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Contributions to Plasma Physics

Free energy of the uniform electron gas: Testing analytical models against first-principles results[†]

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The uniform electron gas is a key model system in the description of matter, including dense plasmas and solid-state systems. However, the simultaneous occurrence of quantum, correlation, and thermal effects makes the theoretical description challenging. For these reasons, over the last half century, many analytical approaches have been developed, the accuracy of which has remained unclear. We have recently obtained the first ab initio data for the exchange correlation free energy of the uniform electron gas, which now provides the opportunity to assess the quality of the mentioned approaches and parameterizations. Particular emphasis is placed on the warm, dense matter regime, where we find significant discrepancies between the different approaches.

KEYWORDS

free energy, quantum Monte Carlo, uniform electron gas, warm dense matter

1 | INTRODUCTION

Over the last decade, there has emerged growing interest in the so-called warm dense matter (WDM), which is of key importance for the description of, for example, astrophysical systems,[1,2] laser-excited solids,[3] and inertial confinement fusion targets.[4–6] The WDM regime is characterized by the simultaneous occurrence of strong (moderate) correlations of ions (electrons), thermal effects, as well as quantum effects of the electrons. In dimensionless units, typical parameters are the Brueckner parameter $r_s = \bar{r}/a_B$ and the reduced temperature $\theta = k_B T/E_F$, both being of the order of unity (more generally in the range 0.1–10). Here, $\bar{r}$ and a_B denote the mean interparticle distance and the Bohr radius, respectively. A third relevant parameter is the classical coupling parameter of the ionic component, $\Gamma_i = Z_i^2 e^2/\bar{r} k_B T$, which is often larger than unity indicating that the ionic component is far from an ideal gas. This makes the theoretical description of this peculiar state of matter particularly challenging, as there is no small parameter to perform an expansion around.

In the ground state, there exists a large toolkit of approaches that allow the accurate description of manifold physical systems, the most successful of which arguably being Kohn–Sham density functional theory (DFT) (e.g., [7,8]). The basic idea of DFT is to map the complicated and computationally demanding quantum many-body problem onto an effective single-particle problem. This would be exact if the correct exchange-correlation functional of the system of interest was available, which is, of course, not the case. In practice, therefore, one has to use an approximation. The foundation of the great success of DFT has been the local density approximation (LDA), that is, the use of the exchange-correlation energy E_{xc} of the uniform electron gas (UEG) with the same density as the more complicated system of interest. Accurate data for E_{xc} of the UEG was obtained by Ceperley and Alder[9] using a quantum Monte Carlo (QMC) method, from which Perdew and Zunger[10] constructed a simple parameterization with respect to density, $E_{xc}(r_s)$, which is still used to this day.

However, the accurate description of WDM requires the extension of DFT to finite temperature. This has been realized long ago by Mermin[11], who used a superposition of excited states weighted with their thermal occupation probability. A

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strict approach to the thermodynamic properties of this system also requires an appropriate finite-temperature extension of the LDA, in particular, replacement of the ground-state energy functionals by free energies, that is $E \rightarrow f = E - TS$. This means, a finite-temperature version of the LDA requires accurate parameterizations of the *exchange correlation free energy* with respect to temperature and density,[12–17] that is, $f_{xc}(r_s, \theta)$, even though in some cases the entropic correction may be small. This seemingly benign task, however, turns out to be far from trivial because accurate data for the free energy are much more involved than the ground-state results. While for the ground state reliable QMC data have been known for a long time, until recently,[18–28] the notorious fermion sign problem[29,30] has prevented reliable QMC simulations in the warm, dense regime. Therefore, during the recent four decades, many theoretical approaches to $f_{xc}(r_s, \theta)$ have been developed that have lead to a variety of parameterizations (for an overview on early works, see e.g., Refs. [31,32]). Some of them have gained high popularity and been successfully applied in many fields, even though their accuracy has not been thoroughly tested. It is the purpose of this paper to present such a quantitative comparison of earlier models with new simulation results.

In Section 2, we introduce a selection of such functions. First, we analyze the purely analytical expression presented by Ebeling et al. (e.g., Ref. [33]). Next, we study functional fits to linear response data based on static local field correction schemes that were suggested by Singwi, Tosi, Land, and Sjölander (STLS)[34] (Section 2.2) and Vashishta and Singwi (VS)[35] (Section 2.3). As a fourth example, we consider the quantum-classical mapping developed by Dharma-wardana and Perrot (PDW)[36,37] (Section 2.4). Finally, we consider the recent parameterization by Karasiev, Sjostrom, Dufty, Trickey (KSDT)[38] (Section 2.5), which is based on the restricted path integral Monte Carlo (RPIMC) data by Brown et al. that became available recently.[39] However, those data have a limited accuracy because of (a) the use of the fixed-node approximation[40] and (b) an inappropriate finite-size correction (see Dornheim et al.[27]), giving rise to systematic errors in the free energy results, as we will show below. In Section 3, we compare all aforementioned parameterizations of f_{xc} to the new, accurate QMC data by Dornheim et al.[27], which are free from any systematic bias and, hence, allow us to gauge the accuracy of models. Particular emphasis is laid on the WDM regime.

