Functional Counterpart of Lagrangian Theorem and Perturbative Density Functional Theory: a Forgotten Idea *

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In this Letter, we truncate the functional expansion of the non-uniform first-order direct correlation function (DCF) around the bulk density at the lowest order. But the truncation is performed formally and exactly by making use of functional counterpart of the Lagrangian theorem of differential calculus. Consequently the expansion coefficient, i.e. the uniform second-order DCF, is replaced by its non-uniform counterpart whose density argument is an appropriate mixture of calculated density distribution and the bulk density with a mixing parameter determined by a hard-wall sum rule. The non-uniform second-order DCF is then approximated by the uniform second-order DCF with an appropriate weighted density as its density argument. The present formally exact truncated functional expansion predicts the density distribution in good agreement with simulation data for hard sphere and Lennard–Jones fluid exerted by an external field.

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Density functional theory (DFT) of non-uniform systems was pioneered by the work of van der Waals on interfaces.[1] It was further motivated by the work of Hohenberg and Kohn[2] for the ground state of quantum systems and it was generalized to finite temperatures by Mermin.[3] Over the past several decades, in the field of classical statistical thermodynamics, we have witnessed great progresses made in DFT. Its status as a powerful theoretical tool has been established for the study of non-uniform systems, such as freezing, adsorption, wetting transition, capillary condensation and filtration, etc.[4] According to different types of approximation used, DFT has evolved into four different versions: including functional perturbative expansion approximation (FPEA),[5] weighted density approximation (WDA),[6] fundamental measure theory (FMT),[7] and our previous DFT that is based on the universality principle of the free energy density functional and test particle trick. Our DFT can be divided into two types: one[8] concerns the bridge functional concept, the other[9] concerns the incorporation of bulk fluid radial distribution function into the density functional. In this Letter, we concentrate on the FPEA, but we do not strive to make approximations for the higher-order direct correlation functions (DCFs) and we include more terms. We truncate the functional expansion series at the lowest order, i.e. the first order, but the truncation is made formally and exactly by applying the Lagrangian theorem of differential calculus to the functional expansion. The validity of the new truncation is tested by applying it to calculate the density profile of the hard-sphere fluid and Lennard–Jones (LJ) fluid exerted by several external potentials.

To calculate the density profile of inhomogeneous fluids, it is convenient to carry out the functional expansion at the level of the first-order DCF, although it is also possible to proceed at the level of free energy.

A formal Taylor expansion of the non-uniform first-order DCF $C^{(1)}(\boldsymbol{r};[\rho])$ around the uniform system of bulk density ρ_b can always be written as

$$\begin{aligned} C^{(1)}(\boldsymbol{r};[\rho]) &= C_0^{(1)}(\rho_b) + \int \mathrm{d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_b)C_0^{(2)}(|\boldsymbol{r}-\boldsymbol{r}_1|;\rho_b) \\ &\quad + \sum_{n=3}^{\infty}\frac{1}{(n-1)!}\int \mathrm{d}\boldsymbol{r}_1\int \mathrm{d}\boldsymbol{r}_2\cdots\int \mathrm{d}\boldsymbol{r}_{n-1}\prod_{m=1}^{n-1} \\ &\quad \cdot[\rho(\boldsymbol{r}_m)-\rho_b]C_0^{(n)}(\boldsymbol{r},\boldsymbol{r}_1,\cdots,\boldsymbol{r}_{n-1};\rho_b), \end{aligned} \tag{1}$$

where each functional derivative, i.e. the expansion coefficient $C_0^{(n)}(\boldsymbol{r},\boldsymbol{r}_1,\cdots,\boldsymbol{r}_{n-1};\rho_b)$, $n\geq 2$, is evaluated at the initial density ρ_b. We do not strive to approximate the expansion coefficients of the higher orders, as done in the previous literature. Instead, we truncate the series at the first order. To make the truncation an accurate representation, one can evaluate the last functional derivative not at the initial ρ_b but at some $\rho_b+\lambda(\rho-\rho_b)$, with λ between 0 and 1.[10] The procedure is the functional counterpart of the Lagrangian theorem of the differential calculus, which has not yet been employed in the studies of DFT in spite of a well-known fact.

