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The density functional theory of classical fluids revisited

J-M Caillol

LPT – CNRS (UMR 8627), Bat. 210, Université de Paris Sud, F-91405 Orsay Cedex, France

E-mail: Jean-Michel.Caillol@th.u-psud.fr

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Abstract

We reconsider the density functional theory of nonuniform classical fluids from the point of view of convex analysis. From the observation that the logarithm of the grand-partition function $\log \Xi[\varphi]$ is a convex functional of the external potential φ it is shown that the Kohn–Sham free energy $\mathcal{A}[\rho]$ is a convex functional of the density ρ. $\log \Xi[\varphi]$ and $\mathcal{A}[\rho]$ constitute a pair of Legendre transforms and each of these functionals can therefore be obtained as the solution of a variational principle. The convexity ensures the uniqueness of the solution in both cases. The variational principle which gives $\log \Xi[\varphi]$ as the maximum of a functional of ρ is precisely that considered in the density functional theory while the dual principle, which gives $\mathcal{A}[\rho]$ as the maximum of a functional of φ, seems to be a new result.

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1. Introduction

The convexity properties of the thermodynamic potentials play an important role in thermodynamics. For instance, in the case of a simple fluid, the entropy $S(U, V, N)$ is a concave function of the internal energy U, the volume V and the number of particles N. As discussed by Wightman [1] this property, supplemented by the hypothesis that the entropy is a homogeneous function of (U, V, N) of the first degree (i.e. $S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$ for any $\lambda > 0$), is fully equivalent to the second law of thermodynamics in Gibbs' formulation [2]. However, it should be stressed that the concavity of S as a function of (U, V, N), and similarly the convexity of U as a function of (S, V, N), are properties which hold only in the thermodynamic limit where the properties of extensivity of S and U are valid [1]. However, there is one family of convexity properties which holds even in a finite volume. That is the convexity of the logarithm of the canonical partition function $\log Z$ as a function of the inverse temperature $\beta = 1/kT$, and the convexity of the logarithm of the grand-partition function $\log \Xi$ in β and $\nu = \beta\mu$ (μ chemical potential) [1].

In this paper we extend the latter property to the case of nonuniform systems. The system of interest is thus a classical fluid in a volume $\mathcal{V}$ and in the presence of an external one-body potential $\varphi(\vec{x})$. It will be shown in section 3 that $\log \Xi$ is a convex functional of the generalized potential

$$u(\vec{x}) = \nu - \beta\varphi(\vec{x}) \tag{1.1}$$

or, alternatively, of the local chemical potential $\mu(\vec{x}) = \mu - \varphi(\vec{x})$. The implications of this mathematical property are studied in detail and are shown to lead to a new formulation of the density functional theory (DFT) of classical fluids. Indeed, the convexity of $\log \Xi[u]$ implies the existence and the uniqueness of a convex functional $\beta\mathcal{A}[\rho]$ of the inhomogeneous density $\rho(\vec{x})$ such that $\log \Xi[u]$ and $\beta\mathcal{A}[\rho]$ are a couple of Legendre transforms. Of course, the functional $\beta\mathcal{A}[\rho]$ identifies with the intrinsic Helmholtz (Kohn–Sham) free energy. Since they are Legendre transforms, both $\log \Xi[u]$ and $\beta\mathcal{A}[\rho]$ can be expressed as the solution of a variational principle. The variational principle which defines $\log \Xi[u]$ as the maximum of a functional of $\rho(\vec{x})$ is precisely the one which was noticed by Kohn *et al* [3, 4] and constitutes the cornerstone of the DFT [3–7]. The dual variational principle, which defines $\beta\mathcal{A}[\rho]$ for a given $\rho(\vec{x})$ as the maximum of a functional of $u(\vec{x})$, seems to have been overlooked.

Our paper is organized as follows. In section 2 we review some mathematical properties of the grand-partition function of a nonuniform fluid. In section 3 we show that $\log \Xi[u]$ is a convex functional of the generalized potential $u(\vec{x})$ which allows us to define its Legendre transform $\mathcal{A}[\rho]$. The link with the DFT is discussed in detail. Conclusions are drawn in section 4. We have found it useful to give easy (formal) proofs of the theorems of convex analysis which are needed in the text in the appendix.

2. The grand-partition function and its functional derivatives

In this section we review known properties of the nonuniform classical fluids and define our notations. We consider a simple fluid made of identical, structureless classical particles in a *finite* volume $\mathcal{V}$. The dimension of space is d. A configuration of the system in the grand-canonical ensemble will be denoted by $\omega \equiv (N, \vec{x}_1, \ldots, \vec{x}_N)$ where $\vec{x}_i$ denotes the position of the ith particle. The grand-canonical partition function $\Xi[u]$ can be written as [8]

$$\Xi[u] = \int \mathrm{d}\mu(\omega) \exp(\langle\hat{\rho}(\omega)|u\rangle) \tag{2.1}$$

where we have introduced the scalar product

$$\langle\hat{\rho}(\omega)|u\rangle \equiv \int_{\mathcal{V}} \mathrm{d}^d\vec{x}\,\hat{\rho}(\vec{x};\omega)u(\vec{x}) \tag{2.2}$$

between the generalized potential $u(\vec{x})$ (cf equation (1.1)) and the microscopic density of particles

$$\hat{\rho}(\vec{x};\omega) = \sum_{i=1}^{N} \delta^d(\vec{x} - \vec{x}_i).$$

In equation (2.1) we have adopted the compact notation

$$\mathrm{d}\mu(\omega) = \mathrm{d}\omega \exp(-\beta W(\omega)) \tag{2.3}$$

where $W(\omega)$ denotes the internal potential energy of N particles in the configuration ω and $\mathrm{d}\omega$ is the grand-canonical measure defined as

$$\int \mathrm{d}\omega \equiv \sum_{N=0}^{\infty} \frac{1}{\Lambda^{dN} N!} \int \mathrm{d}^d\vec{x}_1 \ldots \mathrm{d}^d\vec{x}_N \tag{2.4}$$

where Λ is the de Broglie thermal wavelength. The grand-canonical average of any microscopic variable $\mathcal{A}(\omega)$ can thus be written as

$$\langle \mathcal{A} \rangle = \int \mathrm{d}\mu(\omega) \exp(\langle \hat{\rho}(\omega)|u\rangle)\mathcal{A}(\omega)/\Xi[u]. \tag{2.5}$$

