

# Thermodynamics from Neural Networks: Neural Density Functional Theory

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Korea Institute for Advanced Study

Anna T. Bui and Stephen J. Cox **PRL** (2025)

Stefanie M. Kampa et al. **PRL** (2025)

Florian Sammüller, Matthias Schmidt, and Robert Evans **PRX** (2025)

Florian Sammüller et al. **PNAS** (2023)

2025 **CAINS Workshop** May 28-30

Part I : Thermodynamics & Statistical Mechanics

Part II : **Classical** Density Functional Theory (**cDFT**)

Part III : **Neural** Density Functional Theory (**nDFT**)

Part I : Thermodynamics & Statistical Mechanics

Part II : Classical Density Functional Theory (**cDFT**)

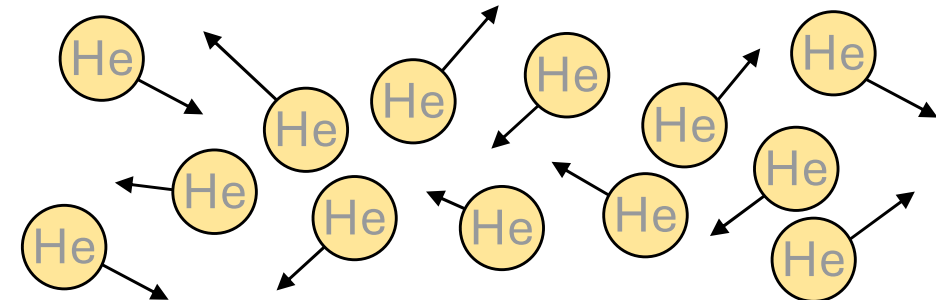
Part III : Neural Density Functional Theory (**nDFT**)

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, entropy, and the physical properties of matter and radiation. The behavior of these quantities is governed by the four laws of thermodynamics, which convey a quantitative description using measurable macroscopic physical quantities but may be explained in terms of microscopic constituents by statistical mechanics. Thermodynamics applies to various topics in science and engineering, especially physical chemistry, biochemistry, chemical engineering, and mechanical engineering, as well as other complex fields such as meteorology.

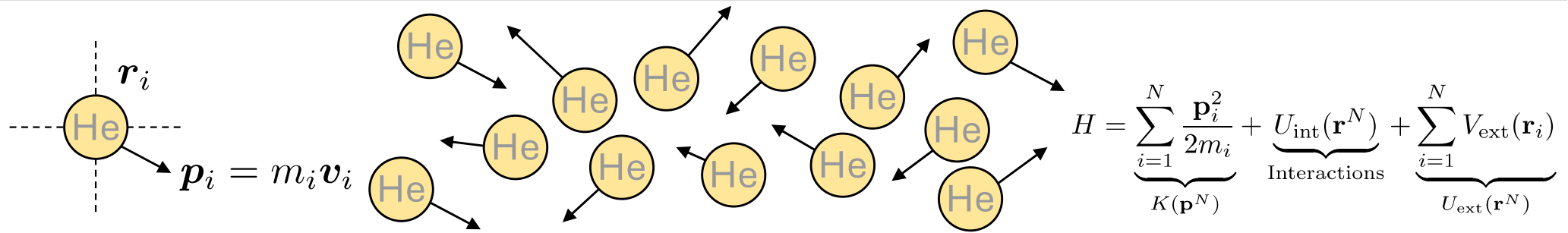
## Macroscopic

Temperature (T), Pressure (P),  
Internal Energy (U), Enthalpy (H),  
Helmholtz Free Energy (F),  
Gibbs Free Energy (G),  
Chemical Potential ( $\mu$ ),  
Heat Capacity ( $C_V$ ),  
Isothermal Compressibility ( $\kappa_T$ )

## Microscopic



$$H = \underbrace{\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i}}_{K(\mathbf{p}^N)} + \underbrace{U_{\text{int}}(\mathbf{r}^N)}_{\text{Interactions}} + \underbrace{\sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i)}_{U_{\text{ext}}(\mathbf{r}^N)}$$



## Temperature

A measure of "hotness" or "coldness" that can be measured with a thermometer

$$T = \frac{2K(\mathbf{p}^N)}{f k_B} \text{ where } f \text{ is kinetic degree of freedom}$$

## Pressure

The force exerted by a system on its surroundings per unit area, which can be measured by a barometer

$$P = \frac{1}{3V} \left[ \sum_i^N m_i v_i^2 + \sum_i^N \mathbf{r}_i \cdot \mathbf{F}_i \right]$$

where  $\mathbf{F}_i$  is the force acting on particle  $i$

$$P = - \left( \frac{\partial F}{\partial V} \right) = k_B T \left( \frac{\partial (\ln Z)}{\partial V} \right) = \frac{\sum_i \left( - \frac{\partial E_i(V, N)}{\partial V} \right) \exp(-\beta E_i(V, N))}{\sum_j \exp(-\beta E_j(V, N))}$$

## Partition Function

### Microcanonical

Counts purely how many distinct microstates exist **at exactly a given energy**, for an isolated system with fixed energy, volume, and particle number.

$$\Omega(N, V, E) = \frac{1}{h^{3N} N!} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} \delta(H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) - E)$$

### Canonical

Adds up every microstate's contribution weighted by **its thermal likelihood at a fixed temperature**, for a system that can exchange heat (but not particles) with a reservoir.

$$Z(N, V, T) = \frac{1}{h^{3N} N!} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} \exp[-\beta H(\mathbf{r}^{3N}, \mathbf{p}^{3N})]$$

### Grandcanonical

Extends that idea by summing over **both microstates and particle numbers**, weighting each by its energy and chemical potential, for a system that can exchange both heat and particles with its surroundings.

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} \exp[-\beta (H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) - \mu N)]$$

Now we can express more thermodynamic variables!

Heat Capacity

$$C_V = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{V,N} \quad \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$C_V = k_B \beta^2 \left( \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 \right)$$

Isothermal  
Compressibility

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial p}{\partial V} \right)_{T,N}^{-1} \quad p = -\frac{\partial F}{\partial V} = \frac{1}{\beta Z} \frac{\partial Z}{\partial V}$$

$$\kappa_T = -\frac{\beta}{V} \left( \frac{1}{Z} \frac{\partial^2 Z}{\partial V^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial V} \right)^2 \right)^{-1}$$

All information is encoded in partition function!

Part I : Thermodynamics & Statistical Mechanics

Part II : **Classical** Density Functional Theory (**cDFT**)

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$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{r}^{3N} d\mathbf{p}^{3N} \exp \left[ -\beta \left( H(\mathbf{r}^{3N}, \mathbf{p}^{3N}) - \mu N \right) \right]$$

**Problem** : Direct calculation of  $\Xi$  is intractable for almost any interacting system due to the high dimensional integrals and sum over  $N$

## Hohenberg-Kohn-Mermin Theorem

Instead of focusing on the positions of all  $N$  particles, can we describe the entire system's equilibrium properties using only its one-body density profile,  $\rho(\mathbf{r})$ ?

### N-particle description

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$$

or

$$P(\mathbf{r}^{3N}, \mathbf{p}^{3N})$$



### One-body density

$$\rho(\mathbf{r})$$

A function of just 3 spatial variables  
Much Simpler!

## One-body density

$$\rho(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle : \text{Fundamental variable of cDFT}$$

## Grand Potential

Free energy like physical quantity

$$\Omega(\mu, V, T) = -k_B T \ln \Xi(\mu, V, T)$$

Hohenberg-Kohn-Mermin Theorem states

## Existence of a Universal Functional

There exists a universal functional of the density,  $F_{\text{int}}[\rho]$ , called intrinsic Helmholtz free-energy functional.

