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An Entropic Approach to Classical Density Functional Theory †

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Abstract: The classical Density Functional Theory (DFT) is introduced as an application of entropic inference for inhomogeneous fluids in thermal equilibrium. It is shown that entropic inference reproduces the variational principle of DFT when information about the expected density of particles is imposed. This process introduces a family of trial density-parametrized probability distributions and, consequently, a trial entropy from which the preferred one is found using the method of Maximum Entropy (MaxEnt). As an application, the DFT model for slowly varying density is provided, and its approximation scheme is discussed.

Keywords: entropic inference; relative entropy; density functional theory; contact geometry; optimal approximations

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1. Introduction

The Density Functional Theory was first developed in the context of quantum mechanics and only later extended to the classical regime. The theory was first introduced by Kohn and Hohenberg (1964) [1] as a computational tool to calculate the spatial density of an electron gas in the presence of an external potential at zero temperature. Soon afterwards, Mermin provided the extension to finite temperatures [2]. Ebner, Saam, and Stroud (1976) [3] applied the idea to simple classical fluids, and Evans (1979) provided a systematic formulation in his classic paper [4]: "The nature of the liquid–vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids".

The majority of physicists and chemists today are aware of the quantum DFT and the Kohn–Sham model [5], while fewer are familiar with the classical DFT; a historical review of quantum DFT and its vast variety of applications is found in [6,7]. The classical DFT, similarly, is a "formalism designed to tackle the statistical mechanics of inhomogeneous fluids" [8], which has been used to investigate a wide variety of equilibrium phenomena, including surface tension, adsorption, wetting, fluids in porous materials, and the chemical physics of solvation.

Just as the Thomas–Fermi–Dirac theory is usually regarded as a precursor of quantum DFT, van der Waals' thermodynamic theory of capillarity under the hypothesis of a continuous variation of density [9] can be regarded as the earliest work on classical DFT without a fundamental proof of existence for such a variational principle.

"The long-term legacy of DFT depends largely on the continued value of the DFT computer programs that practitioners use daily" [6]. The algorithms behind the computer programs, all starting from an original Hartree–Fock method to solve the N-particle Schrödinger equation, have evolved with many approximations and extensions implemented over time by a series of individuals; although the algorithms produce accurate results, they do not mention the HK variational principle. Without the variational principle, the computer codes are suspected of being ad hoc or intuitively motivated without a solid theoretical foundation; therefore, the DFT variational principle not only scientifically justifies the DFT algorithms, but it also provides us with a basis to understand the repeatedly modified algorithms behind the codes.

In this work, we derive the classical DFT as an application of the method of maximum entropy [10–14]. This integrates the classical DFT with other formalisms of classical statistical mechanics (canonical, grand canonical, etc.) as an application of information theory. Our approach not only enables one to understand the theory from the Bayesian point of view, but also provides a framework to construct equilibrium theories on the foundation of MaxEnt. We emphasize that our goal is not derive an alternative to DFT. Our goal is purely conceptual. We wish to find a new justification or derivation of DFT that makes it explicit how DFT fits within the MaxEnt approach to statistical mechanics. The advantage of such an understanding is the potential for future applications that are outside the reach of the current version of DFT.

In Section 2, we briefly review entropic inference as an inference tool that updates probabilities as degrees of rational belief in response to new information. Then, we show that any entropy maximization produces a contact structure that is invariant under the Legendre Transformations; this enables us to take advantage of these transformations for maximized entropy functions (functionals here) found from constraints other than those of thermal equilibrium, as well as thermodynamic potentials.

In Section 3, we briefly review the method of relative entropy for optimal approximation of probabilities, which allows us to derive and then generalize the Bogolyubov variational principle. Then, we apply it for the special case wherein the trial family of probabilities are parametrized by the density function $n(x)$.