We shall denote as usual by $\Omega[u] \equiv -\beta^{-1} \log \Xi[u]$ the grand potential; note that it can be rewritten as a grand-canonical average [5–7]

$$\beta\Omega[u] = \langle \beta W(\omega) + \log f_0(\omega)\rangle - \langle \rho|u\rangle \tag{2.6}$$

$$\rho(\vec{x}) = \langle \hat{\rho}(\vec{x};\omega)\rangle \tag{2.7}$$

where $f_0(\omega) = \Xi^{-1} \exp(-\beta W(\omega) + \langle \hat{\rho}(\omega)|u\rangle)$ is the grand-canonical equilibrium distribution in the phase space.

We shall denote by $\mathcal{U}$ the set of potentials $u(\vec{x})$ such that the rhs of equation (2.1) converges. For the sake of simplicity we shall restrict ourselves to the case of H-stable systems in the sense of Ruelle, i.e. systems such that $W(\omega) \geqslant -N\mathcal{B}$ where the lower bound $\mathcal{B} < \infty$ is some constant independent of N. Most models of interest satisfy this property. We have obviously

$$\Xi[u] \leqslant \exp\left(\frac{1}{\Lambda^d} \exp(\beta\mathcal{B}) \int_{\mathcal{V}} \mathrm{d}^d\vec{x} \exp(u(\vec{x}))\right) \tag{2.8}$$

from which it follows that $\mathcal{U}$ is the set of the functions $u(\vec{x})$ such that $\exp(u(\vec{x}))$ is integrable over the volume $\mathcal{V}$ of the system; i.e. $\mathcal{U} = \left\{u : \mathcal{V} \to \mathbb{R}; \exp(u) \in L^1_{\mathcal{V}}[\mathrm{d}^d\vec{x}]\right\}$. It can be shown that, for H-stable systems, $\mathcal{U}$ is a convex set [9]. Indeed, let u_0 and u_1 be two potentials belonging to $\mathcal{U}$. We define the closed (respectively open) interval $[u_0, u_1]$ (respectively $]u_0, u_1[$) as the set of functions $u_\lambda = (1-\lambda)u_0 + \lambda u_1$ where $0 \leqslant \lambda \leqslant 1$ (respectively $0 < \lambda < 1$). As a consequence of the convexity of the exponential function $\exp((1-\lambda)u_0 + \lambda u_1) \leqslant (1-\lambda)\exp(u_0) + \lambda \exp(u_1)$ and therefore $[u_0, u_1] \subset \mathcal{U}$.

As is well known, $\Xi[u]$ is the generating functional of a hierarchy of correlation functions [8, 10, 11]. Expanding expression (2.1) of $\Xi[u + \delta u]$ in powers of δu one finds for $(u, u + \delta u \in \mathcal{U})$

$$\Xi[u+\delta u]/\Xi[u] = \sum_{n=0}^{\infty} \frac{1}{n!} \int_{\mathcal{V}} \mathrm{d}^d\vec{x}_1 \cdots \mathrm{d}^d\vec{x}_n G^{(n)}(\vec{x}_1,\ldots,\vec{x}_n)\, \delta u(\vec{x}_1)\cdots\delta u(\vec{x}_n) \tag{2.9}$$

where the correlation function $G^{(n)}$ has been defined as

$$\begin{aligned} G^{(n)}(\vec{x}_1,\ldots,\vec{x}_n) &= \frac{1}{\Xi[u]} \frac{\delta^{(n)}\Xi[u]}{\delta u(\vec{x}_1)\cdots\delta u(\vec{x}_n)} \\ &= \left\langle \prod_{i=1}^{n} \hat{\rho}(\vec{x}_i;\omega)\right\rangle. \end{aligned} \tag{2.10}$$

It is sometimes also useful to introduce the connected correlation functions as

$$G_c^{(n)}(\vec{x}_1,\ldots,\vec{x}_n) = \frac{\delta^{(n)} \log \Xi[u]}{\delta u(\vec{x}_1)\cdots\delta u(\vec{x}_n)}. \tag{2.11}$$

The relation between $G_c^{(n)}$ and $G^{(n)}$ can be written symbolically as

$$G_c^{(n)}(\vec{x}_1,\ldots,\vec{x}_n) = G^{(n)}(\vec{x}_1,\ldots,\vec{x}_n) - \sum \prod_{m<n} G_c^{(m)}\left(\vec{x}_{i_1},\ldots,\vec{x}_{i_m}\right) \tag{2.12}$$

where the sum of products is carried out over all possible partitions of the set $(1,\ldots,n)$ into subsets of cardinal $m < n$ [10, 11]. For instance we have

$$G_c^{(2)}(\vec{x}_1,\vec{x}_2) = G^{(2)}(\vec{x}_1,\vec{x}_2) - \rho(\vec{x}_1)\rho(\vec{x}_2) \tag{2.13}$$

where $\rho \equiv G^{(1)} \equiv G_c^{(1)}$ is the mean density of particles. Note that in the theory of liquids one rather defines the correlation functions $\rho^{(n)}$ as the functional derivatives of Ξ with respect to the activity $z = \exp(u)$. More precisely:

$$\rho^{(n)}(\vec{x}_1, \ldots, \vec{x}_n) = \frac{\prod_{1=1}^n z(\vec{x}_i)}{\Xi[z]} \frac{\delta^{(n)} \log \Xi[z]}{\delta z(\vec{x}_1) \cdots \delta z(\vec{x}_n)}. \tag{2.14}$$

The functions $\rho^{(n)}$ and $G^{(n)}$ differ by delta functions [8, 10], for instance $G^{(2)}(\vec{x}_1, \vec{x}_2) = \rho^{(2)}(\vec{x}_1, \vec{x}_2) + \rho(\vec{x}_1)\delta^d(\vec{x}_1 - \vec{x}_2)$.