Given any trial density  $\rho(\mathbf{r})$ , one defines the corresponding grand-potential functional by

$$\Omega[\rho] = F_{\text{int}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) (V_{\text{ext}}(\mathbf{r}) - \mu)$$

## One-body density

$$\rho(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle : \text{Fundamental variable of cDFT}$$

## Grand Potential

Free energy like physical quantity

$$\Omega(\mu, V, T) = -k_B T \ln \Xi(\mu, V, T)$$

Hohenberg–Kohn–Mermin Theorem states

## Variational Principle

The true equilibrium density profile,  $\rho_0(\mathbf{r})$ , is the specific density function that minimizes the grand potential function

$$\left. \frac{\delta \Omega[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=\rho_0} = 0$$

$$\min_{\rho} \Omega[\rho] = \Omega[\rho_0]$$

Ideal part is easy!

$$F_{\text{int}}[\rho; T] = F_{\text{ideal}} + F_{\text{excess}}[\rho; T]$$

$$\beta F_{\text{ideal}} = \int d\mathbf{r} \rho(\mathbf{r}) [\ln(\rho(\mathbf{r}) \Lambda^3(T)) - 1]$$

The collection of all “interesting physics” arising from **interparticle interaction!**

$F_{\text{excess}}[\rho; T]$

$$\delta\Omega[\rho] = \int d\mathbf{r} \left[ \frac{\delta F_{\text{ideal}}[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta F_{\text{excess}}[\rho]}{\delta\rho(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}) - \mu \right] \delta\rho(\mathbf{r}) = 0$$

$$\mu = \frac{\delta F_{\text{ideal}}[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta F_{\text{excess}}[\rho]}{\delta\rho(\mathbf{r})} + V_{\text{ext}}(\mathbf{r})$$

One-body direct correlation function

$$c^{(1)}(\mathbf{r}; [\rho]) \equiv -\beta \frac{\delta F_{\text{excess}}[\rho]}{\delta\rho(\mathbf{r})}$$

measures the reversible work required to insert a “test” particle at a position,  $\mathbf{r}$

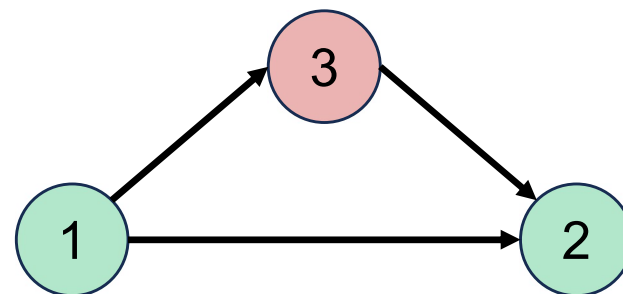
**Self-consistent equation to solve!**

$$\therefore \rho(\mathbf{r}) = \Lambda^{-3} \exp \left[ \beta\mu - \beta V_{\text{ext}}(\mathbf{r}) + c^{(1)}(\mathbf{r}; [\rho]) \right]$$

# Ornstein-Zernike (OZ) equation

## Two-body direct correlation function

$$c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\delta^2 F_{\text{excess}}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}$$



## Ornstein-Zernike equation

The total correlation  $h(r)$  can be written as

$$h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 c^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \rho(\mathbf{r}_3) h^{(2)}(\mathbf{r}_3, \mathbf{r}_2)$$

With uniform and isotropic fluid

$$h(r) = c(r) + \rho_b \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|) h(r)$$

Indirect source

Direct source

$h(r) \equiv g(r) - 1$  where the  $g(r)$  is the radial distribution function

- ❖ We have a single equation, but we have two unknowns

We need **closures** to close the system

- Percus-Yevick (PY) closure**
- works for hard-core-like systems
  - lack of long-range description

$$c_{\text{PY}}(r) = g(r) \left(1 - e^{\beta v(r)}\right) = (h(r) + 1) \left(1 - e^{\beta v(r)}\right)$$

- Hypernetted-Chain (HNC) closure**
- works for soft, long-range potentials
  - underestimates the structuring from exclude-volume effects

$$c_{\text{HNC}}(r) = h(r) - \ln g(r) - \beta v(r)$$

### Mean Spherical Approximation (MSA) closure

$$g(r) = 0, \quad r < \sigma$$
$$c_{\text{MSA}}(r) = -\beta v_{\text{tail}}(r), \quad r \geq \sigma$$

- works for low density ionic/Yukawa fluid
- poor for short range structure

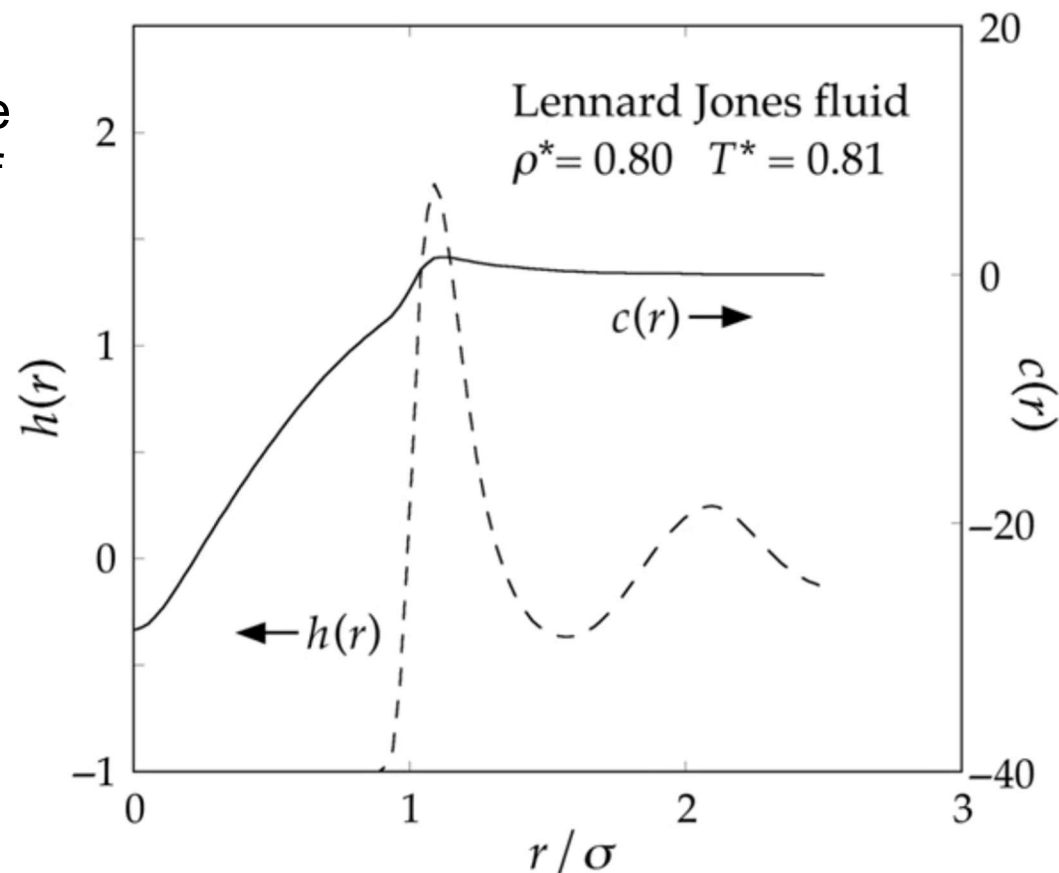
❖ However, no single closure performs reliably in every situation

❖ The appropriate choice must instead be guided by the specific characteristics of the system under study



❖ Strong motivation for neural density functional theory

❖ With simulation you can measure  $c(r)$



$$\rho(\mathbf{r}) = \Lambda^{-3} \exp \left[ \beta \mu - \beta V_{\text{ext}}(\mathbf{r}) + c^{(1)}(\mathbf{r}; [\rho]) \right]$$

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## Neural Density Functional Theory

$$c_1(x_0; [\rho], T) \approx f_\theta(\rho(x - x_c), \dots, \rho(x + x_c), T, L^{-1})$$

