

External Fields, Density Functionals, and the Gibbs Inequality

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Received March 4, 2002; accepted May 22, 2002; revised June 6, 2002

By combining the upper and lower bounds to the free energy as given by the Gibbs inequality for two systems with the same intermolecular interactions but with external fields differing from each other only in a finite region of space Γ , we show that the corresponding equilibrium densities must also differ from each other somewhere in Γ . We note that the basic equations of density functional theory arise naturally from a simple rearrangement and reinterpretation of the terms in the upper bound Gibbs inequality for such systems and briefly discuss some of the complications that occur when the intermolecular interactions of the two systems also differ.

KEY WORDS: Density functional theory; upper and lower bounds; intrinsic free energy functional; Legendre transform; single particle density.

1. INTRODUCTION

Michael Fisher's work has often shown us that important insights can arise from simple starting points through the use of basic principles of statistical mechanics. With this in mind, (but on a much more modest scale!), we will examine here some consequences of one of the earliest fundamental relations of statistical mechanics: the Gibbs inequality, through which Gibbs established the basic convexity properties of the free energy.⁽¹⁾ The usefulness of this inequality in the development of density functional theory (both classical⁽²⁻⁵⁾ and quantum versions^(6,7)) and in perturbation theories of liquids^(4,8,9) has long been recognized.⁽¹⁰⁾ We report here some very simple consequences of the Gibbs inequality for the density response of a fluid to an external field that do not appear to be widely known, and show

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that the basic equations of density functional theory arise directly from a rearrangement and reinterpretation of terms in a special case of the Gibbs inequality.

The Gibbs inequality in its most general form relates the equilibrium properties of a system of interest with Hamiltonian $H(\Phi)$ (with general intermolecular potentials and a generalized single particle potential Φ simply related to the external field ϕ , as discussed below) to those of a "trial" system with Hamiltonian $H_t(\Phi_t)$ with possibly different intermolecular potentials and field Φ_t . We consider here the Grand Canonical ensemble, where the free energy $\Omega = -k_B T \ln \Xi$ and density distribution functions such as the singlet density $\rho(\mathbf{r})$ are functions of the temperature T , volume V and chemical potential μ , and functionals of the external field $\phi(\mathbf{r})$ and of the (pair and any higher order) intermolecular potentials. Here Ξ is the Grand partition function and we will let $\beta = (k_B T)^{-1}$. We are particularly interested in the functional dependence on the external field $\phi(\mathbf{r})$ for fixed values of the thermodynamic variables and the intermolecular potentials. Since the zero of energy can be chosen arbitrarily without affecting the physics, and a constant field acts like a chemical potential shift in the Grand partition function, the relevant quantities actually depend only on the difference⁽³⁾

$$\Phi(\mathbf{r}) \equiv \phi(\mathbf{r}) - \mu \quad (1)$$

as shown in the Appendix. We refer to $\Phi(\mathbf{r})$ as the *singlet field* and write $\Omega([\Phi])$ or $\rho(\mathbf{r}; [\Phi])$ when we want to emphasize this functional dependence.

In this case the Gibbs inequality can be written as:

$$\Omega_t + \langle H(\Phi) - H_t(\Phi_t) \rangle \leq \Omega \leq \Omega_t + \langle H(\Phi) - H_t(\Phi_t) \rangle_t. \quad (2)$$

Here $\langle \rangle$ and $\langle \rangle_t$ denote normalized ensemble averages in the systems with Hamiltonians $H(\Phi)$ and $H_t(\Phi_t)$ respectively, and Ω and Ω_t are the respective free energies. This result follows immediately from Eq. (4) of the basic paper by Mermin;⁽⁶⁾ it holds for general quantum systems and, with modified definitions of the free energies and averages, for other ensembles too. For completeness and to establish notation, we give in the Appendix a derivation for classical systems that uses only convexity properties of the exponential function and seems a little simpler than standard approaches.^(2, 4, 5, 10) As emphasized in the Appendix, the inequalities in Eq. (2) are strict; only if $H(\Phi) = H_t(\Phi_t)$ for *every configuration* with nonzero weight in the averages will $\Omega_t = \Omega$.

