Analytical classical density functionals from an equation learning network

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We explore the feasibility of using machine learning methods to obtain an analytic form of the classical free energy functional for two model fluids, hard rods and Lennard–Jones, in one dimension. The Equation Learning Network proposed in Ref. 1 is suitably modified to construct free energy densities which are functions of a set of weighted densities and which are built from a small number of basis functions with flexible combination rules. This setup considerably enlarges the functional space used in the machine learning optimization as compared to previous works where the functional is limited to a simple polynomial form. As a result, we find a good approximation for the exact hard rod functional and its direct correlation function. For the Lennard–Jones fluid, we let the network learn (i) the full excess free energy functional and (ii) the excess free energy functional related to interparticle attractions. Both functionals show a good agreement with simulated density profiles for thermodynamic parameters inside and outside the training region.

I. INTRODUCTION

Density functional theory (DFT) may be viewed as a great reductionist scheme for classical and quantum many–body systems in equilibrium. The one–to–one correspondence between the one–body density profile of particles and the one–body external potential acting on these particles entails that a unique (free) energy functional of the one–body density contains all of the homogeneous and inhomogeneous equilibrium structure in a given system, and no explicit knowledge of higher–order correlations (i.e. through the phase space distribution of classical particles or the full many–body quantum wavefunction) is needed.

In general, the analytical form of the (free) energy functional is unknown, except for a handful of particular model systems (mostly in one dimension [1D]). In recent years, some effort has gone into approximating ("learning") functionals by machine learning (ML) techniques. In quantum DFT, e.g., interpolating functionals generated by kernel ridge regression have been tested for model 1D systems1,2 and also have been extended to 3D systems.3 Numerically interpolated functionals do not contain sufficient information about functional gradients, therefore both the energy–density map and the external potential–density maps had to be learned by interpolation4. For the 1D Hubbard model, a convolutional network functional has been learned whose numerical functional derivative appears to be more robust.5 However, these approaches hide the energy functional inside an “ML black box” which does not permit much insight from a theory perspective. For the classical case, a 1D LJ like fluid was studied with a convolutional network,6 utilizing an established approach from liquid state theory of splitting the excess free energy functional into a “repulsion” part and an “attraction” part $\mathcal{F}_r, \mathcal{F}_a$. The convolutional network naturally led to an approximation of $\mathcal{F}_a$ in terms of weighted densities $n_i$, which are the essential building blocks in modern classical DFT; however, the free energy density $\mathcal{F}_a(n_i)$ as a function of $n_i$ had to be prescribed as simple polynomials. An interpretable results obtained in6 was the accurate splitting of the interaction potential in the Weeks–Chandler–Andersen (WCA) spirit7.

In this context, the question naturally arises whether ML techniques can be used to learn analytic forms of (free) energy functionals instead of “black boxes” or presumed forms. This question is important also in a more general context: can ML algorithms contribute to theory building in physics? In the ML community, efforts in that direction have utilized genetic algorithms to search a space of simple basis function with multiplication and addition rules.8 More recent work proposes an equation learning network employing gradient–based optimization with simple basis functions and division besides multiplication/addition as combination rules.9 An empirical principle for the “right” formula (choose the simplest one that still predicts well, i.e. Occam’s razor) can be built into the cost function. This principle was also successful in the history of physics in finding analytical models with high predictive power even outside the training/observed regime. For the DFT problem, the extrapolation power to other external potentials is an important aspect, as well as the analytic differentiability of the free energy functional since structural information about the fluid (pair correlations) is obtained via the direct correlation function (two functional derivatives of the excess free energy functional). These aspects are explored below for the model cases of a hard rod (HR) and a Lennard–Jones (LJ) fluid in 1D.

II. CLASSICAL DFT

In classical DFT10,11 the grand potential functional of 1D system is

$$\Omega[\rho(x)] = \mathcal{F}^{id}[\rho(x)] + \mathcal{F}^{ext}[\rho(x)] + \int dx (V^{ext}(x) - \mu) \rho(x),$$

(1)

where $\rho(x)$ is the particle density distribution, $\mathcal{F}^{id}$ is the free energy functional of the ideal gas, $\mathcal{F}^{ext}$ is the excess free energy functional (unique for a given pair potential between par-
FIG. 1: Network architecture of the proposed FEQL for 10 layers ($L = 9$) and one neuron per type ($u = 3, v = 2$) and 6 convolution (weighting) kernels ($n_w = 6$). $\epsilon$ is the coupling strength (equivalent to inverse temperature) in the LJ potential.

particles), $\mu$ is the chemical potential and $V^{\text{ext}}$ is an external potential. The exact form of $F^{\text{id}}$ is:

$$\beta F^{\text{id}} = \int dx \rho(x) \left[ \ln(\rho(x)) \lambda - 1 \right]$$

(2)

with $\beta = 1/(k_B T)$, $T$ the temperature, $k_B$ Boltzmann’s constant, and $\lambda$ the thermal wavelength. In the following we set $\beta = \lambda = 1$.

