Exact conditions on the temperature dependence of density functionals

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(Dated: April 29, 2016)

Universal exact conditions guided the construction of most ground-state density functional approximations in use today. We derive the relation between the entropy and Mermin free energy density functionals for thermal density functional theory. Both the entropy and sum of kinetic and electron-electron repulsion functionals are shown to be monotonically increasing with temperature, while the Mermin functional is concave downwards. Analogous relations are found for both exchange and correlation. The importance of these conditions is illustrated in two extremes: the Hubbard dimer and the uniform gas.

I. INTRODUCTION

Warm dense matter (WDM) is a rapidly growing multidisciplinary field that spans many branches of physics, including for example astrophysics, geophysics, attosecond physics, and nuclear physics[1–9]. In the last decade, quantum molecular dynamics, using DFT with electrons at finite temperatures, has been extremely successful at predicting material properties under extreme conditions, and has become a standard simulation tool in this field[10]. Almost all such simulations use ground-state exchange-correlation (XC) approximations, even when the electrons are significantly heated. Thermal density functional theory (thDFT) was formalized by Mermin[11], when he showed that the reasoning of Hohenberg and Kohn[12] could be extended to the grand canonical potential of electrons coupled to a thermal bath at temperature τ. In recent times, the Mermin-Kohn-Sham (MKS) equations of non-interacting electrons at finite temperature, whose density matches that of the physical system, are being solved to simulate warm dense matter[13, 14]. In most of these calculations, the ground-state approximation (GSA) is made, in which the exchange-correlation (XC) free energy, which typically depends on τ, is approximated by its ground-state value. Accurate results for the uniform gas are still being found[15–18], which provide input to a thermal local density approximation, but LDA is insufficiently accurate for many modern applications, and thermal GGA's are being explored[19].

Many useful exact conditions in ground-state DFT (relation between coupling constant and scaling, correlation scaling inequalities, exchange and kinetic scaling equalities, signs of energy components) were first derived[20] by studying the variational principle in the form of the Levy constrained search[21]. Most of these conditions are satisfied (by construction) by the local density approximation[13] and have been used for decades to constrain and/or improve more advanced approximations[22]. Their finite temperature analogs were derived in Ref. [23] (see also Ref. [24]), and extended in Ref. [25]. Because the kinetic and entropic contributions always appear in the same combination as the so-called kentropic energy (see Eq. (21) and related text), such relations can never be used to extract either component individually.

Many basic thermodynamic relations are proven via quantum statistical mechanics[26]. However, converting these to conditions on density functionals is neither obvious nor trivial. In the present work, we extend these methods to the dependence of the Mermin functional (i.e., the universal part of the free-energy functional) on the *temperature*, rather than on the coupling constant or the scale of the density. We find several new equalities and inequalities which apply to thDFT of all electronic systems. This allows us to separate entropic and kinetic contributions. We show that the entropy density functional is monotonically increasing with temperature, as is the sum of the kinetic and electron-electron repulsion density functionals, and that the temperature derivative of the Mermin functional is the negative of the entropy functional. Thus the Mermin functional is concave downwards as a function of temperature. Applying these conditions to the MKS system yields conditions on the exchange-correlation free energy functionals. Lastly, we illustrate all our findings in the two extreme cases of the uniform gas and the Hubbard dimer. We find a recent parametrization of the XC free energy of the uniform gas violates our conditions, although only for densities that are so low as to be unlikely to significantly affect any property calculated within thLDA.

II. THEORY

For a given average particle number, define the free energy of a statistical density-matrix Γ as

$$A^\tau[\Gamma] = H[\Gamma] - \tau S[\Gamma], \tag{1}$$

where $\hat{H}$ is the Hamiltonian operator, S extracts the entropy, and we use τ to denote temperature. Define

$$F_{\mathrm{I}}[\Gamma] = T[\Gamma] + V_{\mathrm{ee}}[\Gamma], \tag{2}$$

where $\hat{T}$ is the kinetic energy operator and $\hat{V}_{\mathrm{ee}}$ the electron-electron repulsion operator. Then

$$F^{\tau}[\Gamma] = F_{\mathrm{I}}[\Gamma] - \tau\, S[\Gamma]. \tag{3}$$

The Mermin functional, written in terms of a constrained search, is[23]

$$F^{\tau}[n] = \min_{\Gamma \to n} F^{\tau}[\Gamma], \tag{4}$$

where the argument distinguishes functionals of the density from those of the density-matrix. The free energy of a given system can be found from

$$A^{\tau} = \min_{n} \left\{ F^{\tau}[n] + \int d^3 r\, v(\mathbf{r})\, n(\mathbf{r}) \right\}. \tag{5}$$

