Density Functional Theory for Electron Gas and for Jellium

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ABSTRACT: Density functional theory relies on universal functionals characteristic of a given system. Those functionals in general are different for electron gas and for jellium (electron gas with a uniform background). However, jellium is frequently used to construct approximate functionals for an electron gas (e.g., local density approximation and gradient expansions). The precise relationship of the exact functionals for the two systems is addressed here. In particular, it is shown that the exchange-correlation functionals for the inhomogeneous electron gas and inhomogeneous jellium are the same. This justifies theoretical and quantum Monte Carlo simulation studies of jellium to guide the construction of functionals for an electron gas. Related issues of the thermodynamic limit are noted as well.
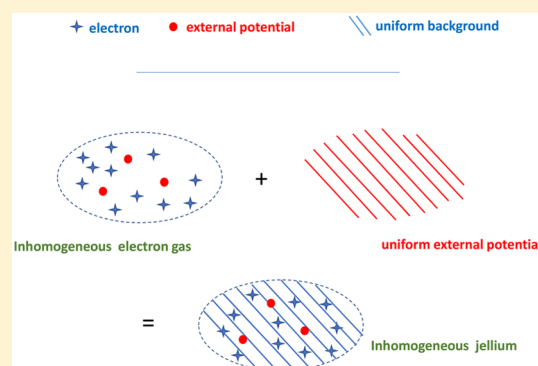
I. INTRODUCTION

Keith Gubbins has been an inspiration to students and colleagues for more than 50 years, through direct mentoring and collaborations and indirectly through his extensive innovative publications. My own collaboration was very early in my career as a new faculty member in the Physics Department at the University of Florida. Keith had just finished his book with Tim Reed showing the relevance of statistical mechanics to applications in chemical and other engineering fields. He continued to demonstrate the importance of formulating practical approximations to complex systems through their firm foundation in basic statistical mechanics. He also demonstrated by example the need to ignore the artificial interfaces between applied and basic disciplines, taking recent developments in the mathematics and physics literature to formulate innovative and accurate descriptions of complex systems via the reinforcement of theory, simulation, and experiment. An example is his early application of nonlocal classical density functional theory (DFT) for adsorption in carbon slit pores, verified by simulation and including a discussion of problems of extracting experimental parameters needed for the calculation.[1] The presentation here has in common the tool of density functional theory for application to a complex system (warm dense matter). But the system is quite different—confined electrons—and hence quantum effects can dominate except at the highest temperatures. The emphasis is on formal relationships to guide practical applications, so it is hoped that Keith will appreciate some of his spirit in the following.

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)[2−5] and one for temperature-dependent classical nonuniform fluids (e.g., two-phase liquids and porous media).[6,7] The former has focused on the determination of the ground-state energy whereas the latter has focused on the classical free energy of thermodynamics.

Their relationship was established by Mermin, who extended the original ground-state theorems of Hohenberg and Kohn to finite temperatures for quantum systems[8,9] described by the Gibbs ensemble of statistical mechanics. This early history is briefly reviewed in refs 5 and 6. Recently, the two paths have rejoined in an effort to describe conditions of warm, dense matter.[10] These are solid density conditions, but temperatures for electrons range from the zero temperature ground state to well above the Fermi temperature. They include domains with atomic and molecular coexistence and with relevant association and dissociation chemistry. A central ingredient is the (intrinsic) free energy functional F, consisting of a non-interacting contribution F_0, a Hartree contribution, F_H, and a remainder called the exchange-correlation free energy functional, F_{xc}. The exact functional form for the Hartree contribution is known, and the contribution from F_0 is treated exactly (numerically) within the Kohn−Sham formulation of DFT[11] extended to finite temperatures. Hence, the primary challenge for applications is the construction of the exchange-correlation density functional.

An important constraint is its equivalence with the corresponding functional for jellium (electrons in a uniform neutralizing background[12]) when evaluated at a uniform density. Although still a difficult quantity to determine, the latter has been studied widely by approximate theoretical methods[12,13] and more recently by quantum simulation methods across the temperature−density plane.[14] An accurate fitting function for practical applications now exists.[15] Its utility for DFT is within the "local density approximation", first

proposed in ref 11 for the zero temperature energy functional and extended to finite temperatures for the free energy functional. It assumes that the nonuniform system F_{xc} can be represented at each point by the uniform jellium F_{xc} evaluated at the density for that point.