In equilibrium, the corresponding density profile $\rho^{\text{eq}}$ minimizes $\Omega$ for a given $\mu$. Thus, with $\frac{\partial \Omega}{\partial \rho} = 0$ and Eq. (2), we obtain

$$\rho^{\text{eq}} = \exp(\mu - \delta F^{\text{id}}/\delta \rho |_{\rho = \rho^{\text{eq}}} - V^{\text{ext}}).$$

(3)

All DFT solutions for test density distributions in this work are obtained by iteratively solving Eq. (3) using the Picard method with mixing.

In this paper, we investigate the HR pair potential:

$$U_{\text{HR}}(x) = \begin{cases} \infty & \text{if } x < \sigma \\ 0 & \text{otherwise} \end{cases}$$

as well as the LJ (–like) potential:

$$U_{\text{LJ}}(x) = \begin{cases} \infty & \text{if } x < \sigma \\ 4 \epsilon \left[ \left( \frac{\sigma}{x} \right)^{12} - \left( \frac{\sigma}{x} \right)^{6} \right] & \text{if } \sigma < x < 16\sigma \\ 0 & \text{otherwise} \end{cases}$$

with $x$ the distance between particle centers, $\sigma$ the diameter of the particles and $\epsilon$ the strength of interaction. In the following we set $\sigma = 1$.

III. MACHINE LEARNING

A. Model

We define a machine learned excess free energy functional $F^{\text{ex,ML}}$ and the resulting ML output density $\rho^{\text{ML}}$ by

$$\rho^{\text{ML}}(x) = \exp(\mu^{\text{ML}} - \frac{\delta F^{\text{ex,ML}}}{\delta \rho} |_{\rho = \rho^{\text{eq}}} - V^{\text{ext}}).$$

(4)

This is the equivalent of a “generative step” of a learned distribution $\rho^{\text{ML}}$ from an input distribution $\rho^{\text{eq}}$ in an ML network (via weighted densities $n_i$, see below). Here, $\mu^{\text{ML}}$ is included in the training process to facilitate convergence. In the end, $\mu^{\text{ML}} \rightarrow \mu$, see also Ref. 2 and SI for details. The test density profiles shown in Figs. 2–4 are obtained by initializing with a constant value and then iteratively minimizing the learned functional with the (physical) $\mu$.

The network we propose, Functional Equation Learner (FEQL), is a $L$–layered feed–forward network with computational units specifically designed for constructing the free energy functional (see Fig. 1). The first layer consists of convolution kernels which compute the weighted densities $n_i$ with
the convolution kernel \( \omega_i \) (i = 1, ..., \( n_w \)) by
\[
n_i(x) = \rho \otimes \omega_i = \int dx' \rho(x') \omega_i(x - x'),
\]
and some of the weighted densities are multiplied by \( \epsilon = 2 \) is a linear, all-to-all mapping of the vector (of functions) \( n = \{n_i(x)\} \) to the vector
\[
z^{(l+1)} = W^{(l)} n
\]
at level \( l \). The layers \( 3, \ldots, L - 4 \) are a sequence of nonlinear and linear transformations. The non-linear transformation at level \( l \) contains \( u \) unary units \( f_i \) and \( v \) binary units \( g_j \) and maps \( z^{(l)}(x) \) (\( u + 2v \)-dimensional) to the layer output \( y^{(l)}(u + v \)-dimensional) as:
\[
y^{(l)} := \left( f_1(z_1^{(l)}), f_2(z_2^{(l)}), \ldots, f_u(z_u^{(l)}) \right),
\]
\[
g_1(z_1^{(l)}, z_2^{(l)}), \ldots, g_v(z_1^{(l)}, z_2^{(l)}, \ldots, z_u^{(l)}, z_{u+1}^{(l)}, \ldots, z_{u+2v}^{(l)}) \right). \tag{7}
\]
The unary units, \( f_1, \ldots, f_u \), receive the respective component, \( z_1, \ldots, z_u \), as inputs, and each unit is one of the following base functions indexed by \( I \in \{0, 1, 2\} \):
\[
f_I(z_i) := \begin{cases} z_i & \text{if } I = 0 \\ \exp(z_i) - 1 & \text{if } I = 1 \\ \ln(z_i + 1) & \text{if } I = 2 \end{cases}
\]
The binary units, \( g_1, \ldots, g_v \), receive the remaining component, \( z_{a+1}, \ldots, z_{a+2v} \), as input in pairs of two, and each unit may be multiplication or division indexed by \( J \in \{0, 1\} \):
\[
g_J(z_i, z_{i+1}) := \begin{cases} z_i \times z_{i+1} & \text{if } J = 0 \\ z_i / (z_{i+1} + 1) & \text{if } J = 1 \end{cases}
\]
Note that \( f_J(0) = g_J(0, z) = 0 \). One may worry about divergences in division and logarithm when \( z \to -1 \). In the beginning of the training procedure, all parameters and convolution kernel are initialized by small numbers so thus \( z \) is close to zero and there are no problems. If \( z \) is too close to -1, the loss will change drastically; thus the network will intrinsically handle this issue. As mentioned in Ref. [9] one could use modified division and logarithm functions and add extra penalties. However, it turns out not to be required here.

