We present here an introductory practical course to classical density functional theory (cDFT). Density functional theories, whether quantum or classical, rely largely on nonintuitive abstract concepts and applied mathematics. They are nevertheless a powerful tool and an active field of research in physics and chemistry that led to the 1998 Nobel prize in chemistry. We here illustrate the DFT in its most mathematically simple and yet physically relevant form: the classical density functional theory of an ideal fluid in an external field, as applied to the prediction of the structure of liquid neon at the molecular scale. This introductory course is built around the production of a cDFT code written by students using the Mathematica language. In this way, they are brought to deal with (i) the cDFT theory itself, (ii) some basic concepts around the statistical mechanics of simple fluids, (iii) the underlying mathematical and numerical problem of functional minimization, and (iv) a functional programming language: Mathematica. Although these computational experiments are presented in a molecular simulation class, they may also be used in a quantum chemistry class to illustrate electronic density functional theory (eDFT), after highlighting the analogies between the quantum and classical DFTs.

Can we study and extract all interesting informations of a quantum system without considering explicitly, i.e., individually, all the electrons? Hohenberg, Kohn and Sham clearly answered yes to these questions when they invented the electronic density functional theory. In their seminal papers published in the middle of the 1960’s, they show that every interesting properties (we call them observables) of a system of particles (electrons) can be extracted not considering individual electrons but their density. This first simplification is followed by the demonstration that everything is “just” about minimizing a functional (a function of a function) of this electronic density [1, 2].

Thanks to its high computational efficiency with respect to theories based on many electrons wavefunctions, electronic density functional theory has imposed as the main theoretical way to treat quantum mechanics problems. As a consequence, it takes a prominent part in the current quantum chemistry classes.

The determination of the energetic and structural equilibrium properties of a given classical system is also an important problem, which is often addressed in statistical thermodynamic or molecular simulations classes for undergraduate students. Along these classes, computational methods which sample the configurations of the system, such as Molecular Dynamics (MD) or Monte-Carlo simulations (MC) [3] are often mentioned. Those sampling methods are not so often introduced to students in a practical way, because writing and using complete MD or MC codes is time-consuming. A framework similar to electronic DFT, with its computational efficiency, also exists for a system composed of a large number of classical molecules. By large, one means from dozens up to the order of magnitude of the Avogadro number.

In our molecular simulation class, we wanted to illustrate the possibility to compute structural properties of a system by using liquid-state theories. For instance, classical density functional theory (cDFT) [4, 5] is as accurate as MC and MD with computational cost reduced by several orders of magnitude.

This is also a good opportunity to mention the problem of computational costs that often are a limitation for everyday research. The structure of this article is the following: first, we introduce quickly the classical density functional theory. This theoretical part gives rise to a discussion around functionals and their minimizations, which are unfamiliar notions to undergraduate students. Then, we present a 2-hours practical, in silico, exercise in which students investigate a model neon fluid. Students are invited to solve this problem by writing a Mathematica program that applies the previously introduce theoretical framework. This program should minimize the free energy functional both analytically and numerically. Note that a solution program is available in Associated Content. We then discuss the results obtained by the students thanks to the program and compare it to experimental data acquired by neutron scattering [6]. Finally, we point out strengths and weaknesses of the theory and approximations made during the course, before concluding.

I. THEORY

Classical density functional theory (cDFT) is the classical analogue of electronic density functional theory (eDFT) introduced by Kohn (Nobel prize in 1998 [7]) together with his collaborators Hohenberg and Sham [1, 2]. cDFT is a well known theory, for which good reviews can easily be found [8]. We just recall here that it is based on (i) the rewriting of the Hamiltonian of a system of
N electrons in an external field (e.g., exerted by the nucleus), as a unique functional of the electronic density, and (ii) the fact that the electronic density that minimizes the functional is the density of the ground state. It has been proved \[3,5\] that this result is still true for classical systems: the minimization of the free energy \( \mathcal{F} \), which is a unique functional of the classical solvent density \( \rho(r) \), with respect to this density, gives access to the equilibrium density \( \rho_{eq}(r) \). This equilibrium density (which is a number of molecules per volume unit) must be understood as the average quantity of solvent molecule at each position \( r \) in the presence of an external perturbation, e.g., a solid surface or a dissolved molecule. Students are asked to think about the fact that \( \mathcal{F} \) is a function of \( \rho \) that is a function of the position \( r \). \( \mathcal{F} \) is thus called a functional and shall be written \( \mathcal{F} [\rho(r)] \). Rigorously \[9\], the free energy functional can be decomposed, as in Eq. [1]. In this equation, students are shown that the scalars \( \mathcal{F}_{\text{id}}[\rho(r)] \) and \( \mathcal{F}_{\text{ext}}[\rho(r)] \) depend of all the values taken by \( \rho \) at all positions \( r \).

