

# Exchange and correlation in finite-temperature TDDFT<sup>\*</sup>

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**Abstract.** We discuss the finite-temperature generalization of time-dependent density functional theory (TDDFT). The theory is directly analogous to that at temperature  $T = 0$ . For example, the finite- $T$  TDDFT exchange-correlation kernel  $f_{xc}(T, n)$  in the local density approximation can again be expressed as a density derivative of the exchange correlation potential  $f_{xc}(T, n) = [\partial v_{xc}(T, n)/\partial n]\delta(\mathbf{r} - \mathbf{r}')$ , where  $n = N/V$  is the electron number density. An approximation for the kernel  $f_{xc}(T, n)$  is obtained from the finite- $T$  generalization of the retarded cumulant expansion applied to the homogeneous electron gas. Results for  $f_{xc}$  and the loss function are presented for a wide range of temperatures and densities including the warm dense matter regime, where  $T \approx T_F$ , the electron degeneracy temperature. The theory also permits a physical interpretation of the exchange and correlation contributions to the theory.

## 1 Introduction

Recently there has been considerable interest in the behavior of condensed matter at finite temperature (FT) and especially in extreme conditions [1–4]. Often such studies are based on the FT extension of density functional theory (DFT) [5]. Indeed, DFT [6,7] has been one of the most useful theories of modern condensed matter physics for describing materials properties. Conventional DFT is formally exact only for ground state properties. However, in principle, thermodynamic equilibrium properties can also be described exactly with Mermin’s (FT) extension of DFT [5]. In a remarkable generalization, an analogous density functional existence theorem has been established for the time-dependent generalization of DFT, i.e., TDDFT [8,9]. The aim of this paper is to discuss the further generalization of TDDFT for finite  $T$ , building on the theory developed e.g., in references [10–12]. In particular we focus on the behavior of the FT exchange-correlation kernel  $f_{xc}(T, n)$  and a few illustrative applications.

Despite their exact properties, DFT and TDDFT are useful in practice only to the extent that the exchange-correlation potential and kernel are accurately known. Unfortunately the task of deriving such functionals has been formidable. Currently practical exchange-correlation functionals at  $T = 0$  are typically based on computationally demanding quantum-Monte-Carlo calculations for the homogeneous electron gas (HEG) [13]. Likewise, FT DFT

functionals are typically based on numerical fits to similar calculations [14,15]. Recently, however, an alternative Green’s function approach has been introduced for calculations of thermodynamic, exchange-correlation, and spectral properties [16]. This approach is based on a FT generalization of the retarded cumulant Green’s function and sum-rules for the energy and electron number-density. For example, the FT total energy per particle is obtained from the Galitskii–Migdal–Koltun sum-rule [17,18], equivalent to that of Martin and Schwinger [19]. Exchange-correlation energies and potentials are also obtained, by subtracting the respective independent particle contributions. Other thermodynamic properties such as the equation of state for the HEG have also been calculated [20]. We generalize this approach here to obtain the FT TDDFT exchange-correlation kernel  $f_{xc}$  within the adiabatic local density approximation (ALDA) over a broad range of temperatures and densities. Details of the behavior of the exchange and correlation parts are also discussed. An advantage of the approach is a physical interpretation of these effects in terms of the behavior of the cumulant. As an application, calculations are also presented for the loss function in the ALDA and compared to the random phase approximation (RPA). Finally we give a brief summary and outlook.

## 2 Finite- $T$ TDDFT

The theory of TDDFT [8,9] and related treatments of linear response within DFT [21,22] have been discussed in detail in several comprehensive reviews [23,24]. The basic formalism can be treated in various ways, both in