2 | FREE-ENERGY PARAMETERIZATIONS

2.1 | Ebeling's Padé formulae

The idea to produce an analytical formula for the thermodynamic quantities that connects known analytical limits via a smooth Padé approximant is due to Ebeling, Kraeft, and Richert et al.[41–44] These approximations have been quite influential in the description of nonideal plasmas and electron–hole plasmas in the 1980s and 1990s, receiving, in part, a substantial number of citations. As they have been improved continuously in the following years, we, therefore, discuss only the more recent versions, compare [33,45] and references therein.

Ebeling et al. used Rydberg atomic units and introduced a reduced thermal density

$$\bar{n} = n\Lambda^3 = 6\sqrt{\pi}r_s^{-3}\tau^{-3/2} \tag{1}$$

with the usual thermal wavelength Λ, and $\tau = k_B T/\text{Ry}$ being the temperature in energy units. The Padé approximation for f_{xc} then reads[33]

$$f_{xc}^{\text{Ebeling,Ry}}(r_s, \tau) = -\frac{f_0(\tau)\bar{n}^{1/2} + f_3(\tau)\bar{n} + f_2\bar{n}^2 \epsilon^{\text{Ry}}(r_s)}{1 + f_1(\tau)\bar{n}^{1/2} + f_2\bar{n}^2} \tag{2}$$

with the coefficients

$$f_0(\tau) = \frac{2}{3}\left(\frac{\tau}{\pi}\right)^{1/4}, \quad f_1(\tau) = \frac{1}{8f_0(\tau)}\sqrt{2}(1 + \log(2)), \quad f_2 = 3, \quad f_3(\tau) = \frac{1}{4}\left(\frac{\tau}{\pi}\right)^{1/2} \tag{3}$$

and the ground-state parameterization for the exchange correlation energy

$$\epsilon^{\text{Ry}}(r_s) = \frac{0.9163}{r_s} + 0.1244 \log\left(1 + \frac{2.117r_s^{-1/2}}{1 + 0.3008\sqrt{r_s}}\right). \tag{4}$$

To achieve better comparability with the other formulas discussed below, we re-express Equation 2 in Hartree atomic units as a function of r_s and the reduced temperature $\theta = k_B T/E_F$:

$$f_{xc}^{\text{Ebeling,Ha}}(r_s, \theta) = -\frac{1}{2}\frac{Ar_s^{-1/2}\theta^{-1/2} + Br_s^{-1}\theta^{-1} + C\theta^{-3}\epsilon^{\text{Ry}}(r_s)}{1 + D\theta^{-1}r_s^{1/2} + C\theta^{-3}}, \quad \text{with} \tag{5}$$

$$A = \frac{2}{3\sqrt{\pi}}\left(\frac{8}{3}\right)^{1/2}\left(\frac{4}{9\pi}\right)^{-1/6}, \quad B = \frac{2}{3\pi}\left(\frac{4}{9\pi}\right)^{-1/3}, \quad C = \frac{64}{3\pi},$$ (6)

$$D = \frac{(1 + \log(2))\sqrt{3}}{4}\left(\frac{4}{9\pi}\right)^{1/6}.$$

Evidently, Equation 5 incorporates the correct ground-state limit

$$\lim_{\theta \to 0} f_{xc}^{\text{Ebeling,Ha}}(r_s, \theta) = -\frac{1}{2}\epsilon^{\text{Ry}}(r_s),$$ (7)

where the pre-factor $1/2$ is due to the conversion between Rydberg and Hartree units. Similarly, in the high-temperature limit, the well-known Debye–Hückel result is recovered, for example Ref. [46]

$$\lim_{\theta \to \infty} f_{xc}^{\text{Ebeling,Ha}}(r_s, \theta) = -\frac{1}{2}A\, r_s^{-1/2}\theta^{-1/2} = -\frac{1}{\sqrt{3}}r_s^{-3/2}T^{-1/2}.$$ (8)

Results for the warm, dense UEG computed from these formulas are included in the following figures. For the Padé approximations to the UEG at strong coupling in the quasi-classical regime, see, for example, Ref. [47].

2.2 | Parameterization by Ichimaru et al.

In the mid-1980s, Tanaka, Ichimaru, and coworkers[48,49] extended the original STLS scheme[34] for the static local field corrections to finite temperature and numerically obtained the interaction energy V (per particle) of the UEG via integration of the static structure factor $S(k)$:

$$V = \frac{1}{2}\int_{k<\infty}\frac{d\mathbf{k}}{(2\pi)^3}[S(\mathbf{k}) - 1]\frac{4\pi}{\mathbf{k}^2}$$ (9)

for 70 parameter combinations with $\theta = 0.1, 1, 5$ and $r_s \sim 10^{-3}, \ldots, 74$. Subsequently, a parameterization for V was introduced as a function of r_s and θ[50,51]

$$V(r_s, \theta) = -\frac{1}{r_s}\frac{a_{\text{HF}}(\theta) + \sqrt{2}\lambda r_s^{1/2}\tanh(\theta^{-1/2})B(\theta) + 2\lambda^2 r_s C(\theta)E(\theta)\tanh(\theta^{-1})}{1 + \sqrt{2}\lambda r_s^{1/2}D(\theta)\tanh(\theta^{-1/2}) + 2\lambda^2 r_s E(\theta)}$$ (10)

with the definitions

$$a_{\text{HF}}(\theta) = 0.610887\tanh\left(\theta^{-1}\right)\frac{0.75 + 3.4363\theta^2 - 0.09227\theta^3 + 1.7035\theta^4}{1 + 8.31051\theta^2 + 5.1105\theta^4},$$ (11)

$$B(\theta) = \frac{x_1 + x_2\theta^2 + x_3\theta^4}{1 + x_4\theta^2 + x_5\theta^4}, \quad C(\theta) = x_6 + x_7\exp\left(-\theta^{-1}\right),$$ (12)

$$D(\theta) = \frac{x_8 + x_9\theta^2 + x_{10}\theta^4}{1 + x_{11}\theta^2 + x_{12}\theta^4}, \quad E(\theta) = \frac{x_{13} + x_{14}\theta^2 + x_{15}\theta^4}{1 + x_{16}\theta^2 + x_{17}\theta^4}.$$ (13)