3. Convexity and Legendre transformations

3.1. *Convexity of* $\log \Xi[u]$

Let us show now that $\log \Xi[u]$ is a strictly convex functional of u, i.e. for any u_1 and $u_2 \neq u_1 \in \mathcal{U}$ we have, for any $0 < \lambda < 1$, the strict inequality

$$\log \Xi[\lambda u_1 + (1-\lambda)u_2] < \lambda \log \Xi[u_1] + (1-\lambda) \log \Xi[u_2]. \tag{3.1}$$

Let $u(\vec{x})$ be an arbitrary potential of $\mathcal{U}$ and $h(\vec{x})$ any non-zero function defined on the volume of the system. Following Percus [12], we can show that the quadratic form

$$(\log \Xi)_u^{(2)}[h] \equiv \int_{\mathcal{V}} \mathrm{d}^d\vec{x}_1 \, \mathrm{d}^d\vec{x}_2 \frac{\delta^{(2)} \log \Xi[u]}{\delta u(\vec{x}_1)\delta u(\vec{x}_2)} h(\vec{x}_1)h(\vec{x}_2) \tag{3.2}$$

is strictly positive which implies strict convexity from theorem 2 of the appendix. Indeed equations (2.10) and (2.11) imply that

$$\begin{aligned}(\log \Xi)_u^{(2)}[h] &= \int_{\mathcal{V}} \mathrm{d}^d\vec{x}_1 \, \mathrm{d}^d\vec{x}_2 G_c^{(2)}(\vec{x}_1, \vec{x}_2)h(\vec{x}_1)h(\vec{x}_2) \\ &= \langle H^2 \rangle - \langle H \rangle^2 > 0 \end{aligned} \tag{3.3}$$

where $H(\omega) = \sum_{i=1}^N h(\vec{x}_i)$.

One can also give an alternative, more direct proof of the convexity of $\log \Xi[u]$. For $u_1, u_2 \neq u_1 \in \mathcal{U}$ and $0 < \lambda < 1$ we have, with slightly simplified notation,

$$\begin{aligned}\Xi[\lambda u_1 + (1-\lambda)u_2] &= \int_{\mathcal{V}} \mathrm{d}\mu \exp(\lambda\langle\hat{\rho}|u_1\rangle) \exp((1-\lambda)\langle\hat{\rho}|u_2\rangle) \\ &< \left[\int_{\mathcal{V}} \mathrm{d}\mu[\exp(\lambda\langle\hat{\rho}|u_1\rangle)]^{1/\lambda}\right]^{\lambda} \times \left[\int_{\mathcal{V}} \mathrm{d}\mu\,[\exp((1-\lambda)\langle\hat{\rho}|u_2\rangle)]^{1/(1-\lambda)}\right]^{(1-\lambda)} \\ &= \Xi[u_1]^{\lambda}\,\Xi[u_2]^{(1-\lambda)} \end{aligned} \tag{3.4}$$

which yields inequality (3.1) by taking the logarithm. In order to write the second line of equation (3.4) we have made use of Hölder's inequality which states that, for any real numbers p, q such that $p > 1, q > 1, 1/p + 1/q = 1$ one has [13]

$$\left|\int \mathrm{d}\mu(\omega) f(\omega)g(\omega)\right| \leqslant \left(\int \mathrm{d}\mu(\omega)|f(\omega)|^p\right)^{1/p} \left(\int \mathrm{d}\mu(\omega)|g(\omega)|^q\right)^{1/q}. \tag{3.5}$$

The case of equality in equation (3.5) occurs only if $|f(\omega)|^p/|g(\omega)|^q$ is almost everywhere equal to a constant. This remark implies the strict inequality in equation (3.1). Note that the grand potential $\beta\Omega[u] = -\log \Xi[u]$ is therefore a strictly concave functional of $u(\vec{x})$ even before the passage to the thermodynamic limit (TL).

3.2. The Kohn–Sham free energy as the Legendre transform of $\log \Xi$

Let us define the functional

$$\beta\mathcal{A}[\rho, u] = \langle\rho|u\rangle - \log \Xi[u]. \tag{3.6}$$

For a given function $\rho(\vec{x})$, $\beta\mathcal{A}[\rho, u]$ is obviously a concave functional of u. Consequently, if $\beta\mathcal{A}[\rho, u]$ has a maximum for some $\bar{u} \in \mathcal{U}$ this maximum is strict and therefore unique. This is theorem 3 of the appendix. By definition, the value of the maximum of $\beta\mathcal{A}[\rho, u]$ is the Legendre transformation $\beta\bar{\mathcal{A}}[\rho]$ of the functional $\log \Xi[u]$ at point ρ, i.e. we have

$$\beta\bar{\mathcal{A}}[\rho] = \sup_{u\in\mathcal{U}} \beta\mathcal{A}[\rho, u] \tag{3.7}$$

$$= \beta\mathcal{A}[\rho, \bar{u}] \tag{3.8}$$

where $\bar{u}$ is the solution of $\delta\mathcal{A}[\rho, u]/\delta u(\vec{x}) = 0$ for a given $\rho(\vec{x})$. If it exists, $\bar{u}$ is therefore the unique solution of

$$\rho(\vec{x}) = \left.\frac{\delta \log \Xi[u]}{\delta u(\vec{x})}\right|_{u=\bar{u}}. \tag{3.9}$$

