Supplement: *Ab Initio* Path Integral Monte Carlo Results for the Dynamic Structure Factor of Correlated Electrons: From the Electron Liquid to Warm Dense Matter

T. Dornheim[1], S. Groth[1], J. Vorberger[2], and M. Bonitz[1]
[1]*Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, Leibnizstraße 15, D-24098 Kiel, Germany*
[2]*Helmholtz-Zentrum Dresden-Rossendorf, D-01328 Dresden, Germany*

I. IMAGINARY-TIME CORRELATION FUNCTIONS

Let us define the imaginary-time density–density correlation function [1–3] as

$$F(\mathbf{q},\tau) = \frac{1}{N}\left\langle n_{\mathbf{q}}(\tau)n_{-\mathbf{q}}(0)\right\rangle \quad , \tag{1}$$

where the densities are evaluated at different imaginary times. Therefore, $F(\mathbf{q},\tau)$ is readily available in path integral Monte Carlo (PIMC) simulations, see, e.g., Refs. [4, 5] for details. Eq. (1) is related to the dynamic structure factor via

$$F(\mathbf{q},\tau) = \int_{-\infty}^{\infty} \mathrm{d}\omega\ S(\mathbf{q},\omega)e^{-\tau\omega} \tag{2}$$

Furthermore, $F(\mathbf{q},\tau)$ gives direct access to the static response function function, which are linked by the imaginary-time version of the fluctuation dissipation theorem, Ref. [6]

$$\chi(\mathbf{q},0) = -n\int_0^\beta \mathrm{d}\tau\ F(\mathbf{q},\tau) \quad . \tag{3}$$

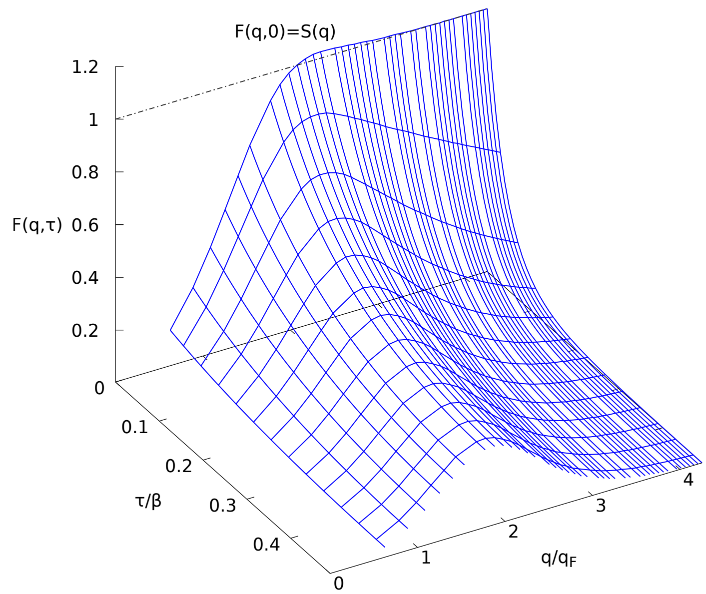

FIG. 1. PIMC data for the imaginary-time density–density correlation function $F(\mathbf{q},\tau)$ for $r_s = 10$, $\theta = 0.75$ and $N = 34$ for $P = 100$ imaginary-time slices (every 4th slice is shown). In the $\tau = 0$ limit, $F(\mathbf{q},\tau)$ approaches the static structure factor $S(\mathbf{q})$. Furthermore, F is symmetric with respect to $\tau = \beta/2$, i.e., $F(\mathbf{q},\tau) = F(\mathbf{q},\beta-\tau)$ (for $\tau \leq \beta/2$).

II. SUM RULES OF THE DYNAMIC STRUCTURE FACTOR

Let us define the k-th frequency moment of $S(\mathbf{q},\omega)$ as

$$\begin{aligned}\langle\omega^k\rangle &= \int_{-\infty}^{\infty}\mathrm{d}\omega\ \omega^k S(\mathbf{q},\omega) \\ &= \int_0^\infty \mathrm{d}\omega\ \omega^k S(\mathbf{q},\omega)\left(1+(-1)^k e^{-\beta\omega}\right) \quad ,\end{aligned} \tag{4}$$

where the second equality follows from the detailed balance condition

$$S(\mathbf{q},\omega) = -S(\mathbf{q},-\omega)e^{-\beta\omega} \quad . \tag{5}$$

In particular, four frequency moments can be computed analytically or from our equilibrium PIMC data:

1. The f sum-rule is simply given by [9]

$$\langle\omega^1\rangle = \frac{q^2}{2} \quad . \tag{6}$$

2. The cubic sum-rule was first reported by Puff [7, 8] and reads [9–11]

$$\begin{aligned}\langle\omega^3\rangle = \frac{q^2}{2}\Bigg(&\left(\frac{q^2}{2}\right)^2 + q^2 n v_q + 2q^2 K \\ &+ \omega_p^2\left(1-I(q)\right)\Bigg) \quad ,\end{aligned} \tag{7}$$

and the potential contribution [9, 11] can be expressed in spherical coordinates as a one-dimensional integral

$$\begin{aligned}I(q) = &\frac{1}{8\pi^2 n}\int_0^\infty \mathrm{d}k\ k^2\left(1-S(k)\right) \\ &\times\left(\frac{5}{3}-\frac{k^2}{q^2}+\frac{\left(k^2-q^2\right)^2}{2kq^3}\log\left|\frac{k+q}{k-q}\right|\right) \quad .\end{aligned} \tag{8}$$

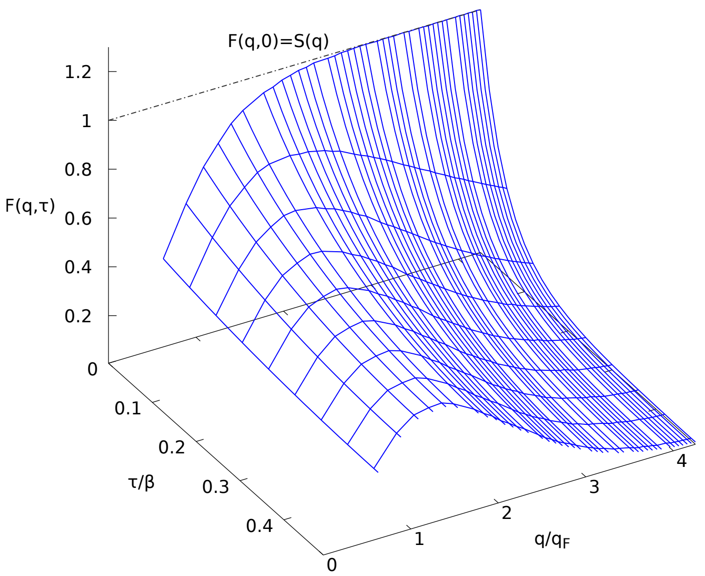

FIG. 2. Same as Fig. 1, but with $\theta = 1$, $P = 50$ and $N = 34$, $r_s = 2$.

3. The inverse frequency moment is directly proportional to the static density response function [10, 12, 13]

$$\langle \omega^{-1} \rangle = -\frac{\chi(\mathbf{q}, 0)}{2n} \quad , \tag{9}$$

where $\chi(\mathbf{q}, 0)$ is computed from Eq. (3).

4. Finally, the normalization of $S(\mathbf{q}, \omega)$ is given by the static structure factor [14]

$$\langle \omega^{0} \rangle = S(\mathbf{q}) \quad . \tag{10}$$

III. DENSITY RESPONSE AND LOCAL FIELD CORRECTION

The dynamic structure factor is directly linked to the imaginary part of the dynamic density response function $\chi(\mathbf{q}, \omega)$ by the fluctuation dissipation theorem [9, 15]

$$S(\mathbf{q}, \omega) = -\frac{\mathrm{Im}\chi(\mathbf{q}, \omega)}{\pi n (1 - e^{-\beta\omega})} \quad . \tag{11}$$

Typically, $\chi(\mathbf{q}, \omega)$ is expressed in terms of the ideal response function $\chi_0(\mathbf{q}, \omega)$ and the dynamic local field correction (LFC) $G(\mathbf{q}, \omega)$, e.g., Refs. [9, 15–17]

$$\chi(\mathbf{q}, \omega) = \frac{\chi_0(\mathbf{q}, \omega)}{1 - v_q \big(1 - G(\mathbf{q}, \omega)\big) \chi_0(\mathbf{q}, \omega)} \quad , \tag{12}$$

with the Fourier transform of the Coulomb interaction

$$v_q = \frac{4\pi}{q^2} \quad . \tag{13}$$

Setting $G(\mathbf{q}, \omega) = 0$ corresponds to the well-known random phase approximation (RPA) and, therefore, the LFC contains all exchange-correlation effects in the density response beyond the mean-field level. In a nutshell, the reconstruction of $S(\mathbf{q}, \omega)$ can be re-cast into the computation of $G(\mathbf{q}, \omega)$. This is very convenient as several properties of the LFC are known exactly, which can be exploited to further improve the reconstruction procedure:

1. The Kramers-Kronig relations link real and imaginary parts [15]:

$$\mathrm{Re}G(\mathbf{q}, \omega) = \mathrm{Re}G(\mathbf{q}, \infty) + \frac{1}{\pi} \int_{-\infty}^{\infty} \mathrm{d}\overline{\omega} \; \frac{\mathrm{Im}G(\mathbf{q}, \overline{\omega})}{\overline{\omega} - \omega} \tag{14}$$

$$\mathrm{Im}G(\mathbf{q}, \omega) = - \frac{1}{\pi} \int_{-\infty}^{\infty} \mathrm{d}\overline{\omega} \; \frac{\mathrm{Re}G(\mathbf{q}, \overline{\omega}) - \mathrm{Re}G(\mathbf{q}, \infty)}{\overline{\omega} - \omega} \tag{15}$$

2. The real and imaginary parts of $G(\mathbf{q}, \omega)$ are even and odd functions with respect to ω, respectively [16].