2. DENSITY RESPONSE TO DIFFERENT SINGLET FIELDS

Consider first the special case where the trial system has exactly the same intermolecular interactions as the system of interest and only the singlet fields may differ. By combining the lower and upper bounds in Eq. (2) for this case we find a simple inequality

$$0 \leq \int d\mathbf{r} [\Phi(\mathbf{r}) - \Phi_t(\mathbf{r})] [\rho_t(\mathbf{r}) - \rho(\mathbf{r})]. \quad (3)$$

Here $\rho_t(\mathbf{r}) \equiv \rho(\mathbf{r}; [\Phi_t])$ is the equilibrium singlet density arising from Φ_t and similarly $\rho(\mathbf{r}) \equiv \rho(\mathbf{r}; [\Phi])$. Equation (3) is valid for any $\Phi_t(\mathbf{r})$. Since the inequalities in Eq. (2) are strict, the right side of Eq. (3) is strictly greater than zero unless $\Phi_t(\mathbf{r}) = \Phi(\mathbf{r})$ for all \mathbf{r} .

Equation (3) has some interesting consequences for the density response of a system to an external field. In particular, it shows *explicitly* that the mapping from the singlet field $\Phi(\mathbf{r})$ to the associated equilibrium density $\rho(\mathbf{r}; [\Phi])$ is one to one: a given singlet field produces a *unique* density response. Thus if $\Phi_t(\mathbf{r})$ differs from $\Phi(\mathbf{r})$ for any \mathbf{r} then the right side of Eq. (3) is strictly greater than zero; for this to be true $\rho_t(\mathbf{r})$ must differ from $\rho(\mathbf{r})$ for some \mathbf{r} . This result plays a central role in density functional theory and is well known. Mermin proved this for quantum systems by contradiction,⁽⁶⁾ and most later discussions of density functional theory⁽²⁻⁵⁾ for classical systems have also relied on proofs by contradiction.⁽¹¹⁾

However Eq. (3) allows us very simply to find more explicit results in some special cases that do not appear to be widely known. For example, suppose $\Phi_t(\mathbf{r})$ differs from $\Phi(\mathbf{r})$ only in a finite region of space Γ , which can be arbitrarily small. Then the integration in Eq. (2) is restricted to Γ and we find the more local result that $\rho_t(\mathbf{r})$ must differ from $\rho(\mathbf{r})$ for some \mathbf{r} in Γ . (This approach gives no information about what happens outside Γ .) This result is obvious in the low density limit where there is a local density response proportional to the Boltzmann factor of $\Phi(\mathbf{r})$ but it holds true in general. If in addition $\Phi_t(\mathbf{r}) > \Phi(\mathbf{r})$ in Γ then $\int_{\Gamma} d\mathbf{r} [\rho(\mathbf{r}) - \rho_t(\mathbf{r})] > 0$. More generally, if Γ denotes the set of points where $\Phi_t(\mathbf{r})$ differs from $\Phi(\mathbf{r})$, then $\rho_t(\mathbf{r})$ must differ from $\rho(\mathbf{r})$ at least for some \mathbf{r} in Γ .

One well known result follows when $\Delta\Phi_t(\mathbf{r}) \equiv \Phi_t(\mathbf{r}) - \Phi(\mathbf{r})$ is very small, as indicated by the notation $\delta\Phi_t(\mathbf{r})$. Then we can use linear response theory to determine the small induced density change:

$$\delta\rho_t(\mathbf{r}) = -\beta \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}'; [\Phi]) \delta\Phi_t(\mathbf{r}'), \quad (4)$$

and Eq. (3) reduces to

$$0 < \int d\mathbf{r} d\mathbf{r}' \delta\Phi_i(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}'; [\Phi]) \delta\Phi_i(\mathbf{r}'), \quad (5)$$

which expresses that fact that the linear response function χ is positive definite^(4,5) (except possibly at a phase transition in zero field where our assumption that linear response theory is accurate for sufficiently small $\delta\Phi_i(\mathbf{r})$ can break down).

3. DENSITY FUNCTIONAL THEORY

The key idea in density functional theory⁽²⁻⁷⁾ is to consider generalized free energies that are functionals of the density $\rho_i(\mathbf{r})$ rather than the field $\Phi_i(\mathbf{r})$. Since the Gibbs inequality shows that a given singlet field produces a unique density response as discussed above, formally any functional of Φ_i can equally well be thought of as a functional of ρ_i . But the Gibbs inequality can play a more central role. We will show that the basic functionals and the minimum principle used in density functional theory arise directly from the Gibbs inequality and its use permits us to see explicitly how the change of variable from singlet fields to densities can be carried out.