We denote by $\Gamma^{\tau}[n]$ the statistical density matrix that minimizes $\hat{F}^{\tau}$ and yields density $n(\mathbf{r})$. Then:

$$\frac{dF^{\tau}[n]}{d\tau} = \frac{\partial F^{\tau}[\Gamma]}{\partial \tau} + \int d\Gamma\, \frac{\partial F^{\tau}[\Gamma]}{\partial \Gamma}\, \frac{d\Gamma^{\tau}[n]}{d\tau}, \tag{6}$$

where all are evaluated at $\Gamma^{\tau}[n]$. Because $\Gamma^{\tau}[n]$ is the minimizer, its derivative with respect to temperature (or any variable) vanishes. Thus

$$\frac{dF^{\tau}[n]}{d\tau} = -S^{\tau}[n]. \tag{7}$$

This is the DFT analog of the standard thermodynamic relation[26], and implies

$$F^{\tau}[n] = F^0[n] - \int_0^{\tau} d\tau'\, S^{\tau'}[n], \tag{8}$$

where $F^0[n]$ is the ground-state functional[12]. We note that Eq. (7) was derived in [9], but only within lattice DFT.

Given a Mermin functional (approximate or exact, interacting or not), Eq. (7) defines what the corresponding entropy functional must be. Since coordinate scaling[23] can separate the kentropic and potential contributions in F, Eq. (7) allows the entropic and kinetic energy functionals to be separated. Alternatively, given an entropy functional, Eq. (7) defines the temperature-dependence of the corresponding Mermin functional. Since the entropy is always positive,

$$dF^{\tau}[n]/d\tau \leq 0, \tag{9}$$

i.e., the Mermin functional is monotonically decreasing.

Now consider what happens when, for a given density and temperature τ, we evaluate the Mermin functional on the density matrix for that density but at a different temperature. By the variational principle, Eq. (5),

$$F^{\tau}[\Gamma^{\tau'}[n]] \geq F^{\tau}[n], \tag{10}$$

for any value of τ'. Thus

$$F_{\mathrm{I}}[\Gamma^{\tau'}[n]] - \tau\, S[\Gamma^{\tau'}[n]] \geq F_{\mathrm{I}}^{\tau}[n] - \tau\, S^{\tau}[n], \tag{11}$$

or

$$F_{\mathrm{I}}^{\tau'}[n] - \tau\, S^{\tau'}[n] \geq F_{\mathrm{I}}^{\tau}[n] - \tau\, S^{\tau}[n]. \tag{12}$$

Since this result is true for any pair of temperatures, we reverse τ and τ' to find:

$$F_{\mathrm{I}}^{\tau}[n] - \tau'\, S^{\tau}[n] \geq F_{\mathrm{I}}^{\tau'}[n] - \tau'\, S^{\tau'}[n]. \tag{13}$$

Addition of Eqs. (12) and (13) yields

$$(\tau - \tau')\,(S^{\tau}[n] - S^{\tau'}[n]) \geq 0, \tag{14}$$

so that the entropy monotonically increases with τ:

$$dS^{\tau}[n]/d\tau \geq 0. \tag{15}$$

Combining this with Eq. (7) implies

$$d^2 F^{\tau}[n]/d\tau^2 \leq 0. \tag{16}$$

Thus $F^{\tau}[n]$ is concave downwards.

We can also isolate the behavior of $F_{\mathrm{I}}^{\tau}[n]$. If we multiply Eq. (12) by τ', and Eq. (13) by τ, and add them together, all entropic contributions cancel, yielding

$$(\tau' - \tau)\,(F_{\mathrm{I}}^{\tau'}[n] - F_{\mathrm{I}}^{\tau}[n]) \geq 0, \quad dF_{\mathrm{I}}^{\tau}[n]/d\tau \geq 0. \tag{17}$$

Both $F_{\mathrm{I}}^{\tau}[n]$ and $S^{\tau}[n]$ are monotonically increasing, but the net effect is that the Mermin free energy is decreasing.