As usual, existence is much more difficult to prove than uniqueness. Clearly, if for some $\vec{x} \in \mathcal{V}$, $\rho(\vec{x}) < 0$ equation (3.9) will not have any solutions in $\mathcal{U}$. It is easy to prove that, for the ideal gas ($W_N \equiv 0\ \forall N$), the condition $\rho(\vec{x}) \geqslant 0$ is sufficient for equation (3.9) to have a solution. For non-trivial models, this condition is in general not sufficient since there exists an upper bound on $\|\rho\|_{L^1}$. However, the beautiful result that for H-stable systems the set $\mathcal{R}$ of densities for which equation (3.9) has a solution is a convex set has been proved by Chayes and Chayes [9].

Some important properties of the functional $\beta\bar{\mathcal{A}}[\rho]$ can easily be deduced from its mere definition. Firstly, note Young's inequality which follows readily from equation (3.7)

$$(\forall u \in \mathcal{U})(\forall\rho \in \mathcal{R}) \log \Xi[u] + \beta\bar{\mathcal{A}}[\rho] \geqslant \langle\rho|u\rangle. \tag{3.10}$$

Secondly, $\beta\bar{\mathcal{A}}$ is a strictly convex functional of ρ. To prove that, let $\rho_1, \rho_2 \neq \rho_1$ be two distinct densities of $\mathcal{R}$ and $0 < \lambda < 1$. Since $\mathcal{R}$ is convex $\rho_\lambda = \lambda\rho_1 + (1-\lambda)\rho_2$ is also a density of $\mathcal{R}$. Let us denote by $\bar{u}_\lambda$ the solution of equation (3.9) corresponding to ρ_λ. It follows from equation (3.7) that

$$\begin{aligned}\beta\bar{\mathcal{A}}[\lambda\rho_1 + (1-\lambda)\rho_2] &= \lambda\beta\mathcal{A}[\bar{u}_\lambda, \rho_1] + (1-\lambda)\beta\mathcal{A}[\bar{u}_\lambda, \rho_2] \\ &< \lambda\beta\bar{\mathcal{A}}[\rho_1] + (1-\lambda)\beta\bar{\mathcal{A}}[\rho_2]\end{aligned} \tag{3.11}$$

which proves the strict convexity. An alternative proof of the convexity of $\beta\bar{\mathcal{A}}[\rho]$ can be found in [9]. Finally the functional derivative of $\beta\bar{\mathcal{A}}[\rho]$ with respect to ρ is easily obtained from equation (3.8). We have

$$\begin{aligned}\frac{\delta\beta\bar{\mathcal{A}}[\rho]}{\delta\rho(\vec{x})} &= \frac{\delta\beta\mathcal{A}[\rho, \bar{u}]}{\delta\rho(\vec{x})} \\ &= \bar{u}(\vec{x}) + \left\langle\rho \left| \frac{\delta\bar{u}}{\delta\rho(\vec{x})}\right.\right\rangle - \left\langle\frac{\delta \log \Xi}{\delta\bar{u}} \left| \frac{\delta\bar{u}}{\delta\rho(\vec{x})}\right.\right\rangle \\ &= \bar{u}(\vec{x})\end{aligned} \tag{3.12}$$

where we have made use of equation (3.9).

Note that it follows from equations (2.6) and (3.8) that we can rewrite

$$\beta\bar{\mathcal{A}}[\rho] = \langle\beta W(\omega) + \log \bar{f}_0(\omega)\rangle \tag{3.13}$$

where $\bar{f}_0(\omega)$ denotes the grand-canonical equilibrium density in the phase space for the system in the presence of the external potential $\bar{u}$. The expression (3.13) of $\beta\bar{\mathcal{A}}[\rho]$ coincides of course with that of the intrinsic Helmholtz (Kohn–Sham) free energy [5–7].

We would now like to comment briefly on equations (3.7) and (3.8). They can be rewritten more explicitly as

$$(\forall u(\vec{x}))\beta\bar{\mathcal{A}}[\rho] \geqslant \int_{\mathcal{V}} \mathrm{d}^d\vec{x}\,\rho(\vec{x})u(\vec{x}) + \beta\Omega[u] \equiv \beta\mathcal{A}[\rho, u] \tag{3.14}$$

where the equality holds for the unique potential $u \equiv \bar{u}$ solution of equation (3.9). Equation (3.14) takes thus the form of a variational principle which asserts that the generalized potential $u(\vec{x})$ which gives rise to a given density $\rho(\vec{x})$ is that which maximizes the functional $\beta\mathcal{A}[\rho, u]$. If it exists it is unique. We have thus obtained a formal solution of the inverse problem to that usually considered in the DFT. To be effective this variational principle requires an exact or at least an approximate knowledge of the functional $\beta\Omega[u]$. Unfortunately, although many efforts have been devoted in the past to find good approximations of $\beta\bar{\mathcal{A}}[\rho]$ [5–7] for many fluids of interest, similar approximations for $\beta\Omega[u]$ are not available, at least to the author's knowledge.