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frequency space [21–24], and real-time [25–27]. The aim of TDDFT is to formulate a DFT for the time-dependent density response  $\delta n(t)$  of an interacting electron system to a time-varying perturbing potential  $\delta v(t')$ . The physical quantity of interest is the linear density response function  $\chi(t, t') = \delta n(t)/\delta v(t')$ . [For simplicity we will drop explicit time, space, frequency, temperature, density or other arguments, unless otherwise needed for clarity.] Formally within TDDFT  $\chi$  satisfies an integral equation

$$\chi = \chi_0 + \chi_0 K \chi, \quad (1)$$

where  $K = v_c + f_{xc}$ ,  $v_c$  is the coulomb potential, and  $f_{xc}$  the exchange-correlation kernel. For example, for the paramagnetic HEG the bare response function in frequency and wave-number space is

$$\chi_0(q, \omega) = 2 \int \frac{d^3 k}{(2\pi)^3} \frac{f_k - f_{k+q}}{\omega - \varepsilon_{k+q} + \varepsilon_k}, \quad (2)$$

where  $f_k(T, \mu) = 1/[\exp[\beta(\varepsilon_k - \mu)] + 1]$  are the Fermi occupation factors,  $\varepsilon_k$  the single-particle energies,  $\mu(T, n)$  the chemical potential at a given density  $n = N/V$  in the thermodynamic limit, and  $\beta = 1/k_B T$ . The temperature and density dependence are implicit in  $f_k$ .

### 3 Finite- $T$ exchange-correlation kernel

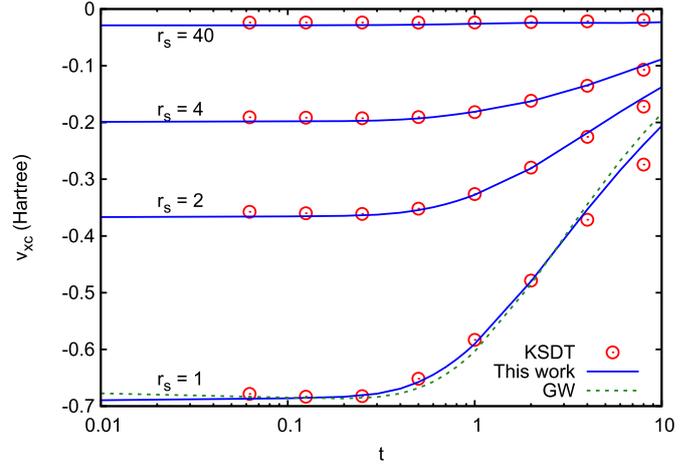
The formal derivation of FT TDDFT proceeds similarly to that at zero  $T$  [21], with *mutatis-mutandis* replacements of the zero temperature occupation numbers by Fermi functions  $f_k(T, \mu)$  calculated with the FT value of the chemical potential  $\mu(T, n)$ . Consequently one deduces (cf. Eqs. (23) and (24) of Ref. [21]) that the adiabatic FT TDDFT kernel is again given by the density derivative of the exchange correlation potential  $v_{xc}(T, n)$ ,

$$f_{xc}(T, n) = \frac{\partial v_{xc}(T, n)}{\partial n} \delta(\mathbf{r} - \mathbf{r}'). \quad (3)$$

The FT exchange-correlation potential  $v_{xc}(T, n)$  can be calculated in different ways using thermodynamic identities. For example, as originally shown by Kohn and Sham [7],  $v_{xc}$  can be obtained from the density derivative of the Helmholtz free energy per particle  $a_{xc} = (A - A_0)/N$ , where  $A = E - TS$  and  $A_0$  is that calculated for electrons in the independent particle approximation. Thus

$$v_{xc}(T, n) = \frac{\partial [na_{xc}(T, n)]}{\partial n}. \quad (4)$$

As expected this expression reduces to the usual expression in terms of the exchange-correlation energy per particle  $v_{xc}(T=0, n) = \partial [n\varepsilon_{xc}]/\partial n$  at  $T=0$ . In the HEG,  $v_{xc}$  is equivalent to the exchange correlation part of the chemical potential  $v_{xc} \equiv \mu_{xc} = \partial A_{xc}/\partial N$ , i.e., the exchange correlation part of the Gibbs free energy per particle  $\mu = G/N$  [7,28]. As an example, Figure 1 illustrates results for  $v_{xc}(T, n)$  from the FT cumulant



**Fig. 1.** Finite- $T$  exchange-correlation potential  $v_{xc}$  vs.  $t = T/T_F$  and the Wigner–Seitz density parameter  $r_s = (3/4\pi n)^{1/3}$  from the FT cumulant Green’s function approach (solid), the GW approximation (dashes), path integral Monte-Carlo calculations (dots) [29], and fitted FT DFT functionals (circles) [14], for a wide range of densities  $r_s$  and temperatures  $T$  compared to the degeneracy temperature  $T_F$ .

