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DIELECTRIC RESPONSE OF THE ELECTRON LIQUID IN GENERALIZED RANDOM-PHASE APPROXIMATION: A CRITICAL ANALYSIS †

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ABSTRACT

We critically examine various approximate theories which have been put forward within the spirit of generalized random-phase approximation (GRPA) for dielectric response of the degenerate electron liquid at metallic densities. The exchange-correlation contribution to the effective field acting on an electron is expressed in terms of a frequency-independent function $G(\vec{q})$ in GRPA. There are requirements of certain sum rules, e.g. the compressibility sum rule, the fluctuation-dissipation theorem and the third frequency moment sum rule, which impose restrictions on $G(\vec{q})$. The theory of Vashishta and Singwi for $G(\vec{q})$ satisfies the compressibility sum rule and the fluctuation-dissipation theorem, while another recent theory by Pathak and Singwi satisfies the third moment sum rule and the fluctuation-dissipation theorem. The second work neglects the correlation contribution to the kinetic energy, while the first one takes it into account through the introduction of an ad hoc parameter. In this note, we show that if the correlation kinetic energy part is correctly taken into account then $G(\vec{q})$ cannot be made to satisfy the compressibility sum rule and the third moment sum rule simultaneously, in the sense that doing this would violate the ground-state energy theorem of Ferrell.

The dielectric response of the electron liquid is conveniently discussed through a frequency and wave-vector-dependent dielectric function [1]. The random-phase approximation (RPA) of Nozières and Pines [2] was the first useful theory for this dielectric function, which is given by

$$\frac{1}{\varepsilon_{RPA}(\vec{q},\omega)} = 1 + \phi(\vec{q})\ \chi_{RPA}(\vec{q},\omega) \tag{1a}$$

where

$$\chi_{RPA}(\vec{q},\omega) = \frac{\chi^0(\vec{q},\omega)}{1 - \phi(\vec{q})\ \chi^0(\vec{q},\omega)} \quad , \tag{1b}$$

$\phi(\vec{q})$ is a Fourier transform of the Coulomb potential and $\chi^0(\vec{q},\omega)$ is the polarizability of free electrons. All the other attempts [3] which have been made to improve upon the RPA result have started from the following form of the density-density response function:

$$\chi(\vec{q},\omega) = \frac{\chi^0(\vec{q},\omega)}{1 - \psi(\vec{q})\ \chi^0(\vec{q},\omega)} \tag{2a}$$

$$\psi(\vec{q}) = \phi(\vec{q})\ (1 - G(\vec{q})) \tag{2b}$$

where an effective potential $\psi(\vec{q})$ enters. The additional term $-\phi(\vec{q})\ G(\vec{q})$ is the correction due to exchange-correlation effects. It is also called the local field correction.

There are a number of exact results which $\chi(\vec{q},\omega)$ should satisfy. We make brief statements about them.

1. <u>Krämer-Krönig relations</u>

$$\chi(\vec{q},\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} d\omega'\ \frac{\mathrm{Im}\ \chi(\vec{q},\omega')}{\omega - \omega' + i\delta} \quad . \tag{3}$$

2. <u>Fluctuation-dissipation theorem</u>

$$S(\vec{q}) = -\frac{1}{\pi n\ \phi(\vec{q})}\int_0^{\infty} \mathrm{Im}\left(\frac{1}{\varepsilon(\vec{q},\omega)}\right) d\omega$$

$$= -\frac{1}{\pi n}\int_0^{\infty} \mathrm{Im}\ \chi(\vec{q},\omega)\ \ d\omega \tag{4}$$

where n is the number density and $S(\vec{q})$ the static structure factor.

3. Frequency moment sum rules

It is convenient to introduce the dynamic structure factor

$$S(\vec{q},\omega) = \sum_{\lambda} \left|\langle\lambda|\rho^{\dagger}_{\vec{q}}|0\rangle\right|^2 \delta(\omega - \omega_{\lambda 0}) \tag{5}$$

where $\rho_{\vec{q}}$ is the Fourier transform of the density operator and $\omega_{\lambda 0} = E_\lambda - E_0$. λ labels the exact eigenstates of the many-body system. We have

$$\chi(\vec{q},\omega) = \int_0^\infty d\omega' \; S(\vec{q},\omega') \left[\frac{1}{\omega - \omega' + i\delta} - \frac{1}{\omega + \omega' + i\delta}\right] \tag{6}$$

and

$$\mathrm{Im}\,\chi(\vec{q},\omega) = -\pi\,[S(\vec{q},\omega) - S(\vec{q},-\omega)] . \tag{7}$$