The linear transformation from level \( l \) to \( l + 1 \) maps the \( (u + v) \)-dimensional input \( y^{(l)} \) to the \( (u + 2v) \)-dimensional intermediate representation \( z^{(l+1)} \) given by
\[
z^{(l+1)} = W^{(l+1)} y^{(l)}. \tag{8}
\]
Thus, the \( n_w \) convolution kernels \( \omega(x) \) in the first layer and the matrices \( W^{(l)} \) are free parameters that are learned during training.

The machine-learned free energy density \( \mathcal{F}^{\mathrm{ML}} \) is a summation of the output of layer \( L - 4 \), the functional derivative
\[
\frac{\delta \mathcal{F}^{\mathrm{ML}}}{\delta \rho} = \sum_i \frac{\partial \mathcal{F}^{\mathrm{ML}}}{\partial \rho_i} \omega_i \ (\text{with } \mathcal{F}^{\mathrm{ML}} = \int dx \mathcal{F}^{\mathrm{ML}}(n)) \text{ and } \sigma \text{ denoting cross-correlation) is used in the final, generative step (Eq. (4)). More details about constructing FEQL can be found in the SI.

### B. Network training

To obtain training data for \( \rho^n \), grand canonical simulation are used in the case of LJ fluid; for the HR fluid, Eq. (1) is directly solved, since the exact functional is known.

FEQL is fully differentiable in its free parameters \( \theta \) = [\( W, \omega \)] and can thus be trained using back-propagation. We adopt the following loss function
\[
L = \frac{1}{N} \sum_{i=1}^{N} \left( \alpha_1 \int |\rho^n - \rho^{\text{HR}}| dx + \alpha_2 |\mu^{ex} - \mu^{\text{ML}}| \right) + \lambda_1 \sum_{i=1}^{n} \sum_{\beta, \gamma} |W_{\beta \gamma}^{(l)}|,
\]
with \( \alpha_1 = 0.9 \) and \( \alpha_2 = 0.1 \). These values have been determined empirically and the exact choice is not critical. For training we choose Adam\textsuperscript{16} with mini-batches:
\[
\theta_{t+1} = \theta_t + \text{Adam} \left( \frac{\partial L(D(i))}{\partial \theta}, \alpha \right)
\]
with \( \alpha \) the stepsize parameter (learning rate) and \( D(i) \) the data in the current mini-batch. The choice of Adam is not critical and standard stochastic gradient descent also works.

Following Sahoo et al.\textsuperscript{13} we adopt a three–step training procedure. At the beginning, we use no regularization (\( \lambda_1 = \lambda_2 = 0 \)), such that parameters can vary freely and reach reasonable starting points. In step 2, we switch on the regularization by setting \( \lambda_1 \) and \( \lambda_2 \) to positive finite values to sparsify the network for obtaining a simpler functional. In step 3, we clamp small parameters with \( |W_{\beta \gamma}^{(l)}| < w_{\text{th}} \) to zero. In this way we keep the sparsity introduced by the lasso\textsuperscript{13} training in step 2 but make sure unbiased parameter values are attained.

In this paper we choose \( \alpha = 10^{-2} \) or \( 10^{-3} \), \( \lambda_1 = 10^{-7} \) and \( w_{\text{th}} = 0.05 \).

### IV. RESULT

#### A. Hard rods

The exact equation of state (eos) for the hard rod (HR) fluid is given by the pressure \( P(\rho) = \frac{\rho^2}{\rho^2 - \rho_0^2} \) and the analytic form of \( \mathcal{F}^{\text{HR}} \) (Percus functional) is one of the few exactly known ones.\textsuperscript{14,15}

The parameter of \( \mathcal{F}^{\text{ML}} \) are trained using 1024 density profiles in a hard wall slit of width 32 \( \sigma \) with 3 additional Gaussian potentials of random strength/width and location inside the slit and with a range of training reservoir densities \( \rho_0 = 0.2...0.55 \). We choose \( n_w = 3 \) and \( (1,1,1,3,1) \) nodes for (identity, exponential, logarithm, multiplication and division) with \( L = 10 \) layers (see Fig. 1) and \( \lambda_2 = 8 \cdot 10^{-5} \) in Eq. (9).
(results for different $\lambda_2$ and arguments for an optimal choice are shown in the SI). $\mathcal{F}^{\text{ex,ML}}$ is not of the form of the Percus functional, since the convolution kernels of the latter are Dirac delta and Heaviside step functions, which are hard to be captured by our network.

In Fig. 2 we show the eos, a density profile inside the thermodynamic training region but not in the training data ($\rho_0 = 0.49$) and a density profile outside the training region ($\rho_0 = 0.80$). The FEQL recovers the almost exact result inside the training region and also performs quite well outside the training region. The ML density profiles are initialized by $\rho = 0.5$ and then iteratively solved using Eq. (5) with $\mathcal{F}^{\text{ex}} = \mathcal{F}^{\text{ex,ML}}$.

The virial expansion

$$P^{\text{ML}}(\rho) \approx \rho + 1.03\rho^2 + 0.71\rho^3 + O(\rho^4)$$  \hspace{1cm} (11)

of the ML eos shows moderate deviation compared to the exact one ($\frac{\rho}{\rho_1} = \rho + \rho^2 + \rho^3 \ldots$).