The functional $\beta\bar{\mathcal{A}}[\rho]$ is the generating functional of the so-called direct correlation functions $\hat{c}^{(n)}(\vec{x}_1, \ldots, \vec{x}_n)$ [11]. These functions play in the theory of liquids the role devoted to the vertex functions in statistical field theory [14]. They are defined as

$$\hat{c}^{(n)}(\vec{x}_1, \ldots, \vec{x}_n) = -\frac{\delta^{(n)}\beta\bar{\mathcal{A}}[\rho]}{\delta\rho(\vec{x}_1)\cdots\delta\rho(\vec{x}_n)}. \tag{3.15}$$

The direct correlation functions $\hat{c}^{(n)}$ and the Ursell correlation functions $G_c^{(n)}$ are related through generalized Ornstein–Zernike relations [11, 14]. In fact, for historical reasons, one rather defines the 'true' direct correlation functions $c^{(n)}(\vec{x}_1, \ldots, \vec{x}_n)$ by

$$\hat{c}^{(n)}(\vec{x}_1, \ldots, \vec{x}_n) = c^{(n)}(\vec{x}_1, \ldots, \vec{x}_n) + \hat{c}_{id}^{(n)}(\vec{x}_1, \ldots, \vec{x}_n) \tag{3.16}$$

where $\hat{c}_{id}^{(n)}$ are the $\hat{c}^{(n)}$ functions of the ideal gas, so that the $c^{(n)}$ are the functional derivatives of minus the excess free energy. It is easily established that

$$\begin{aligned} \hat{c}_{id}^{(1)}(\vec{x}) &= -\log(\Lambda^d\rho(\vec{x})) \\ \hat{c}_{id}^{(n)}(\vec{x}_1, \ldots, \vec{x}_n) &= \frac{(-1)^{n-1}}{\rho(\vec{x}_1)^{n-1}}(n-2)!\prod_{i=2}^{n}\delta^d(\vec{x}_1 - \vec{x}_i)(n \geqslant 2) \end{aligned} \tag{3.17}$$

so that, for instance, we have $c^{(2)}(\vec{x}_1, \vec{x}_2) = \hat{c}^{(2)}(\vec{x}_1, \vec{x}_2) + \delta^d(\vec{x}_1 - \vec{x}_2)/\rho(\vec{x}_1)$. Since the functional $\beta\bar{\mathcal{A}}[\rho]$ is convex, it follows by application of theorem 2 of the appendix that the quadratic form $\beta\bar{\mathcal{A}}_\rho^{(2)}[h]$, where h in an arbitrary nonzero function defined on $\mathcal{V}$, is positive definite, which can be expressed as

$$\int_{\mathcal{V}} \mathrm{d}^d\vec{x}_1\,\mathrm{d}^d\vec{x}_2 \left(\frac{\delta^d(\vec{x}_1 - \vec{x}_2)}{\rho(\vec{x}_1)} - c^{(2)}(\vec{x}_1, \vec{x}_2)\right) h(\vec{x}_1)h(\vec{x}_2) \geqslant 0. \tag{3.18}$$

Note that, in the above equation, *a priori* the inequality is not strict (see the appendix for more details on this point).

3.3. The DFT recovered

As for functions of several variables [2, 15, 17], the Legendre transform of a functional is involutive, i.e. in our case, the Legendre transform of $\beta\bar{\mathcal{A}}[\rho]$ coincides with $\log\Xi[u]$. Indeed, since $\beta\bar{\mathcal{A}}[\rho]$ is a strictly convex functional defined on $\mathcal{R}$, one can define its Legendre transform $\beta\bar{\Lambda}[u]$ for any $u \in \mathcal{U}$. One first defines the two fields functional

$$\beta\Lambda[u,\rho] = \langle\rho|u\rangle - \beta\bar{\mathcal{A}}[\rho] \tag{3.19}$$

which is concave in ρ for a given u. The Legendre transform $\beta\bar{\Lambda}[u]$ is then defined as the maximum of $\beta\Lambda[u,\rho]$ at u fixed, i.e.

$$\beta\bar{\Lambda}[u] = \sup_{\rho\in\mathcal{R}} \beta\Lambda[u,\rho] \tag{3.20}$$

$$= \beta\Lambda[u,\bar{\rho}] \tag{3.21}$$

where $\bar{\rho}$ is the solution of $\delta\Lambda[u,\rho]/\delta\rho(\vec{x}) = 0$ for the given field $u(\vec{x})$. If it exists, $\bar{\rho}$ is therefore the unique solution of

$$u(\vec{x}) = \left.\frac{\delta\beta\bar{\mathcal{A}}[\rho]}{\delta\rho(\vec{x})}\right|_{\rho=\bar{\rho}}. \tag{3.22}$$

In order to prove that $\beta\bar{\Lambda} \equiv \log\Xi$ we insert expression (3.8) of $\beta\bar{\mathcal{A}}[\rho]$ into the rhs of equation (3.21) which yields

$$\beta\bar{\Lambda}[u] = \langle\bar{\rho}|(u-\bar{u})\rangle + \log\Xi[\bar{u}] \tag{3.23}$$

where $\bar{u}$ is the unique solution of

$$\bar{\rho}(\vec{x}) = \left.\frac{\delta\log\Xi}{\delta u(\vec{x})}\right|_{u=\bar{u}}. \tag{3.24}$$

We claim now that $\bar{u} \equiv u$ and therefore $\beta\Lambda \equiv \log\Xi$. Indeed it follows from equation (3.12) that

$$\bar{u}(\vec{x}) = \left.\frac{\delta\beta\bar{\mathcal{A}}[\rho]}{\delta\rho(\vec{x})}\right|_{\rho=\bar{\rho}}$$

and hence, by comparison with equation (3.22) $\bar{u} \equiv u$.