In Section 4, the Density Functional formalism is introduced as an extension of the existing ensemble formalisms of statistical mechanics (canonical, grand canonical, etc.), and we show that the core DFT theorem is an immediate consequence of MaxEnt; we prove that in the presence of an external potential $v(x)$, there exists a trial density functional entropy $S_v(E;n]$ maximized at the equilibrium density. We also prove that this entropy maximization is equivalent to minimization of a density functional potential $\Omega(\beta;n]$ given by

$$\Omega_v(\beta;n] = \int d^3x v(x) n(x) + F(\beta;n] \tag{1}$$

where $F(\beta;n]$ is independent of $v(x)$. This formulation achieves two objectives. (**i**) It shows that the density functional variational principle is an application of MaxEnt for non-uniform fluids at equilibrium, and therefore, varying the density $n(x)$ in $S_v(E;n]$ **does not** imply that the functional represents entropy of any non-equilibrium system. This trial entropy, although very useful, is just a mathematical construct that allows us to incorporate constraints that are related to one another by definition. (**ii**) By this approach, we show that the Bayesian interpretation of probability liberates the fundamental theorem of the DFT from an imaginary grand-canonical ensemble, i.e., the thermodynamic chemical potential is appropriately defined without the need to define microstates for varying numbers of particles.

Finally, in Section 5, as an illustration, we discuss the already well-known example of a slowly varying inhomogeneous fluid. We show that our entropic DFT allows us to reproduce the gradient approximation results derived by Evans [4]. There are two different approximations involved: (**i**) rewriting the non-uniform direct correlation function in terms of the uniform one and (**ii**) the use of linear response theory to evaluate the Fourier transform of direct correlation functions. The former assumes that the density is uniform inside each volume element, and the latter assumes that in of densities for neighboring volume elements is small compared to their average.

2. Entropic Inference

A discussion of the method of maximum entropy as a tool for inference is found in [14]. Given a **prior** Probability Distribution Function (**PDF**) $Q(X)$, we want to find the **posterior** PDF $P(X)$ subject to constraints on expected values of functions of X.

Formally, we need to maximize the relative entropy

$$S_r[P|Q] \equiv -\sum_X (PlogP - PlogQ)\ , \tag{2}$$

under constraints $A_i = \sum_X P(X)\hat{A}_i(X)$ and $1 = \sum_X P(X)$, where A_is are real numbers, $\hat{A}_i$s are real-valued functions on the space of X, and $1 \le i \le m$ for m number of constraints.

The maximization process yields the posterior probability

$$P(X) = Q(X)\frac{1}{Z}e^{-\sum_i \alpha_i \hat{A}_i(X)}\ , \qquad \text{where } Z = \sum_X Q(X)e^{-\sum_i \alpha_i \hat{A}_i(X)}\ , \tag{3}$$

and α_is are Lagrange multipliers associated with A_is.

Consequently, the maximized entropy is

$$S = \sum_i \alpha_i A_i + logZ\ . \tag{4}$$

Now we can show that the above entropy readily produces a contact structure, we can calculate the complete differential of Equation (4) to define the vanishing one-form ω_{cl} as

$$\omega_{cl} \equiv dS - \sum_i \alpha_i dA_i = 0\ . \tag{5}$$

Therefore, any classical entropy maximization with m constraints produces a contact structure $\{\mathbb{T}, \omega_{cl}\}$ in which manifold $\mathbb{T}$ has $2m+1$ coordinates $\{q_0, q_1, \ldots q_m, p_1, \ldots, p_m\}$.

The physically relevant manifold $\mathbb{M}$ is an m-dimensional sub-manifold of $\mathbb{T}$ on which ω_{cl} vanishes; i.e., $\mathbb{M}$ is determined by $1+m$ equations:

$$q_0 \equiv S(\{A_i\})\ , \qquad p_i \equiv \alpha_i = \frac{\partial S}{\partial A_i}\ . \tag{6}$$

The Legendre Transformations, which are defined as

$$q_0 \longrightarrow q_0 - \sum_{j=1}^{l} p_j q_j\ , \tag{7}$$

$$q_i \longrightarrow p_i\ , \quad p_i \longrightarrow -q_i\ , \qquad \text{for } 1 \le i \le l\ ,$$

are coordinate transformations on space $\mathbb{T}$ under which ω_{cl} is conserved. It has been shown [15,16] that the laws of thermodynamics produce a contact structure conforming to the above prescription. Here, we are emphasizing that the contact structure is an immediate consequence of MaxEnt, and therefore, it can be utilized in applications of information theory beyond thermodynamics.