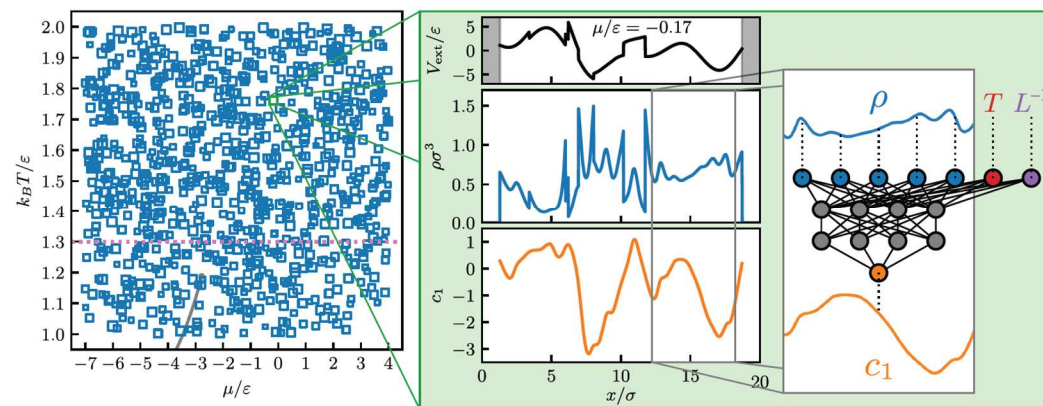
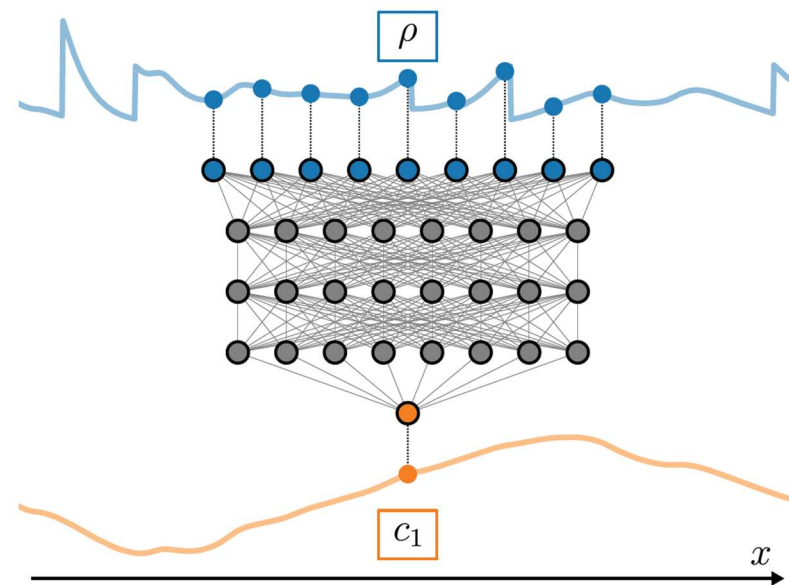
- Neural network itself is a simple MLP
- Grand Canonical Monte Carlo (GCMC) simulation data is used as a training data (# of data : 750-880)

$$-7 < \mu/\epsilon < 4$$

$$1 < k_B T/\epsilon < 2$$

$$x_c = 3.5\sigma \text{ and } \Delta x = 0.01\sigma$$

- Random external potential is applied



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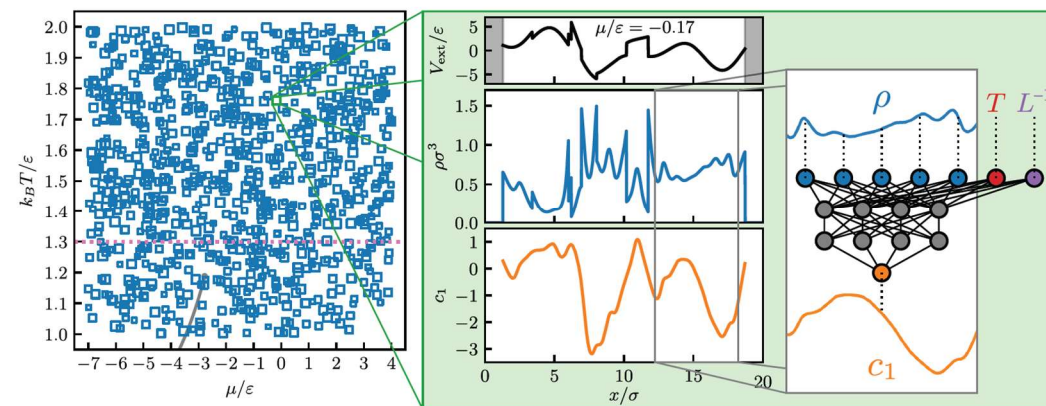
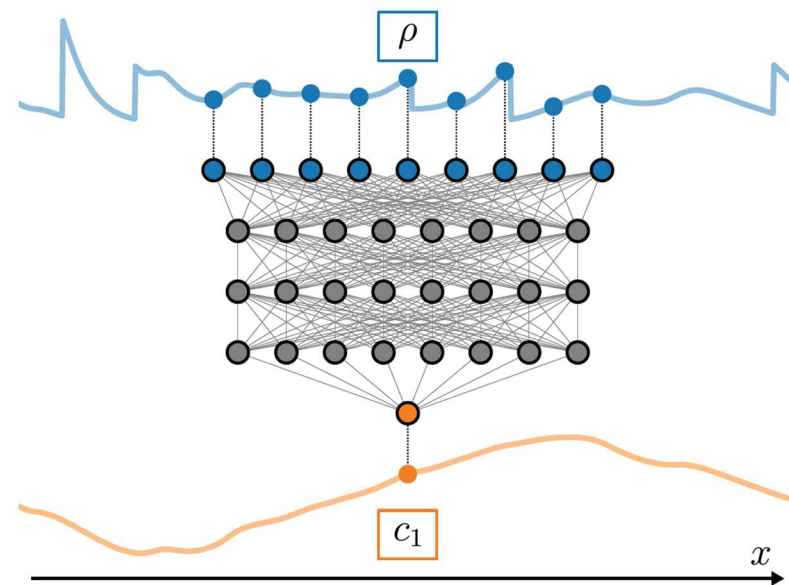
## Neural Density Functional Theory

$$c_1(x_0; [\rho], T) \approx f_\theta(\rho(x - x_c), \dots, \rho(x + x_c), T, L^{-1})$$

- Recalling that  $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\delta^2 F_{\text{excess}}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}$

$$c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta c_1(\mathbf{r}_1; [\rho])}{\delta \rho(\mathbf{r}_2)}$$

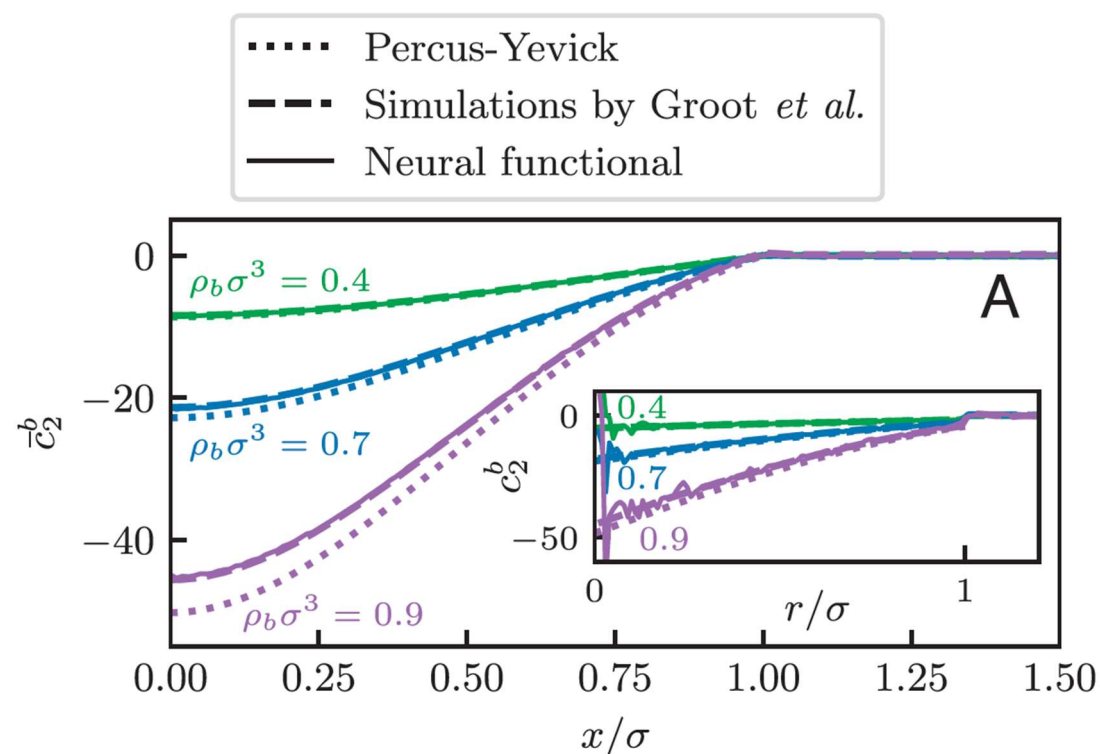
- We can obtain this simply by differentiating the network's output at  $\mathbf{r}_1$  with respect to its input density at  $\mathbf{r}_2$  (via automatic differentiation)