One sees that inaccuracies in these coefficients do not necessarily mean a poor eos. Despite inaccurate coefficients, the higher order terms in the learned eos combine appropriately to give a good representation of the exact eos. This is understandable since no explicit information about virial coefficients is incorporated into the cost function, thus the learning procedure has little incentive to find the correct coefficients.

1. **Splitting between repulsions and attractions**

Following liquid state theory, we split into a contribution from repulsions and one from attractions as follows:

$$\mathcal{F}^{\text{ex,ML}}([\rho]; \epsilon) = \mathcal{F}^{\text{HR}}([\rho]) + \epsilon \mathcal{F}^{\text{ex,ML}}([\rho]; \epsilon),$$  \hspace{1cm} (12)

where the factor $\epsilon$ in front of the $\mathcal{F}^{\text{ex,ML}}$ makes sure $\mathcal{F}^{\text{ex,ML}}(\epsilon \rightarrow 0) = \mathcal{F}^{\text{HR}}$, and $\mathcal{F}^{\text{ex,ML}}$ is to be learned by the network. In Fig. 1 the output from the layer 6 is $\mathcal{F}^{\text{ex,ML}}$; we multiply the output from the layer 8 by $\epsilon$, add contribution from $\mathcal{F}^{\text{HR}}$, and then feed it to the layer 9. In the first layer, we choose $n_w = 4$, 1 kernel multiplied by $\epsilon$ and another 3 without this factor (see Fig. 1), and (1,1,1,2,1) nodes for (identity, exponential, logarithm, multiplication and division). The training parameter $\lambda_2 = 5 \cdot 10^{-5}$ in Eq. (9). Results are shown in Fig. 3. The findings are similar to the HR case with a very good match to simulation data for the eos and test distributions inside and outside the thermodynamic training region. For a 1D system with hard-core repulsive and finite range attractive pair potential, the pressure must be monotonically increasing for arbitrary low temperature (high $\epsilon$), and thus resulting no gas–liquid transition. The corresponding ML pressure shows no van der Waals (vdW) loop for attractions strengths up to $\epsilon = 4.1$, this is a qualitative step forward as compared to Ref. 2.

2. **No splitting**

As a further test of the capability of FEQL, we forego the splitting of the functional such that $\mathcal{F}^{\text{ex}} = \mathcal{F}^{\text{ex,ML}}$. In the first layer, we choose $n_w = 6$, 3 kernels multiplied with $\epsilon$ and another 3 without this factor (see Fig. 1), and (1,1,1,3,1) nodes for (identity, exponential, logarithm, multiplication and division). The training parameter $\lambda_2 = 5 \cdot 10^{-5}$ in Eq. (9). For the training data we also include density profiles from the HR case. In Fig. 4 we show the results. Test distributions match well to simulation data both in the HR limit and the regime of higher attractions. The eos shows an unphysical vdW loop for attractions strengths $\epsilon > 3.7$, much higher than the upper limit of the training data.
FIG. 3: FEQL results for LJ fluid with functional splitting. (a) eos \( P(\rho) \). (b) density profile for \( \epsilon = 1.30, \mu = \ln(1.27) \) inside the training region but \( V_{\text{ext}} \) not in the training data. (c) density profile at a hard wall for \( \epsilon = 1.7, \mu = \ln(1.7) \), outside the training region. Dark solid lines are simulation profiles and blue dashed lines are ML results. Insets in (b) and (c) show \( \Delta \rho = \rho^{MC} - \rho^{ML} \).

FIG. 4: FEQL results for LJ fluid (no splitting). (a) eos \( P(\rho) \). (b) density profile for \( \epsilon = 1.25, \mu = \ln(1.15) \) inside the training region but \( V_{\text{ext}} \) not in the training data. (c,d) density profile at a hard wall for \( \epsilon = 1.9, \mu = \ln(1.9) \) (c) and \( \epsilon = 0, \rho_0 = 0.7 \) (HR limit, (d)). Dark solid lines are simulation profiles and blue dashed lines are ML results. Insets in (b) and (c) show \( \Delta \rho = \rho^{MC} - \rho^{ML} \) and in (d) \( \Delta \rho = \rho^{\text{exact}} - \rho^{ML} \).

C. Direct correlation function

The direct correlation function (dcf) is a central object in DFT which through iterations yields the pair correlation function (Ornstein–Zernike relation, see also Chap. 3 in Ref.[10]). It is given by the second functional derivative of \( \mathcal{F}^{\rho} \):

\[
C^{(2)}(x_1, x_2; \rho_0) = -\frac{\beta \delta^2 \mathcal{F}^{\rho}}{\delta \rho(x_1) \delta \rho(x_2)}, \tag{13}
\]

and it depends only on \( x = |x_1 - x_2| \) in the case of a homogeneous fluid with density \( \rho_0 \).
As the network is only trained on the level of the first functional derivative (see Eq. 4), it is a challenge for FEQL to capture the dcf. In Fig. 5 we show exemplary dcf’s at moderate density for the exact HR functional, LJ from simulation and the corresponding ML results. The direct correlations inside the hard core are captured very well by ML in the HR and LJ cases. Outside the hard core, in the HR case, the \( C^{(2)} \) from the ML shows insignificant correlation. In the case of LJ, the contribution to \( C^{(2)} \) from attraction is semi-quantitatively correct, with a better result in the splitting case.