Applying these conditions to the Mermin-Kohn-Sham electrons[14], we find

$$dF_{\mathrm{s}}^{\tau}[n]/d\tau = -S_{\mathrm{s}}^{\tau}[n], \tag{18}$$

and the inequalities

$$\frac{dT_{\mathrm{s}}^{\tau}[n]}{d\tau}, \frac{dS_{\mathrm{s}}^{\tau}[n]}{d\tau} \geq 0 \geq \frac{dF_{\mathrm{s}}^{\tau}[n]}{d\tau}, \frac{d^2 F_{\mathrm{s}}^{\tau}[n]}{d\tau^2} \tag{19}$$

where subscript s denotes non-interacting, and $F_{\mathrm{s}}^{\tau}[n] = T_{\mathrm{s}}^{\tau}[n] - \tau\, S_{\mathrm{s}}^{\tau}[n]$. Some of these relations have long been invoked for the uniform and slowly-varying gases and for constructing orbital-free density functionals (see Ref. [27] and references therein), but here they have been proven for every inhomogeneous system.

III. ILLUSTRATION

To illustrate these results, we calculate all energy components for an asymmetric Hubbard dimer, i.e. a two-site Hubbard model with a potential $v_1 = -v_2$, as described
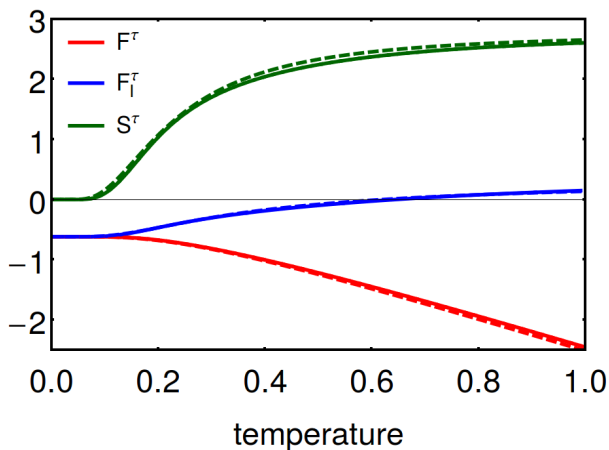
FIG. 1. Energy components for the Hubbard dimer in units of $2t$, where $U = 2t$ and $\Delta n = 0$: $F^\tau, F_{\mathrm{I}}^\tau, S^\tau$, both interacting (solid) and non-interacting (dashed).

in Ref. [28] for the groundstate and [29] for the thermal system. Here t is the hopping parameter, U the on-site repulsion, and Δn the difference in site occupations where the difference comes from having an inhomogeneous potential $\Delta v = v_2 - v_1$. This is the simplest possible model in which one can perform an exact thermal calculation, including the exact thermal correlation components. Fig. 1 shows the energy components, both interacting and non-interacting, as a function of temperature for the homogeneous system with $\Delta n = 0$. All our exact conditions are satisfied for many values of Δn and U.
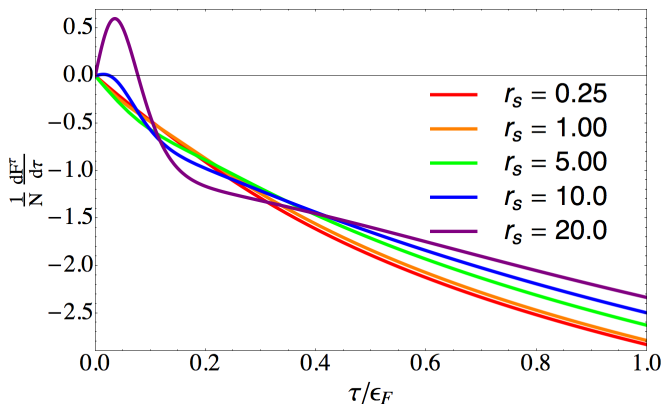

FIG. 2. Temperature dependence of the Mermin functional for spin-unpolarized uniform gas for several values of the Wigner-Seitz radius r_{s}, using the XC parametrization of Ref. [16], where ϵ_{F} is the Fermi energy.

At the other extreme is the uniform electron gas and a modern parametrization of its free energy[16]. In the special case of a uniform density and potential, our formulas become the same as the standard thermodynamic formulas. In Fig. 2, we plot the derivative of the free energy per particle for fixed density (r_{s} value where

$r_{\mathrm{s}} = (3/(4\pi n))^{1/3}$) as a function of temperature, on the scale of the Fermi energy and in atomic units. As $r_{\mathrm{s}} \to 0$, these curves converge to their well known[30] non-interacting value, in which the derivative is negative and decreasing everywhere, in accordance with Eq. (9). Unfortunately, by decreasing the density so that XC effects become relatively more important, we find that the parametrization violates our conditions for $r_{\mathrm{s}} > 10$. Via Eq. (7), this implies that the entropy is unphysically negative. While such low densities are irrelevant to most practical calculations using thLDA, parametrizations of the uniform gas should build in simple exact conditions such as ours. Note that our restrictions apply only to continuous parametrizations. The QMC data on which Ref. [16] is based[15] is for the XC energy at discrete values of the density, and so does not directly give the entropy.

