Contributions to Plasma Physics

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ORIGINAL ARTICLE

Thermodynamics of Non-Uniform Systems and Density Functional Theory

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Received: 28 September 2025 | **Revised:** 28 September 2025 | **Accepted:** 15 October 2025

Keywords: convexity | density functional theory | electrons and ions | functional | statistical mechanics | thermodynamics

ABSTRACT

The relationship of the thermodynamics for non-uniform systems and density functional theory is reviewed. It is observed that the relevant universal functionals are the same in both cases under appropriate conditions for thermodynamics. The variational context arises from the convexity properties of the functionals as represented by equilibrium statistical mechanics. Within thermodynamics a choice of local density or local chemical potential for the local variable can be made. In the latter case a "dual" form for density functional theory applies ("potential functional" theory). The special case of electrons and ions is considered, and the important condition of charge neutrality for thermodynamics is noted. These general results are extended to include the interatomic pair potential as an independent variable. Its conjugate is the equilibrium pair correlation function. As an application, the construction of a classical system to represent a given quantum system in terms of effective potentials is shown to result from the Euler equations of this extended variational formulation.

1 | Introduction

Time-independent density functional theory (DFT) is a method to describe the equilibrium properties of a given system—classical or quantum, at finite or zero temperature. Typically the systems considered are spatially inhomogeneous, for example, electrons in the presence of ions, or fluids with an interface. The properties of interest are expressed as functionals of the local density. Hence the approach requires the determination of the functional forms for the properties and the determination of the equilibrium local density for their evaluation. A central feature is its variational formulation so that non-perturbative approximations, albeit frequently uncontrolled, can be introduced simply. The historical development of DFT has followed two quite different paths, one for quantum systems at zero temperature (e.g., electrons in atoms, molecules, and solids) [1–3] and one for temperature-dependent classical non-uniform fluids (e.g., two-phase liquids, porous media) [4, 5]. The former has focused on the determination of the ground state energy whereas the latter has focused on the classical free energy at finite temperatures. Their unified formulation was established by Mermin who extended the original ground state theorems of Hohenberg and Kohn to finite temperatures for quantum systems [6]. This early history is briefly reviewed in references [4, 7].

In the classical development of DFT and its applications the method is understood as an approach within the thermodynamics of non-uniform systems, complemented by a variational context. The variational context identifies equilibrium states as "extremal states" often characterized by stability conditions originating in the second law of thermodynamics. A more formal origin occurs within axiomatic thermodynamics which requires that a fundamental thermodynamic potential (e.g., entropy or energy) is extensive and a convex or concave function (functional

for non-uniform systems) of its dependent variables [8, 9]. When the thermodynamics is given a foundation in statistical mechanics the variational context is provided by the convexity of the defining thermodynamic "potentials" as well as an explicit representation for those potentials [10]. Reference [9] gives a general and historical perspective on convexity in statistical mechanics and thermodynamics. Although this thermodynamic interpretation of DFT is implicit in Mermin's work it has not been generally recognized nor been found particularly useful within the zero-temperature ground state community; counter examples include [11, 12] and references therein. However, recent experiments and interests in "warm dense matter" [13] have motivated extensions of the zero-temperature methods for electrons to temperatures near the Fermi temperature. Hence the development and application of quantum DFT at finite temperatures is now a problem of significant interest [11, 14], and the potential relevance of its thermodynamic interpretation is of interest as well. A clear summary of the latter is provided by reference [15], and early exploitations are described in references [16, 17]. One objective here is to provide a unified introduction and overview of this initial work with comments and context.

In general the discussion here assumes a finite temperature. A distinction is made between "equilibrium" states and "thermodynamic states". The former are those for which the grand potential of the grand canonical ensemble exists (see Equation 1 below). Thermodynamic states have the additional stronger requirements of being extensive—fundamental global properties that are proportional to the volume for large systems, and fundamental potentials (entropy, internal energy) that are homogeneous first-order functionals of the extensive variables [4, 8]. Indeed, this property is essential for the axiomatic foundations of thermodynamics and its rich theoretical formalism. Furthermore, in this large system limit the thermodynamics based on statistical mechanics is generally the same for microcanonical, canonical, and grand canonical ensembles [9]. With the growing interest in quantum systems at finite temperatures recognizing the thermodynamic context for DFT provides the possibility for a wider class of functionals, their interrelationship, and practical applications. As an example, a variational principle "dual" to density functional theory is noted in the next section, obtained simply by a change of variables from the density to local chemical potential (sometimes referred to as "potential functional theory" [18]). However, it is first necessary to understand which systems qualify for such a thermodynamic context.

To set the stage it is useful to review the calculation of the thermodynamics for a non-uniform system described by the grand canonical ensemble. Consider first a one component system with Hamiltonian $\widehat{H}_N$ for N particles at inverse temperature β and *local* chemical potential $\mu(\mathbf{r})$ in volume V. The grand potential from which all thermodynamic properties follow is defined by [19]

$$\beta\Omega(\beta, V|\mu) \equiv -\ln \sum_{N=0}^{\infty} Tr^{(N)} e^{-\beta\left(\widehat{H}_N - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right)}, \tag{1}$$

where $\widehat{n}(\mathbf{r})$ is the number density operator (see below), and the trace is taken over each N particle Hilbert space of properly symmetrized states (for Bosons or Fermions). The system is spatially inhomogeneous due to an external single particle potential $\phi_{ext}(\mathbf{r})$ which shifts the global chemical potential to $\mu(\mathbf{r}) \equiv \mu - \phi_{ext}(\mathbf{r})$. Thus, the "thermodynamic" variables of the system are the inverse temperature β, the volume V, and local chemical potential $\mu(\mathbf{r})$. The function (functional) of these variables, $\Omega(\beta, V|\mu)$, is entirely characterized by the Hamiltonian $\widehat{H}_N$. This means that the functional form is universal for all choices of $\beta, V, \mu(\mathbf{r})$—only the values of the function (functional) change. In particular, the functional dependence on $\mu(\mathbf{r})$ is universal for all external potentials for which the right side of (1) exists. These are the equilibrium states. Attention is focused here on systems for which, in addition, the thermodynamic limit exists in the sense $\lim_{V\to\infty} \Omega(\beta, V|\mu) = V\omega(\beta|\mu)$, that is, the system becomes extensive for sufficiently large size. Conditions for the thermodynamic limit (including thermodynamic stability and equivalence of equilibrium ensembles) have been established for the case $\phi_{ext}(\mathbf{r}) = 0$. They include stability (lower bound for $\widehat{H}_N$ spectrum proportional to N) and tempering (interactions between groups of particles weaken suffiently fast with separation). A counter example is provided by a system of electrons with Coulomb repulsion confined by a cluster of localized ions for which $\Omega(\beta, V|\mu)$ exists, but the system is not extensive unless supplemented by an additional condition of charge neutrality.

The first objective here is to provide a brief summary of the thermodynamics for a non-uniform system based in equilibrium quantum statistical mechanics, and to show its connection to Mermin's formulation of DFT. It is a straightforward extension of the equilibrium formalism for uniform systems to that for a non-uniform system. Many of the results here summarize earlier discussions in [11] and [12], studies of scaling properties at finite temperatures. The fundamental function is the grand potential $\Omega = \Omega(\beta, V|\mu)$ considered as a function of the temperature $T = 1/k_B\beta$, the volume V, and a functional of the local chemical potential $\mu(\mathbf{r})$. In this representation the local density

$$n(\mathbf{r}, \beta, V|\mu) = -\frac{\delta\Omega(\beta, V|\mu)}{\delta\mu(\mathbf{r})} \tag{2}$$

is a derived quantity, also expressed in terms of these thermodynamic variables. Density functionals appear as a consequence of changing variables from $\mu(\mathbf{r})$ to the local density field $n(\mathbf{r})$. This is effected by a Legendre transformation [20, 21].

$$F(\beta, V|n) = \Omega(\beta, V|\mu) + \int d\mathbf{r} n(\mathbf{r}, \beta, V|\mu)\mu(\mathbf{r}) \tag{3}$$

whereby the grand potential $\Omega(\beta, V|\mu)$ as a functional of $\mu(\mathbf{r})$ is replaced by its "dual" thermodynamic potential, the free energy $F(\beta, V|n)$ as a functional of $n(\mathbf{r})$. In both cases all thermodynamic properties of the system (e.g., entropy, temperature) can be defined from the fundamental thermodynamic potential, $\Omega(\beta, V|\mu)$ or $F(\beta, V|n)$. The existence and uniqueness of this change of variables follows from the concavity of the grand potential. The value of the equilibrium density is also shown to be the extremum of a density functional whose convexity follows from that of the free energy. This constitutes the equivalence with Mermin's formulation. The conjugate roles of $n(\mathbf{r})$ and $\mu(\mathbf{r})$ as simply alternative choices of thermodynamic variables suggests that a variational principle in terms of $\mu(\mathbf{r})$ should be possible in the same way. This is in fact demonstrated below. In the usual case one is given $\mu(\mathbf{r})$ and the variational principle gives a recipe for calculating the equilibrium density. In the

alternative formulation for a given local density $n(\mathbf{r})$ field the variational principle gives a recipe to find the associated $\mu(\mathbf{r})$.