According to the above procedure, Eq. (1) reduces to

$$\begin{aligned} C^{(1)}(\boldsymbol{r};[\rho]) = & C_0^{(1)}(\rho_b) + \int \mathrm{d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1)-\rho_b) \\ & \times C^2(\boldsymbol{r},\boldsymbol{r}_1;[\rho_b+\lambda(\rho-\rho_b)]). \end{aligned} \tag{2}$$

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In the above equations, subscript 0 represents the uniform case, and its removal corresponds to the non-uniform case. It should be noted that the expansion coefficient $C_0^{(2)}$ has been replaced by $C^{(2)}$ in Eq. (2) because of the substitution of the bulk density ρ_b by the non-uniform density distribution $\rho_b + \lambda(\rho - \rho_b)$.

In the formalism of DFT, the density profile equation of non-uniform single component fluid reads

$$\rho(\boldsymbol{r}) = \rho_b \exp\{-\beta\varphi_{\rm ext}(\boldsymbol{r}) + C^{(1)}(\boldsymbol{r};[\rho]) - C_0^{(1)}(\rho_b)\}, \quad (3)$$

where $\varphi_{\rm ext}(\boldsymbol{r})$ is the external potential responsible for the generation of the density distribution $\rho(\boldsymbol{r})$, and $\beta = 1/kT$ with k being the Boltzmann constant and T being the absolute temperature. Substituting Eq. (2) into Eq. (3) yields

$$\rho(\boldsymbol{r}) = \rho_b \exp\Big\{ - \beta\varphi_{\rm ext}(\boldsymbol{r}) + \int {\rm d}\boldsymbol{r}_1(\rho(\boldsymbol{r}_1) - \rho_b) C^{(2)}(\boldsymbol{r}, \boldsymbol{r}_1; [\rho_b + \lambda(\rho - \rho_b)])\Big\}. \quad (4)$$

The key is to approximate the non-uniform second-order DCF $C^{(2)}(\boldsymbol{r}, \boldsymbol{r}_1; [\rho_b + \lambda(\rho - \rho_b)])$ and to choose the appropriate mixing parameter λ.

From Ref. [11], we can approximate the second-order non-uniform DCF through the second-order uniform DCF with a weighted density as the later density argument. Thus, $C^{(2)}(\boldsymbol{r}, \boldsymbol{r}_1; [\rho_b + \lambda(\rho - \rho_b)])$ can be approximated by its uniform counterpart $C_0^{(2)}(|\boldsymbol{r} - \boldsymbol{r}_1|; \tilde{\rho})$ in which $\tilde{\rho}$ is the so-called weighted density. Because the numerical value of $C^{(2)}(\boldsymbol{r}, \boldsymbol{r}_1; [\rho_b + \lambda(\rho - \rho_b)])$ is related to two points, so it is reasonable to make the weighted density $\tilde{\rho}$ in $C_0^{(2)}(|\boldsymbol{r} - \boldsymbol{r}_1|; \tilde{\rho})$ also related to the two points $\boldsymbol{r}$ and $\boldsymbol{r}_1$. Then the natural procedure is to make $\tilde{\rho}$ be related to the mean value of the two points $\boldsymbol{r}$ and $\boldsymbol{r}_1$, i.e. we make the following approximation

$$C^{(2)}(\boldsymbol{r}, \boldsymbol{r}_1; [\rho_b + \lambda(\rho - \rho_b)]) = C_0^{(2)}(|\boldsymbol{r} - \boldsymbol{r}_1|; \tilde{\rho}((\boldsymbol{r} + \boldsymbol{r}_1)/2)). \quad (5)$$