Green’s function approach [16], as discussed in more detail below.

Thus at all temperatures the FT TDDFT kernel in the ALDA can be expressed equivalently as

$$f_{xc}(T, n) = \frac{\partial \mu_{xc}(T, n)}{\partial n} \delta(\mathbf{r} - \mathbf{r}'), \quad (5)$$

$$= \frac{\partial^2 [na_{xc}(T, n)]}{\partial n^2} \delta(\mathbf{r} - \mathbf{r}'). \quad (6)$$

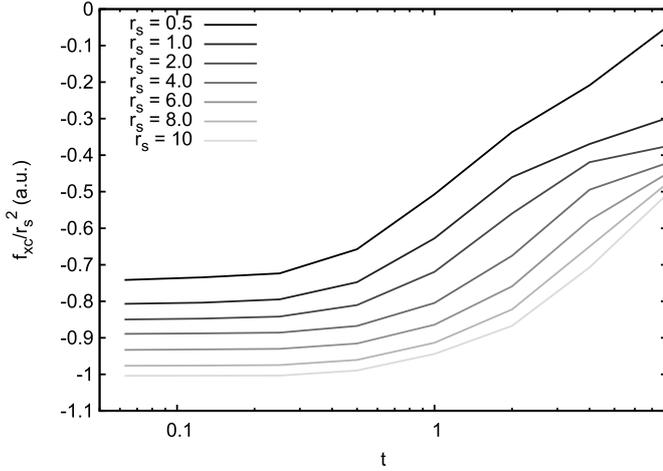
The first form [Eq. (5)] is convenient in practice since it circumvents calculations of the Helmholtz free energy  $A$  and its density derivatives, and can be obtained once a sufficiently accurate approximation for  $\mu_{xc}(T, n)$  is available. As an illustration calculations of  $f_{xc}(T, n)$  in the ALDA from equation (5) for a wide range of temperatures and densities (Fig. 2).

The second [Eq. (6)] is similar to the suggestion of reference [30], apart from the factor of  $n$  in the numerator. These calculations are based on cumulant Green’s function results for  $\mu_{xc}(T, n)$  from reference [16] as outlined below. Then  $f_{xc}$  was calculated by numerical finite differences from equation (5).

Comparisons with previous results for  $r_s = 2$  and 4 are in good agreement. Since  $v_{xc} \sim n^{1/3}$  at low- $T$  being dominated by exchange, one may expect that  $f_{xc}(T, n)$  scales roughly as  $n^{-2/3} r_s^2$  and is hence more strongly dependent on density  $n = (3/4\pi r_s^3)$ . This behavior appears to hold over a broad range of densities, i.e., the results for  $f_{xc}/r_s^2$  in Figure 2 are comparable over a wide range of  $r_s$ .

### 4 Green’s function approach

Our explicit calculations of  $\mu_{xc}$  and  $f_{xc}$  are based on the FT extension of the cumulant Green’s function approach



**Fig. 2.** Finite- $T$  TDDFT exchange-correlation kernel scaled by  $r_s^2$ , i.e.,  $f_{xc}/r_s^2$  vs.  $t = T/T_F$  from the FT cumulant Green's function approach for a range of density parameters  $r_s = (3/4\pi n)^{(1/3)}$ .