The thermodynamic context allows the introduction of other functionals such as entropy and internal energy. A wide range of interrelationships, inequalities and other identities follow directly from the thermodynamics of non-uniform systems. Some examples are provided here for illustration. This broader context for DFT may be of use in constructing or confining practical applications, particularly since the density functionals are now parameterized by temperature as well.

The above analysis applies for fixed interparticle pair potential. Another objective here is to extend the interpretation of the grand potential to be considered a functional of both the external potential (or $\mu(\mathbf{r})$) and the internal pair potential $\phi(\mathbf{r},\mathbf{r}')$. The "thermodynamic" variable conjugate to $\phi(\mathbf{r},\mathbf{r}')$ is the pair correlation function $g(\mathbf{r},\mathbf{r}')$. Convexity properties for functionals of ϕ and of g follow in a manner similar to those of μ and of n, and two variational formulations are established, one for determining n, g for given μ, ϕ, and one for determining μ, ϕ for given n, g. An application of the latter case is illustrated by a definition of a classical system with the same thermodynamics and structure as a chosen quantum system. The motivation is to allow application of classical methods for strong coupling conditions (e.g., molecular dynamics, liquid state theory) to inherently quantum problems. This is accomplished through effective classical properties μ_c, ϕ_c chosen to replicate the quantum system. It is shown that these effective properties are determined via the dual variational form of the extended interpretation presented here. More specifically, for given quantum properties n, g the effective classical properties μ_c, ϕ_c are determined by the extremum Euler equations.

The special case of charged particle systems, for example, a system of electrons and ions, is noted specifically. The conditions discussed above of stability and tempering are more difficult to address in this case, and extensivity requires the additional constraint of charge neutrality. Nevertheless, such systems have a thermodynamic limit [22] based on the two-component grand potential

$$\beta\Omega(\beta,\mu_e,\mu_i,V) \equiv -\ln \sum_{N_i=0}^{\infty} Tr^{(N_i)} \sum_{N_e=0}^{\infty} Tr^{(N_e)} e^{-\beta\left(\hat{H}_e+\hat{H}_i+\hat{H}_{ei}-\mu_e N_e-\mu_i N_i\right)}, \quad (4)$$

here $\hat{H}_e$, $\hat{H}_i$, and $\hat{H}_{ei}$ are the Hamiltonians for the electrons, ions, and their interaction respectively. All charge—charge interactions are Coulomb. The corresponding non-uniform system in the presence of external single particle potentials coupling to the electron and ions define a corresponding inhomogeneous system thermodynamics. Convexity of the free energy functional with respect to both densities leads to a variational formulation but with the additional restriction of charge neutrality. This two-component DFT form has been exploited by Dharma-wardana and Perrot [23] for a hydrogen plasma. The thermodynamic limit for this system is still well-defined.

For practical purposes it is often a good approximation to consider the ions as classical particles (Born-Oppenheimer approximation). Then the average over the electrons can be formally taken for each ion configuration, giving rise to an effective ion potential energy surface chacterized by the electron gas grand potential $\Omega_e(\beta,V|\mu_e)$. The chosen ion configuration now appears as an external potential for the electrons. The remaining ion average is performed classically (e.g., via molecular dynamics). This is the inhomogeneous electron gas addressed by the founders of DFT [1, 6]—interacting electrons in an external potential. Here, however, there can be no connection to a thermodynamic description for $\Omega_e(\beta,V|\mu_e)$ since the Hamiltonian for the electrons alone, $\hat{H}_e$, does not define a thermodynamic functional. In particular, the necessary condition of charge neutrality does not apply except for a special class of external potentials. The formalism of DFT is still applicable, but it is not justified to give it a thermodynamic context nor to use thermodynamic identities.

The relationship to thermodynamics can be recovered by a rearrangement of the electron—ion Hamiltonian to write it as the sum of an electronic jellium, an ionic jellium, and their interaction. A jellium consists of a system of charges interacting with each other and a uniform neutralizing background. In contrast to the electron gas, the thermodynamic limit for jellium has been proved [24]. The evaluation of (4) is then represented in terms of the electronic jellium and classical ionic jellium (called a one component plasma). The electronic average again is formally performed for each ion configuration giving rise to an electron jellium grand potential $\Omega_{eJ}(\beta,V|\mu_{eJ})$. This functional defines a proper thermodynamics such that the full advantage of that formalism can now be exploited. It is noted however that the thermodynamics of jellium is somewhat irregular in several respects.

The references here are not complete and are chosen selectively only to give access to the more extensive literature on the topic of thermodynamics and DFT. This work is dedicated to Professor Michael Bonitz to honor his extensive contributions to the physics of charged particles, guidance to colleagues, and mentorship of students.

2 | Equilibrium Statistical Mechanics, Thermodynamics for A Non-Uniform System, and DFT

Thermodynamics can be presented as a stand-alone theory based on a few axioms [8]. However, its foundation in the ensembles of equilibrium statistical mechanics provides both a basis for the chosen axioms, and a detailed prescription for the calculation of formal functions of these axioms in terms of the microscopic properties of the particular system considered. This origin for thermodynamics is well described for uniform systems in many text books [19]. The general description of thermodynamics for non-uniform quantum systems follows as a straightforward extension of the uniform case, but has had far less attention. As a consequence, perhaps, the growing treatment of non-uniform quantum systems at finite temperatures by DFT [14] generally has not made the connection to thermodynamics more explicit. The objective of this section is to close this gap.

There are further advantages to recognizing the connection of DFT to thermodynamics. The statistical mechanical representation provides a formal means to calculate the relevant

functionals, as well as related structural properties (e.g., correlation functions) beyond the content of thermodynamics. The thermodynamic potentials are generating functionals for these structural properties, as noted below.

2.1 | Thermodynamic Variables $\beta, V, \mu(\mathbf{r})$

For simplicity a one component system of identical particles in a volume V is considered. The Hamiltonian for the isolated system is the sum of their kinetic energies $\hat{K}$ and interparticle potential energy $\hat{U}$. The latter need not be pair-wise additive, but is assumed translationally invariant. In addition, there is an external potential $\phi_{ext}(\mathbf{r})$ that couples to each of the particles.

$$\hat{H} = \hat{K} + \hat{U}, \quad \hat{\Phi}_{ext} = \sum_{i=1}^{N} \phi_{ext}(\hat{\mathbf{r}}_i), \tag{5}$$

where $\hat{\mathbf{r}}_i$ is the position operator for the ith particle. The boundary conditions confining the particles can be assumed to be incorporated in this external potential. Consider the case for which these boundary conditions allow exchange of particles and energy with their surroundings. Within equilibrium statistical mechanics the equilibrium state is described by the grand canonical ensemble whose statistical density operator is

$$\hat{\rho}_G = e^{\beta\Omega(\beta,V|\mu)} e^{-\beta\left(\hat{H}-\mu N+\hat{\Phi}_{ext}\right)} = e^{\beta\Omega(\beta,V|\mu)} e^{-\beta\left(\hat{H}-\int d\mathbf{r}\mu(\mathbf{r})\hat{n}(\mathbf{r})\right)}, \tag{6}$$

where $\hat{n}(\mathbf{r})$ is the particle number density operator

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \hat{\mathbf{r}}_i). \tag{7}$$

The thermodynamic parameters are the temperature $T = 1/k_B\beta$, volume V, and local chemical potential $\mu(\mathbf{r}) = \mu - \phi_{ext}(\mathbf{r})$. The external potential has been combined with the global chemical potential μ by the relationship

$$\mu N - \hat{\Phi}_{ext} = \int d\mathbf{r}\mu(\mathbf{r})\hat{n}(\mathbf{r}), \quad \mu(\mathbf{r}) = \mu - \phi_{ext}(\mathbf{r}). \tag{8}$$

The presence of an external potential $\phi_{ext}(\mathbf{r})$ implies that the system is inhomogeneous (lacks translational invariance). Hence one of the thermodynamic variables, $\mu(\mathbf{r})$, is local.

All thermodynamic properties are defined in terms of the grand potential $\Omega(\beta, V|\mu)$ defined by normalization of $\hat{\rho}_G$

$$\sum_{N=0}^{\infty} Tr^{(N)} \hat{\rho}_G = 1, \tag{9}$$

or

$$\Omega(\beta, V|\mu) \equiv -\beta^{-1} \ln \sum_{N=0}^{\infty} Tr^{(N)} e^{-\beta\left(\hat{H}-\int d\mathbf{r}\mu(\mathbf{r})\hat{n}(\mathbf{r})\right)}. \tag{10}$$

The traces are taken over N-particle Hilbert space with an appropriate restriction on the symmetry of states (Bosons or Fermions). It is a function of β and V, and a functional of $\mu(\mathbf{r})$ which are the independent thermodynamic variables specifying the macroscopic state of the system.