We would like to comment briefly on equations (3.20) and (3.21). They can be recast in the more familiar form

$$(\forall\rho(\vec{x}))\beta\Omega[u] \leqslant \beta\bar{\mathcal{A}}[\rho] - \int_{\mathcal{V}} \mathrm{d}^d\vec{x}\,\rho(\vec{x})u(\vec{x}) \equiv \beta\Omega_{\mathcal{V}}[u,\rho](\equiv -\beta\Lambda[u,\rho]) \tag{3.25}$$

where the equality holds for the unique profile $\rho \equiv \bar{\rho}$ solution of equation (3.22). Equation (3.25) is precisely the DFT variational principle which states that the density $\rho(\vec{x})$ corresponding to the imposed external potential $u(\vec{x})$ is that which minimizes the functional $\beta\Omega_{\mathcal{V}}[\rho,u]$ for a given $u(\vec{x})$ [5–7]. Moreover the solution is unique (if it exists). Note that a similar minimum principle can also be derived in the canonical ensemble; in this case it is the total number of particles $N = \int \mathrm{d}^d\vec{x}\,\rho(\vec{x})$ which is fixed rather than the chemical potential μ [18].

4. Summary and additional comments

In this paper we have studied some of the properties of a nonuniform classical fluid occupying a finite volume $\mathcal{V}$ and in the presence of an external potential $\varphi(\vec{x})$. The thermodynamic and structural properties of the fluid are described by the logarithm of the grand-partition function $\log\Xi[u]$ which is the generating functional of the connected correlation functions $G_c^{(n)}$. $\log\Xi[u]$ is a convex functional of the generalized external potential $u(\vec{x}) \equiv \beta\mu - \beta\varphi(\vec{x})$ and its Legendre transform $\beta\bar{\mathcal{A}}[\rho]$, which identifies with the Kohn–Sham free energy, is a convex functional of the density $\rho(\vec{x})$. $\beta\bar{\mathcal{A}}[\rho]$ is the generating functional of the direct correlation (or vertex) functions $\hat{c}^{(n)}$. The functions $G_c^{(n)}$ and $\hat{c}^{(n)}$ are related by generalized Ornstein–Zernike relations. The Legendre transform is involutive and thus the Legendre transform of $\beta\bar{\mathcal{A}}[\rho]$ coincides with $\log \Xi[u]$. As a consequence of the convexity of $\beta\bar{\mathcal{A}}[\rho]$ and $\log \Xi[u]$ the two following quadratic forms are positive definite

$$\log \Xi_u^{(2)}[h] > 0 \tag{4.1}$$

$$\beta\bar{\mathcal{A}}_\rho^{(2)}[h] \geqslant 0. \tag{4.2}$$

Moreover, for H-stable systems, the set $\mathcal{U}$ of the generalized external potentials u and the set $\mathcal{R}$ of the densities ρ are both convex sets.

For arbitrary potentials $u \in \mathcal{U}$ and densities $\rho \in \mathcal{R}$ we have Young's inequality

$$\beta\bar{\mathcal{A}}[\rho] + \log \Xi[u] \geqslant \langle\rho|u\rangle. \tag{4.3}$$

$\beta\bar{\mathcal{A}}[\rho]$ and $\log \Xi[u]$ are both unique solutions of a variational principle:

$$\beta\bar{\mathcal{A}}[\rho] = \sup_{u\in\mathcal{U}} (\langle\rho|u\rangle - \log \Xi[u]) \qquad (\forall \rho \in \mathcal{R}) \tag{4.4}$$

$$\log \Xi[u] = \sup_{\rho\in\mathcal{R}} (\langle\rho|u\rangle - \beta\bar{\mathcal{A}}[\rho]) \qquad (\forall u \in \mathcal{U}). \tag{4.5}$$

The latter variational principle (4.5) is that of the DFT whereas the dual one (4.4) is a new one.

All the results which are summarized above are valid for any finite domain $\mathcal{V}$, before the passage to the thermodynamic limit, and one can wonder whether they survive in the infinite volume limit. The notion of thermodynamic limit is not easy to define for an inhomogeneous system and we concentrate henceforth on the case of homogeneous systems. The domain $\mathcal{V}$ that we consider now could be a cube of volume $V = L^d$ with periodic boundary conditions, or the surface of a hypersphere, etc. There is no applied external potential and $u = \beta\mu$ reduces to the chemical potential, so that our system is homogeneous even for a finite volume. The grand-canonical pressure p_V is defined by the thermodynamic relation $\log \Xi(\mu) = \beta p_V V$, and similarly we define $a_V(\rho) = \bar{\mathcal{A}}(\rho)/V$. Of course all the results of the paper apply to this peculiar case and one concludes that, for a finite volume V, the pressure $p_V(\mu)$ at given temperature and volume is a *strictly* convex function of the chemical potential and that the specific grand-canonical free energy $a_V(\rho)$ is a strictly convex function of the density. This is true even in the event of a liquid–vapour transition for instance. This behaviour of $a_V(\rho)$ contrasts with that of the canonical free energy $a_V^{\mathrm{can}}(\rho)$ which is a bimodal function of ρ in the two phase region, due to interface effects. But, what happens in the thermodynamic limit? We first note that the *strict* inequalities which enter the definition of strict convexity for both $p_V(\mu)$ and $a_V(\rho)$ can become equalities in the infinite volume limit. Therefore, in the TL, we can only claim that, at a given temperature, $p_\infty(\mu)$ is a convex function of μ and that $a_\infty(\rho)$ is a convex function of the density. Moreover, as is well known, the continuity of some derivatives can also be lost in the TL. This is the case for $p_\infty(\mu)$ which exhibits a kink for some $\mu(T)$ at a temperature T below the critical temperature T_c. One can however still define a Legendre transform in the case of such discontinuities. Let us denote by ρ_g and ρ_l the two distinct values of $\partial p_\infty/\partial\mu$ at the cusp, then $a_\infty(\rho)$ will be a linear function of ρ in the interval $[\rho_g, \rho_l]$. Cusps and intervals correspond in a Legendre transformation [1, 15]. To summarize, in the coexistence region, the *strict* convexity of $a_V(\rho)$ is lost in the TL; by contrast, $p_\infty(\mu)$ remains strictly convex in the TL even in the event of a phase transition, but its derivatives have discontinuity points.