3. The imaginary part of $G(\mathbf{q}, \omega)$ vanishes for high and low frequency [16]:

$$\mathrm{Im}G(\mathbf{q}, 0) = \mathrm{Im}G(\mathbf{q}, \infty) = 0 \tag{16}$$

4. The static limit of $\mathrm{Re}G(\mathbf{q}, \omega)$ can be computed from the static density response function (see Eq. (3)), which is real for $\omega \to 0$ [9]:

$$\mathrm{Re}G(\mathbf{q}, 0) = 1 - \frac{1}{v_q} \left(\frac{1}{\chi_0(\mathbf{q}, 0)} - \frac{1}{\chi(\mathbf{q}, 0)} \right) \tag{17}$$

5. The high frequency limit of $\mathrm{Re}G(\mathbf{q}, \omega)$ [11] is given in terms of the static structure factor $S(\mathbf{q})$ (which is needed for the computation of $I(q)$, see Eq. (8)) and the exchange-correlation contribution to the kinetic energy K_{xc},

$$\mathrm{Re}G(\mathbf{q}, \infty) = I(q) - \frac{2q^2 K_{\mathrm{xc}}}{\omega_p^2} \quad , \tag{18}$$

with the plasma frequency

$$\omega_p = \left(\frac{3}{r_s^3} \right)^{1/2} \quad , \tag{19}$$

and the kinetic term being obtained from the exchange-correlation free energy [18, 19]

$$K_{\mathrm{xc}} = K - U_0 \tag{20}$$

$$= -f_{\mathrm{xc}}(r_s, \theta) - \theta \frac{\partial f_{\mathrm{xc}}(r_s, \theta)}{\partial \theta} \bigg|_{r_s} \tag{21}$$

$$- r_s \frac{\partial f_{\mathrm{xc}}(r_s, \theta)}{\partial r_s} \bigg|_{\theta} \quad . \tag{22}$$

IV. STOCHASTIC LFC RECONSTRUCTION

The task at hand is to find a local field correction $G(\mathbf{q},\omega)\in\mathbb{C}$ that i) fulfills the known exact properties listed in the previous section, ii) is consistent with our PIMC data for $F(\mathbf{q},\tau)$ (see Eq. (2)), and iii) is consistent with the sum-rules for $\langle\omega^k\rangle$ (see Eq. (4)). Being inspired by Refs. [16, 17], we introduce an extended Padé type parametrization of the imaginary part of the form

$$\mathrm{Im}G(\mathbf{q},\omega)=\frac{a_0\omega+a_1\omega^3+a_2\omega^5}{\left(b_0+b_1\omega^2\right)^c}\quad , \tag{23}$$

with a_i, b_i, and c being free (a-priori unknown) parameters. The real part of $G(\mathbf{q},\omega)$ is then computed by numerical integration from Eq. (14), and fixing the static limit to the known value from Eq. (3) (note that the $\omega\to\infty$ limit is fulfilled automatically),

$$\begin{aligned}\mathrm{Re}G(\mathbf{q},0)&\stackrel{!}{=}\mathrm{Re}G(\mathbf{q},\infty) \\ &+\frac{1}{\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega\ \frac{a_0+a_1\omega^2+a_2\omega^4}{\left(b_0+b_1\omega^2\right)^c}\quad ,\end{aligned} \tag{24}$$

determines one free parameter. In practice, Eq. (24) is solved analytically using SymPy [20] to express a_1 in terms of the other parameters. The remaining five free parameters are randomly sampled over ten orders of magnitude to generate trial structure factors $S_{\mathrm{trial},i}(\mathbf{q},\omega)$, which, by design, fulfill all listed exact relations of the LFC. The next step is then to plug the trial solutions into Eqs. (2) and (4) and only keep those that reproduce both $F(\mathbf{q},\tau)$ (for all $\tau\in[0,\beta]$) and $\langle\omega^k\rangle$ ($i\in\{-1,0,1,3\}$) within the statistical uncertainty of the PIMC data. Our final result for $S(\mathbf{q},\omega)$ is computed as the average over $M\sim\mathcal{O}\left(10^3\right)$ independent random solutions,

$$S_{\mathrm{final}}(\mathbf{q},\omega)=\frac{1}{M}\sum_{i=1}^{M}S_{\mathrm{trial},i}(\mathbf{q},\omega)\quad , \tag{25}$$

which also conveniently allows us to estimate the uncertainty of the reconstruction by computing the variance

$$\Delta S(\mathbf{q},\omega)=\left(\frac{1}{M}\left(S_{\mathrm{trial},i}(\mathbf{q},\omega)-S_{\mathrm{final}}(\mathbf{q},\omega)\right)^2\right)^{1/2} \tag{26}$$

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