A proper thermodynamics is associated with $\Omega(\beta, V|\mu)$ whenever the latter exists and is extensive, that is, $\Omega(\beta, V|\mu) \to -Vp(\beta|\mu)$ for $N \to \infty$, $V \to \infty$ at constant N/V. The equation of state is defined by

$$p(\beta|\mu)V \equiv -\Omega(\beta, V|\mu), \tag{11}$$

where $p(\beta|\mu)$ is the equilibrium pressure. It is an intensive (volume independent) property and therefore depends only on β and $\mu(\mathbf{r})$. It is equivalent to that calculated in the microcanonical and canonical ensembles. Sufficient conditions have been proved in the uniform case [25]. They include H stability which requires that the Hamiltonian for N particles be bounded

$$\overline{H}_N > -\frac{B}{N}, \tag{12}$$

for some constant $B \geq 0$ and all N. In addition, the interactions should satisfy a tempering condition that the interaction between groups of distant particles must be negligible. For example, if the potential energy is the sum of pairwise interactions $u(r_{ij})$ then there must exist a $\lambda > d$ (the dimension) and $A \geq 0$, $r_0 > 0$ such that

$$u(r_{ij}) \leq A r_{ij}^{-\lambda}, \quad \text{for } r_{ij} \geq r_0. \tag{13}$$

The extension of the uniform case to non-uniform states with $\mu \to \mu(\mathbf{r})$ effectively defines a class of external potentials for which thermodynamics is still meaningful. This has not been explored here but by "continuity" it is expected to be large.

Other thermodynamic properties follow directly from first derivatives

$$\left.\frac{\partial\Omega(\beta, V|\mu)}{\partial V}\right|_{\mu,\beta} = -p(\beta|\mu), \quad \left.\frac{\delta\Omega(\beta, V|\mu)}{\delta\mu(\mathbf{r})}\right|_{V,\beta} = -n(\mathbf{r}, \beta|\mu) \tag{14}$$

$$\left.\frac{\partial\Omega(\beta, V|\mu)}{\partial\beta}\right|_{\mu,V} = \beta^{-1}\left(U(\beta, V|\mu) + p(\beta|\mu)V - \int d\mathbf{r} n(\mathbf{r}, \beta|\mu)\mu(\mathbf{r})\right). \tag{15}$$

Here the local number density $n(\mathbf{r}, \beta|\mu)$ and the internal energy $U(\beta, V|\mu)$ are identified as equilibrium averages of the corresponding underlying operators

$$n(\mathbf{r}, \beta|\mu) \equiv \sum_{N=0}^{\infty} Tr^{(N)} \hat{\rho}_G \hat{n}(\mathbf{r}), \quad U(\beta, V|\mu) \equiv \sum_{N=0}^{\infty} Tr^{(N)} \hat{\rho}_G \hat{H}. \tag{16}$$

The internal energy $U(\beta, V|\mu)$ is sometimes referred to as the *intrinsic* internal energy since it does not include the external potential energy. The latter is incorporated here in the definition of the local chemical potential $\mu(\mathbf{r})$, equation (8). Finally, the entropy functional is defined by

$$TS(\beta, V|\mu) \equiv U(\beta, V|\mu) + p(\beta|\mu)V - \int d\mathbf{r} n(\mathbf{r}, \beta|\mu)\mu(\mathbf{r}). \tag{17}$$

Note that this is consistent with the microscopic average

$$S(\beta, V|\mu) = -k_B \sum_{N=0}^{\infty} Tr^{(N)} \hat{\rho}_G (\ln \hat{\rho}_G). \tag{18}$$

Equation (15) becomes

$$\beta \frac{\partial \Omega(\beta, V|\mu)}{\partial \beta}\Big|_{\mu,V} = TS(\beta, V|\mu). \tag{19}$$

These first derivative definitions lead directly to the familiar results of thermodynamics. For example using (11–15) gives directly the Gibbs-Duhem equation

$$V\delta p(\beta|\mu) = \int d\mathbf{r} n(\mathbf{r}, \beta|\mu)\delta\mu(\mathbf{r}) + S(\beta, V|\mu)dT. \tag{20}$$

Then, the differential of (17) gives the first law of thermodynamics

$$T\delta S(\beta, V|\mu) = \delta U(\beta, V|\mu) + p(\beta|\mu)dV - \int d\mathbf{r}\mu(\mathbf{r})\delta n(\mathbf{r}, \beta|\mu). \tag{21}$$

The second law follows from the convexity properties discussed below.

In summary, complete thermodynamic information about the system is given by the grand potential $\Omega(\beta, V|\mu)$ as a function or functional of its thermodynamic variables.

2.2 | Thermodynamic Variables $\beta, V, n(\mathbf{r})$

An equivalent alternative thermodynamic description can be given by a change of variables from $\beta, V, \mu(\mathbf{r})$ to variables $\beta, V, n(\mathbf{r})$. The relationship of $n(\mathbf{r})$ to $\mu(\mathbf{r})$ is defined by (14). This is a one-to-one relationship (as follows from the strict concavity of $\Omega(\beta, V|\mu)$, see Appendix A) and so it is invertible to give $\mu(\mathbf{r}) = \mu(\mathbf{r}, \beta|n)$ as a functional of $n(\mathbf{r})$. A new thermodynamic potential $F(\beta, V|n)$ giving all thermodynamic information in terms of the new variables is obtained from $\Omega(\beta, V|\mu)$ by the Legendre transformation [20, 26]

$$\begin{aligned} F(\beta, V|n) &= \left[\Omega(\beta, V|\mu) - \int d\mathbf{r}\frac{\delta\Omega(\beta|\mu)}{\delta\mu(\mathbf{r})}\Big|_{V,\beta}\mu(\mathbf{r})\right]_{\mu(\mathbf{r},\beta|n)} \\ &= \Omega(\beta, V|\mu)|_{\mu(\mathbf{r},\beta|n)} + \int d\mathbf{r} n(\mathbf{r})\mu(\mathbf{r}, \beta|n). \end{aligned} \tag{22}$$

$F(\beta, V|n)$ will be referred to as the thermodynamic potential dual to $\Omega(\beta, V|\mu)$. The interpretation of $F(\beta, V|n)$ is obtained using (11) and (17)

$$\begin{aligned} F(\beta, V|n) &= -p(\beta|\mu)|_{\mu(\mathbf{r},\beta|n)}V + \int d\mathbf{r} n(\mathbf{r})\mu(\mathbf{r}, \beta|n) \\ &= [U(\beta, V|\mu) - TS(\beta, V|\mu)]_{\mu(\mathbf{r},\beta|n)} \\ &\equiv U(\beta, V|n) - TS(\beta, V|n) \end{aligned} \tag{23}$$

Here and below for simplicity the degenerate notation $X(\beta, V|n) \equiv X(\beta, V|\mu)|_{\mu(\mathbf{r},\beta|n)}$ is used. Equation (23) identifies $F(\beta, V|n)$ as the intrinsic Helmholtz free energy ("intrinsic" since U is the intrinsic internal energy as discussed above).

The functional derivative with respect to $n(\mathbf{r})$ gives the inverse of the relationship between $\mu(\mathbf{r})$ and $n(\mathbf{r})$

$$\frac{\delta F(\beta, V|n)}{\delta n(\mathbf{r})}\Big|_{V,\beta} = \mu(\mathbf{r}, \beta|n). \tag{24}$$

Thus (14) and (24) both express the same unique relationship of the pair of functions $\mu(\mathbf{r})$ and $n(\mathbf{r})$.

It is useful to note the microscopic representation of $F(\beta, V|n)$ in terms of the statistical density operator (6) using the definition of $\Omega(\beta, V|\mu)$ in (11)

$$F(\beta, V|n) = \sum_{N=0}^{\infty} Tr^{(N)}\widehat{\rho}_G\left(\beta^{-1}\ln\widehat{\rho}_G + \widehat{H}\right). \tag{25}$$

Here it is understood the $\mu(\mathbf{r}) = \mu(\mathbf{r}, \beta|n)$ in $\widehat{\rho}_G$ such that the statistical density operator gives the specified average density $n(\mathbf{r})$. It is seen that the thermodynamic free energy here is the same as the universal functional $F[n]$ defined by Mermin [6] in his construction of DFT. This is an initial indication that DFT and local thermodynamics may be the same.

Together with (14) the first derivatives of $F(\beta, V|n)$ follow directly from (22)

$$\frac{\partial F(\beta, V|n)}{\partial V}\Big|_{n,\beta} = -p(\beta|n), \quad \frac{\partial F(\beta, V|n)}{\partial \beta}\Big|_{n,V} = \frac{T}{\beta}S(\beta, V|n). \tag{26}$$

The first law (21) is recovered from the variation of (23). All thermodynamic properties are now obtained from $F(\beta, V|n)$ in terms of the variables β, V, and $n(\mathbf{r})$.

