# Status of Free-Energy Representations for Homogeneous Electron Gas

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The homogeneous electron gas (HEG) is a well-studied system at zero temperature as a model for electrons in solids and as a model for fully ionized plasmas at temperatures $T$ well above the Fermi temperature $T_F$. For a long while far less information was available from either theory or simulation at intermediate temperatures and densities, in large part due to lack of motivation. That has changed recently with growing experimental access to observations on states of matter in this domain. Such access is driving growth in the fields of warm dense matter (WDM) and high-energy-density physics. Accordingly, the first quantum Monte Carlo (QMC) simulations for the HEG in this domain were reported only six years ago.[1] Subsequently Dornheim *et al*.[2] produced improved QMC results for temperatures $0.5 \le t = T/T_F \le 8$ over a wide density range (Wigner–Seitz radii $0.1 \le r_s \le 10$). They also developed and used significantly improved finite-size corrections. Those data currently seem to be the most-accurate finite-temperature HEG results available.

For practical purposes a representation interpolating such QMC data and extrapolating it via known theoretical limits is needed. The target is an equation of state for the complete thermodynamics of the HEG, provided by the free energy as a function of $r_s$ and $t$. A rather complete review of the recent simulations and their representations is given in Ref. 3. As noted there, the program for constructing a free energy from theoretical limits and simulation data was originally presented and used in Ref. 4, which presented a representation, "KSDT" (Karasiev–Sjostrom–Dufty–Trickey), based on the original data of Ref. 1 and the $T = 0$ data of Ref. 5. Subsequently, Groth *et al*.[6] used the KSDT approach and protocol to reparametrize the exchange-correlation (XC) contribution to the free energy against the finite-size–corrected QMC results of Ref. 2 along with the Singwi–Tosi–Land–Sjölander (STLS) approximation[7] for low-$t$ ($t < 0.5$) behavior and for connection with the $T = 0$ data of Ref. 5. The resulting representation is denoted as "GDB" (Groth–Dornheim–Bonitz). Essentially simultaneously, a small error in the use of zero-temperature data for KSDT was detected and repaired to yield the corrected KSDT representation "corrKSDT" (see Supplemental Material for Ref. 8).

This work achieved three objectives: The first is based on recent simulation studies of the free energy for the HEG in a domain of the $(r_s,t)$ plane not previously explored. The data combined with thermodynamic consistency and known theoretical limits led to three global representations of the free energy, corrKSDT, its direct antecedent KSDT, and GDB. The equivalence of these for reproducing the simulation data for $f(r_s,t)$ was demonstrated. Furthermore, the equivalence of corrKSDT and GDB for the XC component alone was illustrated, although the original KSDT representation has some inconsequential small errors for $f_{xc}(r_s,t)$ (Ref. 2). Figure 1 demonstrates that the two fits match the available QMC data indistinguishably for $t \ge 0.5$ and are in perfect agreement for $t < 0.5$.

The second objective was to draw attention to the fact that, in spite of these very accurate representations for $f(r_s,t)$, thermodynamic properties obtained by temperature derivatives exhibit striking anomalies. Those occur outside the domain for which simulation data are available and are properties of the extrapolation/interpolation provided by the fitting procedure. This was discussed and it was noted that the entropy per particle (first-order temperature derivative) can become negative for large $r_s$ and small $t$. For the corrKSDT and GDB representations, this corresponds to state conditions beyond the expected spin polarization