Now certain exact odd frequency moment sum rules can be written down:

$$\int_0^\infty S(\vec{q},\omega)\,\omega^{2\ell+1}\,d\omega = \frac{1}{2}\,\langle 0|[\rho_{\vec{q}},[H,\ldots[H,\rho^{\dagger}_{\vec{q}}]\ldots]|0\rangle \tag{8}$$

where H, the Hamiltonian of the system, appears $(2\ell + 1)$ times on the right.

In particular,

$$\int_0^\infty S(\vec{q},\omega)\,\omega\,d\omega = \frac{nq^2}{2m} \tag{9}$$

$$\int_0^\infty S(\vec{q},\omega)\,\omega^3\,d\omega = \frac{nq^2}{2m}\left(\left(\frac{q^2}{2m}\right)^2 + 4\left(\frac{q^2}{2m}\right)\langle KE\rangle\right) + \\ + \frac{n}{2m^2}\sum_{\vec{k}} (\vec{q}\cdot\vec{k})^2\,\phi(\vec{k})\,[S(\vec{q}-\vec{k}) - S(\vec{k})] . \tag{10}$$

Here, $\langle KE\rangle$ is the average kinetic energy per particle. The third moment sum rule [Eq.(10)] can be written in an alternative form:

$$\int_0^\infty S(\vec{q},\omega)\,\omega^3\,d\omega = \frac{nq^2}{2m}\left[\left(\frac{q^2}{2m}\right)^2 + 4\left(\frac{q^2}{2m}\right)\langle KE\rangle\right] +$$

$$+ \frac{n^2}{2m^2}\int d\vec{r}\, g(\vec{r})\,(1-\cos\vec{q}\cdot\vec{r})\,(\vec{q}\cdot\vec{\nabla})^2\,\phi(\vec{r}) \tag{11}$$

where $\phi(\vec{r})$ is the Coulomb potential and $g(\vec{r})$ is the pair correlation function

$$g(\vec{r}) = 1 + \frac{1}{n}\sum_{\vec{q}}\,(S(\vec{q})-1)\,e^{i\vec{q}\cdot\vec{r}} \quad . \tag{12}$$

Now we make a large ω expansion of expressions (3) and (2a) and equate the coefficients of $1/\omega^2$, $1/\omega^4$,... :

$$-\frac{1}{\pi}\int_{-\infty}^{\infty}\omega\,\mathrm{Im}\,\chi(\vec{q},\omega)\,d\omega = -\frac{1}{\pi}\int_{-\infty}^{\infty}\omega\,\mathrm{Im}\,\chi_0(\vec{q},\omega)\,d\omega \tag{13}$$

and

$$-\frac{1}{\pi}\int_{-\infty}^{\infty}\omega^3\,\mathrm{Im}\,\chi(\vec{q},\omega)\,d\omega = -\frac{1}{\pi}\int_{-\infty}^{\infty}\omega^3\,\mathrm{Im}\,\chi_0(\vec{q},\omega)\,d\omega +$$

$$+\,\psi(q)\left[-\frac{1}{\pi}\int_{-\infty}^{\infty}\omega\,\mathrm{Im}\,\chi_0(\vec{q},\omega)\,d\omega\right]^2 . \tag{14}$$

Thus we have

$$-\frac{1}{\pi}\int_{-\infty}^{\infty}\omega\,\mathrm{Im}\,\chi_0(\vec{q},\omega)\,d\,\omega = \frac{nq^2}{m} \tag{15}$$

$$-\frac{1}{\pi}\int_{-\infty}^{\infty}\omega^3\,\mathrm{Im}\,\chi_0(\vec{q},\omega)\,d\omega = \frac{nq^2}{m}\left[\left(\frac{q^2}{2m}\right)^2 + 4\left(\frac{q^2}{2m}\right)\langle KE\rangle_f\right] \quad . \tag{16}$$

Here, $\langle KE\rangle_f$ is the kinetic energy per particle in a non-interacting system.