Florian Sammüller, Matthias Schmidt, and Robert Evans **PRX** (2025)  
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## Neural Density Functional Theory

$$c_1(x_0; [\rho], T) \approx f_\theta(\rho(x - x_c), \dots, \rho(x + x_c), T, L^{-1})$$



- PY closure overestimates repulsion at high density
- Simulation and nDFT have a good agreement

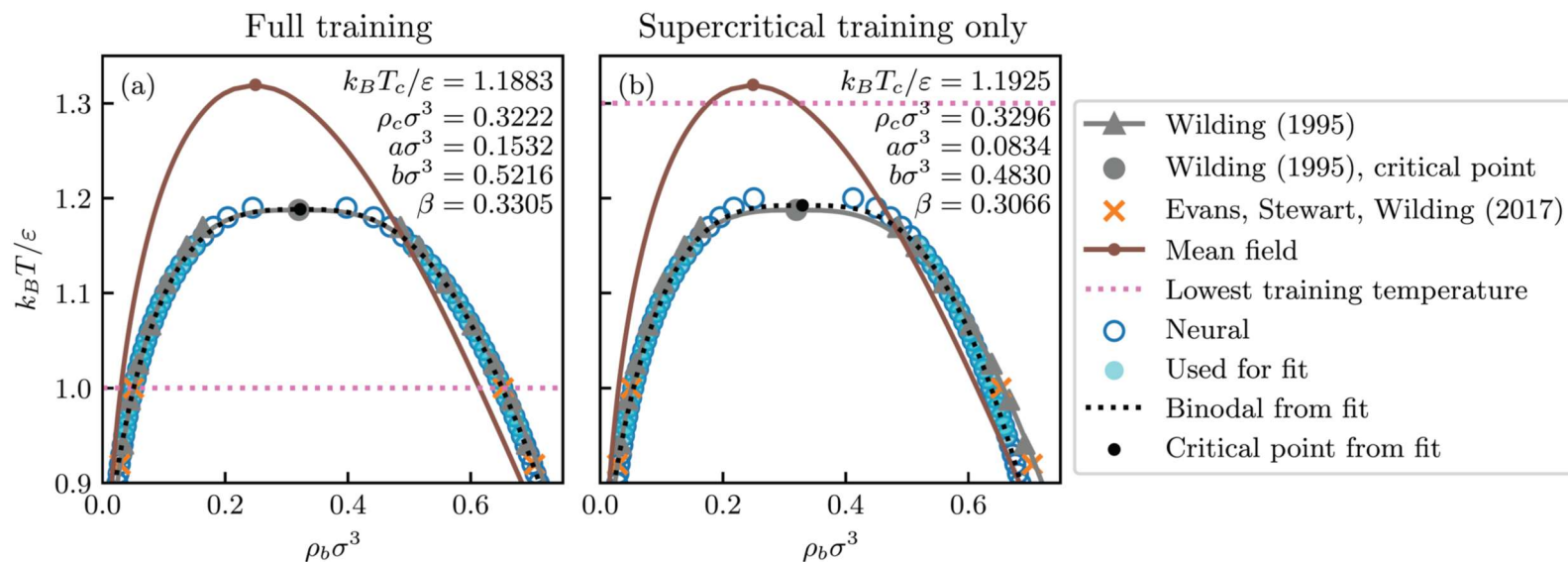
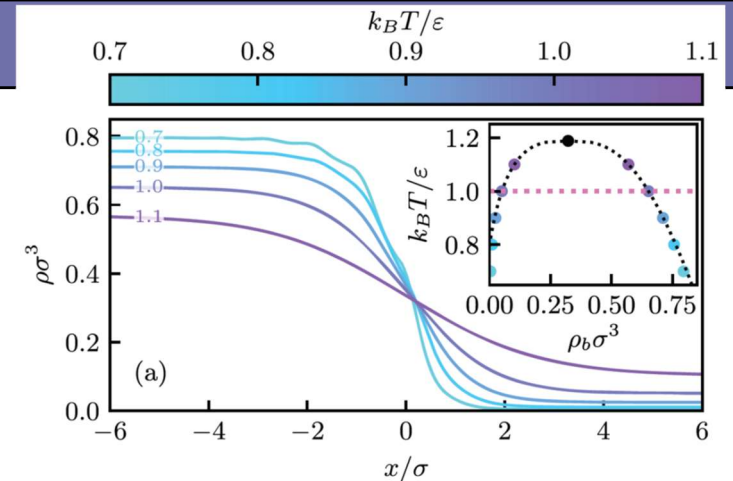
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## Neural Density Functional Theory

$$c_1(x_0; [\rho], T) \approx f_\theta(\rho(x - x_c), \dots, \rho(x + x_c), T, L^{-1})$$

- By initializing with a steplike density profile and minimizing the grand potential, one recovers the equilibrium liquid-gas density distribution.
- The critical point predicted by neural DFT remains reliable even when the sampled temperature range does not include its vicinity.

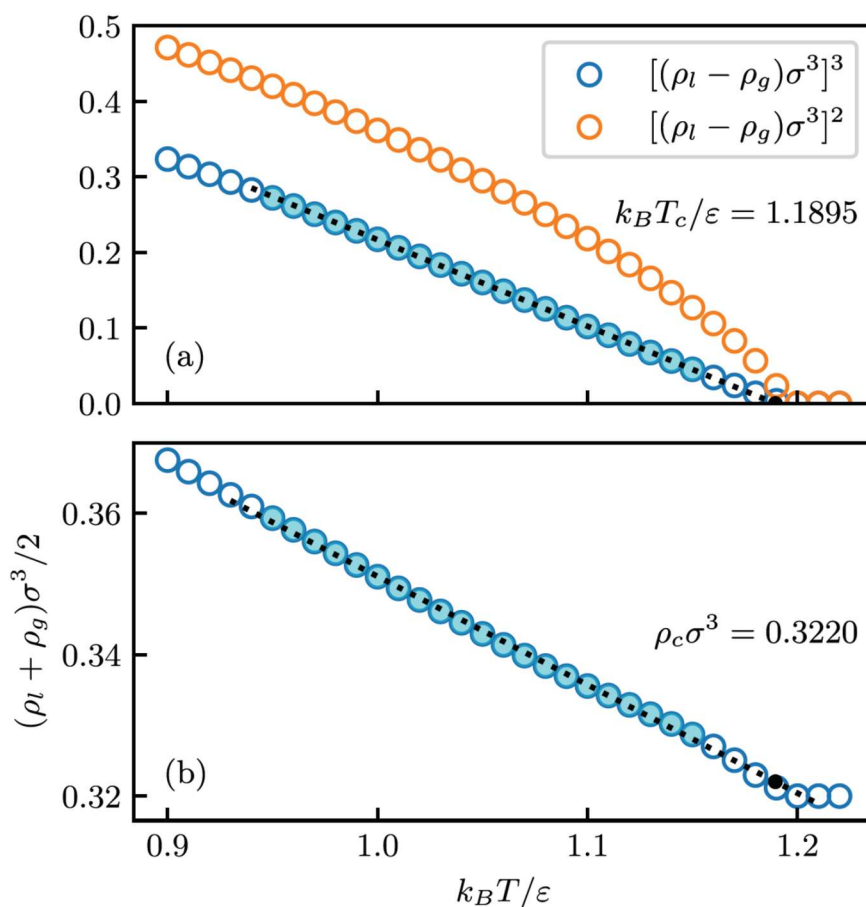


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## Neural Density Functional Theory