3. MaxEnt and Optimal Approximation of Probabilities

The posterior PDF found from entropic inference is usually too complicated to be used for practical purposes. A common solution is to approximate the posterior PDF with a more tractable family of PDFs $\{p_\theta\}$ [17]. Given the exact probability p_0, the preferred member of tractable family p_{θ^*} is found by maximizing the entropy of p_θ relative to p_0:

$$\left.\frac{\delta S_r[p_\theta|p_0]}{\delta\theta}\right|_{\theta=\theta^*} = 0\ . \tag{8}$$

The density functional formalism is a systematic method in which the family of trial probabilities is parametrized by the density of particles; in Section 4, we shall use the method of maximum entropy to determine the family of trial distributions parametrized by $n(x)$, $p_\theta \equiv p_n$. So, we can rewrite Equation (8) as

$$\frac{\delta}{\delta n(x')}\left[S_r[p_n|p_0] + \alpha_{eq}[N - \int d^3x n(x)]\right]_{n(x)=n_{eq}(x)} = 0\,. \tag{9}$$

We will see that the canonical distribution itself is a member of the trial family; therefore, in this case, the exact solution to Equation (9) is p_0 itself:

$$p_n\Big|_{n(x)=n_{eq}(x)} = p_0\,. \tag{10}$$

4. Density Functional Formalism

An equilibrium formalism of statistical mechanics is a relative entropy maximization process consisting of three crucial elements: (i) One must choose the microstates that describe the system of inference. (ii) The prior is chosen to be uniform. (iii) One must select the constraints that represent the information that is relevant to the problem at hand.

In the density ensemble, microstates of the system are given as positions and momenta of all N particles of the same kind, given the uniform prior probability distribution

$$Q(\{\vec{x}_1,\dots,\vec{x}_N;\vec{p}_1,\dots,\vec{p}_N\}) = constant. \tag{11}$$

Keeping in mind that we are looking for **thermal properties of inhomogeneous fluids**, it is natural to choose the density of particles $n(x)$ as a computational constraint and the expected energy E as a thermodynamic constraint, in which $n(x)$ represents the **inhomogeneity** and E defines the thermal equilibrium.

Note that all constraints (computational, thermal, etc.) in the framework can be incorporated as inferential constraints and can be imposed as prescribed in Section 2.

The density constraint holds for every point in space; therefore, we have $1+1+\mathbb{R}^3$ constraints—one for normalization, one for total energy, and one for density of particles at each point in space; thus, we have to maximize the relative entropy

$$S_r[P|Q] = -\frac{1}{N!}\int d^{3N}xd^{3N}p(PlogP - PlogQ) \equiv -Tr_c(PlogP - PlogQ), \tag{12}$$

subject to constraints

$$1 = \langle 1\rangle, \quad E = \langle \hat{H}_v\rangle, \tag{13a}$$

$$n(x) = \langle \hat{n}_x\rangle \quad \text{where} \int d^3xn(x) = N, \tag{13b}$$

where $\langle . \rangle \equiv \frac{1}{N!}\int(.)Pd^{3N}xd^{3N}p$. The classical Hamiltonian operator $\hat{H}$ and the particle density operator $\hat{n}_x$ are given as

$$\hat{H}_v \equiv \sum_{i=1}^{N} v(x_i) + \hat{K}(p_1,\dots,p_N) + \hat{U}(x_1,\dots,x_N), \tag{14}$$

$$\hat{n}_x \equiv \sum_{i}^{N}\delta(x - x_i). \tag{15}$$

The density $n(x)$ is not an arbitrary function; it is constrained by a fixed total number of particles,

$$\int d^3xn(x) = N. \tag{16}$$

Maximizing (12) subject to (13) gives the posterior probability $P(x_1,\dots,x_N;p_1,\dots,p_N)$ as

$$P=\frac{1}{Z_v}e^{-\beta\hat{H}_v-\int d^3x\alpha(x)\hat{n}_x}\quad\text{under condition}\int d^3xn(x)=N. \tag{17}$$

where $\alpha(x)$ and β are Lagrange multipliers.