The first moment sum rule is automatically satisfied by GRPA; the third moment would be satisfied if

$$G_{TM}(\vec{q}) = -\frac{2}{n}\left(\frac{q^2}{4\pi e^2}\right)\left\{\langle KE\rangle - \langle KE\rangle_f\right\}$$

$$-\frac{1}{4\pi n e^2}\sum_{\vec{k}}\left[\frac{(\vec{q}\cdot(\vec{k}+\vec{q}))^2}{q^2}\,\phi(\vec{k}+\vec{q}) - \frac{(\vec{q}\cdot\vec{k})^2}{q^2}\,\phi(\vec{k})\right]\,(S(\vec{k})-1) \quad . \tag{17}$$

In a recent paper, Pathak and Vashishta [4] have utilized the expression for $G(q)$ as given by Eq.(17) but neglected the correlation kinetic energy $\langle KE\rangle_c = \langle KE\rangle - \langle KE\rangle_f$. $G(\vec{q})$ thus becomes a functional of $S(\vec{q})$. The fluctuation-dissipation theorem Eq.(4) is imposed as the self-consistency condition which determines $S(\vec{q})$ and hence $\chi(\vec{q},\omega)$.

We can write down the ground-state energy per particle as

$$E_0 = \langle KE\rangle_f + \int_0^1 \frac{d\lambda}{\lambda} \langle PE\rangle_\lambda$$

or alternatively

$$E_0 = \langle KE\rangle + \langle PE\rangle$$

so that

$$\begin{aligned}\langle KE\rangle_c &= \int_0^1 \frac{d\lambda}{\lambda} \langle PE\rangle_\lambda - \langle PE\rangle \\ &= -\frac{4}{\pi}\left(\frac{9\pi}{4}\right)^{1/3}\left[\frac{1}{r_s^2}\int_0^{r_s}\bar{\gamma}(x)\,dx - \frac{\bar{\gamma}(r_s)}{r_s}\right] \text{ Rydbergs}\end{aligned} \tag{18}$$

where $\bar{\gamma}(r_s)$ is given by

$$\bar{\gamma}(r_s) = -\frac{1}{2k_F}\int_0^\infty (S(q,r_s) - 1)\,dq \tag{19}$$

$$= -\frac{k_F^2}{3}\int_0^\infty r(g(r,r_s) - 1)\,dr\,. \tag{20}$$

For the derivation of Eq.(18), we refer to Vashishta and Singwi [5].

The expression of $G_{TM}(\vec{q})$ can now be written in the form

$$\begin{aligned}G_{TM}(\eta) = {} & 3\left\{\frac{1}{r_s}\int_0^{r_s}\bar{\gamma}(x)\,dx - \bar{\gamma}(r_s)\right\}\eta^2 \\ & - \frac{3}{4}\int_0^\infty d\eta'\,\eta'^2\,(s(\eta') - 1)\left[\frac{5}{6} - \frac{\eta'^2}{2\eta^2}\right. \\ & \left. + \frac{\eta'^2 - \eta^2}{4\eta'\eta^3}\,\ln\left|\frac{\eta + \eta'}{\eta - \eta'}\right|\right]\,.\end{aligned} \tag{21}$$

Here $\eta = q/k_F$. It can be written in an alternative form which can easily be derived starting from Eq.(11) instead of Eq.(10):

$$G_{TM}(\eta) = 3 \left\{ \frac{1}{r_s} \int_0^{r_s} \bar{\gamma}(x)\, dx - \bar{\gamma}(r_s) \right\} \eta^2$$

$$- 2 \int_0^{\infty} \frac{d\rho}{\rho} \, (g(\rho, r_s) - 1)\, j_2(\eta\rho) \quad . \tag{22}$$

Here $\rho \equiv rk_F$ and $j_2(\eta\rho)$ is the spherical Bessel function of order two.

4. Compressibility sum rule

The $\vec{q} \to 0$ limit of the static dielectric function is given by

$$\lim_{\vec{q} \to 0} \mathcal{E}(\vec{q},0) = 1 + \frac{k_{TF}^2/q^2}{1 - \gamma(k_{TF}^2/k_F^2)} \tag{23}$$

here

$$\gamma = \lim_{\vec{q} \to 0} \frac{G(\vec{q})}{(q^2/k_F^2)} \tag{24}$$

and k_{TF} is the Thomas-Fermi wave number. The isothermal compressibility κ is given by

$$\frac{\kappa_{free}}{\kappa} = 1 - \gamma \left(\frac{k_{TF}^2}{k_F^2} \right) \quad . \tag{25}$$

The compressibility sum rule states that the volume of compressibility determined from the ground-state energy of the system or from the virial equation of state should be the same as given by Eq.(25).