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Appendix. Convex functionals

Functionals are a simple generalization of functions of several variables; they can be defined as 'functions of functions'. In this appendix we give formal proofs of the theorems on convex functionals [16] which are needed in the text, without aiming at any mathematical rigour. The proofs given below are a mere transcription of the material of any standard textbook on functions of several variables [17].

We consider a convex set X of real functions defined on a domain $\mathcal{V} \subset \mathbb{R}^d$ with a norm $\|\varphi\| (\varphi \in X)$. We define a functional F as a mathematical object which associates with each element φ a real number $F[\varphi]$. F will be said to be differentiable at point φ of X if there exists a linear functional $F_\varphi^{(1)}$ such that

$$F[\varphi + \delta\varphi] = F[\varphi] + F_\varphi^{(1)}[\delta\varphi] + \epsilon[\delta\varphi]\|\delta\varphi\| \tag{A1}$$

$$\lim_{\|\delta\varphi\| \to 0} \epsilon[\delta\varphi] = 0 \tag{A2}$$

where we have noted

$$F_\varphi^{(1)}[\delta\varphi] = \int_{\mathcal{V}} \mathrm{d}^d\vec{x}\, \frac{\delta F}{\delta\varphi(\vec{x})} \delta\varphi(\vec{x}) \tag{A3}$$

where $\delta F/\delta\varphi(\vec{x})$ is the functional derivative of F with respect to the field $\varphi(\vec{x})$. One deduces from equation (A1) a useful expression for the derivative of F in the direction $\delta\varphi$:

$$F_\varphi^{(1)}[\delta\varphi] = \lim_{\lambda \to 0} \frac{F[\varphi + \lambda\delta\varphi] - F[\varphi]}{\lambda} \qquad (\forall \delta\varphi \in X). \tag{A4}$$

It is easy to prove by applying Rolle's theorem to the real function $g(t) = F(\varphi + t\delta\varphi)$ that a Taylor–MacLaurin expansion also holds for functionals:

$$F[\varphi + \delta\varphi] = F[\varphi] + F_{\varphi+\lambda\delta\varphi}^{(1)}[\delta\varphi] \qquad (0 < \lambda < 1). \tag{A5}$$

If F is twice differentiable it generalizes as

$$F[\varphi + \delta\varphi] = F[\varphi] + F_\varphi^{(1)}[\delta\varphi] + \tfrac{1}{2} F_{\varphi+\lambda\delta\varphi}^{(2)}[\delta\varphi] \qquad (0 < \lambda < 1) \tag{A6}$$

where

$$F_\varphi^{(2)}[\delta\varphi] = \int_{\mathcal{V}} \mathrm{d}^d\vec{x}\, \mathrm{d}^d\vec{y}\, \frac{\delta^{(2)} F}{\delta\varphi(\vec{x})\delta\varphi(\vec{y})} \delta\varphi(\vec{x})\delta\varphi(\vec{y}). \tag{A7}$$

It will be necessary to distinguish carefully between convex and strictly convex functionals. $F[\varphi]$ will be said to be convex if $(\forall \varphi_1, \varphi_2 \in X)$ and for all $0 \leqslant \lambda \leqslant 1$ one has $F[\lambda\varphi_1 + (1-\lambda)\varphi_2] \leqslant \lambda F[\varphi_1] + (1-\lambda)F[\varphi_2]$, whereas it will be said to be strictly convex if $(\forall \varphi_1, \varphi_2 \neq \varphi_1 \in X)$ and for all $0 < \lambda < 1$ one has $F[\lambda\varphi_1 + (1-\lambda)\varphi_2] < \lambda F[\varphi_1] + (1-\lambda)F[\varphi_2]$. $F[\varphi]$ will be said to be concave (respectively strictly concave) if $-F[\varphi]$ is convex (respectively strictly convex). Henceforth we shall assume moreover that all the considered functionals are at least twice differentiable. Let us establish our first theorem which states that a convex functional lies above its tangent plane, i.e. more precisely

Theorem 1.

- *F convex* $\Longleftrightarrow$ $(\forall\varphi_1,\varphi_2\in X)F[\varphi_2]\geqslant F[\varphi_1]+F^{(1)}_{\varphi_1}[\varphi_2-\varphi_1]$.
- *F strictly convex* $\Longleftrightarrow$ $(\forall\varphi_2\neq\varphi_1\in X)F[\varphi_2]>F[\varphi_1]+F^{(1)}_{\varphi_1}[\varphi_2-\varphi_1]$.

Proof. Suppose F is convex, $0<\lambda<1$ and $(\varphi_1,\varphi_2\neq\varphi_1\in X)$. The convexity of F implies that

$$\frac{F[\varphi_1+\lambda(\varphi_2-\varphi_1)]-F[\varphi_1]}{\lambda}\leqslant F[\varphi_2]-F[\varphi_1].$$

Taking the limit $\lambda\to 0$ and making use of equation (A4) yields $F[\varphi_2]\geqslant F[\varphi_1]+F^{(1)}_{\varphi_1}[\varphi_2-\varphi_1]$. If F is strictly convex the above proof does not imply the strict inequality, more care is needed. Let $0<\omega<1$. Since

$$(1-\lambda)\varphi_1+\lambda\varphi_2=\frac{\omega-\lambda}{\omega}\varphi_1+\frac{\lambda}{\omega}(\varphi_1+\omega(\varphi_2-\varphi_1))$$

for $0\leqslant\lambda\leqslant\omega$ we have $0\leqslant(\omega-\lambda)/\omega\leqslant 1$ and therefore

$$F[\varphi_1+\lambda(\varphi_2-\varphi_1)]\leqslant\frac{\omega-\lambda}{\omega}F[\varphi_1]+\frac{\lambda}{\omega}F[\varphi_1+\omega(\varphi_2-\varphi_1)].$$

If F is strictly convex one thus has for $0<\lambda\leqslant\omega$

$$\frac{F[\varphi_1+\lambda(\varphi_2-\varphi_1)]-F[\varphi_1]}{\lambda}\leqslant\frac{F[\varphi_1+\omega(\varphi_2-\varphi_1)]-F[\varphi_1]}{\omega}<F[\varphi_2]-F[\varphi_1].$$

Taking the limit $\lambda\to 0$ and making use of equation (A4) yields the strict inequality: $F[\varphi_2]>F[\varphi_1]+F^{(1)}_{\varphi_1}[\varphi_2-\varphi_1]$, since, by hypothesis, $\omega<1$.