2.3 | Convexity and Variational Forms for Thermodynamics

The two thermodynamic potentials $\Omega(\beta, V|\mu)$ and $F(\beta, V|n)$ have important properties arising from their origin within statistical mechanics as representing "extremal" or "most probable" states. For example, define the functional of statistical density operators normalized to unity $\widehat{\rho}$ by

$$\Omega[\widehat{\rho}] \equiv \sum_{N=0}^{\infty} Tr^{(N)}\widehat{\rho}\left(\beta^{-1}\ln\widehat{\rho} + \widehat{H} - \int d\mathbf{r}\widehat{n}(\mathbf{r})\mu(\mathbf{r})\right). \tag{27}$$

It follows that $\widehat{\rho} = \widehat{\rho}_G$ provides a lower bound, whose value is the grand potential Ω [6]

$$\Omega[\widehat{\rho}_G] = \Omega(\beta, V|\mu) < \Omega[\widehat{\rho}] \tag{28}$$

Similar inequalities can be obtained for the entropy (18) and free energy (25) by appropriately constrained variation of $\widehat{\rho}$. At the level of thermodynamics these origins are reflected by the fact that $\beta\Omega(\beta, V|\mu)$ is the extremum of a strictly concave functional of β and $\mu(\mathbf{r})$, and $\beta F(\beta, V|n)$ is the extremum of a strictly convex functional of β and $n(\mathbf{r})$. The terminology "strict" means that it has a unique extremum. A brief overview of the proof with references is given in Appendix A.

These convexity properties imply a variational formulation of thermodynamics. To illustrate, suppose the functional $F(\beta, V|n)$ is considered and it is desired to find the appropriate density $n_e(\mathbf{r})$ for its equilibrium evaluation, given a specific $\mu(\mathbf{r})$. Construct the functional

$$\Omega_\mu(\beta, V|n) \equiv F(\beta, V|n) - \int d\mathbf{r} n(\mathbf{r})\mu(\mathbf{r}). \tag{29}$$

Here $n(\mathbf{r})$ and $\mu(\mathbf{r})$ are independent functions. Since $F(\beta, V|n)$ is a convex functional of $n(\mathbf{r})$ so is $\Omega_\mu(\beta, V|n)$. Its minimum is given by the Euler equation

$$\left.\frac{\delta\Omega_\mu(\beta, V|n)}{\delta n(\mathbf{r})}\right|_{n_e} = 0, \tag{30}$$

or more explicitly

$$\left.\frac{\delta F(\beta, V|n)}{\delta n(\mathbf{r})}\right|_{n_e} = \mu(\mathbf{r}). \tag{31}$$

Furthermore, evaluation of $\Omega_\mu(\beta, V|n)$ at the density $n_e(\mathbf{r})$ that satisfies (31) gives the grand potential

$$\Omega_\mu\big(\beta, V|n_e\big) = \Omega(\beta, V|\mu). \tag{32}$$

Hence the extremum of $\Omega_\mu(\beta, V|n)$ gives the equilibrium density and the equilibrium thermodynamic potential.

A dual variational principle can be given in terms of $\mu(\mathbf{r})$. Define the functional

$$F_n(\beta, V|\mu) \equiv \Omega(\beta, V|\mu) + \int d\mathbf{r} n(\mathbf{r})\mu(\mathbf{r}). \tag{33}$$

Again, $n(\mathbf{r})$ and $\mu(\mathbf{r})$ are independent functions. It is desired to find the equilibrium value $\mu_e(\mathbf{r})$ for a given $n(\mathbf{r})$. Since $\Omega(\beta, V|\mu)$ is a concave functional of $\mu(\mathbf{r})$ so is $F_n(\beta, V|\mu)$. Its maximum is given by the Euler equation

$$\left.\frac{\delta\Omega(\beta, V|\mu)}{\delta\mu(\mathbf{r})}\right|_{\mu_e} = -n(\mathbf{r}), \tag{34}$$

which is the equilibrium condition (14). Furthermore, the evaluation of $F_n(\beta, V|\mu)$ at the solution to this equation, $\mu_e(\mathbf{r})$ is the equilibrium free energy functional

$$F_n\big(\beta, V|\mu_e\big) = F(\beta, V|n) \tag{35}$$

Thus, the extremum of $F_\mu(\beta, V|\mu)$ gives the equilibrium local chemical potential and the equilibrium thermodynamic potential.

2.4 | Equivalence of DFT and Thermodynamics

The variational principle based on (29) is precisely the traditional density functional theory [11, 14]. Its equivalent dual, based on (33), is the "potential" functional theory. Their origin in equilibrium statistical mechanics provides definitions for the functionals $\Omega(\beta, V|\mu)$ and $F(\beta, V|n)$ as ensemble averages whose dependence on the thermodynamic variables is explicit. Thus, for example, derivatives with respect to β can be calculated directly from these definitions or can be obtained from the thermodynamic formalism. As an example, (19) follows directly from the microscopic definitions of the local number density $n(\mathbf{r}, \beta|\mu)$, internal energy $U(\beta, V|\mu)$, and entropy $S(\beta, V|\mu)$. Then from the definition of $F(\beta, V|n)$ as the Legendre transform of $\Omega(\beta, V|\mu)$ the β derivative of $F(\beta, V|n)$ in (26) is obtained

$$\left.\frac{\partial F(\beta, V|n)}{\partial\beta}\right|_{n,V} = \frac{T}{\beta}S(\beta, V|n). \tag{36}$$

The corresponding thermodynamic route is obtained from the identification $\Omega(\beta, V|\mu) = -p(\beta|\mu)V$ and differentiating the Legendre transform to get

$$\left.\frac{\partial F(\beta, V|n)}{\partial\beta}\right|_{n,V} = -\left.\frac{\partial p(\beta|\mu)}{\partial\beta}\right|_{\mu,V} V = \frac{T}{\beta}S(\beta, V|n). \tag{37}$$

The second equality follows from the Gibbs-Duhem equation (20). It is seen that the thermodynamic context opens the door to a wide range of properties and relationships among first derivatives of the functionals that are central to finite temperature DFT (e.g., Maxwell relations, thermodynamic response functionals).

Second derivatives of a thermodynamic potential provide properties that are often more experimentally accessible than those of first derivatives. For example, the second derivative of $\beta F(\beta, V|n)$ at constant n, V is proportional to the specific heat at constant volume

$$\begin{aligned} C_V(\beta, V|n) &\equiv \left.\frac{\partial U(\beta, V|n)}{\partial T}\right|_{n,V} = \left.\frac{\partial}{\partial T}(F(\beta, V|n) + TS(\beta, V|n))\right|_{n,V} \\ &= \left.\frac{\partial}{\partial T}\left(F(\beta, V|n) + \beta\left.\frac{\partial F(\beta, V|n)}{\partial\beta}\right|_{n,V}\right)\right|_{n,V} \\ &= -\frac{\beta}{T}\frac{\partial^2\beta F(\beta, V|n)}{\partial\beta^2}. \end{aligned} \tag{38}$$

Second derivatives with respect to the local variables $\mu(\mathbf{r})$ or $n(\mathbf{r})$ provide thermodynamic properties of structure. For example, the density response function $\chi\big(\mathbf{r}, \mathbf{r}'; \beta, V|\mu\big)$ is obtained from

$$\left.\frac{\delta^2\Omega(\beta, V|\mu)}{\delta\mu(\mathbf{r})\delta\mu(\mathbf{r}')}\right|_{\beta,V} = -\frac{\delta n(\mathbf{r})}{\delta\mu(\mathbf{r}')} \equiv -\chi\big(\mathbf{r}, \mathbf{r}'; \beta, V|\mu\big). \tag{39}$$

Use of the microscopic definition for $\Omega(\beta, V|\mu)$, (10), gives the representation as an equilibrium correlation function

$$\chi\big(\mathbf{r}, \mathbf{r}'; \beta V|\mu\big) = -\frac{1}{\beta}\int_0^\beta d\beta' \big\langle e^{\beta' H}\delta\widehat{n}(\mathbf{r})e^{-\beta' H}\widehat{n}\big(\mathbf{r}'\big); \beta|\mu\big\rangle. \tag{40}$$

The second derivative of the free energy is the inverse of this response function

$$\left.\frac{\delta^2 F(\beta, V|n)}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{\beta,V} = \frac{\delta\mu(\mathbf{r})}{\delta n(\mathbf{r}')} = \chi^{-1}\big(\mathbf{r}, \mathbf{r}'; \beta, V|\mu\big). \tag{41}$$

The inverse is defined as

$$\int d\mathbf{r}''\chi^{-1}\big(\mathbf{r}, \mathbf{r}''; \beta, V|\mu\big)\chi\big(\mathbf{r}'', \mathbf{r}'; \beta, V|\mu\big) = \delta\big(\mathbf{r} - \mathbf{r}'\big) \tag{42}$$

If $F(\beta, V|n)$ is separated into its non-interacting (ideal) part and a remainder, the contributions of the latter to the density derivatives are called "direct correlation functions". In the classical limit, the identity (42) becomes the Ornstein-Zernike equation relating the pair and direct correlation functions, a fundamental component of classical liquid theory.