The objective here is to clarify the precise relationship of the DFT functionals for the two different systems, electron gas and jellium, for general nonuniform densities. The primary new result is that the exchange-correlation functionals for the two systems are equivalent and the total free energies (intrinsic plus external potential) are the same. In the analysis, it noted that jellium is usually considered in the thermodynamic limit, $\overline{N} \to \infty$, $V \to \infty$, $\overline{N}/V = $ constant, where $\overline{N}$ and V are the average particle number and volume, respectively. It has been proven that the jellium free energy is well defined in this limit,[16] whereas that for the electron gas is not (it does not scale as the volume for large system size due in part to a lack of charge neutrality). Nevertheless, the exchange-correlation component of the free energy for the electrons does have a proper thermodynamic limit as a consequence of the equivalence demonstrated here. In the next section, Hamiltonians for the isolated electron gas and jellium are defined. Next, the statistical mechanical basis for DFT is described for the grand canonical ensemble. The grand potential (proportional to the pressure) is defined as a functional of a given external potential $v_{ex}(\mathbf{r})$ (occurring through a local chemical potential $\mu(\mathbf{r}) = \mu - v_{ex}(\mathbf{r})$), and the corresponding functionals for the inhomogeneous electron gas and inhomogeneous jellium are related. Associated with $\mu(\mathbf{r})$ are the densities $n_e(\mathbf{r})$ and $n_j(\mathbf{r})$ for the two systems. Their relationship is established. Next, the strict concavity of the grand potential functionals assures a one-to-one relationship of the densities to $\mu(\mathbf{r})$ so that a change in variables is possible. This is accomplished by Legendre transformations which define the free energy density functionals. It is noted that the free energy density functional obtained in this way is precisely that of Mermin's DFT. The free energies differ by the potential energy of the background charge. It is shown that this cancels the differences between the corresponding Hartree free energy contributions, resulting in the desired equivalence of the exchange-correlation functionals.

II. INHOMOGENEOUS ELECTRON AND JELLIUM FUNCTIONALS

The Hamiltonian for an isolated system of N electrons in a volume V is given by

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

where m and e are the electron mass and charge, respectively, and $\delta(\mathbf{r})$ is the Dirac delta function. The number density operator for position $\mathbf{r}$ is

$$\hat{n}(\mathbf{r}) = \sum_{\alpha=1}^{N} \delta(\mathbf{r} - \hat{\mathbf{q}}_\alpha) \tag{2}$$

The position and momentum operators for electron α are $\hat{\mathbf{q}}_\alpha$ and $\hat{\mathbf{p}}_\alpha$, respectively. A caret over a symbol denotes the operator corresponding to that variable. The related jellium Hamiltonian is

$$\hat{H}_j = \sum_{\alpha=1}^{N} \frac{\hat{p}_\alpha^2}{2m} + \frac{1}{2}e^2 \int d\mathbf{r}\, d\mathbf{r}' \frac{(\hat{n}(\mathbf{r}) - n_b)(\hat{n}(\mathbf{r}') - n_b) - \hat{n}(\mathbf{r})\,\delta(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3}$$

The constant n_b denotes the density of a uniform neutralizing background for the electrons. When the grand canonical ensemble is considered, it is given by $n_b = \overline{N}/V$, where $\overline{N}$ is the average particle number. The two Hamiltonians are seen to be related by

$$\hat{H}_j = \hat{H}_e + \int d\mathbf{r}\, v_b(\mathbf{r})\,\hat{n}(\mathbf{r}) + E_b \tag{4}$$

with

$$v_b(\mathbf{r}) = -e^2 \int d\mathbf{r}' \frac{n_b}{|\mathbf{r} - \mathbf{r}'|} \tag{5}$$

The second term on the right side of eq 4 is the potential of interaction between the electrons and the background, and the third term is the background self-energy

$$E_b = \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}' \frac{(n_b e)^2}{|\mathbf{r} - \mathbf{r}'|} = -\frac{1}{2} \int d\mathbf{r}\, n_b v_b(\mathbf{r}) \tag{6}$$

Equation 3 is the usual definition of jellium as the electron system plus a uniform neutralizing background.