For extremely high temperatures, sums over KS eigenstates become impractical, and only pure DFT can be applied. Because the uniform gas satisfies our conditions, and because Thomas-Fermi (TF) theory uses local approximations to the kinetic and entropic contributions which satisfy the conditions pointwise, we deduce that TF theory satisfies our conditions. However, recent attempts to go beyond TF theory, such as using generalized gradient approximations for the energy[19, 31, 32], should be tested for satisfaction of these constraints.

IV. EXCHANGE-CORRELATION

In the final section of this paper, we apply this reasoning to the MKS method. The Mermin functional is written in terms of the MKS quantities and a correction:

$$F^\tau[n] = F_{\mathrm{S}}^\tau[n] + U_{\mathrm{H}}[n] + A_{\mathrm{XC}}^\tau[n], \qquad (20)$$

called the exchange-correlation (XC) free energy. (The Hartree energy, $U_{\mathrm{H}}[n]$, has no explicit temperature dependence). The XC free energy is a sum of three components:

$$A_{\mathrm{XC}}^\tau[n] = K_{\mathrm{XC}}^\tau[n] + U_{\mathrm{XC}}^\tau[n] = T_{\mathrm{XC}}^\tau[n] - \tau S_{\mathrm{XC}}^\tau[n] + U_{\mathrm{XC}}^\tau[n], \qquad (21)$$

where U_{XC}^τ is the potential contribution and K_{XC}^τ is the kentropic contribution, which in turn consists of T_{XC}^τ, the kinetic contribution, and $-\tau S_{\mathrm{XC}}^\tau$, where S_{XC}^τ is the entropic contribution.

Subtract Eq. (18) from Eq. (7) to find

$$\frac{dA_{\mathrm{XC}}^\tau[n]}{d\tau} = -S_{\mathrm{XC}}^\tau[n], \qquad (22)$$

or

$$A_{\mathrm{XC}}^\tau[n] = E_{\mathrm{XC}}[n] - \int_0^\tau d\tau' \, S_{\mathrm{XC}}^{\tau'}[n]. \qquad (23)$$

All thermal XC effects are contained in the XC contribution to the entropy. This provides an intriguing alternative to the adiabatic connection formula of Ref. [23]

or the thermal connection formula of Ref. [25]. Our inequalities do not yield definite signs for XC quantities, just weak constraints that would be difficult to impose universally on an XC approximation:

$$\frac{dT_{\mathrm{XC}}^\tau}{d\tau} \geq -\frac{dT_{\mathrm{s}}^\tau}{d\tau}, \quad \frac{dS_{\mathrm{XC}}^\tau}{d\tau} \geq -\frac{dS_{\mathrm{s}}^\tau}{d\tau}. \quad (24)$$

We can also combine these with the coupling-constant derivatives of Ref. [25] to find Maxwell-style relations:

$$\left(\frac{\partial U_{\mathrm{XC}}}{\partial \tau}\right)_\lambda = -\lambda \left(\frac{\partial S_{\mathrm{XC}}}{\partial \lambda}\right)_\tau \quad (25)$$

where λ denotes evaluation at coupling-constant λ, holding the density fixed[23].

Exchange can be isolated by considering the limit of either weak interaction or scaling to the high-density limit[23]. The exchange free energy is

$$A_{\mathrm{X}}^\tau[n] = V_{\mathrm{ee}}[\Gamma_{\mathrm{S}}^\tau[n]] - U_{\mathrm{H}}[n] \quad (26)$$

in a case of no degeneracies (the only case we consider here). Because Γ_{S}^τ minimizes the kentropy alone, to first order in λ, kentropic corrections must be zero. Thus

$$K_{\mathrm{X}}^\tau[n] = 0, \quad T_{\mathrm{X}}^\tau[n] = \tau S_{\mathrm{X}}^\tau[n] = -\tau dA_{\mathrm{XC}}^\tau[n]/d\tau. \quad (27)$$