In addition to the exact limits for $\theta \to 0$ and $\theta \to \infty$, the parameterization from Equation 10 also approaches the well-known Hartree–Fock limit for high density:

$$\lim_{r_s \to 0} V(r_s, \theta) = -\frac{a_{\text{HF}}(\theta)}{r_s},$$ (14)

which has been parameterized by Perrot and Dharma-wardana,[52] see Equation 11. Naturally, the free parameters x_i, $i = 1, \ldots, 17$ have been determined by fitting Equation 10 to the STLS data for V, and the resulting values are listed in Table 1. From the interaction energy $V(r_s, \theta)$, the free exchange-correlation energy is obtained by integration:

$$f_{xc}(r_s, \theta) = \frac{1}{r_s^2}\int_0^{r_s} d\bar{r}_s\, \bar{r}_s V(\bar{r}_s, \theta).$$ (15)

TABLE 1 Fit parameters by Ichimaru[51] for the $f_{xc}(r_s, \theta)$ parameterization from Equation 16, fitted to STLS data[49]

x_1	x_2	x_3	x_4	x_5
3.4130800×10^{-1}	1.2070873×10	1.148889×10^0	1.0495346×10	1.326623×10^0
x_6	x_7	x_8	x_9	x_{10}
8.72496×10^{-1}	2.5248×10^{-2}	6.14925×10^{-1}	1.6996055×10	1.489056×10^0
x_{11}	x_{12}	x_{13}	x_{14}	x_{15}
1.010935×10	1.22184×10^0	5.39409×10^{-1}	2.522206×10^0	1.78484×10^{-1}
x_{16}	x_{17}			
2.555501×10^0	1.46319×10^{-1}			

Plugging in the expression for $V(r_s, \theta)$ from Equation 10 into 15 gives the final parameterization for $f_{xc}(r_s, \theta)$:

$$f_{xc}(r_s, \theta) = -\frac{1}{r_s}\frac{c(\theta)}{e(\theta)} \tag{16}$$

$$
- \frac{\theta}{2e(\theta)r_s^2\lambda^2}\left[\left(a_{\mathrm{HF}}(\theta) - \frac{c(\theta)}{e(\theta)}\right) - \frac{d(\theta)}{e(\theta)}\left(b(\theta) - \frac{c(\theta)d(\theta)}{e(\theta)}\right)\right]
$$

$$
\times \log\left|\frac{2e(\theta)\lambda^2 r_s}{\theta} + \sqrt{2}d(\theta)\lambda r_s^{1/2}\theta^{-1/2} + 1\right|
$$

$$
- \frac{\sqrt{2}}{e(\theta)}\left(b(\theta) - \frac{c(\theta)d(\theta)}{e(\theta)}\right)\frac{\theta^{1/2}}{r_s^{1/2}\lambda}
$$

$$
+ \frac{\theta}{r_s^2\lambda^2 e(\theta)\sqrt{4e(\theta) - d^2(\theta)}}\left[d(\theta)\left(a_{\mathrm{HF}}(\theta) - \frac{c(\theta)}{e(\theta)}\right)\right.
$$

$$
\left. + \left(2 - \frac{d^2(\theta)}{e(\theta)}\right)\left(b(\theta) - \frac{c(\theta)d(\theta)}{e(\theta)}\right)\right]
$$

$$
\times \left[\mathrm{atan}\left(\frac{2^{3/2}e(\theta)\lambda r_s^{1/2}\theta^{-1/2} + d(\theta)}{\sqrt{4e(\theta) - d^2(\theta)}}\right) - \mathrm{atan}\left(\frac{d(\theta)}{\sqrt{4e(\theta) - d^2(\theta)}}\right)\right]
$$

with the abbreviations

$$b(\theta) = \theta^{1/2}\tanh\left(\theta^{-1/2}\right)B(\theta), \quad c(\theta) = C(\theta)e(\theta), \tag{17}$$
$$d(\theta) = \theta^{1/2}\tanh\left(\theta^{-1/2}\right)D(\theta), \quad e(\theta) = \theta\tanh\left(\theta^{-1}\right)E(\theta).$$

2.3 | VS parameterization

Despite the overall good performance of STLS in the ground state,[53] it has long been known that this scheme does not fulfill the compressibility sum rule (CSR, see e.g., Ref. [54] for a detailed discussion). To overcome this obstacle, Vashishta and Singwi[35] introduced modified local field corrections (VS), where the CSR is automatically fulfilled. This idea had been extended in an approximate way to finite temperature by Stolzmann and Rösler,[55] and more recently Sjostrom and Dufty[54] obtained an exhaustive dataset of results that are exact within the VS framework.