The Lagrange multiplier function $\alpha(x)$ is implicitely determined by

$$\frac{\delta logZ_v}{\delta\alpha(x)}=-n(x) \tag{18}$$

and by Equation (16)

$$-\int d^3x\frac{\delta logZ_v}{\delta\alpha(x)}=N\,. \tag{19}$$

Substituting the trial probabilities from (17) into (12) gives the **trial** entropy $S_v(E;n]$ as

$$S_v(E;n]=\beta E+\int d^3x\alpha(x)n(x)+logZ_v, \tag{20}$$

where $Z_v(\beta;\alpha]$ is the **trial** partition function defined as

$$Z_v(\beta;\alpha]=Tr_c e^{-\beta\hat{H}_v-\int d^3x\alpha(x)\hat{n}_x}\,. \tag{21}$$

The equilibrium density $n_{eq}(x)$ is that which maximizes $S_v(E;n]$ subject to $\int d^3xn(x)=N$:

$$\frac{\delta}{\delta n(x')}\left[S_v(E;n]+\alpha_{eq}[N-\int d^3xn(x)]\right]=0\quad\textit{for fixed }E. \tag{22}$$

Next, perform a Legendre transformation and define the Massieu functional $\tilde{S}_v(\beta,n]$ as

$$\tilde{S}_v\equiv S_v-\beta E, \tag{23}$$

so that we can rewrite Equation (22) as

$$\frac{\delta}{\delta n(x')}\left[\tilde{S}_v(\beta;n]-\alpha_{eq}\int d^3xn(x)\right]=0\quad\textit{for fixed }\beta\,. \tag{24}$$

Combine (20), (23), and (24) and use the variational derivative identity $\frac{\delta n(x)}{\delta n(x')}=\delta(x-x')$ to find

$$\int d^3x\left[\frac{\delta logZ_v(\beta;\alpha]}{\delta\alpha(x)}+n(x)\right]\frac{\delta\alpha(x)}{\delta n(x')}=\alpha_{eq}-\alpha(x'). \tag{25}$$

The LHS of equation (25) vanishes by (16), and therefore, the RHS must vanish for an arbitrary $n(x)$, which implies that

$$\alpha(x)=\alpha_{eq}\,,\quad\text{and}\quad\frac{\delta logZ_v}{\delta\alpha(x)}\bigg|_{\alpha_{eq}}=-n_{eq}(x)\,. \tag{26}$$

Substituting (26) into (17) yields the equilibrium probability distribution

$$P^*(x_1,\dots,x_N;p_1,\dots,p_N)=\frac{1}{Z_v^*}e^{-\beta\hat{H}_v-\alpha_{eq}\int d^3x\hat{n}_x}=\frac{1}{Z_v^*}e^{-\beta\hat{H}_v-\alpha_{eq}N} \tag{27}$$

where $Z_v^*(\beta,\alpha_{eq})=Tr_c e^{-\beta\hat{H}_v-\alpha_{eq}N}$.

From the inferential point of view, **the variational principle for the grand potential and the equilibrium density** [4] is proved at this point; we showed that for an arbitrary classical Hamiltonian $\hat{H}_v$, there exists a trial entropy $S_v(E;n(x)]$ defined by Equation (20), which assumes its maximum at fixed energy and varying $n(x)$ under the condition $\int d^3xn(x) = N$ at the equilibrium density and gives the posterior PDF (Equation (27)) equal to that of the canonical distribution.