$$c_1(x_0; [\rho], T) \approx f_\theta(\rho(x - x_c), \dots, \rho(x + x_c), T, L^{-1})$$



$$\Delta\rho = \rho_l - \rho_g$$

$$\tau = \frac{T_c - T}{T_c}$$

In mean-field picture,  $\Delta\rho \sim \tau^{\beta_{\text{MF}}}$

where  $\beta_{\text{MF}} = 0.5$

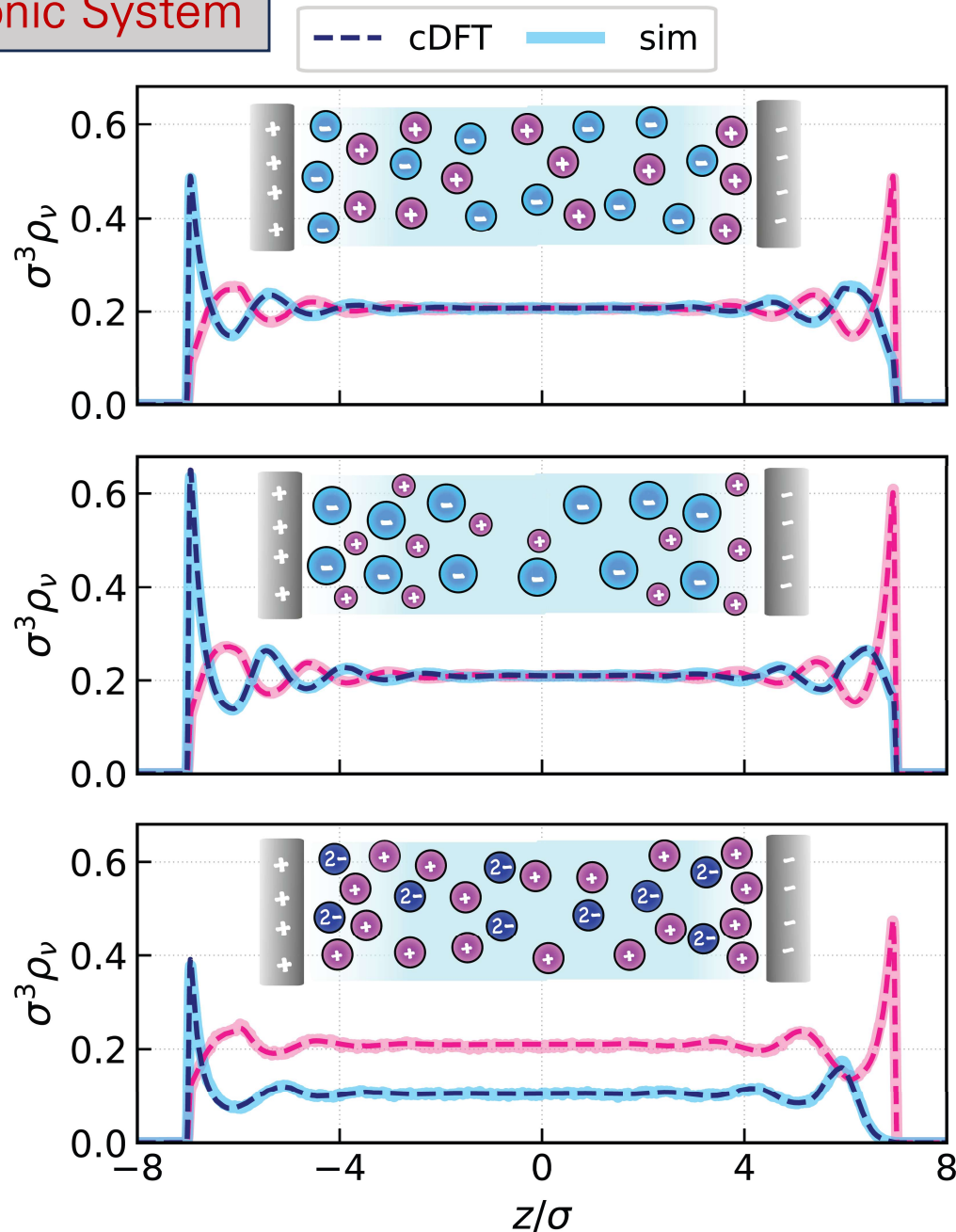
- The nDFT, however, shows a  $\beta = 0.33$  which indicates non-mean-field exponent.
- This value is very close to  $\beta_{\text{Ising}}^{3D} = 0.326$

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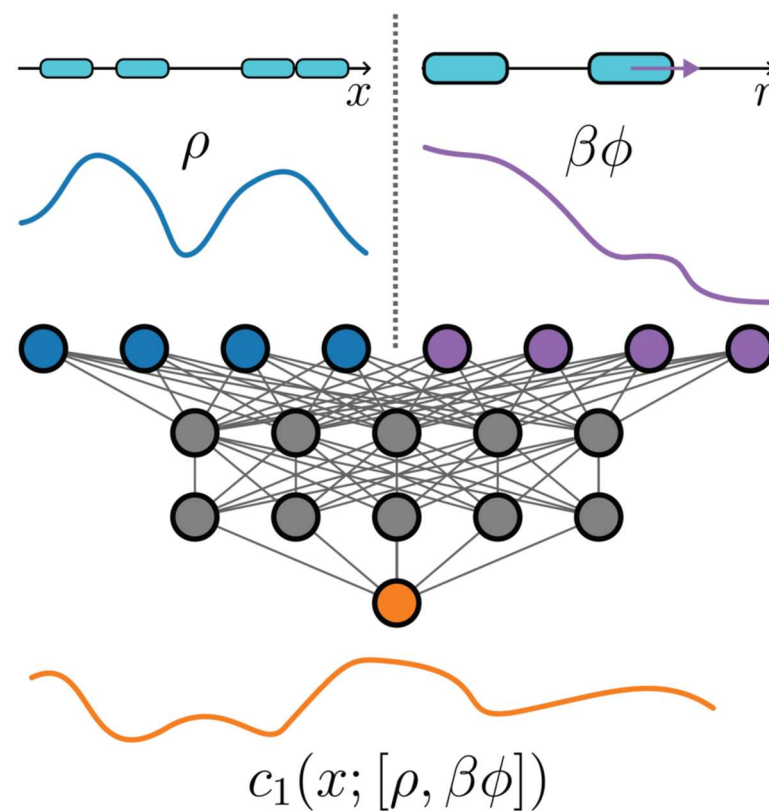


## Ionic System



Anna T. Bui and Stephen J. Cox **PRL** (2025)