As already explained in the previous section for the STLS data, they first calculated the static structure factor $S(k)$, computed the interaction energy V by integration (Equation 9), fitted the parameterization from Equation 10 to this data, and thereby obtained the desired parameterization of $f_{xc}(r_s, \theta)$ as given in Equation 16 (albeit with the new fit parameters listed in Table 2).

2.4 | PDW parameterization

Dharma-wardana and Perrot[36,37] introduced an independent, completely different idea. In particular, they employed a *classical mapping* such that the correlation energy of the electron gas at $T = 0$ (that has long been known from QMC calculations [9,10]) is exactly recovered by the simulation of a classical system at an effective "quantum temperature" T_q. However, due to the lack of accurate data at finite T, an exact mapping had not been possible, and the authors introduced a modified temperature T_c, where they assumed an interpolation between the exactly known ground state and classical (high T) regimes, $T_c = \sqrt{T^2 + T_q^2}$. Naturally, at WDM conditions this constitutes a largely uncontrolled approximation.

TABLE 2   Fit parameters by Sjostrom and Dufty[54] for the $f_{xc}(r_s, \theta)$ parameterization from Equation 16, fitted to VS data

x_1	x_2	x_3	x_4	x_5
1.8871493×10^{-1}	1.0684788×10	1.1088191×10^2	1.8015380×10	1.2803540×10^2
x_6	x_7	x_8	x_9	x_{10}
8.3331352×10^{-1}	$-1.1179213 \times 10^{-1}$	6.1492503×10^{-1}	1.6428929×10	2.5963096×10
x_{11}	x_{12}	x_{13}	x_{14}	x_{15}
1.0905162×10	2.9942171×10	5.3940898×10^{-1}	5.8869626×10^4	3.1165052×10^3
x_{16}	x_{17}			
3.8887108×10^4	2.1774472×10^3			

TABLE 3   Fit parameters by Perrot and Dharma-wardana[37] for the $f_{xc}(r_s, \theta)$ parameterization from Equation 18

k	$a_{1,k}$	$b_{1,k}$	$c_{1,k}$	$a_{2,k}$	$b_{2,k}$	$c_{2,k}$	v_k	r_k
1	5.6304	−2.2308	1.7624	2.6083	1.2782	0.16625	1.5	4.4467
2	5.2901	−2.0512	1.6185	−15.076	24.929	2.0261	3	4.5581
3	3.6854	−1.5385	1.2629	2.4071	0.78293	0.095869	3	4.3909

To obtain the desired parameterization for f_{xc}, extensive simulations of the UEG in the range $r_s = 1$–10 and $\theta = 0$–10 were performed. These were used as input for a fit (see Table 3 for the corresponding fit parameters) with the functional form

$$f_{xc}(r_s, \theta) = \frac{\epsilon(r_s) - P_1(r_s, \theta)}{P_2(r_s, \theta)}, \tag{18}$$

$$P_1(r_s, \theta) = \left(A_2(r_s)u_1(r_s) + A_3(r_s)u_2(r_s)\right)\theta^2 Q^2(r_s) + A_2(r_s)u_2(r_s)\theta^{5/2}Q^{5/2}(r_s),$$

$$P_2(r_s, \theta) = 1 + A_1(r_s)\theta^2 Q^2(r_s) + A_3(r_s)\theta^{5/2}Q^{5/2}(r_s) + A_2(r_s)\theta^3 Q^3(r_s),$$

$$Q(r_s) = \left(2r_s^2\lambda^2\right)^{-1}, \quad n(r_s) = \frac{3}{4\pi r_s^3}, \quad u_1(r_s) = \frac{\pi n(r_s)}{2}, \quad u_2(r_s) = \frac{2\sqrt{\pi n(r_s)}}{3},$$

$$A_k(r_s) = \exp\left(\frac{y_k(r_s) + \beta_k(r_s)z_k(r_s)}{1 + \beta_k(r_s)}\right), \quad \beta_k(r_s) = \exp\left(5(r_s - r_k)\right),$$

$$y_k(r_s) = v_k \log(r_s) + \frac{a_{1,k} + b_{1,k}r_s + c_{1,k}r_s^2}{1 + r_s^2/5}, \quad z_k(r_s) = r_s \frac{a_{2,k} + b_{2,k}r_s}{1 + c_{2,k}r_s^2},$$

which becomes exact for $\theta \to 0$ and $\theta \to \infty$, but is limited to the accuracy of the classical mapping data in between. Further, it does not include the exact Hartree–Fock limit for $r_s \to 0$, so that it cannot reasonably be used for $r_s < 1$. For completeness, we mention that a functional form similar to Equation 18 was recently used by Brown et al. [56] for a fit to their RPIMC data[39].

Similar ideas of quantum-classical mappings were recently investigated by Dufty and Dutta (see e.g., Ref. [57,58]).

2.5 | Parameterization by Karasiev et al.