A. Grand Potential Functionals. Now consider the addition of an external single-particle potential $v_{ex}(\mathbf{r})$ to the electron and jellium Hamiltonians. The equilibrium properties for the corresponding inhomogeneous systems are defined by the grand canonical potentials

$$\beta\Omega_e(\beta, V|\mu) = -\ln \sum_{N=0}^{\infty} Tr^{(N)} e^{-\beta(\hat{H}_e - \int d\mathbf{r}\, \mu(\mathbf{r})\,\hat{n}(\mathbf{r}))} \tag{7}$$

$$\beta\Omega_j(\beta, V|\mu) = -\ln \sum_{N=0}^{\infty} Tr^{(N)} e^{-\beta(\hat{H}_j - \int d\mathbf{r}\, \mu(\mathbf{r})\,\hat{n}(\mathbf{r}))} \tag{8}$$

Here, the local chemical potential is defined by

$$\mu(\mathbf{r}) = \mu - v_{ex}(\mathbf{r}) \tag{9}$$

These grand potentials are functions of the inverse temperature β and the volume V and *functionals* of the local chemical potential $\mu(\mathbf{r})$. The functionals themselves, $\Omega_e(\beta, V|\cdot)$ and $\Omega_j(\beta, V|\cdot)$, are characterized by $\hat{H}_e$ and $\hat{H}_j$, respectively (the notation $\Omega(\beta, V|\cdot)$ is used to distinguish the functional from its value $\Omega(\beta, V|\mu)$ when evaluated at μ). Because the latter two are different, the functionals are different. However, from eq 4 they have the simple relationship

$$\beta\Omega_j(\beta, V|\mu) = \beta E_b + \beta\Omega_e(\beta, V|\mu - v_b) \tag{10}$$

In fact, all average properties in the corresponding grand ensembles have a similar relationship. For example, a property represented by the operator $\hat{X}$ has the averages

$$X_e(\beta, V|\mu) \equiv \sum_{N=0}^{\infty} Tr^{(N)} e^{\beta\Omega_e} e^{-\beta(\hat{H}_e - \int d\mathbf{r}\, \mu(\mathbf{r})\,\hat{n}(\mathbf{r}))} \hat{X} \tag{11}$$

$$X_j(\beta, V|\mu) \equiv \sum_{N=0}^{\infty} Tr^{(N)} e^{\beta\Omega_j} e^{-\beta(\hat{H}_j - \int d\mathbf{r}\, \mu(\mathbf{r})\,\hat{n}(\mathbf{r}))} \hat{X} \tag{12}$$

so with eqs 4 and 10 they are related by

$$X_j(\beta, V|\mu) = X_e(\beta, V|\mu - v_b) \tag{13}$$

B. Free Energy Density Functionals. The local number densities are

$$n_{\rm e}({\bf r}, \beta, V|\mu) = -\frac{\delta\beta\Omega_{\rm e}(\beta, V|\mu)}{\delta\beta\mu({\bf r})}, \quad n_{\rm j}({\bf r}, \beta, V|\mu) = -\frac{\delta\beta\Omega_{\rm j}(\beta, V|\mu)}{\delta\beta\mu({\bf r})}$$

$$(14)$$

The derivative of $\Omega_{\rm j}(\beta, V|\mu)$ is taken at constant $n_{\rm b}$. Using eq 10 or 13, it is seen that the number densities are related by

$$n_{\rm j}({\bf r}, \beta, V|\mu) = n_{\rm e}({\bf r}, \beta, V|\mu - v_{\rm b})$$