The specification of $\tilde{\rho}$ can be made by following and extending the spirit of the simple weighted density approximation (SWDA)[12] for the non-uniform first-order DCF which employs the normalized uniform second-order DCF as the weighting function for the calculation of the weighted density to its second-order counterpart, i.e. $\tilde{\rho}$ is defined by

$$\tilde{\rho}(\boldsymbol{r}) = \int {\rm d}\boldsymbol{r}'(\lambda(\rho(\boldsymbol{r}') - \rho_b) + \rho_b) w(|\boldsymbol{r} - \boldsymbol{r}'|; \rho_b) \quad (6)$$

with $w(|\boldsymbol{r} - \boldsymbol{r}'|; \rho_b)$ defined by

$$w(|\boldsymbol{r} - \boldsymbol{r}'|; \rho_b) = C_0^{(2)}(|\boldsymbol{r} - \boldsymbol{r}'|; \rho_b)/C_0^{(1)'}(\rho_b). \quad (7)$$

Here $C_0^{(1)'}(\rho_b)$ is the first-order density derivative of the uniform first-order DCF $C_0^{(1)}(\rho_b)$ which can be obtained by numerical integration

$$C_0^{(1)'}(\rho_b) = \int {\rm d}\boldsymbol{r} C_0^{(2)}(\boldsymbol{r}; \rho_b). \quad (8)$$

In this Letter, we specify the mixing parameter λ by making the theoretical prediction of Eq. (4) satisfy the sum rule which specifies bulk pressure P by hard-wall contact density ρ_w

$$P = \rho_w kT. \quad (9)$$

Here ρ_w can be obtained from $\rho(0.5)$ in Eq. (4) when the external potential has the following form

$$\varphi_{\rm ext}(z) = \infty \quad z/\sigma < 0.5, \qquad = 0 \quad 0.5 < z/\sigma, \quad (10)$$

where σ represents the fluid particle diameter. The specified numerical value of λ is also suitable for other cases of the external potential following the universality of the free energy density functional, which means the independence of the free energy density functional (and its functional derivative, i.e. the non-uniform first-order DCF) on the concrete external potential responsible for the formation of the density distribution profile.[8,9,13]

To test the present formally exact truncation, firstly we apply the present DFT approach to a hard-sphere fluid near a single hard wall and confined in a spherical cavity. For the former case, the external potential is of the form of Eq. (10). For the latter case, it is in the following form

$$\varphi_{\rm ext}(\boldsymbol{r}) = \infty, \quad |\boldsymbol{r}|/\sigma > R, \qquad = 0, \quad |\boldsymbol{r}|/\sigma < R, \quad (11)$$

where R is the spherical cavity radius.

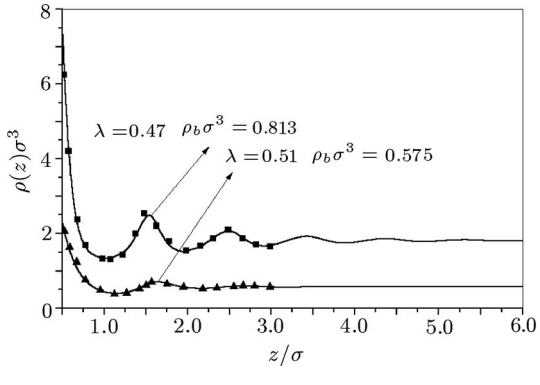


Fig. 1. Density profiles of a hard-sphere fluid near a hard wall for two cases of bulk density. The lines correspond to the predictions of the present method, and the symbols represent the corresponding simulation data.[16] The coordinate for the upper curve should be shifted down by one unit.