Karasiev et al.[38] (KSDT) utilized as the functional form for f_{xc} an expression similar to Equation 10, which Ichimaru and coworkers[50,51] suggested for the interaction energy:

$$f_{xc}(r_s, \theta) = -\frac{1}{r_s} \frac{a_{HF}(\theta) + b(\theta)r_s^{1/2} + c(\theta)r_s}{1 + d(\theta)r_s^{1/2} + e(\theta)r_s}, \tag{19}$$

$$b(\theta) = \tanh\left(\theta^{-1/2}\right)\frac{b_1 + b_2\theta^2 + b_3\theta^4}{1 + b_4\theta^2 + \sqrt{1.5}\lambda^{-1}b_3\theta^4}, \quad c(\theta) = \left[c_1 + c_2\exp\left(-\frac{c_3}{\theta}\right)\right]e(\theta),$$

$$d(\theta) = \tanh\left(\theta^{-1/2}\right)\frac{d_1 + d_2\theta^2 + d_3\theta^4}{1 + d_4\theta^2 + d_5\theta^4}, \quad e(\theta) = \tanh\left(\theta^{-1}\right)\frac{e_1 + e_2\theta^2 + e_3\theta^4}{1 + e_4\theta^2 + e_5\theta^4}.$$

Further, instead of fitting to the interaction energy V, they used the relation

$$E_{xc}(r_s, \theta) = f_{xc}(r_s, \theta) - \theta \frac{\partial f_{xc}(r_s, \theta)}{\partial \theta}\bigg|_{r_s} \tag{20}$$

TABLE 4 Fit parameters by Karasiev et al. [38] for the $f_{xc}(r_s, \theta)$ parameterization from Equation 19

b_1	b_2	b_3	b_4	c_1	c_2	c_3
0.283997	48.932154	0.370919	61.095357	0.870089	0.193077	2.414644

d_1	d_2	d_3	d_4	d_5	e_1	e_2
0.579824	94.537454	97.839603	59.939999	24.388037	0.212036	16.731249

e_3	e_4	e_5				
28.485792	34.028876	17.235515				

and fitted the rhs of Equation 20 to the recently published RPIMC data for the exchange correlation energy E_{xc} by Brown et al. [39] that are available for the parameters $r_s = 1$–40 and $\theta = 0.0625$–8 (see Table 4 for the corresponding fit parameters).

3 | RESULTS

In this section we analyze the behavior of the analytical approximations for the exchange-correlation free energies that were summarized above by comparison with our recent simulation results that cover the entire relevant density range for temperatures $\theta \geq 0.5$. These data have an unprecedented accuracy on the order of 0.1% (for details, see Refs. [27,28]).

3.1 | Temperature dependence

In Figure 1, we show the temperature dependence of the exchange-correlation free energy as a function of the reduced temperature θ for two densities that are relevant for contemporary WDM research, namely $r_s = 1$ (left) and $r_s = 6$ (right). For both cases, all depicted parameterizations reproduce the correct classical limit for large θ [cf. Equation 8] and four of them (Ebeling, KSDT, STLS, and PDW) are in excellent agreement for the ground state as well. For completeness, we note that the small differences between KSDT and Ebeling and PDW are due to different ground-state QMC input data. In particular, Karasiev et al. used more recent QMC results by Spink et al.,[59] although in the context of WDM research the deviations to older parameterizations are negligible. The VS parameterization, on the other hand, does not incorporate any ground-state limit and, consequently, the behavior of $f_{xc}^{VS}(r_s, \theta)$ becomes unreasonable below $\theta = 0.0625$. Similarly, the lowest temperature (despite the ground-state limit) included in the fit for $f_{xc}^{PDW}(r_s, \theta)$ is $\theta = 0.25$ and the rather unsmooth connection between this point and $\theta = 0$ does not appear to be trustworthy as well.

Let us now check the accuracy of the different models at intermediate WDM temperatures. As a reference, we use the recent accurate QMC results for the macroscopic UEG by Dornheim et al.,[27] that is, the red squares. For $r_s = 1$, the semi-analytic expression by Ebeling (blue) exhibits the largest deviations exceeding $\Delta f_{xc}/f_{xc} = 25\%$ for $\theta \sim 1$. For lower density, $r_s = 6$, the Ebeling parameterization is significantly more accurate, although here, too, appear deviations of $\Delta f_{xc}/f_{xc} \sim 10\%$ to the exact data at intermediate temperature. Therefore, this parameterization produces reliable data in the two limiting cases of zero and high temperature, but is less accurate in between.

Next we consider the STLS curve (black). It is in very good agreement with the QMC data, and the error does not exceed $\Delta f_{xc}/f_{xc} = 4\%$ over the entire θ range for both depicted r_s values. The largest deviations appear for intermediate temperatures as well.

Third, we consider the VS model (yellow line). For $r_s = 1$, the VS parameterization by Sjostrom and Dufty[54] exhibits the same trends as the STLS curve, albeit with larger deviations, $\Delta f_{xc}/f_{xc} > 5\%$. Further, for $r_s = 6$, f_{xc}^{VS} exhibits much larger deviations to the exact result and the error reaches $\Delta f_{xc}/f_{xc} \approx 8\%$. Evidently, the constraint to automatically fulfill the CSR does not improve the accuracy of other quantities, in particular the interaction energy V (which was used as an input for the parameterization (see Section 2.3) or the static structure factor $S(k)$ itself).

Fourth, the parameterization based on the classical mapping (PDW, light blue) exhibits somewhat opposite trends as compared to Ebeling, STLS, and VS and predicts too large an exchange-correlation free energy for all θ. The magnitude of the deviations is comparable to VS and does not exceed $\Delta f_{xc}/f_{xc} = 5\%$.