2.5 | Convexity and Stability Conditions

The stability criteria of thermodynamics arise from the convexity or concavity of a chosen thermodynamic potential. For example,

$\beta\Omega(\beta, V|\mu)$ is a concave function (functional) of β ($\mu(\mathbf{r})$), as discussed in Appendix A. Then, for example

$$\left.\frac{\partial^2 \beta\Omega(\beta, V|\mu)}{\partial\beta^2}\right|_{\mu,V} < 0, \tag{43}$$

or equivalently

$$\left.\frac{\partial^2 p(\beta, V|\mu)}{\partial T^2}\right|_{\mu,V} > 0. \tag{44}$$

Convexity properties of other thermodynamic potentials can be obtained from their origins as Legendre transforms. To see this consider the generic Legendre transform to change variables from a to b

$$B(b) = A(a) + ab, \quad \frac{dA(a)}{da} = -b, \quad \frac{dB(b)}{db} = a. \tag{45}$$

It follows that

$$\frac{d^2A(a)}{da^2} = -\frac{db}{da} = -\left(\frac{d^2B(b)}{db^2}\right)^{-1}. \tag{46}$$

If $d^2A(a)/da^2 > 0$ then $A(a)$ is strictly convex and $B(b)$ is strictly concave—the Legendre transform reverses convexity of the original function. As an example, rewrite (17) as

$$U(\beta, V|\mu) = \Omega(\beta, V|\mu) - \int d\mathbf{r}\frac{\delta\Omega(\beta, V|\mu)}{\delta\mu(\mathbf{r})}\mu(\mathbf{r}) - T\left.\frac{d\Omega(\beta, V|\mu)}{dT}\right|_{\mu,V} \tag{47}$$

where use has been made of (19) in the form

$$\left.\frac{d\Omega(\beta, V|\mu)}{dT}\right|_{\mu,V} = -S(\beta, V|\mu). \tag{48}$$

It is seen that (47) is the Legendre transform for a change of variables $\beta, \mu(\mathbf{r}), V$ to $S, n(\mathbf{r}), V$ giving the internal energy as a function of the latter variables $U(\beta, V|\mu) \to U(S, V|n)$. Now, since $\Omega(\beta, V|\mu)$ is a concave function of β and concave functional of $\mu(\mathbf{r})$ it follows that $U(S, V|n)$ is a convex function of S and convex functional of $n(\mathbf{r})$. For example,

$$\left.\frac{d^2U(S, V|n)}{dS^2}\right|_{n,V} = \left.\frac{dT}{dS}\right|_{n,V} > 0. \tag{49}$$

The entropy is an increasing function of the temperature at constant n, V.

As a second example, rewrite (23) as

$$F(\beta, V|n) = U(S, V|n) - S\frac{dU(S, V|n)}{dS}. \tag{50}$$

This is seen to be the Legendre transformation for a change of variables $S, n(\mathbf{r}), V$ to $T, n(\mathbf{r}), V$. Since $U(S, V|n)$ is a convex function of S then $F(\beta, V|n)$ is a concave function of T

$$\frac{d^2F(\beta, V|n)}{dT^2} = -\frac{dS(\beta, V|n)}{dT} < 0. \tag{51}$$

Use has been made of (36) in the first equality. Equation (51) agrees with (49). Finally, the positivity of the specific heat in (38) is confirmed

$$C_V(\beta, V|n) = -\frac{\beta}{T}\frac{\partial^2\beta F(\beta, V|n)}{\partial\beta^2} = T\frac{dS(\beta, V|n)}{dT} > 0. \tag{52}$$

The analysis here has been thermodynamic, but as has been stressed above, its foundation in statistical mechanics often provides explicit microscopic representations. In the present case, (18) can be differentiated directly to get the same result,

$$\frac{dS(\beta, V|\mu)}{dT} = \frac{1}{T^2}\sum_{N=0}^{\infty} Tr^{(N)}\hat{\rho}_G\left(\ln\hat{\rho}_G - \left\langle\ln\hat{\rho}_G\right\rangle\right)^2 > 0. \tag{53}$$

3 | Electrons and Ions

Now consider a system of N_e electrons and N_i ions of charge number Z. The system is at equilibrium described by the grand ensemble with thermodynamic parameters V, β, μ_e, μ_i (volume, inverse temperature, chemical potentials). The Hamiltonian operator is given by

$$\hat{H} = \hat{H}_e + \hat{H}_i + \hat{U}_{ei}, \tag{54}$$

where the Hamiltonian for the electrons, $\hat{H}_e$, the ions, $\hat{H}_i$, and their interaction $\hat{U}_{ei}$ are

$$\hat{H}_e = \sum_{\alpha=1}^{N_e}\frac{\hat{p}_{e\alpha}^2}{2m_e} + \frac{1}{2}e^2\int d\mathbf{r}d\mathbf{r}'\frac{\hat{n}_e(\mathbf{r})\hat{n}_e(\mathbf{r}') - \hat{n}_e(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{55}$$

$$\hat{H}_i = \sum_{\alpha=1}^{N_i}\frac{\hat{p}_{i\alpha}^2}{2m_i} + \frac{1}{2}Z^2e^2\int d\mathbf{r}d\mathbf{r}'\frac{\hat{n}_i(\mathbf{r})\hat{n}_i(\mathbf{r}') - \hat{n}_i(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{56}$$

$$\hat{U}_{ei} = -Ze^2\int d\mathbf{r}d\mathbf{r}'\frac{\hat{n}_i(\mathbf{r})\hat{n}_e(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{57}$$

The corresponding grand potential is

$$\beta\Omega(\beta, \mu_e, \mu_i, V) \equiv -\ln\sum_{N_e=0,N_i=0}^{\infty} Tr^{(N_e)}Tr^{(N_i)}e^{-\beta\left(\hat{H}-\mu_eN_e-\mu_iN_i\right)}. \tag{58}$$

Several problems are now evident for the special case with Coulomb interactions. H stability is not self-evident due to the singular electron-ion Coulomb divergence at small r_{ij}. In fact, this precludes the existence of the grand potential for classical systems, but the bound for quantum Fermions can be proved [22], so $\beta\Omega(\beta, \mu_e, \mu_i, V)$ converges in this case. The additional condition of tempering is not satisfied for the Coulomb interaction. However, for charge neutral systems it was shown that screening effects due to the long range nature of the Coulomb interactions lead to effective interactions that are tempered. Consequently, the thermodynamic limit for a charge neutral system of electrons and ions exists [22]. Furthermore the grand potential is a concave function of its chemical potentials and the free energy is a convex function of the density, just as for the shorter ranged particles of the last section.

The objective here is to extend the discussion to inhomogeneous systems, as in the last section, and to address the differences due to the constraint of charge neutrality. Consider two external single-particle potentials coupling to the electrons and ions, respectively

$$\hat{\Phi}_{ext} = \int d\mathbf{r}\big(\hat{n}_e(\mathbf{r})\phi_e(\mathbf{r}) + \hat{n}_i(\mathbf{r})\phi_i(\mathbf{r})\big). \tag{59}$$

Then (58) becomes a functional of $\mu_e(\mathbf{r}) = \mu_e - \phi_e(\mathbf{r})$ and $\mu_i(\mathbf{r}) = \mu_i - \phi_i(\mathbf{r})$

$$\begin{aligned}&\beta\Omega\big(\beta, V|\mu_e, \mu_i\big)\\ &\quad\equiv -\ln \sum_{N_e=0,N_i=0}^{\infty} Tr^{(N_e)} Tr^{(N_i)} e^{-\beta\left(\hat{H} - \int d\mathbf{r}\left(\hat{n}_e(\mathbf{r})\mu_e(\mathbf{r}) + \hat{n}_i(\mathbf{r})\mu_i(\mathbf{r})\right)\right)},\end{aligned} \tag{60}$$

At this point $\mu_e(\mathbf{r})$ and $\mu_i(\mathbf{r})$ are independent functions. However, for a charge neutral system there is a constraint on the average particle numbers

$$\overline{N}_e\big(\beta, V|\mu_e, \mu_i\big) = Z\overline{N}_i\big(\beta, V|\mu_e, \mu_i\big), \tag{61}$$

This can be imposed by the stronger constraint $N_e = ZN_i$ on each term of the double sum in (60) to define a grand potential for a system of charge neutral electrons and ions

$$\begin{aligned}&\beta\Omega'\big(\beta, V|\mu_e, \mu_i\big)\\ &\quad\equiv -\ln \sum_{N_i=0}^{\infty} Tr^{(N_e=ZN_i)} Tr^{(N_i)} e^{-\beta\left(\hat{H}' - \int d\mathbf{r}\left(\hat{n}'_e(\mathbf{r})\mu_e(\mathbf{r}) + \hat{n}_i(\mathbf{r})\mu_i(\mathbf{r})\right)\right)}.\end{aligned} \tag{62}$$

There is only a single summation over the ion total numbers, and the electron number density operator is now

$$\hat{n}'_e(\mathbf{r}) = \sum_{i=1}^{ZN_i} \delta\big(\mathbf{r} - \hat{\mathbf{r}}_{ie}\big). \tag{63}$$

Similarly, the Hamiltonian $\hat{H}'$ is the same as in (55–57) except with the replacement $N_e = ZeN_i$. The average number densities associated with $\Omega'\big(\beta, V|\mu_e, \mu_i\big)$ are

$$\begin{aligned}n_e\big(\mathbf{r}, \beta, V|\mu_e, \mu_i\big) &= -\frac{\delta\Omega'\big(\beta, V|\mu_e, \mu_i\big)}{\delta\mu_e(\mathbf{r})}\\ n_i\big(\mathbf{r}, \beta, V|\mu_e, \mu_i\big) &= -\frac{\delta\Omega'\big(\beta, V|\mu_e, \mu_i\big)}{\delta\mu_i(\mathbf{r})}.\end{aligned} \tag{64}$$

The integrals of these densities satisfy (61) by construction since each term of the sum in (62) is charge neutral.