V. CONCLUSION

The adaptation of EQL\(^3\) to the classical DFT problem of finding \( \mathcal{F}^{\mu} \) has shown satisfactory results for the exemplary case of the 1D HR and LJ fluid. The new network FEQL is very flexible and goes significantly beyond the polynomial ansatz used in Ref. \(^2\). The analytic form allows for more easily transferable output and further calculations to obtain, e.g., direct correlation functions. An application to more realistic systems in 3D and perhaps also complex fluids such as water appears to be promising.\(^18\) From the results of this work we conclude that the incorporation of results from liquid state theory (separation of repulsion and attraction) is not essential here; however, it increases the reliability and trainability of the ML functional. Future work should include information on virial or high density expansions as well as correlation functions (via test particles) and should develop more quantitative measures for extrapolative capabilities of ML functionals.

SUPPLEMENTARY INFORMATION

See supplementary information for more discussion about the training procedure, FEQL, \( \mu_{\text{ex}} \), comparison of Ref. \(^2\) explicit \( \mathcal{F}^{\mu_{\text{ex}}} \) and convolution kernels \( \omega(x) \).

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I. EXACT HARD ROD FUNCTIONAL

The exact form of the excess free energy functional for hard rods (HR) $F_{HR}$ is\textsuperscript{1, 2}

$$F_{HR} = \int \phi[n] \, dx = \int -n_0 \ln(1 - n_1) \, dx \quad (1)$$

with $n_i(x) = \rho \otimes \omega^\text{exact}_i(\text{convolution})$, where $\omega^\text{exact}_i(x) = \Theta(\sigma/2 - |x|)$ and $\omega^\text{exact}_0(x) = \frac{1}{2}\delta(\sigma/2 - |x|)$. Here, $\sigma$ is the length of the rod, $\Theta(x)$ is the Heaviside step function and $\delta(x)$ the Dirac delta function. Thus,

$$\frac{\partial F_{HR}}{\partial \rho} = \sum_i \frac{\partial \phi[n]}{\partial n_i} \ast \omega^\text{exact}_i. \quad (2)$$

with $\ast$ denoting cross-correlation. Eqs. (2) and (1) are used to generate the training profiles in the HR case. In the Lennard–Jones (LJ) case, $F_{HR}$ describes the repulsive part of the free energy functional.

![Graph](image)

FIG. 1: Loss as a function of number of iterations for 4 different values of $\lambda_2$. Dashed lines are validation loss and solid circles are training loss.

II. HARD RODS: LEARNING PROCEDURE AND DEPENDENCE ON LOSS FUNCTION PARAMETER $\lambda_2$

In the main paper, we have defined the loss function

$$L = \frac{1}{N} \sum_{i=1}^{N} \left( \alpha_1 \int |\rho^\text{eq}_i - \rho^\text{ML}_i| \, dx + \alpha_2 |\mu^\text{eq}_i - \mu^\text{ML}_i| \right) + \lambda_1 \int |\omega_i| + \lambda_2 \sum_{l,\delta} |W^{(l)}_{\delta\gamma}|. \quad (3)$$

The first term quantifies the deviation between generated and input density profile (ground truth) and the corresponding chemical potentials. The second term is a regularizer to avoid numerically large weight functions during

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the training procedure, and it is not very important for final results. The third term with coefficient \( \lambda_2 \) is used as a substitute for the number of nonzero entries in the matrices \( W(i) \) which is not differentiable directly. Nevertheless, minimizing the absolute norm tends to produce sparse solutions, see also Lasso regression\(^3\), and thus favors simpler functionals.

Before training, we prepare 1024 density profiles with a range of reservoir densities \( \rho_0 = 0.2...0.55 \), and randomly divided into 921 density profiles as training set and 103 as validating set. The training procedure only uses training set for updating trainable parameters and evaluates the value of the loss on the training set and on the validating set (called training loss and validation loss) at the end of each iteration\(^4\). Additionally, we also prepare 256 density profiles with a range of reservoir densities \( \rho_0 = 0.6...0.8 \), outside the training region, as a measurement for extrapolative capabilities. Then, as described in the main paper, we have used a three-step training procedure. In Fig. 1 we show the evolution of the training and validation loss throughout the training for 4 different values of \( \lambda_2 \). For the higher values of \( \lambda_2 \) (10\(^{-2}\) and 10\(^{-3}\)) there is a marked increase of \( L \) at the beginning of step 2. For \( \lambda = 10^{-4} \) the beginning of step 2 without increase of \( L \) and then further decreases.