It may seem odd to consider a kinetic contribution to exchange (impossible in the ground state), but T_{X}^τ vanishes as $\tau \to 0$ in Eq. (27). For a uniform gas, the thermal exchange energy is well-known[30]. But for our Hubbard dimer[29], when $\langle N \rangle = 2$, we find $E_{\mathrm{X}}[n] = -U_{\mathrm{H}}[n]/2$, so that $T_{\mathrm{X}}^\tau = S_{\mathrm{X}}^\tau = 0$.
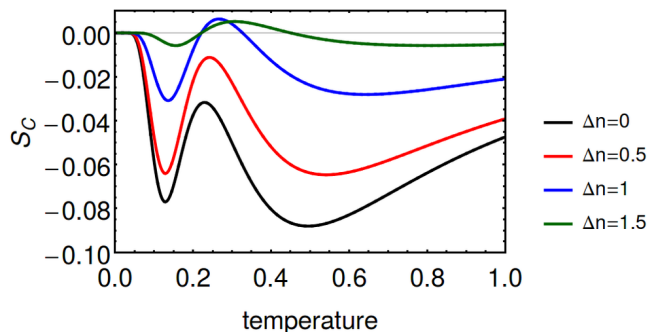

FIG. 3. Correlation entropy in the Hubbard dimer for several values of Δn as a function of temperature, in units of $2t$, where $U = 2t$.

The results of Eq. (23) apply to correlation alone and can be used in either direction, just as the relation for the full functional. They are well-known for the uniform gas from statistical mechanics[33–35]. But for an inhomogeneous system, they are non-trivial, and so we illustrate them on the asymmetric Hubbard dimer. In Fig. 3, we plot the entropic correlation as a function of temperature for several values of Δn, the occupation difference that arises from the asymmetric potential. Eq. (23) is satisfied within numerical precision. The derivative of S_{C}^τ

can change sign, even though both $S^\tau(\Delta n)$ and $S_{\mathrm{s}}^\tau(\Delta n)$ are monotonically increasing (This explains the small dip seen in Fig. 7 of Ref. [29]).

V. DISCUSSION AND CONCLUSIONS

Finally, we explain the apparent success of the ground-state approximation (GSA) for $A_{\mathrm{XC}}^\tau[n]$ in MKS equilibrium calculations. Almost all present-day calculations of WDM use this approximation, and a recent calculation on the Hubbard dimer[29] found that GSA worked well when neither the temperature nor the strength of the correlations were large (the conditions corresponding to most WDM calculations). Now we explain why. Write

$$F^{\tau,\mathrm{GSA}}[n] = F_{\mathrm{s}}^\tau[n] + U_{\mathrm{H}}[n] + E_{\mathrm{XC}}[n]. \quad (28)$$

Clearly, all temperature dependence is contained only in the KS part (usually a very dominant piece). Since the KS piece satisfies all the different inequalities and equalities, then so does any GSA calculation. But attempt to add corrections to a GSA calculation by writing

$$A_{\mathrm{XC}}^{\tau,\mathrm{GSA}}[n] = E_{\mathrm{XC}}^{\mathrm{GSA}}[n] + \Delta A_{\mathrm{XC}}^\tau[n]. \quad (29)$$

Only the thermal correction appears in the exact conditions we have derived, since they all contain temperature derivatives. But there is no simple way to know if the corrections will satisfy the exact conditions for all possible systems. The only case would be using local approximations for all temperature-dependent quantities, and then using energy densities from the uniform gas. Thus a TF calculation, with thermal LDA corrections, would satisfy these conditions, since they would be satisfied pointwise, as the uniform gas satisfies these conditions for every density. But in any MKS calculation using approximate thermal XC corrections, this is not guaranteed. Unless special care is taken to guarantee satisfaction of our conditions, *only* GSA automatically does this. This is analogous to the situation in TDDFT (at zero temperature): The adiabatic LDA, which ignores the history dependence that is known to exist in the TDDFT functionals, satisfies most exact conditions, while the time-dependent LDA (the Gross-Kohn approximation[36]) violates several important constraints[37]. All this explains why the GSA has been working well in many situations[1, 38]. The GSA appears to be correct in both the low- and high-temperature limits and, at least for model systems, reproduces the exact KS orbitals accurately[29]. Of course, this depends on the specific property being calculated and the acceptable level of error, and does not preclude moderate deviations, especially between these extremes, i.e., warm dense matter. But any calculation that includes, e.g., semilocal thermal XC corrections, risks violating the exact conditions listed here that GSA automatically satisfies, and should be checked for such violations. On the other hand, the Hartree-Fock approximation (or rather, the DFT equivalent, called EXX[39]), must satisfy the conditions since any expansion in powers of the

coupling constant up to some order must satisfy all our conditions.

To conclude, the formulas presented here are exact conditions applying to every thermal electronic system when treated with DFT, and should guide the future construction of approximate functionals.

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