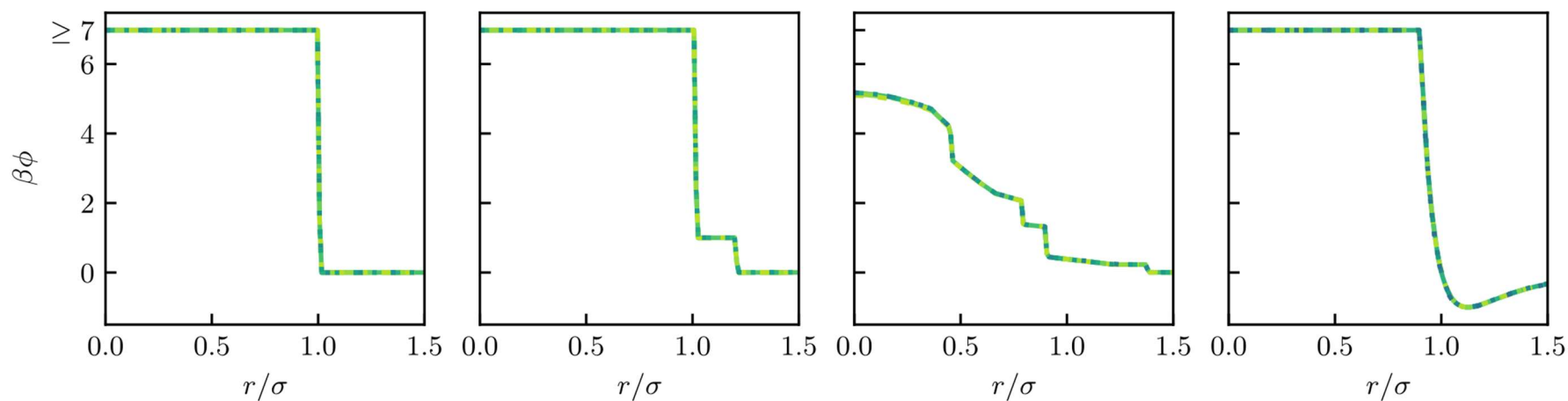
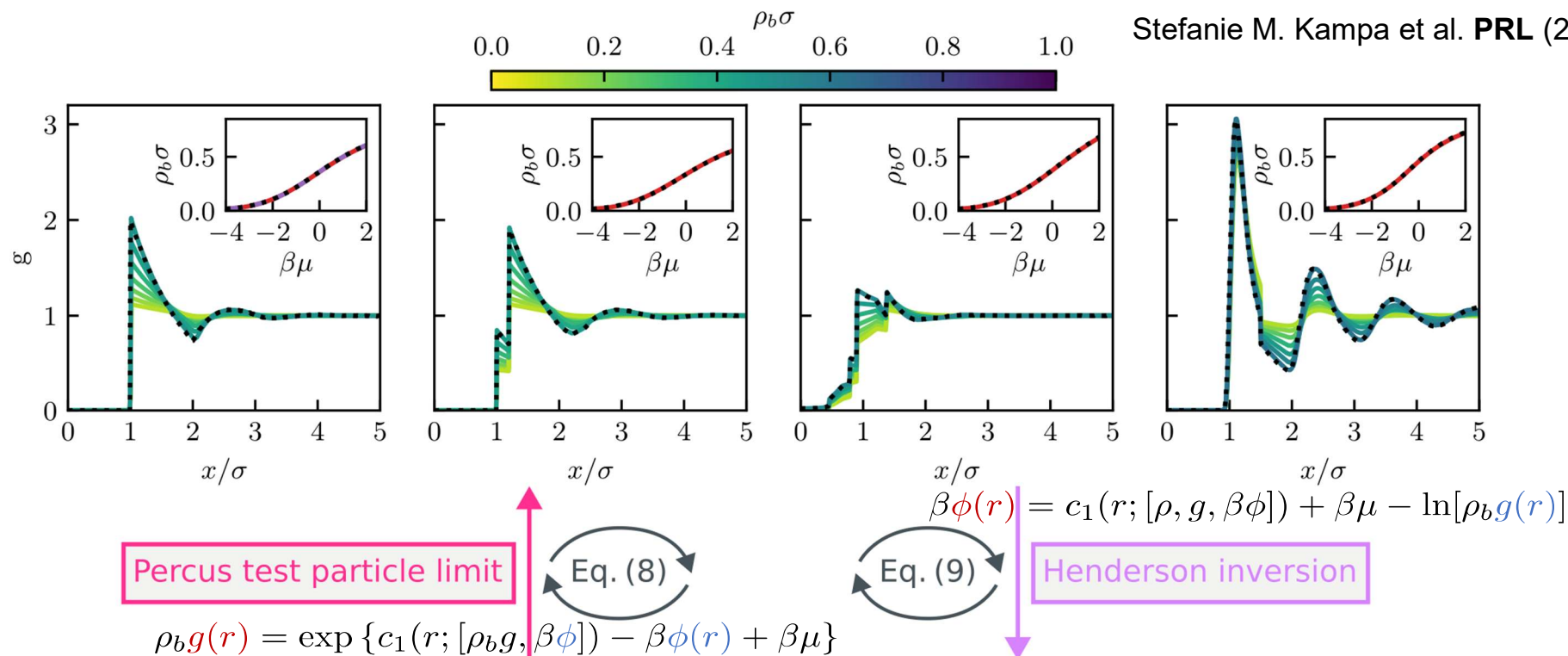
## Metadensity Functional Theory for inverse problem



Stefanie M. Kampa et al. **PRL** (2025)

Radial distribution function  $\longleftrightarrow$  Potential function

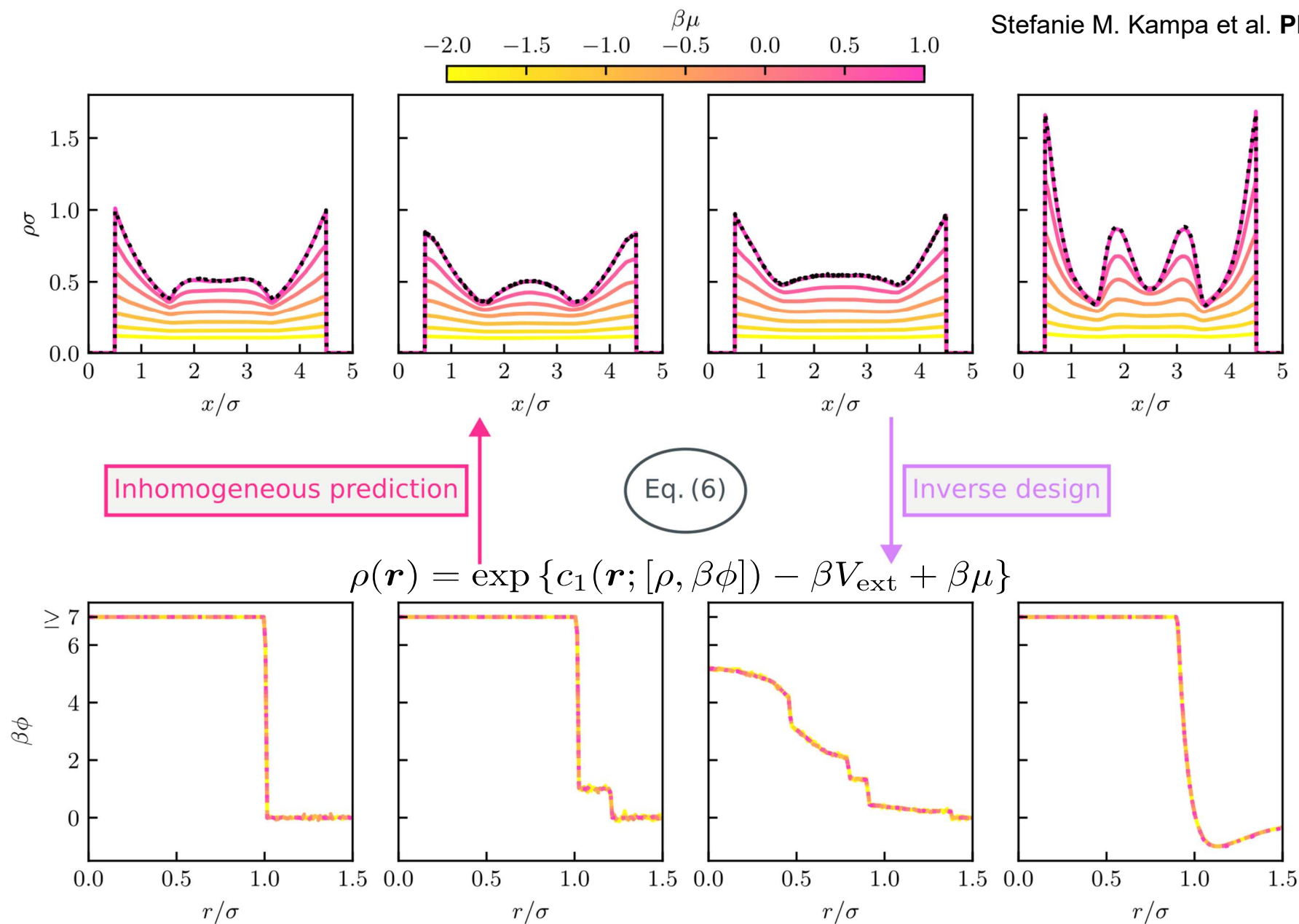
Stefanie M. Kampa et al. **PRL** (2025)