It has been shown in the uniform case (i.e., $\mu_e(\mathbf{r}) \to \mu_e$ and $\mu_i(\mathbf{r}) \to \mu_i$) that the thermodynamic limit for both $\Omega\big(\beta, \mu_e, \mu_i, V\big)$ (with average charge neutrality (61)), and $\Omega'\big(\beta, \mu_e, \mu_i, V\big)$ exist and are equal in this limit [22]. The contributions to (60) from $N_e \neq ZN_i$ give negligible weight to the sum in the thermodynamic limit. As in the previous section, it is assumed now that the proof of the thermodynamic limit for the uniform system extends to a wide class of external potentials of the form (59) so that the functionals $\Omega\big(\beta, V|\mu_e, \mu_i\big)$ and $\Omega'\big(\beta, V|\mu_e, \mu_i\big)$ exist as well.

The thermodynamics for the ions and electrons in terms of the variables $\beta, V, \mu_e(\mathbf{r}), \mu_i(\mathbf{r})$ is obtained from $\Omega'\big(\beta, V|\mu_e, \mu_i\big)$ to define the two component pressure analogous to (11)

$$p\big(\beta|\mu_e, \mu_i\big)V \equiv -\Omega'\big(\beta, V|\mu_e, \mu_i\big). \tag{65}$$

Related thermodynamic functionals are defined in terms of the first derivatives, as described in the previous section. A change of variables to $\beta, V, n_e(\mathbf{r}), n_i(\mathbf{r})$ is effected by the double Legendre transformation

$$F\big(\beta, V|n_e, n_i\big) = \Omega'\big(\beta, V|\mu_e, \mu_i\big) + \int d\mathbf{r}\big(n_e(\mathbf{r})\mu_e(\mathbf{r}) + n_i(\mathbf{r})\mu_i(\mathbf{r})\big). \tag{66}$$

where it is understood that the right side is evaluated at $\mu_e\big(\mathbf{r}, \beta|n_e, n_i\big)$ and $\mu_i\big(\mathbf{r}, \beta|n_e, n_i\big)$ obtained by inverting (64). That equilibrium relationship of the pairs $n_e(\mathbf{r}), n_i(\mathbf{r})$ and $\mu_e(\mathbf{r}), \mu_i(\mathbf{r})$ is now expressed equivalently in terms of the free energy functional

$$\begin{aligned}\mu_e\big(\mathbf{r}, \beta, V|n_e, n_i\big) &= \frac{\delta F\big(\beta, V|n_e, n_i\big)}{\delta n_e(\mathbf{r})}\\ \mu_i\big(\mathbf{r}, \beta, V|n_e, n_i\big) &= \frac{\delta F\big(\beta, V|n_e, n_i\big)}{\delta n_i(\mathbf{r})}.\end{aligned} \tag{67}$$

The method of Appendix A can be extended in a straightforward way to prove the joint concavity of $\Omega'\big(\beta, V|\mu_e, \mu_i\big)$ in $\mu_e(\mathbf{r})$ and $\mu_i(\mathbf{r})$. Similarly $F\big(\beta, V|n_e, n_i\big)$ is a jointly convex functional in the densities $n_e(\mathbf{r})$ and $n_i(\mathbf{r})$. Consequently the variational functional (29) can be generalized to

$$\begin{aligned}\Omega_{\mu_e,\mu_i}\big(\beta, V|n_e, n_i\big) &\equiv F\big(\beta, V|n_e, n_i\big)\\ &\quad - \int d\mathbf{r}\big(n_e(\mathbf{r})\mu_e(\mathbf{r}) + n_i(\mathbf{r})\mu_i(\mathbf{r})\big),\end{aligned} \tag{68}$$

where now the pairs $n_e(\mathbf{r}), n_i(\mathbf{r})$ and $\mu_e(\mathbf{r}), \mu_i(\mathbf{r})$ are independent. Then from the convexity of $F\big(\beta, V|n_e, n_i\big)$ it follows that $\Omega_{\mu_e,\mu_i}\big(\beta, V|n_e, n_i\big)$ also is a convex functional of the densities, with a minimum at

$$\frac{\delta F\big(\beta, V|n_e, n_i\big)}{\delta n_e(\mathbf{r})} = \mu_e(\mathbf{r}), \quad \frac{\delta F\big(\beta, V|n_e, n_i\big)}{\delta n_i(\mathbf{r})} = \mu_i(\mathbf{r}). \tag{69}$$

This is a coupled set of Euler equations that determine $n_e(\mathbf{r}), n_i(\mathbf{r})$ for given $\mu_e(\mathbf{r}), \mu_i(\mathbf{r})$. It is just the equilibrium condition (67). Furthermore, when evaluated at these densities $\Omega_{\mu_e,\mu_i}\big(\beta, V|n_e, n_i\big)$ becomes the grand potential $\Omega'\big(\beta, V|\mu_e, \mu_i\big)$ from (66). Hence (68) is a variational principle for thermodynamics, in terms of a universal free energy functional $F\big(\beta, V|n_e, n_i\big)$. DFT is recovered for this system of electrons and ions.

The complementary variational principle similar to (33) can be constructed for this case as well. Define the variational functional

$$\begin{aligned}F_{n_e,n_i}\big(\beta, V|\mu_e, \mu_i\big) &\equiv \Omega'\big(\beta, V|\mu_e, \mu_i\big)\\ &\quad + \int d\mathbf{r}\big(n_e(\mathbf{r})\mu_e(\mathbf{r}) + n_i(\mathbf{r})\mu_i(\mathbf{r})\big).\end{aligned} \tag{70}$$

Again, the pairs $n_e(\mathbf{r}), n_i(\mathbf{r})$ and $\mu_e(\mathbf{r}), \mu_i(\mathbf{r})$ are independent functions. Since $\Omega'\big(\beta, V|\mu_e, \mu_i\big)$ is a concave functional of $\mu_e(\mathbf{r}), \mu_i(\mathbf{r})$

so is $F_{n_e,n_i}(\beta, V|\mu_e, \mu_i)$. Its maximum is given by the Euler equations that determine $\mu_e(\mathbf{r})$, $\mu_i(\mathbf{r})$ for given $n_e(\mathbf{r})$, $n_i(\mathbf{r})$

$$\frac{\delta\Omega'(\beta, V|\mu_e, \mu_i)}{\delta\mu_e(\mathbf{r})} = -n_e(\mathbf{r}), \quad \frac{\delta\Omega'(\beta, V|\mu_e, \mu_i)}{\delta\mu_i(\mathbf{r})} = -n_i(\mathbf{r}). \quad (71)$$

This is the equilibrium condition (64), and evaluation of $F_{n_e,n_i}(\beta, V|\mu_e, \mu_i)$ at this solution gives the equilibrium free energy functional $F(\beta, V|n_e, n_i)$..

The pair of Euler equations (69) has been applied to the description of a Hydrogen plasma within the context of DFT by Dharma-wardana and Perrot [23]. They consider the densities as independent variables and include the condition of charge neutrality via a Lagrange multiplier. Here, the inversion of (64) necessarily leads to densities whose total number satisfies charge neutrality. Hence all variations are understood to be among functions of this class. The Lagrange multiplier is perhaps a more practical implementation of the constraint.