We start from the upper bound to the free energy Ω that follows from Eq. (2) in the special case where only the singlet fields differ:

$$\Omega \leq \Omega_i + \int d\mathbf{r} [\Phi(\mathbf{r}) - \Phi_i(\mathbf{r})] \rho_i(\mathbf{r}). \quad (6)$$

The standard density functional relations⁽²⁻⁵⁾ follow immediately by simply rearranging and reinterpreting terms in this equation. Thus we rewrite Eq. (6) as

$$\Omega = \min_{\Phi_i} \left[\left\{ \Omega_i - \int d\mathbf{r} \rho_i(\mathbf{r}) \Phi_i(\mathbf{r}) \right\} + \int d\mathbf{r} \rho_i(\mathbf{r}) \Phi(\mathbf{r}) \right]; \quad (7)$$

here the minimum is taken over all possible fields Φ_i and is achieved only when $\Phi_i = \Phi$ for all \mathbf{r} .

Equation (7) may seem to be a particularly hard and inefficient way to calculate Ω but we can proceed as follows. Since the density is related to the functional derivative of the free energy by

$$\rho_i(\mathbf{r}) \equiv \rho(\mathbf{r}; [\Phi_i]) = \delta\Omega([\Phi_i]) / \delta\Phi_i(\mathbf{r}), \quad (8)$$

the terms in curly brackets in the right side of Eq. (7) represent a (functional) Legendre transform⁽⁷⁾ from $\Omega_t \equiv \Omega([\Phi_t])$ to a so-called *intrinsic free energy density functional* $F([\rho_t])$, where

$$F([\rho_t]) \equiv \Omega([\Phi_t]) - \int d\mathbf{r} \rho_t(\mathbf{r}) \Phi_t(\mathbf{r}) \quad (9)$$

denotes the terms in curly brackets. As the notation indicates, F is a functional of the equilibrium density $\rho_t(\mathbf{r})$ and not of the field; thus the $\Phi_t(\mathbf{r})$ on the right side is the field that corresponds to the density $\rho_t(\mathbf{r})$. By standard properties of the Legendre transform the associated field formally satisfies

$$\delta F([\rho_t]) / \delta \rho_t(\mathbf{r}) = -\Phi_t(\mathbf{r}). \quad (10)$$

The transformation of variables from fields to densities in F can be seen more explicitly if we rewrite Eq. (9) in the following equivalent form:

$$F([\rho_t]) \equiv \min_{\Phi'_t} \left[\Omega([\Phi'_t]) - \int d\mathbf{r} \rho_t(\mathbf{r}) \Phi'_t(\mathbf{r}) \right]. \quad (11)$$

The minimum is taken over all possible external fields Φ'_t at fixed $\rho_t(\mathbf{r})$. The minimum occurs when the functional derivative with respect to Φ'_t of the term in square brackets vanishes; from Eq. (8) this occurs when Φ'_t equals the field Φ_t associated with the density distribution $\rho_t(\mathbf{r})$, as in Eq. (9). Thus $F([\rho_t])$ is certainly well-defined in principle, though Eq. (11) does not present a very useful way to calculate it in practice.

Having made this change of variable, the only remaining dependence on the field Φ_t on the right side of Eq. (7) is through the associated equilibrium density $\rho_t(\mathbf{r})$, and the minimum can be taken over all such density distributions. Thus Eq. (7) can be rewritten as

$$\Omega = \Omega([\Phi]) = \min_{\rho_t} \left[F([\rho_t]) + \int d\mathbf{r} \rho_t(\mathbf{r}) \Phi(\mathbf{r}) \right]. \quad (12)$$

This is the basic equation of density functional theory. The term in square brackets on the right side is usually interpreted as a generalized *Grand free energy density functional* $\Omega_\Phi([\rho_t])$:⁽³⁾

$$\Omega_\Phi([\rho_t]) \equiv F([\rho_t]) + \int d\mathbf{r} \rho_t(\mathbf{r}) \Phi(\mathbf{r}). \quad (13)$$