[16] applied to the HEG. Formally the chemical potential  $\mu(T, n)$  is determined self-consistently by enforcing charge conservation  $(1/V)\Sigma_k n_k = \langle N(T)/V \rangle = n$  where

$$n(\mu, T) = \frac{1}{V} \sum_k \int d\omega A_k(\omega) f(\omega). \quad (7)$$

Subtracting the chemical potential  $\mu_0(T, n)$  for the non-interacting system gives the exchange correlation part, i.e.  $\mu_{xc} \equiv \mu(T, n) - \mu_0(T, n)$ . We have checked that our calculations of  $\mu_0(T, n)$  agree well with those of reference [28], and that the total energies  $E_0$  agree with those of reference [13]. The single-particle occupation numbers  $n_k(T)$  given by the integral in equation (7) are calculated in terms of the spectral function  $A_k(\omega)$  [19]. Note that in this work, the self-consistency condition for the chemical potential is only applied to the explicit calculation of  $n(\mu, T)$  in equation (7). However, additional self-consistency could be investigated, since the spectral function itself is dependent on the single particle energies and chemical potential through the self-energy and dielectric function. Thus our procedure is analogous to a “one-shot” GW calculation. The spectral function  $A_k(\omega)$  characterizes the energy distribution of a given one-particle state  $k$ . In contrast to the independent particle approximation  $A_k(\omega) = \delta(\omega - \varepsilon_k)$ , the spectral function generally has a distribution that reflects the many-body exchange and correlation effects in the system. This spectrum can be expressed as the imaginary part of the one-particle Green's function  $G_k(\omega)$  for the interacting electron system

$$A_k(\omega) = -\frac{1}{\pi} \text{Im} \int d\omega e^{i\omega t} G_k(t). \quad (8)$$

Formally the Green's function  $G_k(t)$  can be represented exactly using the Hedin equations with a self-energy  $\Sigma = GW\Gamma$  [31], where  $W$  is the screened-Coulomb interaction and  $\Gamma$  the vertex function. However, owing to the

extreme difficulty of calculating  $\Gamma$ , the GW approximation  $\Gamma \equiv 1$  is often used. Although the GW approximation describes quasi-particle behavior well, it generally gives a poor description of satellite features in the spectral function beyond the quasi-particle peaks [31]. Recently however, it has been found that the retarded cumulant Green's function gives an improved description of the spectral function, including the satellites [32,33]. This approach has recently been generalized to finite temperatures [16]. Briefly the method is based on an exponential ansatz for the FT Green's function in the time-domain for a given single-particle state  $k$  in which  $G$  is assumed to be diagonal,  $G_k(t) = -i\theta(t)e^{-i\varepsilon_k^x t} e^{\tilde{C}_k(t)}$ . Another advantage of this formulation is that the static exchange and dynamic correlation contributions are separable  $C_k(t) = -i\Sigma_k^x t + \tilde{C}_k(t)$ . All correlation effects are thus included in the dynamic part  $\tilde{C}_k(t)$  of the total cumulant which can be expressed in Landau form [34],

$$\tilde{C}_k(t) = \int d\omega \frac{\beta_k(\omega)}{\omega^2} (e^{-i\omega t} + i\omega t - 1). \quad (9)$$

Here the kernel  $\beta_k(\omega) = (1/\pi) |\text{Im} \Sigma_k(\omega + \varepsilon_k)|$  reflects the excitation spectrum in the system, with peaks proportional to those in the loss function,

$$L(q, \omega) = |(1/\pi) \text{Im} \epsilon^{-1}(q, \omega)|. \quad (10)$$

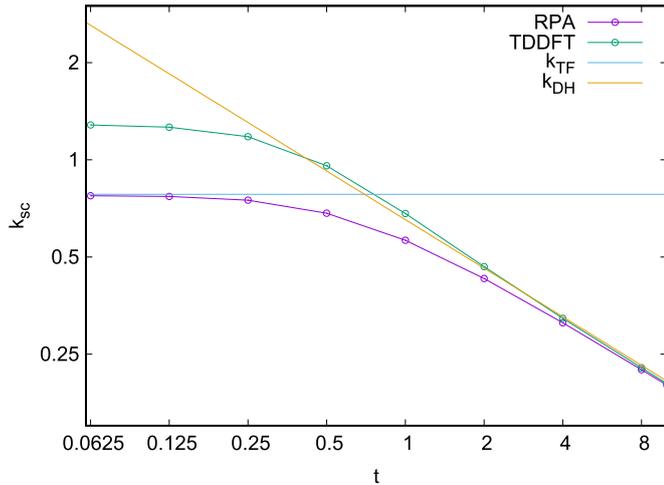
Lastly the FT self energy in  $\beta_k$  is calculated to leading order in  $W$  using the FT generalization of the GW approximation,