Finally, we consider the recent parameterization by Karasiev et al. (KSDT, green),[38] which is based on RPIMC results[39]. For $r_s = 6$, there is excellent agreement with the new reference QMC data with a maximum deviation of $\Delta f_{xc}/f_{xc} \sim 1\%$ for $\theta = 4$. This is, in principle, expected since the main sources of error for their input data, that is, the nodal error and the insufficient finite-size correction, are less important for larger r_s. However, for $r_s = 1$ there appear significantly larger deviations exceeding $\Delta f_{xc}/f_{xc} = 5\%$ at high temperature. In fact, for $r_s = 1$ and the largest considered temperature, $\theta = 8$, the KSDT parameterization exhibits the largest deviations of all depicted parameterizations.
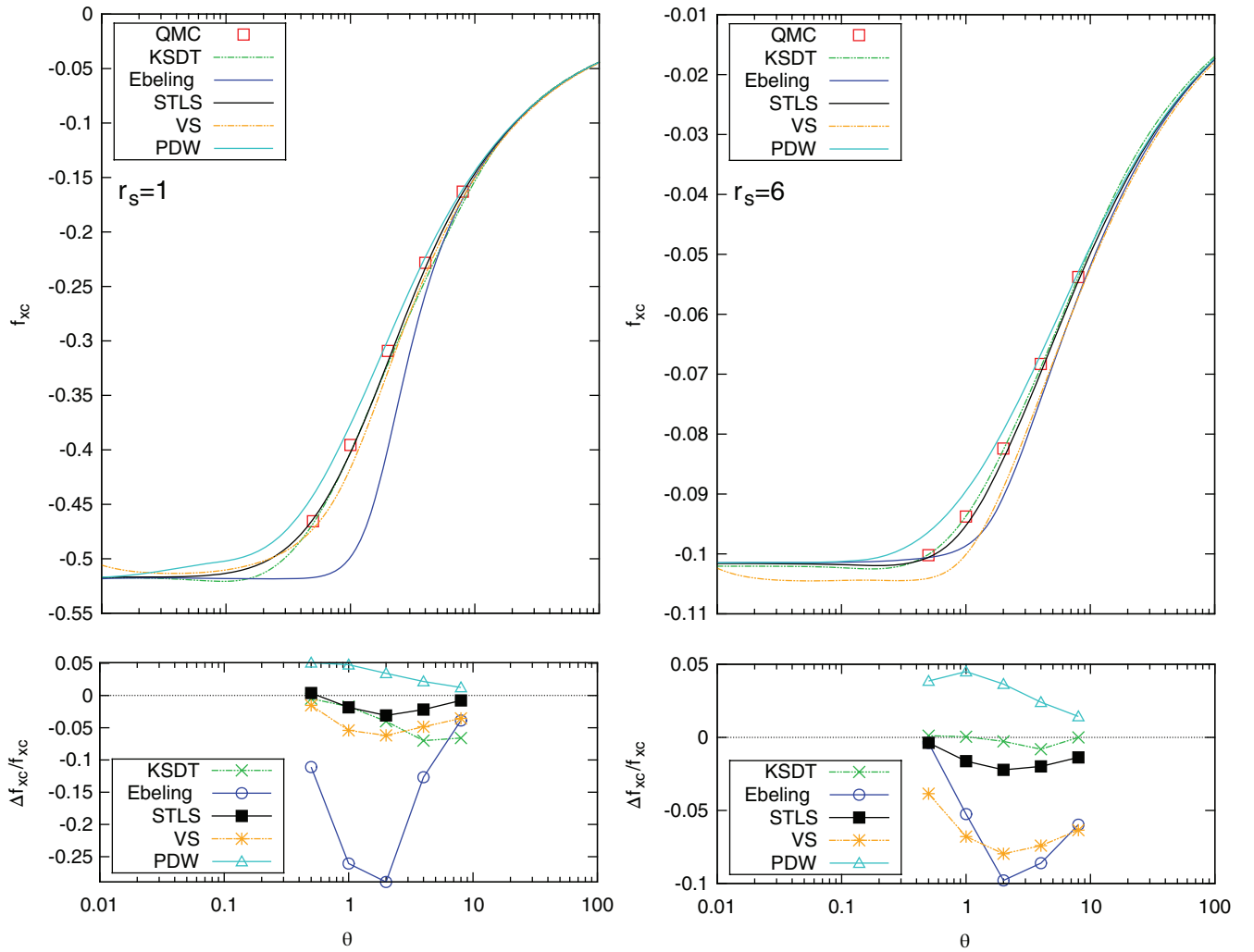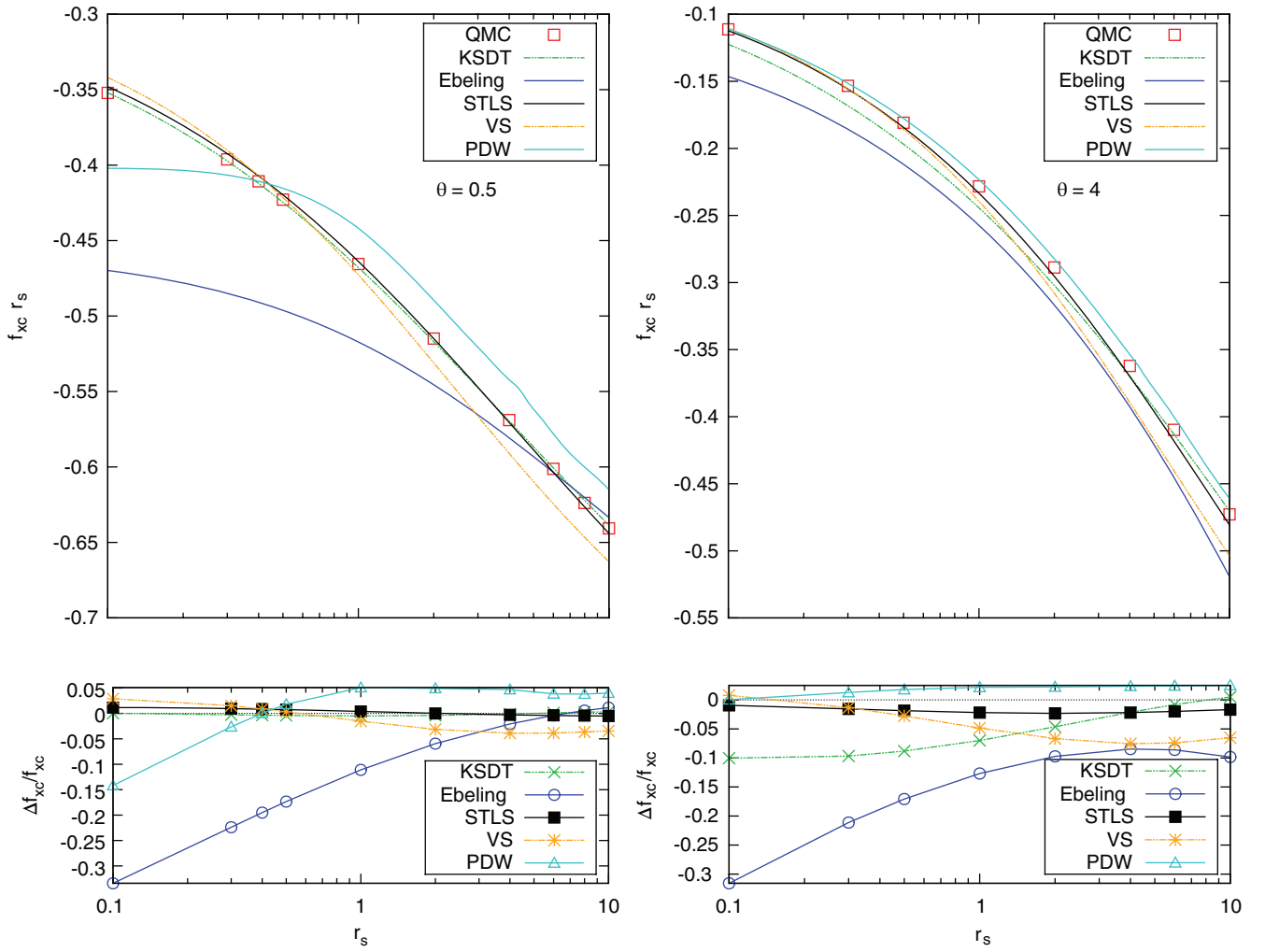
FIGURE 1   Temperature dependence of f_{xc} at fixed density $r_s = 1$ (left) and $r_s = 6$ (right). Top: Quantum Monte Carlo (QMC) data (symbols) taken from Dornheim et al.,[27] a parameterization of RPIMC data by Karasiev, Sjostrom, Dufty, Trickey (KSDT),[38] a semi-analytic Padé approximation by Ebeling,[33] a parameterization fitted to Singwi, Tosi, Land, and Sjölander (STLS) and Vashishta and Singwi (VS) data by Ichimaru[51] and Sjostrom and Dufty,[54] respectively, and a fit to classical mapping data by Perrot and Dharma-wardana (PDW).[37] Bottom: Relative deviation to the QMC data.