\[
\mathcal{F}[\rho(r)] = \mathcal{F}_{\text{id}}[\rho(r)] + \mathcal{F}_{\text{exc}}[\rho(r)] + \mathcal{F}_{\text{ext}}[\rho(r)] - \mu \int \rho(r) \, dr,
\]

with

\[
\mathcal{F}_{\text{id}}[\rho(r)] = k_B T \int \rho(r) \left( \ln \left( \Lambda^3 \rho(r) \right) - 1 \right) dr,
\]

\[
\mathcal{F}_{\text{ext}}[\rho(r)] = \int v_{\text{ext}}(r) \rho(r) \, dr,
\]

where \( \mu \) is the chemical potential, \( k_B \) is the Boltzmann constant, \( T \) the temperature in Kelvin, \( \Lambda = \sqrt{\frac{\hbar^2}{2\pi m}} \) is the thermal wavelength, \( \hbar \) is the Planck constant (6.62606957 \times 10^{-34} \text{ J.s}) and \( m \) is the mass of the solvent molecule. \( \mathcal{F}_{\text{id}}[\rho(r)] \) is the ideal term of a non interacting fluid. It is purely entropic and its expression, given in Eq. [2], is exact. Students are asked to think about the potential relation between the information entropy as expressed by Shannon and this ideal term, since they look very similar. \( \mathcal{F}_{\text{exc}}[\rho(r)] \) is the term due to an external potential, \( v_{\text{ext}} \). It represents the effect of any perturbation on the solvent. It can be, for instance, any interaction of the solvent with a molecular solute, an interface... \( \mathcal{F}_{\text{ext}}[\rho(r)] \) is the excess term, due to solvent-solvent interactions. Exact expression for this term is in the general case still unknown. Finding the best approximation for it, especially for water, is one intense field of research which goes far beyond this introduction \[10\]. Note that this excess term is the equivalent of the Hartree plus exchange correlation term in electronic DFT in the sense that it requires some approximations. In our first approach of cDFT, we will neglect it. Interested students may refer to [9] for a review of the various approaches of this term.

With an approximation for this excess term and given an external potential, it is possible to minimize the functional which means to find the value of the solvent density \( \rho(r) \) in all the points of the space such as \( \mathcal{F} \) is minimum. Once this minimization has been done, the equilibrium density, and thus all the structural properties are known.

In order to get used to this functional approach, students are now asked to minimize both numerically and analytically the simplest form for \( \mathcal{F} \), i.e., to find the solvent density \( \rho(r) \) for all \( r \) that minimizes the free energy functional. They will then be able to deduce the structural properties of a fluid close to liquid neon \[9\].

II. STUDENT EXERCISE AND COMPUTATIONAL METHOD

To illustrate the use of cDFT we proposed to students to write a Mathematica program \[11\]. This 2 hours practical course has been planned for a class of a dozen of undergraduate students. It requires one computer per student with Wolfram Mathematica version 9 or superior. This software has been chosen because of (i) its symbolic possibilities, and (ii) its functional programming paradigm that allows students not to focus on programming but on algorithms.

In order to limit this practical course to 2 hours, the minimization will be carried in one dimension, reducing the computational and programming efforts. Interested students are proposed to extend their code to three-dimensional cases. The spatial coordinates \( r \), are thus discretized on an regular grid: \( \{r_i\} \).

We would like to treat a case that makes the students able to compare the analytical and numerical minimizations. For this purpose we omit, in the following the problematic excess term of Eq. [1], as discussed in the previous section. Neglecting this excess term decreases the computational cost of the numerical minimization of the functional by one order of magnitude. Indeed the ideal and the external term require a simple integration over the spacial coordinates \( r \), as can be seen in Eqs. [2] and [3]. The computational cost of such integration scales as \( O(N) \), where \( N \) is the number of grid nodes used to discretize space. The excess term would have required, at least, a double integration on space, and consequently scales at best as \( O(N^2) \). Furthermore, the excess term makes the analytical functional minimization much more complex, if not impossible, for undergraduate students. Nevertheless, this approximation is a good opportunity to discuss numerical and practical problems, if they are kept clearly informed by their supervisor that there are no more correlations in between the molecules of the solvent, that can now be considered as an ideal fluid.