Reciprocally, we assume that

$$(\forall\varphi_1,\varphi_2\in X)\qquad F[\varphi_2]\geqslant F[\varphi_1]+F^{(1)}_{\varphi_1}[\varphi_2-\varphi_1].$$

Let φ_1 and φ_2 be two distinct points of X and $0<\lambda<1$, we have

$$F[\varphi_1]\geqslant F[\lambda\varphi_1+(1-\lambda)\varphi_2]+F^{(1)}_{\lambda\varphi_1+(1-\lambda)\varphi_2}[(1-\lambda)(\varphi_1-\varphi_2)] \tag{A8}$$

$$F[\varphi_2]\geqslant F[\lambda\varphi_1+(1-\lambda)\varphi_2]+F^{(1)}_{\lambda\varphi_1+(1-\lambda)\varphi_2}[\lambda(\varphi_2-\varphi_1)]. \tag{A9}$$

It is now sufficient to add the two above inequalities, multiplied respectively by λ and $1-\lambda$, to obtain

$$\lambda F[\varphi_1]+(1-\lambda)F[\varphi_2]\geqslant F[\lambda\varphi_1+(1-\lambda)\varphi_2]$$

which establishes the convexity of F or its strict convexity if the inequalities are strict. □

Let us now prove the following theorem.

Theorem 2.

- *F convex* $\Longleftrightarrow$ $(\forall\varphi_1,\varphi_2\in X)\ F^{(2)}_{\varphi_1}[\varphi_2-\varphi_1]\geqslant 0$
- $(\forall\varphi_1,\varphi_2\neq\varphi_1\in X)\ F^{(2)}_{\varphi_1}[\varphi_2-\varphi_1]>0\Longrightarrow$ *F strictly convex.*

Proof. Let us first assume that F is convex and let φ_1 be an arbitrary function of X. We define $G[\varphi]=F[\varphi]-F^{(1)}_{\varphi_1}[\varphi-\varphi_1]$. It follows from the convexity of F and from theorem 1 that $(\forall\varphi\in X)\ G[\varphi]-G[\varphi_1]\geqslant 0$. We now perform a second-order Taylor–MacLaurin expansion of G about φ_1 (cf equation (A6)) which yields

$$G[\varphi_1+t\varphi]-G[\varphi]=\frac{t^2}{2}\left(F^{(2)}_{\varphi_1}[\varphi]+\epsilon(t)\|\varphi\|^2\right)\geqslant 0\qquad\lim_{t\to 0}\epsilon(t)=0. \tag{A10}$$

Taking the limit $t\to 0$ yields $F^{(2)}_{\varphi_1}[\varphi]\geqslant 0$.

Reciprocally, let φ_1 and φ_2 ($\varphi_2 \neq \varphi_1$) be two arbitrary functions of X. There must exist some $\varphi \in]\varphi_1, \varphi_2[$ such that (cf equation (A6))

$$F[\varphi_2] = F[\varphi_1] + F^{(1)}_{\varphi_1}[\varphi_2 - \varphi_1] + \tfrac{1}{2}F^{(2)}_{\varphi}[\varphi_2 - \varphi_1]. \tag{A11}$$

We define the (strictly) positive number ρ by $\varphi_2 - \varphi_1 = \rho(\varphi - \varphi_1)$ which allows us to rewrite (A11) as

$$F[\varphi_2] - F[\varphi_1] - F^{(1)}_{\varphi_1}[\varphi_2 - \varphi_1] = \frac{\rho^2}{2}F^{(2)}_{\varphi}[\varphi - \varphi_1].$$

Assuming the positiveness of the quadratic form of the rhs yields, by application of theorem 1, to the convexity of F and to its strict convexity in the case of strict positiveness. □

The last result we need is theorem 3:

Theorem 3.

- *If F is convex and has a local minimum at $\varphi_1 \in X$, then the minimum is global.*
- *If F is strictly convex then F has at most one minimum and this is a strict minimum.*

Proof. Let $\varphi = \varphi_1 + \delta\varphi$ be an arbitrary function in X and $0 \leqslant \lambda \leqslant 1$. Since F is convex

$$F[\varphi_1 + \lambda\delta\varphi] \leqslant (1 - \lambda)F[\varphi_1] + \lambda F[\varphi]$$

hence $F[\varphi_1 + \lambda\delta\varphi] - F[\varphi_1] \leqslant \lambda(F[\varphi] - F[\varphi_1])$. Assuming the existence of a local minimum of F at φ_1 implies that for some $0 < \lambda_0 < 1$ we have $F[\varphi_1 + \lambda_0\delta\varphi] - F[\varphi_1] \geqslant 0$ from which it follows that $F[\varphi] - F[\varphi_1] \geqslant 0$. Therefore the minimum is global. If F is strictly convex the same demonstration leads to the inequalities

$$0 \leqslant F[\varphi_1 + \lambda_0\delta\varphi] - F[\varphi_1] < \lambda_0\,(F[\varphi] - F[\varphi_1])$$

which prove that the minimum is strict and therefore unique. □

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