$$\Sigma_{\mathbf{k}}(\omega, T) = \int d\omega' \frac{d^3 q}{(2\pi)^3} |\text{Im} W(\mathbf{q}, \omega')| \times \left[ \frac{f(\varepsilon_{\mathbf{k}-\mathbf{q}}) + N(\omega')}{\omega + \omega' - \varepsilon_{\mathbf{k}-\mathbf{q}} + i\delta} + \frac{1 - f(\varepsilon_{\mathbf{k}-\mathbf{q}}) + N(\omega')}{\omega - \omega' - \varepsilon_{\mathbf{k}-\mathbf{q}} + i\delta} \right], \quad (11)$$

where  $N(\omega) = 1/(e^{\beta\omega} - 1)$  is the Bose factor at frequency  $\omega$ . The imaginary part of  $\Sigma_{\mathbf{k}}(\omega)$  then yields the excitation spectrum  $\beta_k(\omega)$ . At very high- $T$  compared to  $T_F$ , the behavior of the  $\beta_k$  is dominated by the Bose factors  $N(\omega) \sim k_B T/\omega$  and becomes strongly symmetric about  $\omega = 0$ . To obtain the screened interaction  $W = v/\epsilon$  we use the FT-RPA approximat for the dielectric function  $\epsilon = 1 + (4\pi/q^2)\chi_0$ , as in reference [16].

## 5 Calculations

Once  $f_{xc}(T, n)$  is known, FT TDDFT calculations of spectra can be carried out for a variety of applications [23]. As an example we show calculations of the the screening constant  $k_{sc}(T)$  from the static limit  $\epsilon(q, T) = 1 + k_{sc}^2/q^2$ . This is shown in Figure 3, and compared to the low temperature Thomas-Fermi (TF) approximation, as well as the high temperature Debye-Hückel (DH) form. The RPA screening limits to each of these at low and high



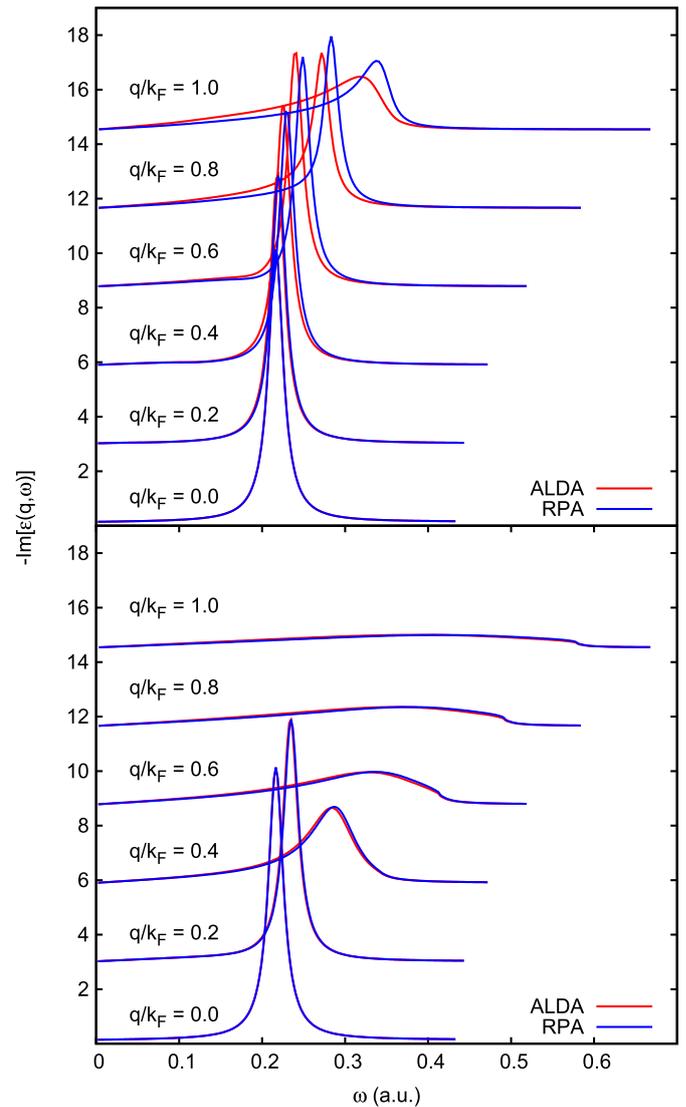
**Fig. 3.** FT screening constant  $k_{sc}(T)$  from TDDFT (green) and RPA (violet) for  $r_s = 4$ . Note that  $k_{sc}$  in TDDFT always exceeds the Thomas–Fermi limit and that in the RPA and rapidly asymptotes to the Debye–Hückel limiting behavior at high  $T$ .