$$(15)$$

It can be shown that $\Omega_{\rm e}(\beta, V|\cdot)$ and $\Omega_{\rm j}(\beta, V|\cdot)$ (again with constant $n_{\rm b}$) are strictly concave functionals so that eq 14 defines the one-to-one invertible relationships $n_{\rm e} \Leftrightarrow \mu$ and $n_{\rm j} \Leftrightarrow \mu$. Consequently, a change in variables $\beta, V, \mu \to \beta, V, n_{\rm e}$ for the inhomogeneous electron system and $\beta, V, \mu \to \beta, V, n_{\rm j}$ for inhomogeneous jellium is possible. The corresponding Legendre transformations then define the free energy functionals of these densities

$$F_{\rm e}(\beta, V|n_{\rm e}) = \Omega_{\rm e}(\beta, V|\mu) + \int {\rm d}{\bf r} \, \mu({\bf r}) \, n_{\rm e}({\bf r}, \beta, V|\mu)$$

$$(16)$$

$$F_{\rm j}(\beta, V|n_{\rm j}) = \Omega_{\rm j}(\beta, V|\mu) + \int {\rm d}{\bf r} \, \mu({\bf r}) \, n_{\rm j}({\bf r}, \beta, V|\mu)$$

$$(17)$$

These are precisely the density functionals of DFT (e.g., defined by Mermin[8]).

Their relationship follows using eqs 4 and 15

$$\begin{aligned} F_{\rm j}(\beta, V|n_{\rm j}) &= \beta E_{\rm b} + \Omega_{\rm e}(\beta, V|\mu - v_{\rm b}) \\ &+ \int {\rm d}{\bf r} \, (\mu({\bf r}) - v_{\rm b}({\bf r})) n_{\rm e}({\bf r}, \beta, V|\mu - v_{\rm b}) \\ &+ \int {\rm d}{\bf r} \, v_{\rm b}({\bf r}) n_{\rm e}({\bf r}, \beta, V|\mu - v_{\rm b}) \\ &= F_{\rm e}(\beta, V|n_{\rm e}(|\mu - v_{\rm b})) + \int {\rm d}{\bf r} \, v_{\rm b}({\bf r}) \, n_{\rm e}({\bf r}, \beta, V|\mu - v_{\rm b}) + \beta E_{\rm b} \end{aligned}$$

$$(18)$$

and using eq 15 again gives the desired result.

$$F_{\rm j}(\beta, V|n_{\rm j}) = F_{\rm e}(\beta, V|n_{\rm j}) + \int {\rm d}{\bf r} \, v_{\rm b}({\bf r}) \, n_{\rm j}({\bf r}|\mu) + \beta E_{\rm b}$$

$$(19)$$

Because $\mu({\bf r})$ is arbitrary, so also is $n_{\rm j}({\bf r}|\mu)$ and eq 19 can be written more simply as

$$F_{\rm j}(\beta, V|n) = F_{\rm e}(\beta, V|n) + \int {\rm d}{\bf r} \, v_{\rm b}({\bf r}) \, n({\bf r}) + \beta E_{\rm b}$$

$$(20)$$

III. EXCHANGE-CORRELATION FUNCTIONAL EQUIVALENCE

Traditionally, the free energy density functional is separated into a noninteraction contribution, F_0, a mean-field Hartree contribution, $F_{\rm H}$, and the remaining exchange-correlation contribution, $F_{\rm xc}$

$$F = F_0 + F_{\rm H} + F_{\rm xc}$$

$$(21)$$

Clearly, F_0 is the same for the electron and jellium systems, as follows from eq 20 because $v_{\rm b}({\bf r}) = 0$ in this case. However, the Hartree terms (defined as the average intrinsic internal energy with the pair correlation function equal to unity) are different

$$F_{\rm eH}(\beta, V|n) = \frac{1}{2}e^2 \int {\rm d}{\bf r} \, {\rm d}{\bf r}' \frac{n({\bf r}) \, n({\bf r}')}{|{\bf r} - {\bf r}'|}$$

$$(22)$$

$$F_{\rm jH}(\beta, V|n) = \frac{1}{2}e^2 \int {\rm d}{\bf r} \, {\rm d}{\bf r}' \frac{(n({\bf r}) - n_{\rm b})(n({\bf r}') - n_{\rm b})}{|{\bf r} - {\bf r}'|}$$

$$(23)$$

In particular, their system size dependence is quite different. For example, in the uniform density limit (assuming a spherical volume) $F_{\rm eH}(\beta, V|n) \to C(n_{\rm e})^2 V^{5/3}$ (with $C = (4\pi)^2(1/15)(3/(4\pi))^{5/3} \simeq 0.967$), whereas $F_{\rm jH}(\beta, V|n)$ vanishes in this limit. This difference is the reason (along with charge neutrality) that $F_{\rm j}(\beta, V|n)$ has a proper thermodynamic limit[16] while $F_{\rm e}(\beta, V|n)$ does not (because it does not scale linearly with the volume).