First, the students are requested to find analytically the expression of the functional derivative of the free energy, that reads:

\[
\frac{\delta \mathcal{F}[\rho(r)]}{\delta \rho(r)} = \beta^{-1} \ln \left( \Lambda^3 \rho(r) \right) + v_{\text{ext}}(r) - \mu,
\]

where \( \beta = (k_B T)^{-1} \). Some time must be dedicated to
explain functional derivation, as this step is often difficult for students. Because DFT is a variational principle, we are looking for the functional root of this equation, that is:

$$\rho_{eq}(r) = \frac{\exp(\beta \mu)}{\Lambda^3} \exp(-\beta v_{ext}(r)),$$

(5)

where the chemical potential, $\mu$, is chosen so that $\exp(\beta \mu) / \Lambda^3 = \rho_b$, the homogeneous, bulk solvent density. We see that without external perturbation, the solvent is homogeneous, i.e., the equilibrium density is a constant, equal to $\rho_b$. On the contrary, where the perturbation is very repulsive ($v_{ext} \gg \beta^{-1}$), the equilibrium density is zero.

In order to illustrate the powerful variational principle of all DFTs and to be able to extend this course to more complex cases, students are requested to minimize directly the free energy $F$ numerically. For this purpose, they are asked to discretize Eqs. 2-3:

$$F_{id}[\rho\{r_i\}] = k_B T \sum_i \Delta_i \rho(r_i) \left[ \ln (\Lambda^3 \rho(r_i)) - 1 \right],$$

(6)

$$F_{ext}[\rho\{r_i\}] = \sum_i \Delta_i \rho(r_i) v_{ext}(r_i),$$

(7)

where $\Delta_i$ is the element of integration. It is for instance the distance between two radial nodes in one dimension. Then, Eqs. 6-7 must be implemented into the Mathematica program. An example is given in Associated Content.

To minimize the functional, they need to chose a starting point for the density at all nodes: naively, students often propose the homogeneous solvent density $\rho_b$, which is often good enough a guess. Then, they obtain and plot the equilibrium density profile corresponding to different external potentials: an hard wall, a gaussian repulsive field...

In order to compare with a physical system, we propose to focus on liquid neon, of bulk density $\rho_b = 0.033$ molecules/Å$^3$ at 35.05 K. Such a system was studied by neutron scattering by de Graaf and Mozer. They reported the radial distribution function (rdf) of liquid neon, which is the probability to find a Ne atom at distance $r$ of another Ne, normalized by the bulk density $\rho_b$. Rdf is related to the density at a distance $r$ of a reference solvent molecule by

$$g(r) = \frac{\rho(r)}{\rho_b},$$

(8)

where $r$ is the distance between the two Ne atoms. As we decided not to include any excess term, there are no Ne-Ne interactions. All the interactions are put into the external term. We use the most common and widely-employed interatomic potential for Van der Waals interactions, the Lennard-Jones potential:

$$v_{ext}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^12 - \left( \frac{\sigma}{r} \right)^6 \right],$$

(9)

with parameters given in Table 1. Students have previously been taught about this potential.

### III. RESULTS AND DISCUSSION

Numerical minimization of the free energy $F$, for a model neon, results in the equilibrium solvent density, from which we compute the rdf with Eq. 8. It is plotted in full black line in figure 1. In this same figure, it is compared to the rdf obtained analytically from Eq. 9.

It can be noticed that the radial distribution profiles obtained by analytical and numerical minimizations are identical. Students can be convinced that numerical methods can reproduce exact results predicted by theory. This justifies the use of numerical methods when problems can not be solved analytically.