This is further confirmed in the Fig. 2a, which shows the final value of \( L \) from the training, validating, and extrapolating set as a function of \( \lambda_2 \). The loss shows underfitting for \( \lambda_2 > 10^{-3} \) and overfitting for \( \lambda_2 < 10^{-7} \). Near–optimal choices are \( 10^{-6} < \lambda_2 < 10^{-4} \). The complexities (the number of nonzero entries in \( W \)) increase with decreasing of \( \lambda_2 \) (Fig. 2b). For a broad range of complexities, the loss is almost constant (Fig. 2c).

![Fig. 2](image)

(a) Final loss versus \( \lambda_2 \).
(b) Complexity versus \( \lambda_2 \).
(c) Complexity versus loss.

FIG. 2: The interdependence of loss, complexity and \( \lambda_2 \).

The effect of \( \lambda_2 \) on the bulk equation of state (eos) is shown in Fig. 3. The relative deviation of the ML pressure from the exact one (Fig. 3a) is close to zero for \( \lambda_2 < 10^{-3} \). In Fig. 3b we analyze the virial coefficients \( a_2...a_4 \) \( (P = \sum_{m=1}^3 \rho^m a_m ; a_1 = 1 \) (ideal gas) and all \( a_i = 1 \) for the exact eos) Therefore, we finally choose \( \lambda_2 = 8 \cdot 10^{-5} \) as a near-optimal compromise between low loss, complexity and eos.

![Fig. 3](image)

(a) The relative pressure difference as a function of density \( \rho \).
(b) Second to fourth virial coefficient as a function of \( \lambda_2 \).

FIG. 3: Properties of the bulk fluid: pressure and virial coefficients.
III. CONSISTENCY OF \( \mu \)

Following Ref. 5, we define \( \rho_{\text{ML}}^i \) of the \( i \)-th data set (Eq.(4) in the main paper) by

\[
\rho_{\text{ML}}^i(x) = \exp \left( \mu_{\text{ML}}^i - \delta \frac{F_{\text{ex,ML}}}{\delta \rho} \bigg|_{\rho = \rho_{eq}^i} - V_{\text{ext}}^i \right) .
\]

Here \( \mu_{\text{ML}}^i \) is determined by demanding that \( \int (\rho_{\text{ML}}^i - \rho_{eq}^i)^2 \) is minimal, which entails that \( \mu_{\text{ML}}^i \) varies during the iterations. This choice of \( \mu_{\text{ML}}^i \) stabilizes the training process, and \( \mu_{\text{ML}}^i \) is directly determined by

\[
\frac{\partial}{\partial \mu_{\text{ML}}^i} \int (\rho_{\text{ML}}^i - \rho_{eq}^i)^2 = 0 \Rightarrow \mu_{\text{ML}}^i = \ln \left( \frac{\int \rho_{\text{ML}}^i \rho_{\text{ML}}^i}{\int \rho_{eq}^i \rho_{eq}^i} \right) ,
\]

where \( \rho_{\text{ML}}^i = \exp \left( -\delta \frac{F_{\text{ex,ML}}}{\delta \rho} \bigg|_{\rho = \rho_{eq}^i} - V_{\text{ext}}^i \right) \). If the training converges, \( \mu_{\text{ML}}^i \) will converge to \( \mu_{eq}^i \). In Fig.4 we show \( \Delta \mu = \mu_{eq}^i - \mu_{\text{ML}}^i \) versus \( \mu_{eq}^i \) at the end of training for the three cases in the main paper, and \( \mu_{\text{ML}}^i \) is indeed close to \( \mu_{eq}^i \).

Furthermore, we also check \( \mu(\rho) = \frac{\partial}{\partial \rho} \) (i.e. from the equation of state), where \( \rho \) here refers to the density of the bulk fluid. In Fig. 5 we show \( \mu(\rho) \) by exact functional, ML, and MC simulations for the three cases as in the main paper. Deviations only occur for the LJ case well outside the training region.

![FIG. 4: \( \Delta \mu = \mu_{eq}^i - \mu_{\text{ML}}^i \) versus \( \mu_{eq}^i \). (a) HR (b) LJ with splitting (c) LJ, no splitting.](image)

![FIG. 5: \( \mu(\rho) \) versus \( \rho \). (a) HR (b) LJ with splitting (c) LJ, no splitting. In (b) and (c), the circles are ML and dashed lines are MC simulations.](image)
In principle, one could also fix $\mu_{ML}^i = \mu_i$ (the chemical potential of the data set) and then choose $\alpha_1 = 1$ and $\alpha_2 = 0$ in Eq. (3), but this requires smaller learning rates and results in much longer training processes. For example, the HR case with parameters as in the main paper can be done with learning rate $= 10^{-5}$ and the number of training iterations doubled.

**IV. COMPARISON AMONG $F_{ex,ML}$ FOR LJ FLUID**

In Ref. 5, the $F_{ex,ML}$ is limited to the polynomial ansatz and the best one is given by

$$F_{ex,ML} = F_{HR} + \epsilon \left( \int dx \sum_{ij} \beta_{ij} n_i n_j + \sum_{i,j,k} \gamma_{ijk} n_i n_j n_k \right)$$

(5)

with $i,j,k$ run from 0 to 7, thus we have 16 weighted densities in total. In Fig. 6 we show the equation of state $P(\rho)$ with $\epsilon = 2.5$ and $\rho(x)$ with $\epsilon = 1.7$ and $\mu = \ln(1.7)$ at a hard wall. Both results show that FEQL is better than the polynomial ansatz in Ref. 5.

