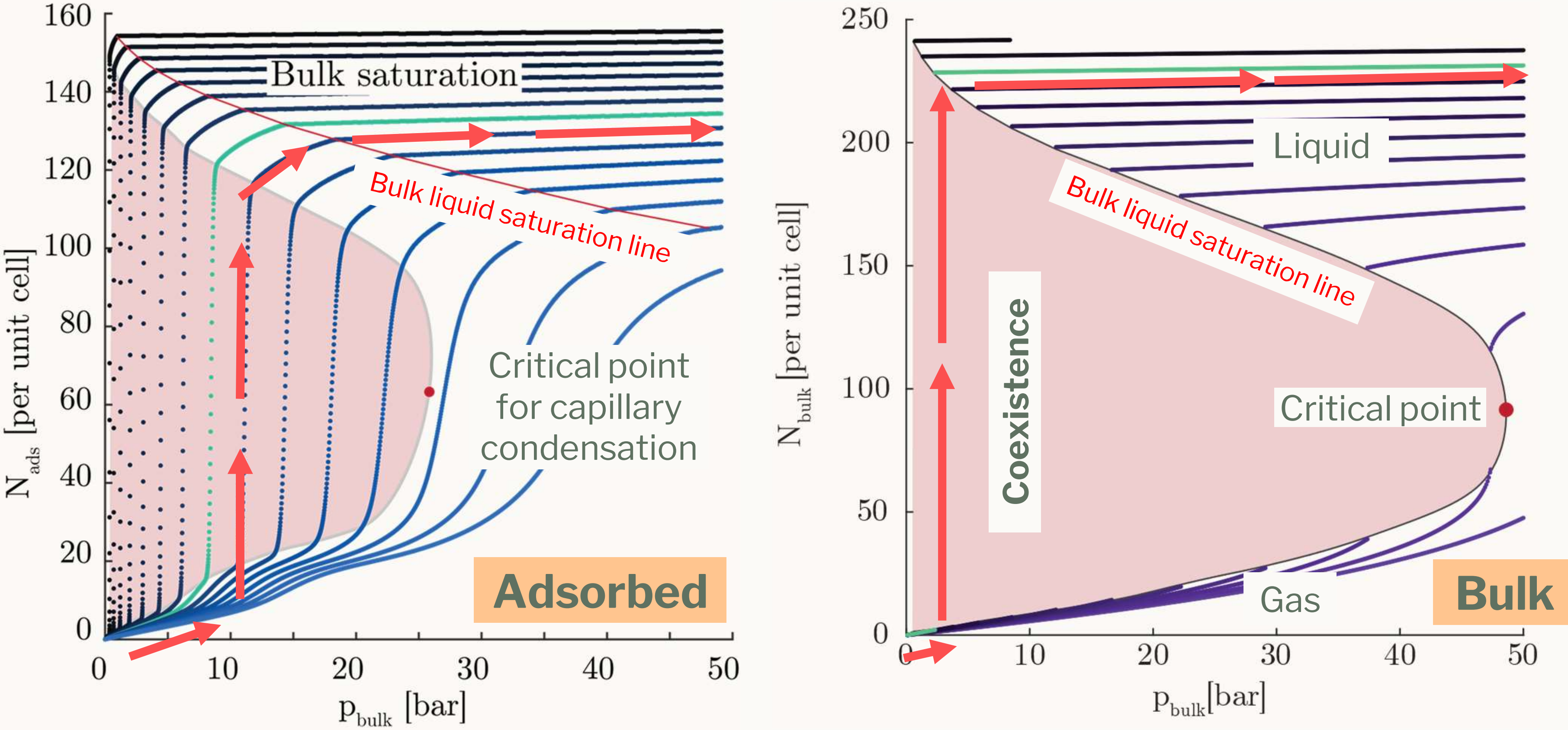
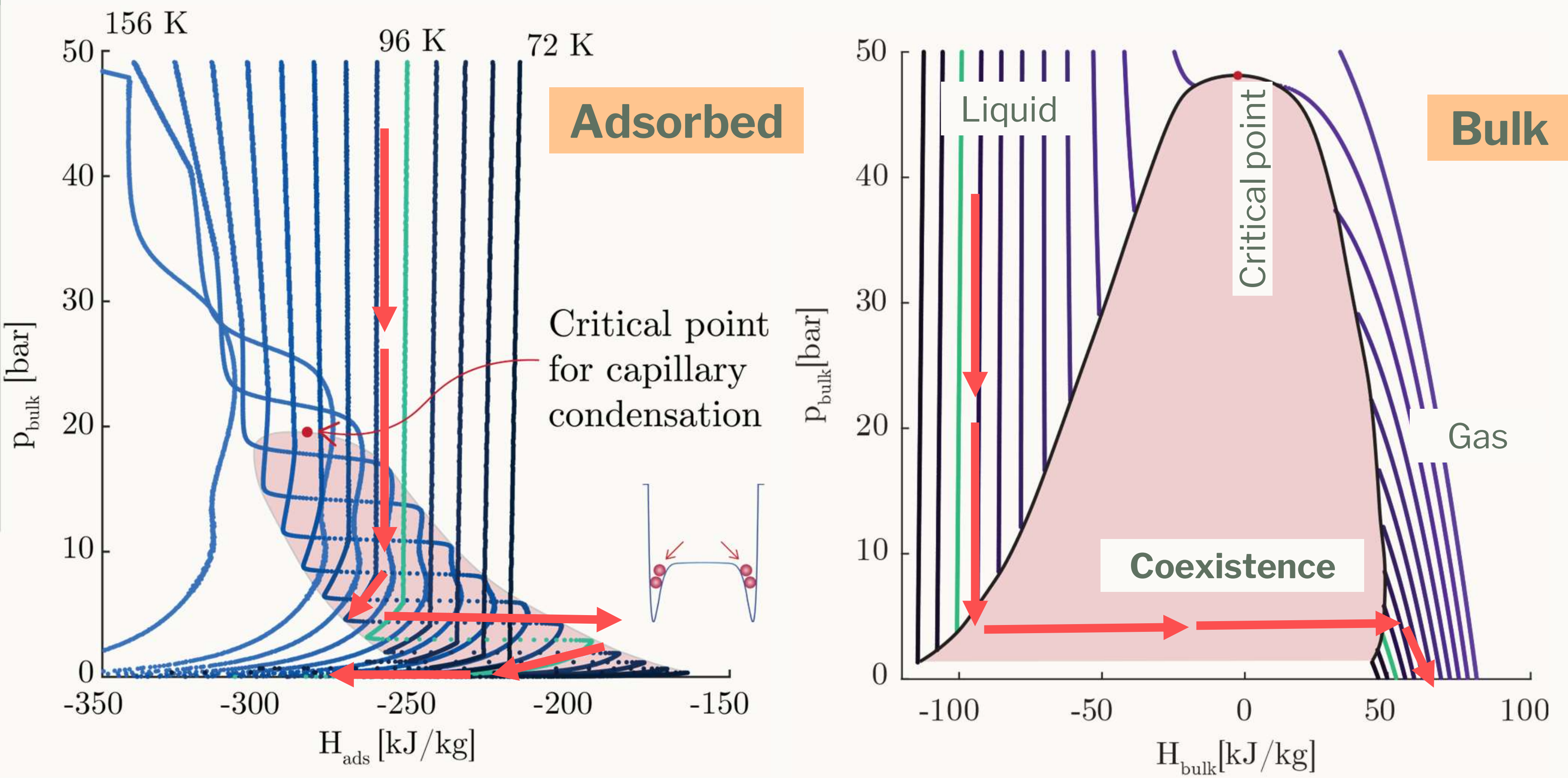