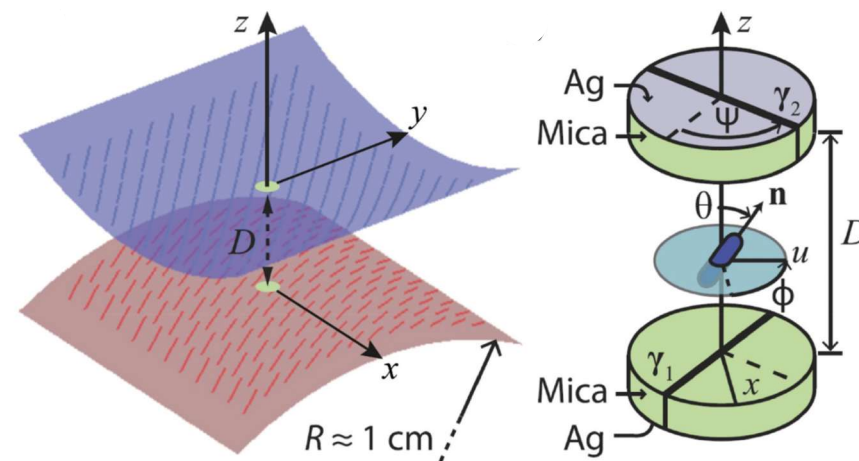
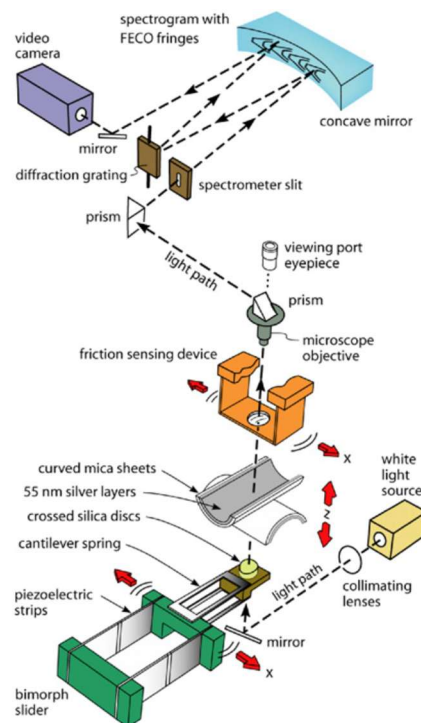
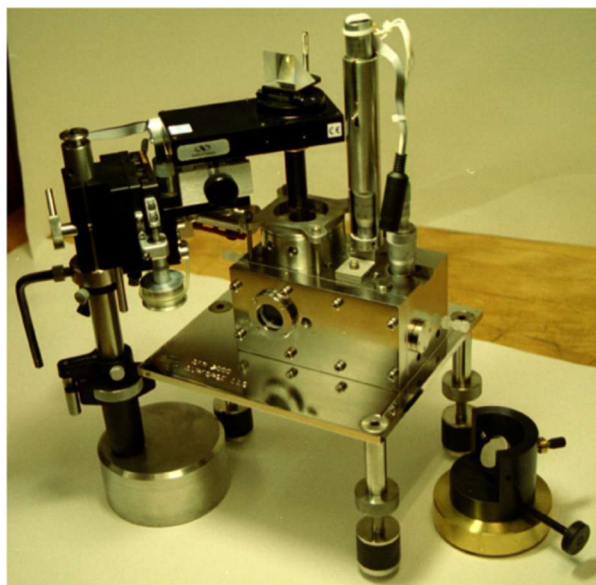
Density profile

Potential function

Stefanie M. Kampa et al. **PRL** (2025)