temperatures, respectively, while the TDLDA screening deviates from the TF value at low  $T$ , and more quickly approaches the linear DH behavior than that of the RPA.

As a second example, we calculate the loss function  $L(q, \omega)$ , (Fig. 4) for various values of  $q$  from 0 to  $k_F$  and  $T$ . Note that for low temperature there are appreciable differences in the plasmon dispersion between TDDFT and RPA, while at high temperature these differences are small. Various optical constants can then be obtained in terms of  $\epsilon_1$  and  $\epsilon_2$  in the long-wavelength limit [35]  $q \rightarrow 0$ . In this limit the effect of  $f_{xc}$  is small compared to  $v$ , as illustrated by the small differences between the ALDA and RPA in Figure 4. We also find that at large  $q$ , ALDA and RPA are virtually equivalent, whereas there are visible differences in the plasmon frequency for intermediate  $q$ .

## 6 Summary and outlook

The extension of TDDFT to finite temperatures is directly analogous to the zero temperature development. For example, the exchange-correlation kernel  $f_{xc}(T, n)$  is again given by the density derivative of the exchange-correlation part of the chemical potential but calculated at temperature  $T$  as in equation (5). Given its simplicity compared to GW/BSE, TDDFT can be advantageous for practical calculations of time-dependent response once a reliable estimate of  $f_{xc}$  is available. Illustrative calculations of  $f_{xc}$  for the HEG in the ALDA have been obtained from the FT retarded cumulant Green’s function formalism. Interestingly the temperature dependence of  $f_{xc}$  is only weakly varying at low temperatures  $T < T_F$  so the zero temperature theory is usually a good approximation at normal conditions. As observed for  $v_{xc}$  and  $\epsilon_{xc}$  [16], correlation effects in  $f_{xc}$  remain strong even at relatively high temperatures  $T \approx T_F$  while exchange effects diminish rapidly



**Fig. 4.** Finite- $T$  TDDFT loss function in the ALDA from equation (11) and the RPA response function in equation (2) vs.  $q$  for low and high  $T$ :  $T/T_F = 0.1$  (top), and 10 (bottom) vs.  $q = 0$  (bottom) to  $q = k_F$  (top) of each in steps of  $0.2 k_F$ .

above  $T_F$ , corresponding to a cross-over from exchange to Coulomb correlation dominated behavior. It is also of interest to compare TDDFT with the GW Bethe-Salpeter equation approach, which is similar to that for TDDFT except for the form of the kernel  $K$  in equation (1) [36]. It is not obvious that the ALDA  $f_{xc}(T, n)$  is an adequate approximation for all physical properties since it is real, local, and static. In contrast, the importance of quasi-particle corrections in the GW/BSE at low  $T$  [36] suggest that inelastic losses are also important at high  $T$  for various spectra.

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## Author contribution statement

All the authors were involved in the preparation of the manuscript. All the authors have read and approved the final manuscript.

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