Note that $\Omega_\Phi([\rho_i])$, unlike $F([\rho_i])$, is a functional of the field Φ as well as the density ρ_i . (Of course, both Ω_Φ and F remain functionals of all the intermolecular interaction potentials). Equation (12) shows explicitly that the minimum value of $\Omega_\Phi([\rho_i])$ with respect to ρ_i at fixed Φ is the desired free energy $\Omega([\Phi])$. The density that minimizes this functional is $\rho(\mathbf{r})$ and at that minimum we have

$$\frac{\delta\Omega_\Phi([\rho_i])}{\delta\rho_i(\mathbf{r})} = 0. \quad (14)$$

This derivation highlights the following points. The minimum in Eq. (12) must be taken over equilibrium densities ρ_i arising from a system with the same intermolecular interactions but a different singlet field. While the mapping from arbitrary fields to equilibrium densities is one to one, it is not necessarily true that an arbitrary function of the density must correspond to the equilibrium density of a system with a given H in some field (unless the field is trivially taken to be so much stronger than the intermolecular interactions that there is an essentially local response). Thus, a density distribution predicting 14 nearest neighbors about a fixed particle in a hard sphere system is unphysical and should not be included in the trial density set for Eq. (12). In practice, we suspect this is not a serious problem in most cases where only limited density variations are considered and for non hard core systems the inverse mapping can generally be carried out.⁽¹²⁾

Analogous equations hold in the Canonical ensemble, but then the trial density set should include only densities yielding the fixed number of particles. In this case workers have found it more convenient to work in the Grand ensemble where this restriction does not apply and then subtract out the lowest order effects of particle number fluctuations.⁽¹³⁾

4. DIFFERENT INTERMOLECULAR INTERACTIONS

More problematic is the fact that the functional dependence on ρ_i is also affected by the intermolecular interactions. While the exact $F([\rho_i])$ is a "universal" functional of ρ_i for a given set of intermolecular interactions, it remains an essentially unknown functional of the intermolecular interactions, which in classical applications can have a variety of forms. Any approximate expression for $F([\rho_i])$ must implicitly or explicitly take this functional dependence into account. Thus a density functional that can accurately describes the properties of a nonuniform hard sphere fluid may not be appropriate for a system with softer repulsive intermolecular

interactions. This problem seems much more severe when there are attractive intermolecular interactions. Then F must describe critical properties, capillary waves, and a variety other phenomena where the functional dependence on w plays an essential role, and we have little idea of its form.⁽¹⁴⁾ (And of course knowing the exact form, as we do for the original free energy $\Omega([\Phi])$ through the partition function, does not mean we can carry out practical calculations!)

In many cases where long wavelength fluctuations are not important, a mean field treatment of the attractive interactions may suffice. For the simple Lennard-Jones (LJ) fluid with pair interactions $w_{\text{LJ}}(r_{12})$ this can arise by approximating the structure of the nonuniform LJ fluid by that of a *reference fluid* with purely repulsive pair interactions $u_0(r_{12})$ giving repulsive forces equal to those of the LJ potential and a singlet field $\Phi_0(\mathbf{r})$ that incorporates the averaged effects of the attractive interactions.⁽¹⁴⁾ The free energy can again be estimated using the Gibbs inequality, but now in a more general form than Eq. (6) or (12), since the intermolecular pair potentials as well as the singlet fields differ. We use the subscript 0 to denote the trial system in this special case. Equation (2) then becomes

$$\begin{aligned} \Omega_0 - \int d\mathbf{r} \rho(\mathbf{r}) \Delta\Phi(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) u_1(r_{12}) \\ \leq \Omega \leq \Omega_0 - \int d\mathbf{r} \rho_0(\mathbf{r}) \Delta\Phi(\mathbf{r}) \\ + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2) u_1(r_{12}). \end{aligned} \quad (15)$$

Here $u_1(r_{12}) = w_{\text{LJ}}(r_{12}) - u_0(r_{12})$.

To get an upper bound to the free energy from the last inequality, we need an accurate expression for the pair distribution function $\rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ as well as $\rho_0(\mathbf{r})$. However, since $u_0(r_{12})$ is different than $w_{\text{LJ}}(r_{12})$ the Gibbs inequality shows there is no choice of $\Phi_0(\mathbf{r})$ for which the upper bound gives the exact free energy. Nevertheless, if $\Phi_0(\mathbf{r})$ is chosen so that $\rho_0(\mathbf{r})$ closely approximates $\rho(\mathbf{r})$, it seems physically plausible that $\rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ could also rather closely resemble $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, at least at high density when correlations arising from packing of the repulsive cores are most important.⁽¹⁴⁾ When this is true, the upper and lower bounds in Eq. (15) are close to each other and the upper bound provides a reasonable estimate for the exact free energy. The basic equations of perturbation theory of *uniform* fluids can be established from this perspective and accurate results for the free energy of the dense LJ uniform fluid are found⁽¹⁵⁾ from the upper bound in Eq. (15).