We now compare theoretical predictions to the experimental rdf for liquid neon, extracted from Ref. 3, that is also plotted in Fig. 1. The simple model studied here is able to reproduce the good position for the first peak in the rdf. This peak corresponds to the position of the molecules of the so-called first solvation shell. However there is no presence of further extrema in the

| $\epsilon$ (kJ/mol) | $\sigma$ (Å) |
|---------------------|-------------|
| 1.6                 | 2.6         |

Table 1: Lennard-Jones parameters for the external potential, $v_{ext}$, of Eq. 9.
calculated cDFT results. This is expected because the model does not contain any interactions between the solvent molecules. The second peak should be understood as a response to the presence of the first peak. Indeed, molecules in the first shell also have a first solvation shell, and thus induce a second peak (for second nearest neighbors), in the rdf we are looking at. This is thus solvent induced and cannot be recovered by our (ideal) approximation of the excess (solvent-solvent) term. This means that a model as simple as an ideal fluid perturbed by a Lennard-Jones solute is sufficient to model the first solvation shell of a neon fluid.

Students are also asked to evaluate the number of Ne neighbors in the first solvation shell of a given Ne. This can be done by integrating the radial distribution function from 0 to the end of the experimental first peak and multiply by $4\pi\rho B$. The $4\pi$ term is due to the threedimensional nature of the solvation shell. Both experimental and cDFT rdf lead to a number of molecules that is close to 12, which corresponds to a compact packing between neon atoms.

At this point, we emphasis to students that the extraction of particular physical data can be easier with some computational techniques than with others. For instance, the generation of density maps such as in Fig. 2 is completely straightforward from cDFT as it is a direct output of the theory. It can be interesting to discuss with them how they would compute the same quantities with a MD or MC simulation.

It is the moment to highlight the simplicity of the model and the crudeness of setting the excess term to zero. More complex systems can be studied with more sophisticated cDFT. For instance, cDFT predictions now require $\approx 1$ min to get a rdf in quantitative agreement with Molecular Dynamics or Monte Carlo simulations, that require $\approx 10$ CPU-hours [12].

**IV. CONCLUSIONS**

We have proposed to our undergraduate students an introductory course to classical density functional theory to illustrate that liquid state theories are an alternative to the much more time-consuming but widely used Molecular Dynamics and Monte Carlo simulations. In order to illustrate how a cDFT code works, we proposed a practical course to study a simple system: liquid neon modeled by an ideal fluid.

This practical course consisted in writing a Mathematica program that minimizes a functional both numerically and analytically. This little program, given in Associated Content, can be written in 2 hours. With a simple model and their own code, students are able to reproduce the main feature of the radial distribution function of liquid neon, i.e., the position and height of the first solvation shell.

![Figure 2: On top, the density map predicted by cDFT for Ne in the approximation described in the text. At bottom, the density map reconstructed from the experimental radial distribution function. A single neon atom is at coordinates $(x, y) = (0, 0)$.](image)

Even if this is a small program written to treat a simple physical problem, it permits to introduce the problematic of numerical minimization and more generally to mention some computational aspects (scaling of a method, approximations, agreement with exact theoretical predictions and experimental data ...). This practical activity has helped our students to make a first contact with computational chemistry and actual theoretical research.

[1] Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas, *Phys. Rev.* 1964, B864-B871
[2] Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys Rev.* 1965, 140, A1133–A1138
[3] Frenkel, D.; Smit, B. *Understanding Molecular Simula-
[4] Evans, R. The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids, *Adv. Phys.* **1979**, *28*, 143-200

[5] Mermin, N. Thermal Properties of the Inhomogeneous Electron Gas, *Phys. Rev.* **1965**, *137*, A1441–A1443

[6] de Graaf, L. A.; Mozer, B. Structure Study of Liquid Neon by Neutron Diffraction, *J. Chem. Phys.* **1971**, *55*, 4967

[7] www.nobelprize.org/nobel_prizes/chemistry/laureates/1998

[8] Parr, R. G. Density Functional Theory, *Annu. Rev. Phys. Chem.* **1983**, *34*, 631–656

[9] Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*. Academic Press, 2013

[10] Jeanmairet, G.; Levesque, M.; Vuilleumier, R.; Borgis, D. Molecular Density Functional Theory of Water, *J. Phys. Chem. Lett.* **2013**, *4*, 619–624

[11] Wolfram Research, Inc., *Mathematica*, Version 9.0, Champaign, IL (2012).

[12] Levesque, M.; Marry, V.; Rotenberg, B.; Jeanmairet, G.; Vuilleumier, R.; Borgis, D. Solvation of complex surfaces via molecular density functional theory, *J. Chem. Phys.* **2012**, *137*, 224107