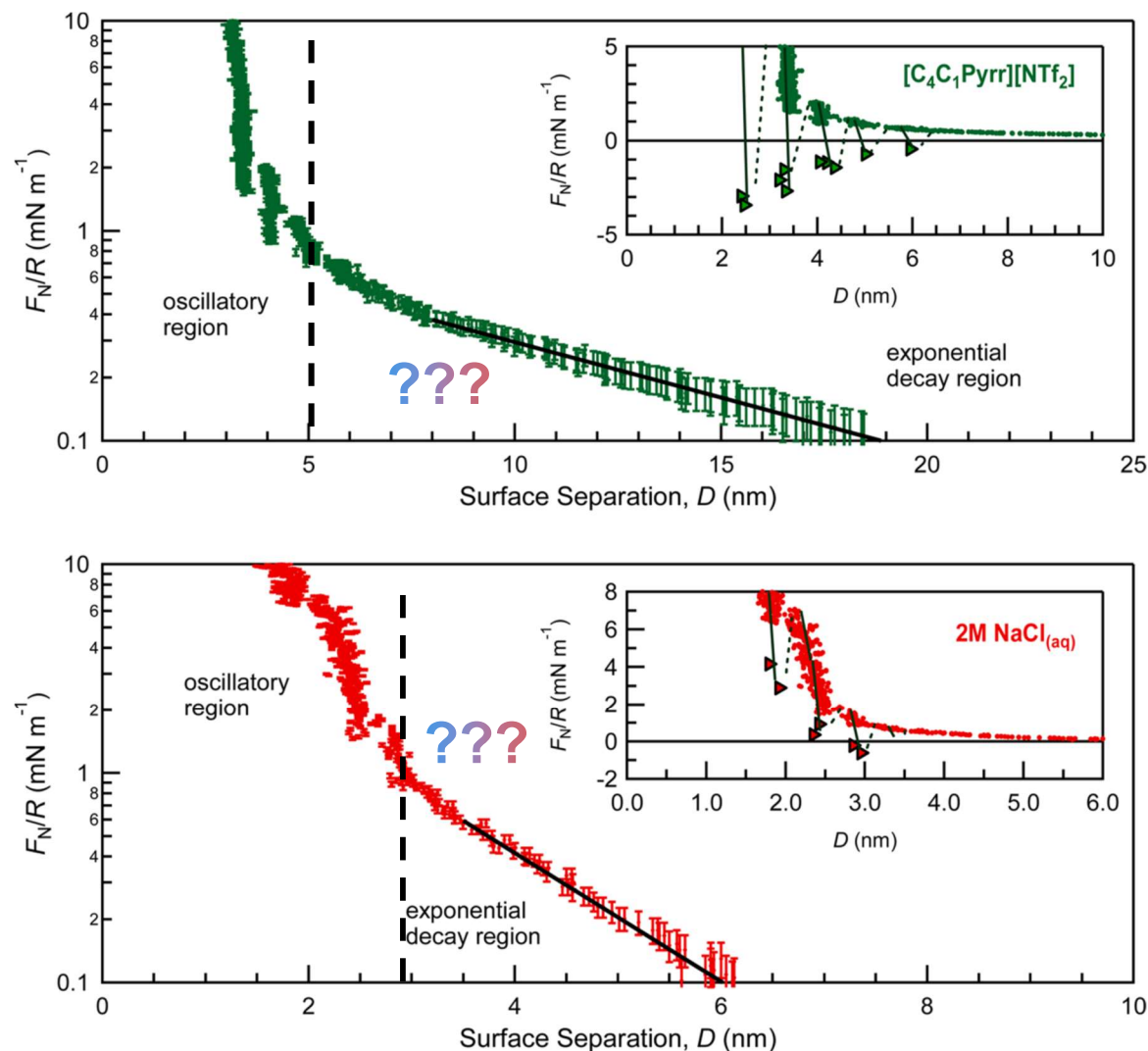


J. Israelachvili et al, *Rep. Prog. Phys.* (2010)

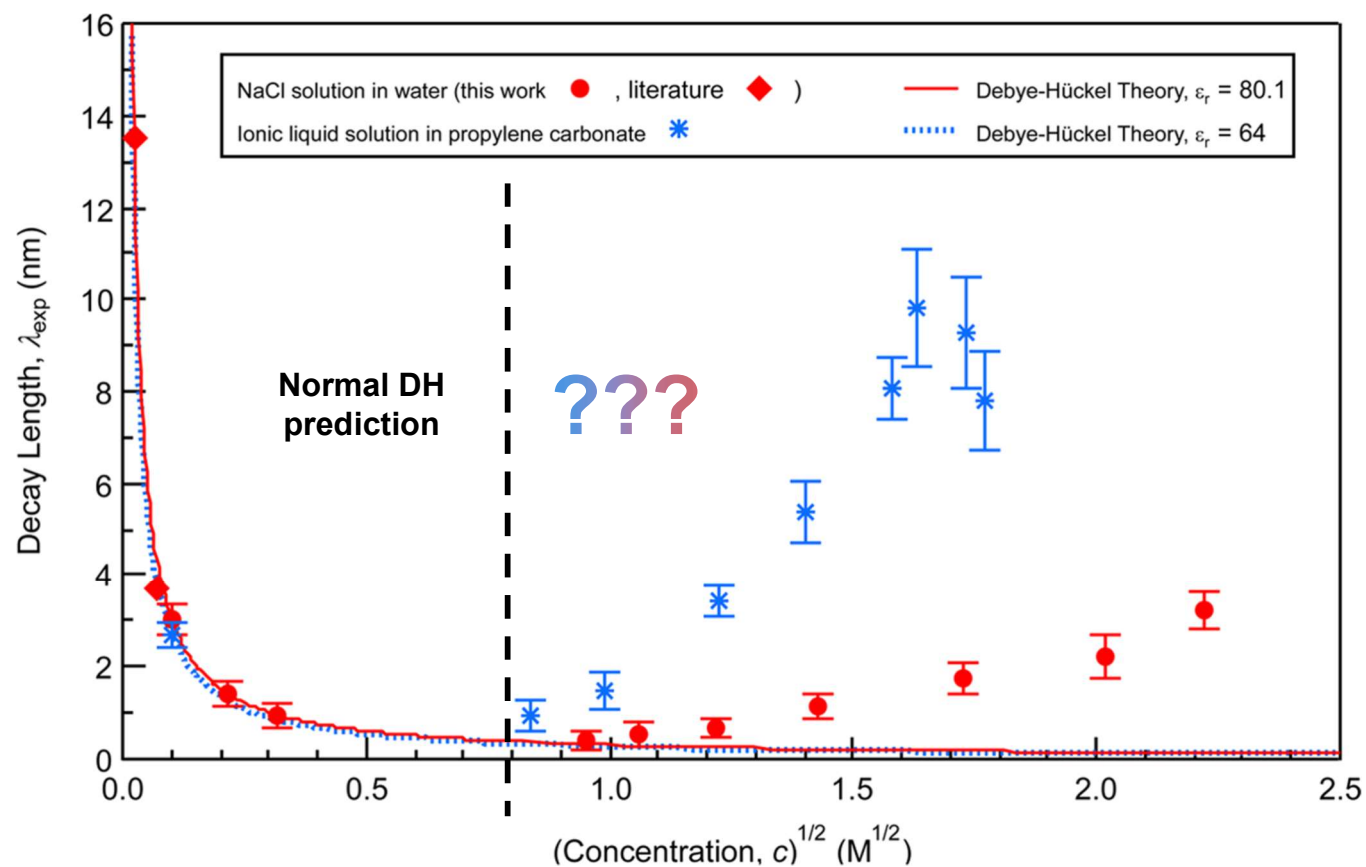
Bruno Zappone & Marina Ruths, *Liq. Cryst.* (2024)

## Surface Force Apparatus (SFA)

- It uses **interferometric techniques** to precisely measure the separation between two surfaces
- A calibrated **differential force spring** measures the **force exerted between the surfaces**



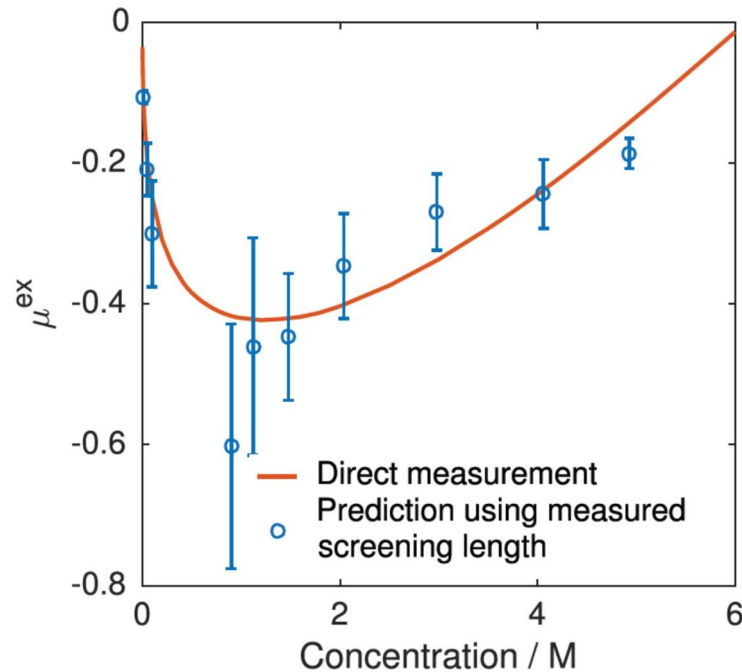
- Without depending on the chemical identity of charge carrier (Either salt or ionic liquid), one can observe **systematic underscreening at long-range separation**



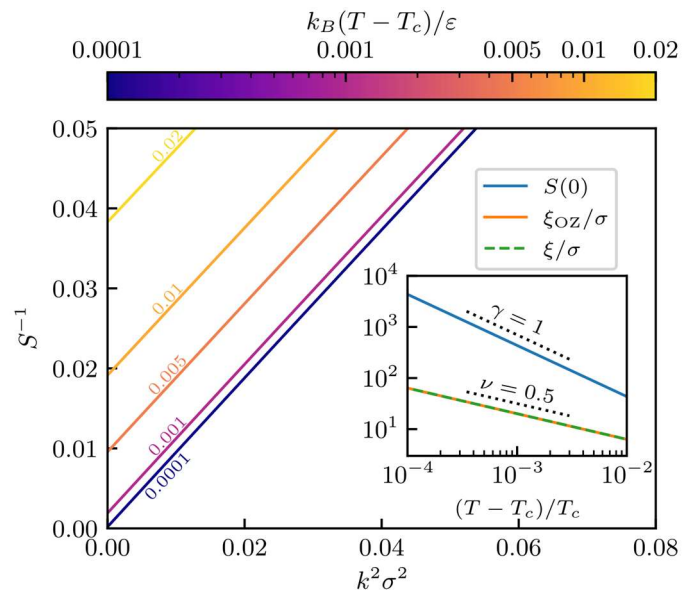
A. M. Smith, A. A. Lee, and S. Perkin, *JPCL* (2016)

- Without depending on the chemical identity of charge carrier (Either salt or ionic liquid), one can observe **systematic underscreening at long-range separation**

$$\lambda_D = \left( \frac{\epsilon_r \epsilon_0 k_B T}{\sum_i \rho_{\infty, i} e^2 z_i^2} \right)^{1/2}$$



A. A. Lee et al., **Faraday Discussions** (2017)  
A. A. Lee et al., **PRL** (2017)



- Excess chemical potential can be directly estimated from

$$\mu_{\text{ex}} = -k_B T c^{(1)}([\rho_b])$$

$$\frac{\mu_{\text{ex}}}{k_B T} = -\frac{1}{2} \frac{l_B}{l_S + a}$$

- Correlation length can be explicitly extracted from

$$S(k) = \frac{1}{1 - \rho_b \tilde{c}_b^{(2)}(k)}$$

$$S(k) \approx \frac{S(0)}{1 + \xi_{OZ}^2 k^2}$$

$$\xi_{OZ}^2 = R^2 S(0)$$

### Neural DFT is more than just fitting data

- ❖ It's about learning a fundamental physical relationship.
- ❖ The mapping from a system's configuration (density, interaction potential) to its correlations and free energy.
- ❖ Not just predicting properties of a given material, but designing the material (i.e., the interparticle potential  $\phi(r)$ ) to achieve desired properties or structures.

### Known Limitations

- ❖ Long-range interaction
- ❖ Formulation of complex molecular structure

Thank you!  
Q&A