An upper bound for the free energy from the last inequality is guaranteed only if we use accurate values for $\rho_0(\mathbf{r})$ and $\rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$. In many applications of density functional theory $\rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is replaced by the product $\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)$ for computational simplicity.⁽³⁾ A minimization of the approximate free energy when this approximation is made cannot be justified by any upper bound principle, though it may be useful for other purposes. In a uniform fluid this approach yields a constant value for $\Phi_0(\mathbf{r})$, which gives a constant reference density equal to the LJ density, and the resulting free energy is only qualitatively accurate, sometimes being larger and sometimes smaller than the correct result.^(14, 16)

APPENDIX A

Consider a classical system with interaction potentials

$$H(\phi) = \sum_{i=1}^N \phi(\mathbf{r}_i) + \sum_{i<j}^N w^{(2)}(\mathbf{r}_i, \mathbf{r}_j) + \dots \quad (\text{A.1})$$

We explicitly denote only the dependence of H on the external field ϕ ; the intermolecular interactions $w^{(j)}$ are general and can include 3, 4, ..., N body terms. The Grand partition function \mathcal{E} for a system with chemical potential μ , and temperature $k_B T \equiv \beta^{-1}$ is given by

$$\mathcal{E} \equiv e^{-\beta\Omega} = \text{Tr} e^{-\beta H(\phi) + \beta\mu N} = \text{Tr} e^{-\beta H(\Phi)}, \quad (\text{A.2})$$

where

$$\text{Tr}(\cdot) \equiv \sum_N [N! \Lambda^{3N}]^{-1} \int d\mathbf{r}^N(\cdot). \quad (\text{A.3})$$

Here $\Lambda \equiv (\beta h^2 / 2\pi m)^{1/2}$ is the thermal de Broglie wavelength. In the last equality in Eq. (A.2) we combined the chemical potential terms with the external field terms in Eq. (A.1) to exhibit the functional dependence only on the the singlet field $\Phi(\mathbf{r}) \equiv \phi(\mathbf{r}) - \mu$. Finally we use pointed brackets to define a normalized ensemble average:

$$\langle\langle \cdot \rangle\rangle \equiv e^{\beta\Omega} \text{Tr} e^{-\beta H(\Phi)}(\cdot). \quad (\text{A.4})$$

To arrive at the Gibbs inequality, we consider an arbitrary ‘‘trial’’ system with different interaction potentials $H_t(\Phi_t)$ and note that the partition function $\mathcal{E} = e^{-\beta\Omega}$ can be written as

$$e^{-\beta\Omega} = \text{Tr} e^{-\beta H_t(\Phi_t)} e^{-\beta[H(\Phi) - H_t(\Phi_t)]} \quad (\text{A.5})$$

or

$$e^{-\beta\Omega} = e^{-\beta\Omega_t} \langle e^{-\beta[H(\Phi) - H_t(\Phi_t)]} \rangle_t. \quad (\text{A.6})$$

If x is a random variable and $\langle x \rangle$ denotes its average over any normalized probability distribution we have $e^{x - \langle x \rangle} \geq 1 + x - \langle x \rangle$ for all real x . Taking averages we find the familiar result $\langle e^x \rangle \geq e^{\langle x \rangle}$ with the strict inequality holding if there is any configuration in the average with $x \neq \langle x \rangle$. Applying this to Eq. (A.6) gives

$$e^{-\beta\Omega} \geq e^{-\beta\Omega_t} e^{-\beta\langle [H(\Phi) - H_t(\Phi_t)] \rangle_t}. \quad (\text{A.7})$$

This yields the final result

$$\Omega \leq \Omega_t + \langle H(\Phi) - H_t(\Phi_t) \rangle_t, \quad (\text{A.8})$$

where the equality holds only when $H(\Phi) = H_t(\Phi_t)$ for all configurations in the average. Swapping $H(\Phi)$ and $H_t(\Phi_t)$ yields the lower bound as given in Eq. (2). By redefining the averages and free energies appropriately these results also hold in the Canonical ensemble, and they are valid for quantum systems as well.⁽⁶⁾

ACKNOWLEDGMENTS

It is a pleasure to dedicate this paper to Michael Fisher on the happy occasion of his 70th birthday and to thank him for his unfailing support, insight, and advice over the many years we have known each other. We are also grateful to Yng-Gwei Chen and Ted Kirkpatrick for helpful discussions. This work is supported by the National Science Foundation through Grant CHE-0111104.

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