At first sight, this seems at odds with eq 20 because the left side has a thermodynamic limit whereas each term on the right separately does not. However, the second and third terms cancel the singular volume dependence of $F_{\rm eH}$ so that

$$F_{\rm eH}(\beta, V|n) + \int {\rm d}{\bf r} \, v_{\rm b}({\bf r}) \, n({\bf r}) + \beta E_{\rm b} = F_{\rm jH}(\beta, V|n)$$

$$(24)$$

This observation, together with the equavalence of the noninteracting contributions, leads to the equivalence of the exchange-correlation contributions for the electron gas and jellium

$$F_{\rm jxc}(\beta, V|n) = F_{\rm exc}(\beta, V|n)$$

$$(25)$$

Note that this equivalence applies for general inhomogeneous densities, extending the familiar relationship for uniform systems.

These are two different inhomogeneous systems, yet their correlations are the same for every admissable density. The functionals are universal in the sense that their forms are independent of the underlying external potential. However, the potential associated with the chosen density of their argument is different in each case. To see this, consider the functional derivative of eq 20 with respect to the density

$$\frac{\delta F_{\rm j}(\beta, V|n)}{\delta n({\bf r})} = \mu({\bf r}) = \frac{\delta F_{\rm e}(\beta, V|n)}{\delta n({\bf r})} + v_{\rm b}({\bf r})$$

$$(26)$$

Hence, the density n is determined from the jellium functional by

$$\frac{\delta F_{\rm j}(\beta, V|n)}{\delta n({\bf r})} = \mu({\bf r}) = \mu - v_{\rm ex}({\bf r})$$

$$(27)$$

Alternatively, the same density is determined from the electron functional by

$$\frac{\delta F_{\rm e}(\beta, V|n)}{\delta n({\bf r})} = \mu({\bf r}) - v_{\rm b}({\bf r}) = \mu - (v_{\rm ex}({\bf r}) + v_{\rm b}({\bf r}))$$

$$(28)$$

For jellium, the potential is $v_{\rm ex}({\bf r})$, and for the electron gas, it is $v_{\rm ex}({\bf r}) + v_{\rm b}({\bf r})$. The two solutions to eqs 27 and 28 have the same relationship as expressed in eq 15.

IV. DISCUSSION

Practical approximations for the electron gas exchange-correlation functional are typically introduced at the level of its density, defined by

$$F_{\rm exc}(\beta, V|n) = \int {\rm d}{\bf r} \, f_{\rm exc}({\bf r}, \beta, V|n)$$

$$(29)$$

A formal functional expansion about the density at point $\bf r$ can be performed

$$f_{exc}(\mathbf{r}, \beta, V|n) = f_{exc}(\mathbf{r}, \beta, V|n)|_{n(\mathbf{r})}$$
$$+ \int d\mathbf{r}' \frac{\delta f_{exc}(\mathbf{r}, \beta, V|n)}{\delta n(\mathbf{r}')}\bigg|_{n(\mathbf{r})} (n(\mathbf{r}') - n(\mathbf{r}))$$

$$+ \int d\mathbf{r}' \, d\mathbf{r}'' \frac{\delta f_{exc}(\mathbf{r}, \beta, V|n)}{\delta n(\mathbf{r}')\delta n(\mathbf{r}'')}\bigg|_{n(\mathbf{r})} (n(\mathbf{r}') - n(\mathbf{r}))(n(\mathbf{r}'') - n(\mathbf{r})) + \dots$$

$$(30)$$

The coefficients are evaluated at the uniform density $n(\mathbf{r})$; i.e., all functional density dependence is evaluated at the same value. Consequently, the lead term is just the uniform electron gas exchange-correlation free energy per unit volume