The necessary quantities, i.e. the uniform second-order DCF $C_0^{(2)}(r; \rho_b)$, can be obtained from the Percus–Yevick approximation.[14] The employed equation of state for the bulk hard-sphere fluid is from the

Carnahan–Starling empirical approximation.[15] The calculated density distribution is plotted against the corresponding simulation data[16,17] in Figs. 1 and 2 for the two cases of the external potentials. It can clearly be seen that the predictions from the present truncation are in good agreement with the corresponding simulation data and are even more accurate than that of the available most accurate DFTs,[8,9] although we have not plotted the predictions of the DFTs in Refs. [8] and [9] for clarity.

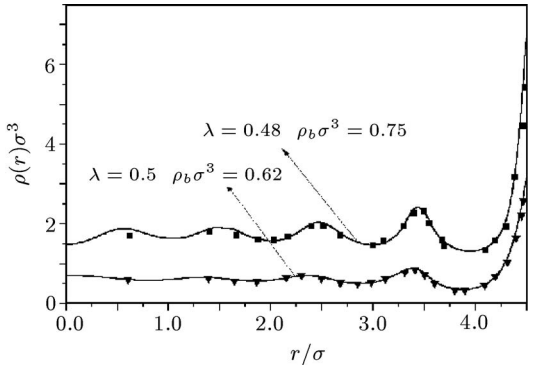


Fig. 2. Density profiles of a hard-sphere fluid confined in a spherical cavity with a hard wall $R = 4.5\sigma$ for two cases of bulk density. The lines correspond to the predictions of the present method, and the symbols represent the corresponding simulation data.[17] The coordinates for the upper curve should be shifted down by one unit.

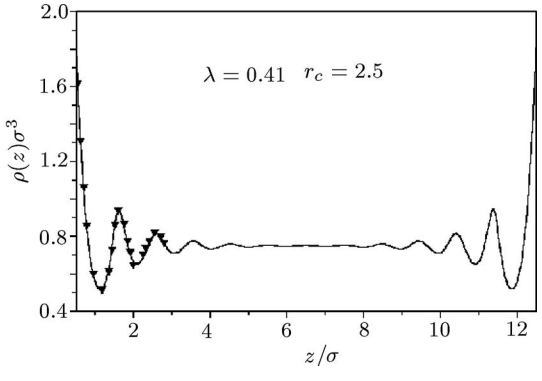


Fig. 3. Density profile of a LJ fluid ($\rho_b\sigma^3 = 0.75, kT/\varepsilon = 1.304$) confined between two hard walls with $H/\sigma = 13$. The line corresponds to the prediction of the DFT, and the triangles represent the corresponding Monte Carlo results.[19] Only half the slit for the simulation data is shown.

To test further the validity of the present formally exact DFT, we apply it to the LJ fluid confined between two hard walls situated at $z = 0$ and $z = H$ respectively. In this case the external potential is given by

$$\beta\varphi_{\rm ext}(z) = \begin{cases} 0 & 0.5\sigma < z < H - 0.5\sigma \\ \infty & \text{otherwise} \end{cases} . \qquad (12)$$

The interaction potential of the LJ fluid model is in the form of

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \qquad (13)$$

where σ and ε characterize the interaction range and strength, respectively.

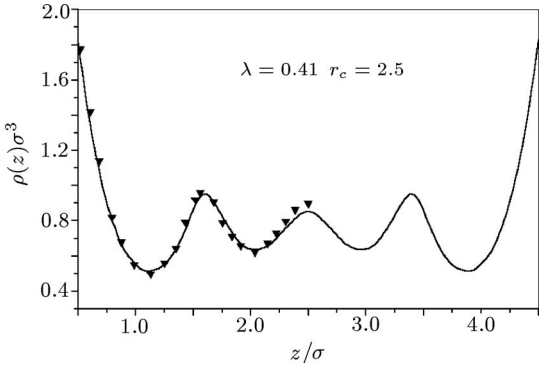


Fig. 4. The same as in Fig. 3, but with $H/\sigma = 5$.