3.1 | Inhomogeneous Electron Gas

An alternative approach to the thermodynamics of the electron–ion system used in practice is to perform the electron and ion averages in sequence. Since the ions are semi-classical under most conditions of interest, the ion average can be performed classically via molecular dynamics simulation. To elaborate this, return to the grand potential without external potentials (58) and perform the average over the electron subsystem formally to give

$$\beta\Omega(\beta, \mu_e, \mu_i, V) = -\ln \sum_{N_i=0}^{\infty} Tr^{(N_i)} e^{-\beta\left(\hat{H}_i + \Omega_e(\beta, V|\mu_e) - \mu_i N_i\right)}, \quad (72)$$

where the electronic grand potential $\beta\Omega_e(\beta, V|\mu_e)$ is identified as

$$\beta\Omega_e(\beta, V|\mu_e) = -\ln \sum_{N_e=0}^{\infty} Tr^{(N_e)} e^{-\beta\left(\hat{H}_e - \int d\mathbf{r}\mu_e(\mathbf{r})\hat{n}_e(\mathbf{r})\right)}, \quad (73)$$

and

$$\mu_e(\mathbf{r}) \equiv \mu_e - \int d\mathbf{r}' \frac{-Ze^2\hat{n}_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (74)$$

Now as above define the corresponding quantities obtained by including only charge neutral terms, $N_e = ZN_i$

$$\beta\Omega'(\beta, \mu_e, \mu_i, V) = -\ln \sum_{N_i=0}^{\infty} Tr^{(N_i)} e^{-\beta\left(\hat{H}_i + \Omega'_e(\beta, V|\mu_e) - \mu_i N_i\right)}, \quad (75)$$

where now the electron grand potential is defined for $N_e = ZN_i$

$$\beta\Omega'_e(\beta, V|\mu_e) = -\ln Tr^{(N_e=ZN_i)} e^{-\beta\left(\hat{H}'_e - \int d\mathbf{r}\mu_e(\mathbf{r})\hat{n}'_e(\mathbf{r})\right)}. \quad (76)$$

The prime on electron properties indicates that the electron number is $N_e = ZN_i$ for each term in the summation, for example, $\hat{n}'_e(\mathbf{r})$ is given by (63).

The large ion mass implies its thermal deBroglie wavelength λ_i is small compared to other length scale of the problem (e.g., average interparticle distance) and its Fermi energy is small compared to β^{-1} for most conditions. Then the quantum trace over the ions can be represented as a classical phase space average over the ion degrees of freedom [27]

$$\beta\Omega'(\beta, \mu_e, \mu_i, V) \to -\ln \sum_{N_i=0}^{\infty} \frac{1}{\lambda_i^{3N_i} N_i!} \int d\mathbf{X}_i e^{-\beta(U_{ii} + \Omega'_e(\beta, V|\mu_e) - \mu_i N_i)}. \quad (77)$$

Here U_{ii} is the ion-ion Coulomb repulsion energy and the set of ionic coordinates $\{\mathbf{X}_{i,1} \ldots \mathbf{X}_{i,N_i}\}$ is denoted $\mathbf{X}_i$. Furthermore, this classical ion average can be implemented efficiently via molecular dynamics simulation under the assumption of ergodicity. The effective ion force on ion α for such a simulation is

$$\begin{aligned} \mathrm{F}_\alpha &= -\nabla_{\mathbf{X}_\alpha}\left(U_{ii} + \Omega'_e(\beta, V|\mu)\right) \\ &= -\nabla_{\mathbf{X}_\alpha} U_{ii} - \int d\mathbf{r} n_e(\mathbf{r}, \beta|\mu)\nabla_{\mathbf{X}_\alpha} \int d\mathbf{r}' \frac{-Ze^2\hat{n}_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (78)$$

This is the method of choice in most current calculations of thermodynamic properties for warm, dense matter [13]. An approximate electron DFT calculation for the forces between ions is performed at each time step of the MD simulation.

It appears that the calculation of $\beta\Omega'_e(\beta, V|\mu_e)$ is the same as the generic form of (1). In fact this is the *inhomogeneous electron gas* problem as originally considered by Hohnberg and Kohn [1] and by Mermin [6]. It is a system of electrons with Coulomb interactions in the presence of an external potential. However, for general $\mu(\mathbf{r})$ the conditions on $\hat{H}_e$ for the thermodynamic limit are not satisfied in this case and the functional $\Omega_e(\beta, V|\mu)$ does not exist as a thermodynamic potential. This is due in part to the lack of charge neutrality for the electron system alone. Of course it is well-defined outside of the thermodynamic context, such as for self-bound clusters, atoms, molecules. The specific case of the external potential in (57) is due to a given configuration of ions, $\hat{n}'_i(\mathbf{r})$, and includes such stable non-extensive systems for which $\Omega_e(\beta, V|\mu)$ is a well-defined functional. Its Legendre transform $F_e(\beta, V|n)$ is the free energy density functional of DFT. However, they are not the thermodynamic potentials for an extended electron gas.

4 | Pair Potential as a Variable

For simplicity, return to the case of a one-component system of uncharged particles. In this section the grand potential of (10) is written in an equivalent form to make its dependence on the pair potential explicit

$$\Omega(\beta, V|\mu) \equiv -\beta^{-1} \ln \sum_{N=0}^{\infty} Tr^{(N)} e^{-\beta\left(\hat{K} + \hat{U} - \int d\mathbf{r}\mu(\mathbf{r})\hat{n}(\mathbf{r})\right)}. \quad (79)$$

For the special case of pair potentials $\hat{U}$ has the form

$$\begin{aligned} \hat{U} &= \frac{1}{2}\sum_{i\neq j}^{N} u(\hat{\mathbf{r}}_i, \hat{\mathbf{r}}_j) \\ &= \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' u(\mathbf{r}, \mathbf{r}')\left(\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') - \hat{n}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')\right). \end{aligned} \quad (80)$$

It is now interesting to consider (79) as repesenting a class of systems for different choices of the pair potential $u(\mathbf{r},\mathbf{r}')$, and define the corresponding functional of *both* $\mu(\mathbf{r})$ and $u(\mathbf{r},\mathbf{r}')$

$$\Omega(\beta,V|\mu,u) \equiv -\beta^{-1}\ln\sum_{N=0}^{\infty} Tr^{(N)} e^{-\beta\left(\hat{K}+\int d\mathbf{r}d\mathbf{r}'u(\mathbf{r},\mathbf{r}')(\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')-\hat{n}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}'))-\int d\mathbf{r}\mu(\mathbf{r})\hat{n}(\mathbf{r})\right)}. \quad (81)$$

The first functional derivatives are

$$\left.\frac{\delta\Omega(\beta,V|\mu,u)}{\delta\mu(\mathbf{r})}\right|_u = -\langle\hat{n}(\mathbf{r});\mu,u\rangle = -n(\mathbf{r}|\mu,u), \quad (82)$$

$$\left.\frac{\delta\Omega(\beta,V|\mu,u)}{\delta u(\mathbf{r},\mathbf{r}')}\right|_\mu = \left\langle\left(\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')-\hat{n}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right);\mu,u\right\rangle, \equiv n(\mathbf{r}|\mu,u)n(\mathbf{r}'|\mu,u)g(\mathbf{r},\mathbf{r}'|\mu,u) \quad (83)$$

The brackets $\langle\ \ ;\mu,u\rangle$ denote a quantum grand canonical equilibrium average with parameters μ,u. The function $g(\mathbf{r},\mathbf{r}'|\mu,u)$ is the pair correlation function and is the first order characterization of structure.

As in the previous sections the pair $u(\mathbf{r},\mathbf{r}')$ and $g(\mathbf{r},\mathbf{r}')$ are conjugate functions in the same sense as $\mu(\mathbf{r})$ and $n(\mathbf{r})$. Equations (82) and (83) provide the one-to-one correspondence between the functions and their conjugates. The convexity proofs including $u(\mathbf{r},\mathbf{r}')$ follow in an analogous way as in Appendix A. A change of representation from $\mu(\mathbf{r}),u(\mathbf{r},\mathbf{r}')$ to $n(\mathbf{r}),g(\mathbf{r},\mathbf{r}')$ can be implemented via a Legendre transformation

$$F(\beta,V|n,g) = \Omega(\beta,V|\mu,u) + \int d\mathbf{r}n(\mathbf{r})\mu(\mathbf{r}) + \int d\mathbf{r}d\mathbf{r}'g(\mathbf{r},\mathbf{r}')u(\mathbf{r},\mathbf{r}'). \quad (84)$$

Equations (81–83) provide the complete thermodynamics and structure for a quantum system with given $\mu(\mathbf{r}),u(\mathbf{r},\mathbf{r}')$, or $n(\mathbf{r}),g(\mathbf{r},\mathbf{r}')$. An interesting application is to use these equations to define a corresponding classical system with the same thermodynamics and structure [28]. This is possible by introducing the classical temperature, local chemical potential, and pair potentials β_c^{-1}, $\mu_c(\mathbf{r})$, $u_c(\mathbf{r},\mathbf{r}')$. The classical system has a functional $\Omega_c(\beta_c,V|\mu_c,u_c)$ defined as above, but for a system with classical mechanics. The classical parameters are then determined by the equivalence conditions

$$\Omega_c(\beta_c,V|\mu_c,u_c) \equiv \Omega(\beta,V|\mu,u) \quad (85)$$

$$\left.\frac{\delta\Omega_c(\beta_c,V|\mu_c,u_c)}{\delta\mu_c(\mathbf{r})}\right|_{u_c} \equiv \left.\frac{\delta\Omega(\beta,V|\mu,u)}{\delta\mu(\mathbf{r})}\right|_u \quad (86)$$

$$\left.\frac{\delta\Omega_c(\beta_c,V|\mu_c,u_c)}{\delta u_c(\mathbf{r},\mathbf{r}')}\right|_{\mu_c} \equiv \left.\frac{\delta\Omega(\beta,V|\mu,u)}{\delta u(\mathbf{r},\mathbf{r}')}\right|_\mu \quad (87)$$

A motivation for the mapping to a classical system is to allow application of effectice classical methods for evaluation of various properties. For example, with β_c^{-1}, $\mu_c(\mathbf{r})$, $u_c(\mathbf{r},\mathbf{r}')$ known the methods of classical liquid state theory and molecular dynamics simulation can be applied. Of course the inversion of (85–87) for the classical parameters is a difficult task in general. However, a specific example showing the effectiveness of this approach has been demonstrated for the electron gas [29, 30].