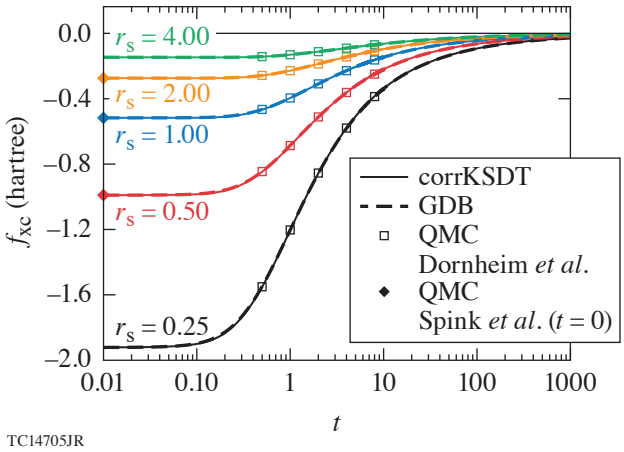


Figure 1
Comparison between $f_{xc}$ values from the corrKSDT and GDB parametrizations and QMC data from Ref. 9 for the unpolarized HEG at $r_s$ = 0.25, 0.5, 1, 2, and 4. The ground-state limit ($t$ = 0, Ref. 5) QMC values also are shown.

transition and therefore outside the domain of their intended application. A second more-serious anomaly occurs for the specific heat $c_V$ (second derivative with respect to $T$). In that case, all of the representations predict unusual oscillatory behavior for $t$ between 0.1 and 1 and $r_s \geq 10$. Figure 2 shows $c_V$ calculated for the noninteracting and interacting HEG from the corrKSDT and GDB representations. As anticipated, the specific heat curves from the two parametrizations are practically identical, a consequence of the small procedural differences of parameter fitting in the two. Even though the oscillatory behavior might be an indication of some kind of critical point, it is far more plausible that it is an artifact introduced by the QMC data of Ref. 2 and the way that corrKSDT and GDB represent those data. Without any theoretical or simulation guidance, this must be seen as a possible flaw in the representation function.

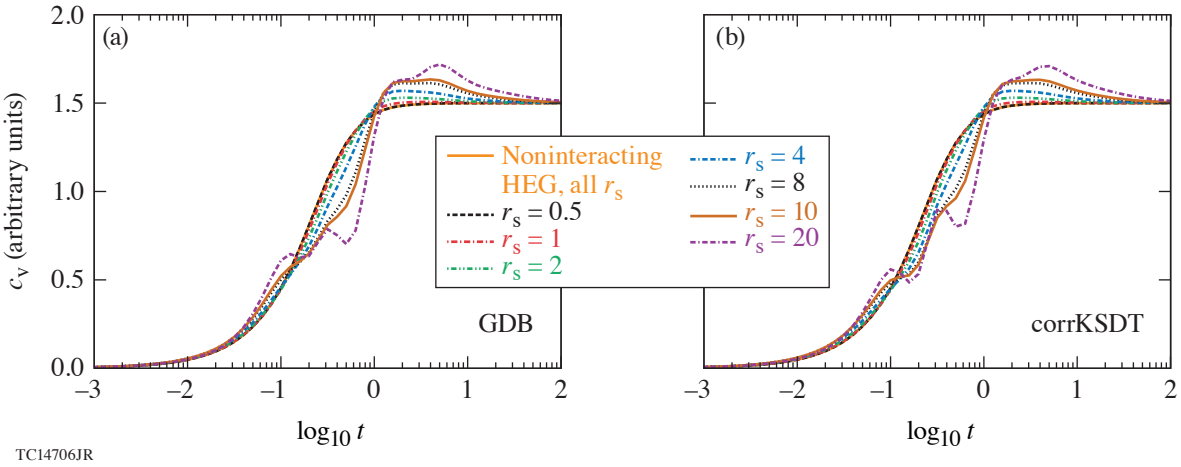


Figure 2
Electron specific heat $c_V$ for the noninteracting and interacting HEG calculated with (a) GDB and (b) corrKSDT parametrizations.

The third objective was to verify the use of the three representations as essentially interchangeable for use as local density approximation (LDA) functionals in free-energy DFT calculations and in more-refined $f_{xc}$ approximations. It is helpful to note the parallel with most $T$ = 0 DFT calculations. They are based in a similar way on ground-state HEG simulations. Generalized gradient approximations, for example, have the LDA (consequently the HEG) as a limiting case. Therefore, the extensions discussed here to the entire ($r_s$,$t$) plane constitute an essential prerequisite for addressing WDM in an accurate, practical fashion. A first example of a nonempirical semilocal free-energy density functional for matter under extreme conditions, built on the LDA representations here, was noted.[8]

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