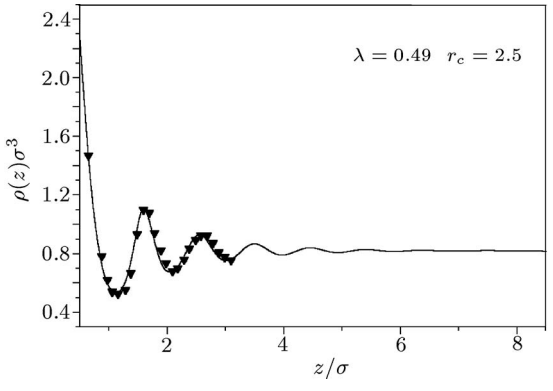


Fig. 5. Density profile of a LJ fluid ($\rho_b\sigma^3 = 0.82, kT/\varepsilon = 1.35$) near a single hard wall. The line corresponds to the prediction of the DFT, and the triangles represent the corresponding Monte Carlo results.[20]

There is no analytical expression for the second-order DCF for the uniform LJ fluid, but we can solve the Ornstein–Zernike (OZ) equation at several state points near the considered bulk state point. Then we tabulate these data prior to the iteration procedure, and employ the interpolation procedure to obtain the required second-order uniform DCF during iteration. Thus, the difficulty without the analytical expression for the second-order uniform DCF can be overcome easily. Here we choose the Malijevsky–Labik bridge function from various existing bridge functions, such as the Percus–Yevick bridge function, the hypernetted-chain bridge function, and the Martynov–Sarkisov bridge function, etc.[18] When the predictions from the Malijevsky–Labik bridge function for the second-order uniform DCF are employed as the input, the present theory supplies the best predictions of the density distribution profile for the calculated non-uniform LJ fluid. The calculated density profile at one state point for different external potential is

plotted in Figs. 3 and 4 with the corresponding simulation data.[19] The figures show the prediction power of the present theory for the non-hard sphere fluid as a whole. Furthermore, we calculate the density distribution profile for the LJ fluid near a single hard wall at another state point. The calculated results and the corresponding simulation data[20] are plotted in Fig. 5. To compare the present theoretical predictions with the corresponding simulation data, we truncate the LJ fluid potential range at $r_c = 2.5\sigma$ for the calculation of Figs. 3–5. In short, Figs. 1–5 indicate that the present truncation can supply very good predictions for the density distribution.

Compared with previous DFTs, the advantages of the present FPEA can be summed up as follows. Firstly, it is conceptually very simple, it is based on a well-known mathematical theorem, and it does not associate with a complicated principle. The universality of its mathematical basis determines the theoretical universality for applications to various interaction potential fluids. Secondly, the required input parameters of the present theory, the second-order uniform DCF and the equation of state can be obtained from the highly mature integral equation theory (IET) of fluid state physics. In particular, the widely used thermodynamically self-consistent IET can produce reliable second-order uniform DCF and the pressure. Thus, the input parameters of the present DFT can be obtained self-consistently by a single self-consistent IET. Thirdly, the present DFT is also computationally very simple. Compared to the WDA, the present theory employs the SWDA to approximate the non-uniform second-order DCF, but achieves higher accuracy than that of the complicated WDA[6] which is more accurate than the SWDA but inferior to the available most accurate DFTs[8,9] in accuracy. Therefore, the present DFT keeps the computational simplicity of the SWDA but achieves even higher accuracy than the available most accurate DFTs[8,9]. The underlying spirit of the present theory can, if it is carried out at the level of the free energy, directly predict the excess Helmholtz free energy of the non-uniform systems, which is crucial in the construction of the phase diagram. We will report the related numerical results elsewhere. It is well known that the perturbation expansion is a basic tool to solve theoretical physics problems. From the point of view of mathematics, the Lagrangian theorem can be applied to any Taylor expansion, so the methodology explored here can be extended to various problems concerning any Taylor expansion in theoretical physics.

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