![Graphs](image)

FIG. 6: Comparison among three $F_{ex,ML}$ for LJ fluid, two from the main paper and $F_{ex,ML}$ from Ref. 5. (a) $P(\rho)$ with $\epsilon = 2.5$. (b) $\rho(x)$ at a hard wall with $\epsilon = 1.7$ and $\mu = \ln(1.7)$. (c) $\Delta \rho(x) = \rho^{ML}(x) - \rho^{MC}(x)$ with the same condition as (b). Note that the training data are $\epsilon = 1.0...1.5$ for $F_{ex,ML}$ and $\epsilon = 0.5...1.5$ for two $F_{ex,ML}$ form the main paper.

**V. FULL $F_{ex,ML}$**

Here we show the full functional of $F_{ex,ML}[n]$, with $n_i(x) = \int dx' \rho(x') \omega_i(x-x')$. The coefficients in $F_{ex,ML}$ are single precision; for displaying purposes, all coefficients are rounded to the one decimal place and then rationalized. For $F_{ex,ML}$ with full digits, we provide test function.ipynb (Jupyter notebook). Also, in test function.ipynb and other notebooks, we demonstrate how to use trained functional to obtain equilibrium density profiles, eos, and direct correlation function$^6$.

**A. $F_{ex,ML}$ for hard rod**

The FEQL result for hard rod is

$$F_{ex,ML} = \int dx \left( \frac{n_i^2}{4} + \frac{n_i n_j y_0 - n_i^2}{4} \right) + y_2 \left( -\frac{n_i^2}{5} - \frac{n_0^2}{10} n_0 - \frac{3}{10} n_0^2 + \frac{3}{10} \right) + e y_1 - 1$$

(6)

with $y_0 = \frac{2 n_i}{5} + \frac{n_0}{10}$, $y_1 = \frac{3 n_i}{5}$, $y_2 = \frac{2 n_i}{5} - \frac{n_0}{10} + \frac{n_0^2}{10}$, $y_3 = \frac{n_0^2}{10}$ and convolution kernels $\omega_i$ shown in Fig. 7a.
B. $F^{\text{ex,ML}}$ for LJ with splitting

$$F^{\text{ex}} = F^{\text{th}} + e F^{\text{ex,ML}}$$, where

$$F^{\text{ex,ML}} = \int dx \frac{3}{5} y_0 y_1 \left( \frac{-\epsilon n_3}{2} - \frac{n_0}{10} - \frac{n_1}{10} - \frac{n_2}{5} + \frac{y_0 y_1}{10} - \frac{y_2 y_3}{5} - \frac{2 y_4}{5} \right) - \frac{y_0 y_1}{10} - \frac{y_2 y_3}{5}$$

$$+ \left( \frac{3 \epsilon n_3}{10} + \frac{n_0}{10} + \frac{3 n_2}{5} - \frac{y_0 y_1}{10} - \frac{9 y_2 y_3}{10} + \ln y_0 - \frac{\epsilon n_3}{10} + \frac{n_0}{10} + \frac{n_1}{10} + \frac{y_0 y_1}{10} - \frac{11 y_2 y_3}{10} \right)$$

$$+ \left( \frac{-3 \epsilon n_3}{10} - \frac{n_0}{10} - \frac{n_1}{10} - \frac{2 n_2}{5} + \frac{3 y_0 y_1}{10} - \frac{3 y_2 y_3}{10} + \frac{e^{\psi}}{5} - \frac{1}{5} - \frac{9 y_4}{10 y_5} \right) + e^{-2 \epsilon n_3 - \psi} + \ln \left( -\frac{y_2 y_3}{5} + 1 \right) - 1$$

(7)

with

$$y_0 = \frac{n_0}{10} + \frac{2 n_1}{5} - \frac{n_2}{10}, \quad y_1 = \frac{-\epsilon n_3}{2} - \frac{n_0}{10} - \frac{3 n_1}{10} + \frac{2 n_2}{5} + \frac{3 y_0 y_1}{10} + 1, \quad y_2 = \frac{\epsilon n_3}{10} + \frac{n_0}{10} + \frac{n_1}{10} + \frac{3 n_2}{10},$$

$$y_4 = -\epsilon n_3 - \frac{n_0}{10} - \frac{n_1}{10} - \frac{11 n_2}{10}, \quad y_5 = \frac{-2 \epsilon n_3}{10} - \frac{6 n_1}{10} + \frac{1}{5}, \quad y_6 = \frac{-3 \epsilon n_3}{10} + \frac{n_0}{10} + \frac{n_1}{10} + 1, \quad y_7 = \frac{-\epsilon n_3}{5} + \frac{2 n_0}{5}$$

and convolution kernels $\omega_i$ shown in Fig. 7b.