5 | Discussion

The objective here has been to clarify the relationship of finite temperature density functional theory to the thermodynamics of non-uniform systems. The primary results can be summarized as follows:

- All information about equilibrium states is contained in the fundamental potential $\Omega(\beta,V|\mu)$ given by (1). Its representation in terms of the grand canonical ensemble provides an explicit basis for its evaluation in terms of the state variables β,V, and $\mu(\mathbf{r})$. An equivalent representation is given by the free energy functional $F(\beta,V|n)$ of (22) in terms of the variables β,V, and $n(\mathbf{r})$.
- DFT describes the equilibrium states of a broad class of systems for which the grand potential $\Omega(\beta,V|\mu)$ exists, as given by Mermin's formulation [6]. Thermodynamics describes a subset of those states with the additional conditions of being sufficiently large that its global properties are extensive. For such states, DFT is a special equivalent representation of thermodynamics.
- For thermodynamic states the variational feature of DFT follows from the convexity properties of fundamental thermodynamic potentials.
- The equivalence of DFT and thermodynamics gives the former a wider context through relationship to various functionals obtained by a change of variables via Legendre transformation. Thermodynamic identities and properties of first and second derivatives provide exact constraints that may be of use in practical construction of functionals, and describing experimental conditions of interest.
- Thermodynamics for systems of electrons and ions with Coulomb interactions requires the additional constraint of charge neutrality. For the specific case of charge neutral electrons and one component of ions the grand potential $\Omega(\beta,V|\mu_e,\mu_i)$ exists and has all the properties required for thermodynamics; equivalence with DFT still applies.
- The current practical approach of separating $\Omega(\beta,V|\mu_e,\mu_i)$ into a partial average over electrons, followed by a classical average over ions, leads to an intermediate electron potential $\Omega_e(\beta,V|\mu_e,\mu_i)$. The latter describes the effect of electrons on the ion-ion forces, needed to implement the final classical ion average via molecular dynamics simulation. However, $\Omega_e(\beta,V|\mu_e,\{\mu_i\})$ does not satisfy the conditions for a thermodynamics and the associated DFT is not equivalent to thermodynamics.
- The extension of these functional to include the pair potential as an independent variable was described. It was used to define an equivalent classical system with the same thermodynamics an structure. The succesful application of such a classical representation for the electron gas was noted.

Acknowledgments

The author thanks Sam Trickey and Jeffrey Wrighton for helpful comments. This research was supported by the US Office of Energy,

Department of Science, Basic Energy Sciences under award number DE-SC0002139. There is no conflict of interest associated with this work.

Funding

This work was supported by Basic Energy Sciences, DE-SC0002139.

Conflicts of Interest

The author declares no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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Appendix A

Concavity of $\Omega(\beta, V|\mu)$ and Convexity of $F(\beta, V|n)$

Consider first the grand potential $\Omega(\beta, V|\mu)$ defined by (10). Strict concavity of $\Omega(\beta, V|\mu)$ with respect to $\mu(\mathbf{r})$ is defined by

$$\Omega\big(\beta, V|\lambda\mu_1 + (1-\lambda)\mu_2\big) > \lambda\Omega\big(\beta, V|\mu_1\big) + (1-\lambda)\Omega\big(\beta, V|\mu_2\big), \quad \text{(A1)}$$

for all λ in the closed interval $[0, 1]$ and $\mu_1 \neq \mu_2$. To prove this first note the inequality [31]

$$Tr^{(N)} e^{\lambda\hat{A}+(1-\lambda)\hat{B}} \leq \left(Tr^{(N)} e^{\hat{A}}\right)^{\lambda}\left(Tr^{(N)} e^{\hat{B}}\right)^{(1-\lambda)}, \quad \text{(A2)}$$

and therefore

$$\ln Tr^{(N)} e^{\lambda\hat{A}+(1-\lambda)\hat{B}} \leq \lambda \ln\left(Tr^{(N)} e^{\hat{A}}\right) + (1-\lambda)\ln Tr^{(N)} e^{\hat{B}}. \quad \text{(A3)}$$

Choose for $\hat{A}$ and $\hat{B}$ the special cases

$$\hat{A} = -\beta\left(\hat{H} - \int d\mathbf{r}\mu_1(\mathbf{r})\hat{n}(\mathbf{r})\right), \quad \hat{B} = -\beta\left(\hat{H} - \int d\mathbf{r}\mu_2(\mathbf{r})\hat{n}(\mathbf{r})\right). \quad \text{(A4)}$$

Then with (10) concavity of $\Omega(\beta, V|\mu)$ is proved

$$\Omega\big(\beta, V|\lambda\mu_1 + (1-\lambda)\mu_2\big) \geq \lambda\Omega\big(\beta, V|\mu_1\big) + (1-\lambda)\Omega\big(\beta, V|\mu_2\big). \quad \text{(A5)}$$

The equality holds only for $\mu_1 = \mu_2$ or $\lambda = 0, 1$. So strict concavity follows with the restrictions $\mu_1 \neq \mu_2$ and $\lambda \in (0, 1)$. The importance of strict concavity is that it ensures the invertibility of the relationship of μ and n given by (14)

$$\left.\frac{\delta\Omega(\beta, V|\mu)}{\delta\mu(\mathbf{r})}\right|_{V,\beta} = -n(\mathbf{r}), \quad \text{(A6)}$$

such that for each μ there is a unique n.

Next consider the convexity of $F(\beta, V|n)$ with respect to $n(\mathbf{r})$. The proof here follows that for the classical case in reference [10]. Define a functional of n and μ by

$$F(\beta, V|\mu, n) \equiv \Omega(\beta, V|\mu) + \int d\mathbf{r} n(\mathbf{r})\mu(\mathbf{r}). \tag{A7}$$

Here $\Omega(\beta, V|\mu)$ is the same functional as for the grand potential, but n and μ are now independent. Since $\Omega(\beta, V|\mu)$ is concave it follows that $F(\beta, V|\mu, n)$ also is concave. Its maximum occurs for the solution to

$$\left.\frac{\delta\Omega(\beta, V|\overline{\mu})}{\delta\mu(\mathbf{r})}\right|_{V,\beta} = -n(\mathbf{r}), \tag{A8}$$

denoted by $\overline{\mu}(\mathbf{r}) = \mu(\mathbf{r}, \beta|n)$. Then

$$F(\beta, V|\mu, n) < F(\beta, V|\overline{\mu}, n) = F(\beta, V|n). \tag{A9}$$

The last equality follows from the definition of $F(\beta, V|n)$ as the Legendre transformation (14). Now define the density $n_\lambda = \lambda n_1 + (1-\lambda)n_2$ and denote the solution to (A8) corresponding to n_λ by $\overline{\mu}_\lambda$. Then it follows that

$$\begin{aligned} F\left(\beta, V|n_\lambda\right) &= \lambda F\left(\beta, V|\overline{\mu}_\lambda, n_1\right) + (1-\lambda)F\left(\beta, V|\overline{\mu}_\lambda, n_2\right) \\ &< \lambda F\left(\beta, V|n_1\right) + (1-\lambda)F\left(\beta, V|n_2\right), \end{aligned} \tag{A10}$$

which demonstrates the convexity of $F\left(\beta, V|n_\lambda\right)$.

A similar analysis follows directly to prove concavity with respect to β

$$\Omega\left(\lambda\beta_1 + (1-\lambda)\beta_2, V|\mu\right) > \lambda\Omega\left(\beta_1, V|\mu\right) + (1-\lambda)\Omega\left(\beta_2, V|\mu\right), \tag{A11}$$

with the choice

$$\widehat{A} = -\beta_1\left(\widehat{H} - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right), \quad \widehat{B} = -\beta_2\left(\widehat{H} - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right) \tag{A12}$$

in (A3).