$$f_{exc}(\mathbf{r}, \beta, V|n)|_{n(\mathbf{r})} = \frac{1}{V} F_{exc}(\beta, V, n_e)|_{n_e = n(\mathbf{r})}$$

$$(31)$$

This is known as the local density approximation. Similarly, subsequent terms in eq 30 are the response functions for the uniform electron gas. From the above analysis, all of these can now be identifed with those for jellium, which has been studied extensively. As noted in the Introduction, an accurate analytic fit for $F_{jxc}(\beta, V, n_e)$ is now available across the entire β, n_e plane,[15] so the local density approximation is known explicitly. Similarly, the first few response functions for jellium are known as well.[12]

More generally, approximations for exchange correlations away from the uniform limit (e.g., generalized gradient approximations) can be addressed for *inhomogeneous* jellium as well. Although this is a difficult problem, it is placed in a more controlled thermodynamic context due to charge neutrality and extensivity.

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Notes

The author declares no competing financial interest.

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■ REFERENCES

(1) Lastoskie, C.; Gubbins, K.; Quirke, N. Pore sizeheterogeneity and the carbon slit pore: a density functional theory model. *Langmuir* **1993**, *9*, 2693−2702.

(2) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, 864−871.

(3) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford: New York, 1989.

(4) Dreizler, R. M.; Gross, E. K. U. *DensityFunctional Theory: An Approach to the Quantum Many-Body Problem*; Springer Verlag: Berlin, 1990.

(5) Jones, R. O. Density functional theory: Itsorigins, rise to prominence, and future. *Rev. Mod. Phys.* **2015**, *87*, 897−923.

(6) Evans, R. Density Functionals in the Theory of Non-Uniform Fluids. In *Fundamentals of Inhomogeneous Fluids*, Henderson, D., Ed.; Marcell Dekker: New York, 1992; pp 85−176. The nature of theliquid-vapour interface and other topics in the statistical mechanics ofnon-uniform, classical fluids. *Adv. Phys.* **1979**, *28*, 143−200. Density Functional Theory for Inhomogenous Fluids: Statics, Dynamics, and Applications. In *3rd Warsaw School of Statistical Physics*; Cichocki, B., Napiówski, M., Piasecki, J., Eds.; Warsaw University Press: Warsaw, 2010; pp 43−85.

(7) Lutsko, J. Recent Developments in Classical DensityFunctional Theory. *Adv. Chem. Phys.* **2010**, *144*, 1−93.

(8) Mermin, D. Thermal Properties of the InhomogeneousElectron Gas. *Phys. Rev.* **1965**, *137*, 1441−1443.

(9) Eschrig, H. T > 0 Ensemble-state Density Functional Theory via Legendre Transform. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82*, 205120.

(10) *Frontiers and Challenges in Warm Dense Matter*; Graziani, F. et al., Eds.; Spinger Verlag: Heidelberg, 2014.

(11) Kohn, W.; Sham, L. J. Self-Consistent Equations IncludingExchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, 1133−1138.

(12) Giuliani, G.; Vignale, G.; *Quantum Theory of the Electron Liquid*; Cambridge University Press: New York, 2005.

(13) Sjostrom, T.; Dufty, J. Uniform electron gas atfinite temperatures. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, 115123. and references therein.

(14) Dornheim, T.; Groth, S.; Sjostrom, T.; Malone, F.; Foulkes, W.; Bonitz, M. Ab initio Quantum Monte Carlo simulation of the warmdense electron gas in the thermodynamic limit. *Phys. Rev. Lett.* **2016**, *117*, 156403. and references therein.

(15) Karasiev, V.; Sjostrom, T.; Dufty, J.; Trickey, S. B. Accurate Homogeneous Electron Gas Exchange-Correlation Free Energy for LocalSpin-Density Calculations. *Phys. Rev. Lett.* **2014**, *112*, 076403.

(16) Lieb, E.; Narnhofer, H. The thermodynamic limit for jellium. *J. Stat. Phys.* **1975**, *12*, 291−310.