3.2 │ Density dependence

As a complement to Section 3.1, in Figure 2 we investigate in more detail the density dependence of the different parameterizations for two relevant temperatures, $\theta = 0.5$ (left) and $\theta = 4$ (right).

Most notably, the Ebeling and PDW parameterizations do not include the correct high-density ($r_s \rightarrow 0$) limit, that is Equation 11, and therefore are not reliable for $r_s < 1$. For $\theta = 0.5$, f_{xc}^{Ebeling} is in qualitative agreement with the correct results, but the deviations rapidly increase with density and exceed $\Delta f_{xc}/f_{xc} = 10\%$, for $r_s = 1$. At higher temperature, $\theta = 4$, the situation is worse, and the Ebeling parameterization shows systematic deviations over the entire density range. The STLS fit displays a similarly impressive agreement with the exact data as for the θ dependence (cf. Figure 1), and the deviations do not exceed $\Delta f_{xc}/f_{xc} \sim 3\%$ for both depicted θ values. On the other hand, the VS results are again significantly less accurate than STLS although the deviation remains below $\Delta f_{xc}/f_{xc} = 8\%$ for both temperatures. Further, we notice that the largest deviations occur for $r_s \geq 2$, that is, toward stronger coupling, which is expected since here the pair distribution function exhibits unphysical negative values at short distance (see e.g., Ref. [54]). Again, the incorporation of the CSR has not improved the quality of the interaction energy or the structure factor compared to STLS. The classical mapping data (PDW) does exhibit deviations not exceeding $\Delta f_{xc}/f_{xc} = 5\%$ for $r_s \geq 1$, that is, in the range where numerical data have been incorporated into the fit. Overall, the quality of this parameterization is comparable to the VS curve although the relative deviation appears to be almost constant with respect to the density. This is not surprising, as the approximation has not been conducted with respect to coupling (the effective classical system is solved with the hypernetted chain method, which is expected to be accurate in this regime) but, instead, in the interpolation of the effective temperature T_c. Further, we notice a peculiar nonsmooth and almost oscillatory behavior of f_{xc}^{PDW} around $r_s = 5$, which is more pronounced for $\theta = 0.5$ and the origin of which remains unclear. Finally, we again consider