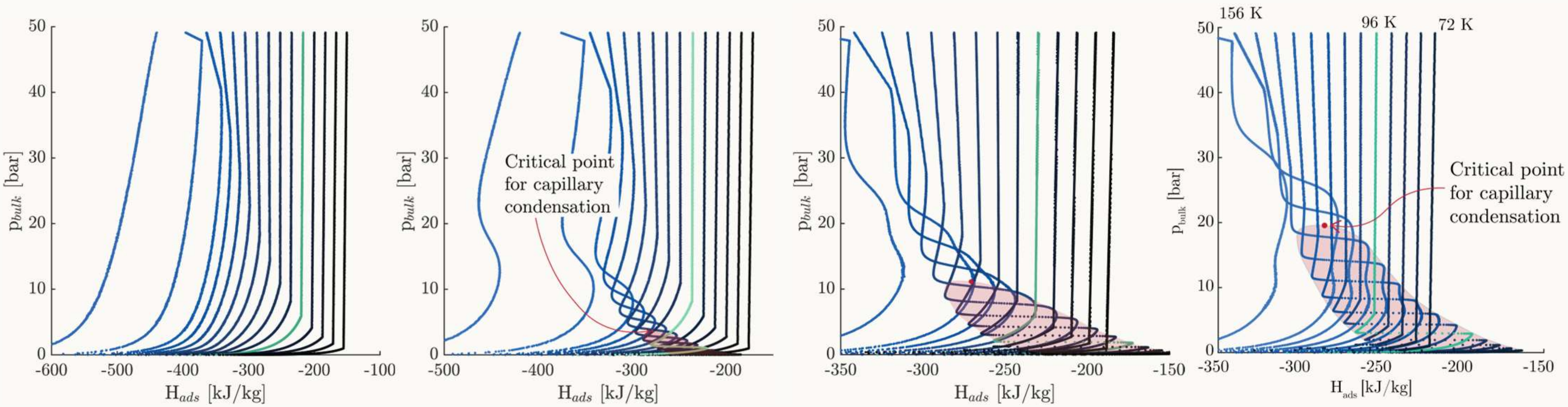