The massieu function $\tilde{S}_v(\beta; n(x)]$ from Equation (23) defines the **density functional potential** $\Omega_v(\beta; n(x)]$ by

$$\Omega_v(\beta; n] \equiv \frac{-\tilde{S}_v(\beta; n]}{\beta} = -\int d^3x \frac{\alpha(x)}{\beta} n(x) - \frac{1}{\beta} log Z_v(\beta; \alpha] \,, \tag{28}$$

so that the maximization of $S_v(E; n]$ (20) in the vicinity of the equilibrium is equivalent to the minimization of $\Omega_v(\beta; n(x)]$ (28) around the same equilibrium point

$$\frac{\delta}{\delta n(x')} \left[\Omega_v(\beta; n] + \frac{\alpha_{eq}}{\beta} \int d^3xn(x) \right] = 0 \,. \tag{29}$$

After we find Ω_v, we just need to recall that $\alpha(x) = -\beta \frac{\delta \Omega_v}{\delta n(x)}$ and substitute in Equation (26) to recover the "core integro-differential equation" [4] of the DFT as

$$\nabla \left(\frac{\delta \Omega(\beta; n]}{\delta n(x)} \right)_{eq} = 0 \tag{30}$$

which implies that

$$\Omega_{v;eq} \leq \Omega_v(\beta; n], \tag{31}$$

where

$$\Omega_{v,eq}(\beta; n] = -\frac{\alpha_{eq}}{\beta} \int d^3xn(x) - \frac{1}{\beta} log Z^*_v(\beta, \alpha_{eq}). \tag{32}$$

From Equation (28), it is clear that

$$\Omega_v(\beta; n] = \int d^3xv(x)n(x) + \langle \hat{K} + \hat{U} \rangle - \frac{S_v(E; n]}{\beta} \,. \tag{33}$$

It is convenient to define the **intrinsic density functional potential** F_v as

$$F_v(\beta; n] \equiv \langle \hat{K} + \hat{U} \rangle - \frac{S_v}{\beta} \tag{34}$$

to have

$$\Omega_v(\beta; n] = \int v(x)n(x) + F_v(\beta; n] \,. \tag{35}$$

Now we are ready to restate the fundamental theorem of the classical DFT:

Theorem 1. *The intrinsic functional potential F_v is a functional of density $n(x)$ and is independent of the external potential:*

$$\frac{\delta F_v(\beta; n]}{\delta v(x')} = 0 \quad \textit{for fixed } \beta \textit{ and } n(x). \tag{36}$$

Proof. The crucial observation behind the DFT formalism is that P and Z_v depend on the external potential $v(x)$ and the Lagrange multipliers $\alpha(x)$ only through the particular combination $\bar{\alpha}(x) \equiv \beta v(x) + \alpha(x)$. Substitute Equation (20) into (34) to get

$$\beta F_v(\beta; n] = log Z(\beta; \bar{\alpha}] + \int d^3x \bar{\alpha}(x) n(x), \tag{37}$$

where $Z(\beta;\bar{\alpha}] = Z_v(\beta;\alpha] = Tr_c e^{-\beta(\hat{K}+\hat{U})-\int d^3x\bar{\alpha}(x)\hat{n}_x}$. The functional derivative of βF_v at fixed $n(x)$ and β is

$$\frac{\delta(\beta F_v(\beta;n])}{\delta v(x')}\Big|_{\beta,n(x)} = \int d^3x'' \frac{\delta}{\delta\bar{\alpha}(x'')}\left[logZ(\beta;\bar{\alpha}] + \int d^3x\bar{\alpha}(x)n(x)\right]\frac{\delta\bar{\alpha}(x'')}{\delta v(x')}\Big|_{\beta,n(x)} . \tag{38}$$