FIGURE 2 Density dependence of f_{xc} at fixed temperature $\theta = 0.5$ (left) and $\theta = 4$ (right). Top: Quantum Monte Carlo (QMC) data taken from Dornheim et al.,[27] a parameterization of RPIMC data by Karasiev, Sjostrom, Dufty, Trickey (KSDT),[38] a semi-analytic Padé approximation by Ebeling,[33] a parameterization fitted to Singwi, Tosi, Land, and Sjölander (STLS) and Vashishta and Singwi (VS) data by Ichimaru[51] and Sjostrom and Dufty,[54] respectively, and a fit to classical mapping data by Perrot and Dharma-wardana (PDW).[37] Bottom: Relative deviation to the QMC data.

the KSDT fit based on the RPIMC data by Brown et al. [39] (a similar analysis for more temperatures can be found by Dornheim et al.[27]). For $\theta = 0.5$, this parameterization is in excellent agreement with the reference QMC data and the deviations are in the sub-percent regime over the entire depicted r_s range. However, for larger temperatures there appear significant errors that, at $\theta = 4$, reach a maximum of $\Delta f_{xc}/f_{xc} \sim 10\%$ for $r_s = 0.1$, that is, at parameters where STLS, VS, and PDW are in very good agreement with the reference QMC data. Interestingly, these deviations vanish only for $r_s \leq 10^{-4}$. Naturally, the inaccuracies of the KSDT fit are a direct consequence of the systematic errors of the input data and the lack of accurate simulation data for $r_s < 1$, prior to Dornheim et al.[27]

4 | DISCUSSION

In summary, we have compared five different parameterizations of the exchange-correlation free energy of the unpolarized UEG to the recent QMC data by Dornheim et al.[27] and, thereby, have been able to gauge their accuracy with respect to θ and r_s over large parts of the WDM regime. We underline that all these parameterizations are highly valuable, the main merit being their easy and flexible use and rapid evaluation. At the same time, an unbiased evaluation of their accuracy had not been done and appears highly important, as this allows constraining the field of applicability of these models and indicating directions for future improvements.

Summarizing our findings, we have observed that the semi-analytic parameterization by Ebeling[33] is mostly reliable in the high and zero temperature limits but exhibits substantial deviations in between. The STLS fit given by Ichimaru and coworkers[50,51], on the other hand, exhibits a surprisingly high accuracy for all investigated r_s–θ combinations with a typical

relative systematic error of $\sim 2\%$. The more recent VS results,[54] which automatically fulfill the CSR, display a qualitatively similar behavior but are significantly less accurate everywhere. The classical mapping suggested by Perrot and Dharma-wardana[37] constitutes an approximation rather with respect to temperature than to the coupling strength and, consequently, exhibits different trends. In particular, we have found that the relative systematic error is nearly independent of r_s, but decreases with increasing θ and eventually vanishes for $\theta \to \infty$. Overall, the accuracy of the PDW parameterization is comparable to VS and, hence, inferior to STLS. Finally, the more recent fit by Karasiev et al. [38] to RPIMC data[39] is accurate for large r_s and low temperature, where the input data is not too biased by the inappropriate treatment of finite size errors in the underlying RPIMC results. For higher temperatures (where the exchange-correlation free energy constitutes only a small fraction of the total free energy), there occur relative deviations of up to $\sim 10\%$.

Thus we conclude that an accurate parameterization of the exchange-correlation free energy that is valid for all r_s–θ combinations is presently not available. However, the recent QMC data by Dornheim et al.[27] most certainly constitute a promising basis for the construction of such a functional. In the mean time, of all the considered parameterizations, KSDT appears to be the most accurate at low θ and large r_s while the STLS fit exhibits smaller deviations elsewhere. Further, thermal DFT calculations in the local spin-density approximation require a parameterization of f_{xc} also as a function of the spin polarization $\xi = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$, that is, $f_{xc}(r_s, \theta, \xi)$ for all WDM parameters. Obviously, this will require an extension of the QMC simulations beyond the unpolarized case, $\xi \in (0, 1]$; in addition, reliable data for $\theta < 0.5$ are indispensable. This work is presently under way. We also note that the quality of the currently available KSDT fit for $f_{xc}(r_s, \theta, \xi)$ remains to be tested for $\xi > 0$. The accuracy of this parameterization is limited by (a) the quality of the RPIMC data (for the spin-polarized UEG ($\xi = 1$), they are afflicted with a substantially larger nodal error than for the unpolarized case that we considered in the present paper, see Ref. [22]), and (b) by the quality of the PDW results[37] that have been included as the only input to the KSDT fit for $0 < \xi < 1$ at finite θ. Therefore, we conclude that the construction of a new accurate function $f_{xc}(r_s, \theta, \xi)$ is still of high importance for thermal DFT and semi-analytical models, for comparisons with experiments, but also for explicitly time-dependent approaches such as time-dependent DFT and quantum hydrodynamics.[60,61]

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