Comparison with the bulk argon



Effect of pore size

11 Å 15 Å 20 Å 24 Å



- No coexistence region
- ~ Bulk above critical point
- Second-order phase change

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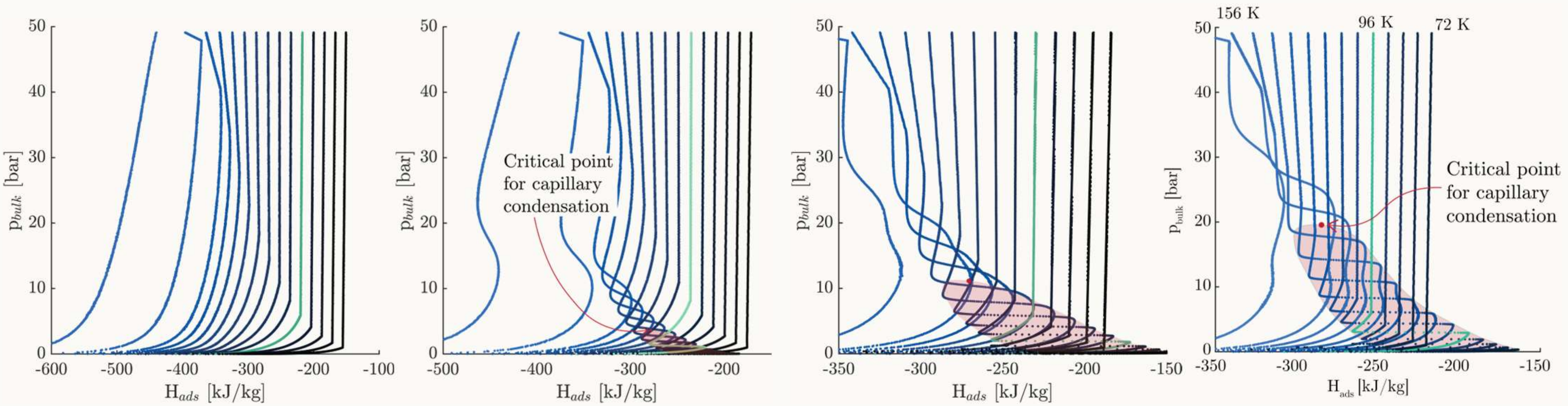

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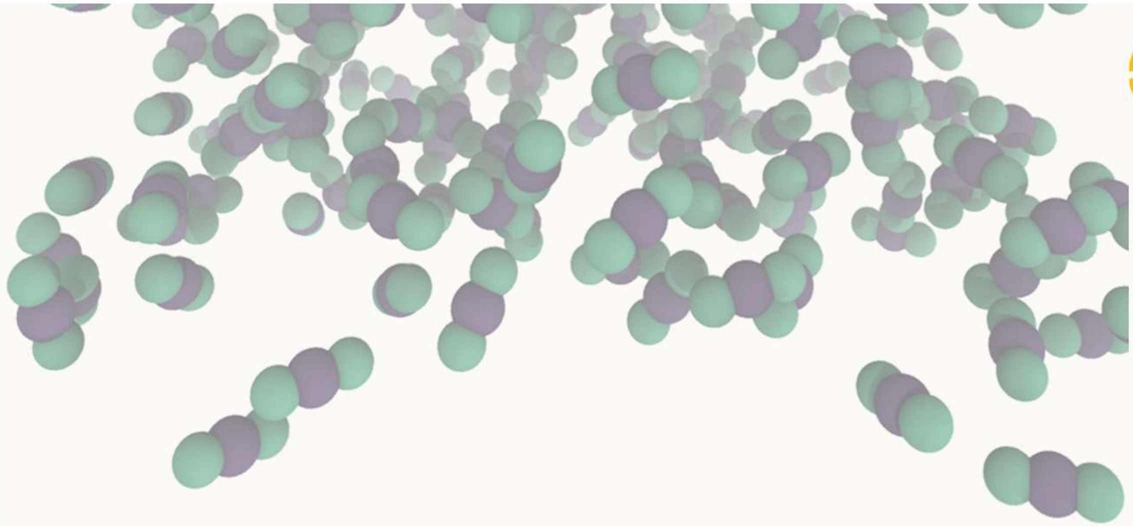

Thank you

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Japan Science and Technology Agency

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