Since $n(x') = -\frac{\delta logZ(\beta;\bar{\alpha}]}{\delta\bar{\alpha}(x')}$, keeping $n(x)$ fixed is achieved by keeping $\bar{\alpha}(x)$ fixed:

$$\frac{\delta\bar{\alpha}(x'')}{\delta v(x')}\Big|_{\beta,n(x)} = \frac{\delta\bar{\alpha}(x'')}{\delta v(x')}\Big|_{\beta,\bar{\alpha}(x)} = 0\,, \tag{39}$$

so that

$$\frac{\delta F_v(\beta,n]}{\delta v(x')}\Big|_{\beta,n(x)} = 0\,, \tag{40}$$

which concludes the proof; thus, we can write down the intrinsic potential as

$$F(\beta,n(x)] = F_v(\beta,n(x)]\,. \tag{41}$$

□

Remark 1. *Note that since a change in the external potential $v(x)$ can be compensated by a suitable change in the multiplier $\alpha(x)$ in such a way as to keep $\bar{\alpha}(x)$ fixed, such changes in $v(x)$ will have no effect on $n(x)$. Therefore, keeping $n(x)$ fixed on the left-hand side of (37) means that $\bar{\alpha}(x)$ on the right side is fixed too.*

Now, we can substitute Equation (35) into (29) and define the chemical potential

$$\mu \equiv \frac{-\alpha_{eq}}{\beta}\,, \tag{42}$$

to have

$$\frac{\delta}{\delta n(x')}\left[\int d^3x v(x)n(x) + F(\beta;n] - \mu\int d^3x n(x)\right]_{n(x)=n_{eq}(x)} = 0\,. \tag{43}$$

We can also substitute (35) into (30) to find

$$v(x) + \frac{\delta F}{\delta n(x)}\Big|_{eq} = \mu, \tag{44}$$

which allows us to define and **interpret** $\mu_{in}(x;n] \equiv \frac{\delta F}{\delta n(x)}$ as the **intrinsic chemical potential** of the system. To proceed further, we also split F into that of ideal gas plus the interaction part as

$$F(\beta;n] = F_{id}(\beta;n] - \phi(\beta;n]. \tag{45}$$

Differentiating with $\frac{\delta}{\delta n(x)}$ gives

$$\beta\mu_{in}(x;n] = log(\lambda^3 n(x)) - c(x;n]\,, \tag{46}$$

where, for a monatomic gas, $\lambda = \left(\frac{2\pi\hbar^2}{m}\right)^{1/2}$. The additional one-body potential $c(x;n] = \frac{\delta\phi}{\delta n(x)}$ is related to the Ornstein–Zernike direct correlation function of non-uniform fluid [18–20] by

$$c^{(2)}(x,x';n] \equiv \frac{\delta c(x;n]}{\delta n(x')} = \frac{\delta^2\phi(\beta;n]}{\delta n(x)\delta n(x')}\,. \tag{47}$$

5. Slowly Varying Density and Gradient Expansion

We have proved that the solution to Equation (43) is the equilibrium density. However, the functional $F(\beta; n]$ needs to be approximated because the direct calculation of F involves calculating the canonical partition function, the task that we have been avoiding to begin with. Therefore, different models of the DFT may vary in their approach to guessing $F(\beta; n]$. Now assume that we are interested in a monatomic fluid with a slowly varying external potential. In our language, it means that we use the approximation $\int d^3x \equiv \sum (\Delta x)^3$, where Δx is much longer than the density correlation length, and the change in density in each volume element is small compared to the average density. This allows us to interpret each volume element $(\Delta x)^3$ as a fluid at grand canonical equilibrium with the rest of the fluid as its thermal and particle bath.

Similarly to [4], we expand $F(\beta; n]$ as

$$F(\beta; n] = \int d^3x \Big[f_0(n(x)) + f_2(n(x)) |\nabla n(x)|^2 + \mathcal{O}(\nabla^4 n(x)) \Big] \,. \tag{48}$$

Differentiating with respect to $n(x)$, we have

$$\mu_{in}(x; n] = \frac{\delta F}{\delta n(x)} = f_0'(n(x)) - f_2'(n(x)) |\nabla n(x)|^2 - 2 f_2(n(x)) \nabla^2 n(x). \tag{49}$$