C. $F^{\text{ex,ML}}$ for LJ without splitting

The result of $F^{\text{ex}}$ given by FEQL is

$$F^{\text{ex,ML}} = \int dx \frac{3}{10} y_0 \ln y_1 + \frac{y_2 y_3}{10} + \frac{y_4 y_5}{10} + \ln \left( \frac{y_2 y_3}{10} + 1 \right)$$

$$+ \left( -\frac{3 \epsilon n_3}{5} - \frac{n_0}{5} + \frac{n_2}{5} + \frac{y_2 y_3}{2} - \frac{9 \ln y_1}{5} \right) + \left( -\frac{\epsilon n_3}{5} + \frac{n_0}{10} + \frac{n_2}{10} + \frac{3 y_4 y_5}{10} - \frac{\epsilon n_3}{10} - \frac{n_0}{10} - \frac{n_1}{10} + \frac{y_6 y_7}{5} \right)$$

$$+ e^{-2 \epsilon n_3 - \psi} + \ln \left( \frac{y_2 y_3}{10} + 1 \right) - 1$$

(8)

with

$$y_0 = \frac{3 \epsilon n_3}{5} + \frac{n_0}{10}, \quad y_1 = -\frac{7 n_0}{10} + \frac{7 n_2}{10} + 1, \quad y_2 = 3 \epsilon n_5 + \frac{n_0}{5} - \frac{n_2}{10} + \frac{y_0 y_1}{10} + 1, \quad y_3 = 3 \epsilon n_5 + \frac{n_0}{5} - \frac{n_0}{10} - \frac{n_1}{10} - \frac{n_2}{10},$$

$$y_4 = \frac{3 \epsilon n_3}{10} + \frac{n_0}{10} + \frac{n_0}{10} + \frac{n_2}{5} + \frac{3 n_2}{10}, \quad y_5 = \frac{-2 n_0}{5} + \frac{2 n_2}{5} + \frac{3 n_2}{10},$$

$$y_6 = \frac{3 \epsilon n_3}{10} - \frac{n_0}{10} + \frac{n_0}{10} + \frac{n_2}{5} + \frac{3 n_2}{10}, \quad y_7 = -\frac{\epsilon n_3}{5} + \frac{n_0}{10} + \frac{n_1}{10} + 1$$

and convolution kernels $\omega_i$ shown in Fig. 7c.

VI. FEQL BUILDING AND PHYSICAL CONSTRAINTS

To build FEQL, we first use $SymPy^7$ to determine $F^{\text{ex,ML}}$ and $\frac{\partial F^{\text{ex,ML}}}{\partial n_m}$ with a given number of weighted densities $n_m$, levels and nodes. Second, we feed the $\frac{\partial F^{\text{ex,ML}}}{\partial n_m}$ and trainable parameters into Tensorflow$^8$; then add other layers to fit the DFT structure (convolutions and Eq.(4) in the main paper). Finally, the network is trained by Keras$^9$ with Tensorflow backend.
Since $F^{\omega_{\text{ML}}}$ approximates $F^{\omega}$, we must consider two physical constraints: (i) $F^{\omega_{\text{ML}}} (\rho = 0) = 0$ and (ii) $\frac{\partial F^{\omega_{\text{ML}}}}{\partial \rho} |_{\rho = 0} = 0$. To enforce (i), we choose the linear mapping without bias and $f(0) = g(0, z) = 0$ in the non-linear mapping. Condition (ii) can be enforced by setting appropriate parameters form the matrix $W^{(l)}$ of the final level to zero. This requires to determine the analytic form of $\frac{\partial F^{\omega_{\text{ML}}}}{\partial \rho} |_{\rho = 0}$ to identify those parameters. For example, for a FEQL with $n_w = 2$, 2 levels and (1,1,1,1) nodes for (identity, exponential, logarithm, multiplication and division),

\[
\begin{align*}
\frac{\partial F^{\omega_{\text{ML}}}}{\partial \rho} |_{\rho = 0} &= a_2 L_2 (a_1 L_0 n_0 + a_1 L_1 n_1) + a_2 L_2 \left( a_1 L_2 n_0 + a_1 L_3 n_1 + a_1 L_1 n_1 \right) + a_2 L_2 (a_1 L_0 n_0 + a_1 L_1 n_1) + a_2 L_2 (a_1 L_0 n_0 + a_1 L_1 n_1) + a_2 L_2 (a_1 L_0 n_0 + a_1 L_1 n_1) + a_2 L_2 (a_1 L_0 n_0 + a_1 L_1 n_1) + a_2 L_2 (a_1 L_0 n_0 + a_1 L_1 n_1) \quad \text{(a)}
\end{align*}
\]

Consequently, we set $a_2 L_0$ to zero in order to keep $\frac{\partial F^{\omega_{\text{ML}}}}{\partial \rho} |_{\rho = 0} = 0$. 

FIG. 7: $\omega$ for all cases. (a)HR. The $\omega^{\omega_{\text{ML}}}$ are the exact weighting kernels in Eqs. (1) and (2). (b)LJ, splitting (c) LJ, no splitting. The maximum allowed range for the kernels is $[-4\sigma, 4\sigma]$ in the HR case and $[-8\sigma, 8\sigma]$ in the LJ case.
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