In the absence of an external potential, $v(x) = 0$, the second and the third terms in the RHS of (49) vanish, and from Equation (44), $\mu_{in} = \mu$; therefore, we have

$$f_0'(n) = \mu(n(x)), \tag{50}$$

where $\mu(n(x))$ is the chemical potential of a uniform fluid with density $n = n(x)$. On the other hand, with the assumption that each volume element behaves as if it is in grand canonical ensemble for itself under influence of both external potential and additional one-body interaction $c(x; n]$, we know that the second derivative of F is related to Ornstein–Zernike theory by

$$\beta \frac{\delta^2 F}{\delta n(x) \delta n(x')} = \frac{\delta(x - x')}{n(x)} - c^{(2)}(x, x'; n] \,. \tag{51}$$

Therefore we have a Taylor expansion of F around the uniform density as

$$\begin{aligned} F[n(x)] =& F[n] + \int d^3x \Big[\frac{\delta F}{\delta n(x)} \Big]_{n_{eq}(x)} \tilde{n}(x) \\ &+ \frac{1}{2\beta} \int \int d^3x d^3x' \Big[\frac{\delta(x - x')}{n(x)} - c^{(2)}(|x - x'|; n] \Big]_{n_{eq}(x)} \tilde{n}(x) \tilde{n}(x') + \dots, \end{aligned} \tag{52}$$

where $\tilde{n}(x) \equiv n(x) - n$, and $c^{(2)}(|x - x'|; n]$ is the direct correlation function of a uniform fluid with density $n = n(x)$. The Fourier transform of the second integral in (52) gives

$$\begin{aligned} \frac{1}{2\beta} \int \int d^3x d^3x' \Big[\frac{\delta(x - x')}{n(x)} - c^{(2)}(|x - x'|; n] \Big]_{n_{eq}(x)} \tilde{n}(x) \tilde{n}(x') \\ = \frac{-1}{2\beta V} \sum_q \Big(c^{(2)}(q; n] - \frac{1}{n(q)} \Big) \tilde{n}(q) \tilde{n}(-q) \,, \end{aligned} \tag{53}$$

and comparing with (48) yields

$$f_0''(n) = \frac{-1}{\beta} \big(a(n) - \frac{1}{n} \big) \,, \qquad f_2(n) = \frac{-b(n)}{2\beta}, \tag{54}$$

where the functions $a(n)$ and $b(n)$ are defined as coefficients of the Fourier transform of the Ornstein–Zernike direct correlation function by $c^2(q;n] = a(n(q)) + b(n(q))q^2 + \ldots$. $b(n)$ is evaluated with linear response theory to find that

$$f_2(n(x)) = \frac{1}{12\beta}\int d^3x'|x-x'|^2 c^{(2)}(|x-x'|;n]. \tag{55}$$

We can substitute Equations (55) and (50) into (49) and use the equilibrium identity $\nabla\mu = 0$ to find the integro-differential equation

$$\nabla\left[v(x) + \mu(n(x)) - f_2'(n(x))|\nabla n(x)|^2 - 2f_2(n(x))\nabla^2 n(x)\right]_{n(x)=n_{eq}(x)} = 0, \tag{56}$$

which determines the equilibrium density $\hat{n}_{eq}(x)$ in the presence of external potential $v(x)$ given the Ornstein–Zernike direct correlation function of uniform fluid $c^{(2)}[n(x),|x-x'|]$.

6. Conclusions

We have shown that the variational principle of classical DFT is a special case of applying the method of maximum entropy to construct optimal approximations in terms of the variables that capture the relevant physical information, namely, the particle density $n(x)$. It is worth emphasizing once again: In this paper, we have pursued the purely conceptual goal of finding how the DFT fits within the MaxEnt approach to statistical mechanics. The advantage of achieving such an insight is the potential for future applications that lie outside the reach of the current versions of DFT. As an illustration, we have discussed the already well-known example of a slowly varying inhomogeneous fluid. Future research can be pursued in three different directions: (**i**) To show that the method of maximum entropy can also be used to derive the quantum version of DFT, (**ii**) to approach the Dynamic DFT [21], generalizing the idea to non-equilibrium systems by following the theory of maximum caliber [22], and (**iii**) to revisit the objective of Section 5 and construct weighted DFTs [23,24] by using the method of maximum entropy.

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