Using the relation

$$\kappa = \left(n \frac{\partial p}{\partial n} \right)^{-1}$$

and the virial equation of state

$$p = \frac{2}{3} n \langle KE \rangle - \frac{1}{6} n^2 \int d\vec{r}\, [g(\vec{r}) - 1]\, (\vec{r} \cdot \vec{\nabla})\, \phi(\vec{r}) \tag{26}$$

we get

$$\frac{\kappa_{free}}{\kappa} = 1 - \frac{1}{(k_F^2/2m)} \left[-\frac{\partial}{\partial n} (n \langle KE \rangle_c) + \right.$$

$$\left. + \left\{ 1 + \frac{n}{2}\frac{\partial}{\partial n} \right\} \left\{ \int d\vec{r}\, (g(\vec{r},n) - 1)\, (\vec{r}\cdot\vec{\nabla})\, \phi(\vec{r}) \right\} \right] . \quad (27)$$

A comparison of Eqs.(25) and (27) gives

$$\gamma = \frac{\pi}{2e^2 k_F} \left[-\frac{\partial}{\partial n} (n \langle KE \rangle_c) + \right.$$

$$\left. + \left[1 + \frac{n}{2}\frac{\partial}{\partial n} \right] \left\{ \int d\vec{r}\, (g(\vec{r},n) - 1)\, (\vec{r}\cdot\vec{\nabla})\, \phi(\vec{r}) \right\} \right] . \quad (28)$$

Thus a $G(q)$ which gives the above small q behaviour is given by

$$G_c(\vec{q}) = \frac{\pi}{2e^2 k_F^3} \left\{ -\frac{\partial}{\partial n} [n \langle KE \rangle_c] \right.\, \vec{q}^{\,2}$$

$$+ \left[1 + \frac{n}{2}\frac{\partial}{\partial n} \right] \left[-\frac{1}{n} \int \frac{d\vec{q}\,'}{(2\pi)^3} (S(\vec{q}-\vec{q}\,') - 1) \right] \quad (29a) .$$

or

$$G_c(\eta) = -\frac{\gamma_s}{3} \left[\frac{5\bar{\gamma}(r_s)}{r_s} - \frac{d\bar{\gamma}(r_s)}{dr_s} - \frac{5}{r_s^2} \int_0^{r_s} \bar{\gamma}(x)\, dx \right] \eta^2 +$$

$$+ \left\{ 1 + \frac{n}{2}\frac{\partial}{\partial n} \right\} \left[\eta \int_0^{\infty} (1 - g(\rho))\, j_1(\eta\rho)\, d\rho \right] . \quad (29b)$$

In a series of papers, Singwi et al.[5),6),7)] have developed a succession of approximations for the function $G(q)$. The basic philosophy is to include the short-range correlations responsible for the local field corrections in a self-consistent manner. In the last paper, they propose the following form for $G(q)$:

$$G_{VS}(q) = \left\{ 1 + a\, n \frac{\partial}{\partial n} \right\} \left[-\frac{1}{n} \int \frac{d\vec{q}\,'}{(2\pi)^3} (S(\vec{q}-\vec{q}\,') - 1) \right]$$

$$= \left\{ 1 + a\, n \frac{\partial}{\partial n} \right\} \left[\eta \int_0^{\infty} (1 - g(x))\, j_1(\eta x)\, dx \right] . \quad (30)$$

Now, it may be noted that in this expression for $G(q)$ (compare with Eq.(29)), the $\langle KE \rangle_c$ term has been neglected and in its place a parameter "a" has been introduced in the derivative term. Later, we shall comment about this parameter.

It is clear that a $G(q)$ which is either tailored to satisfy the compressibility sum rule or the third moment sum rule, together with the fluctuation-dissipation theorem imposed as the self-consistency condition, can be constructed. Here, we wish to look at the problem from another angle. Is it possible to construct $G(q)$ which satisfies both the compressibility sum rule and the third moment sum rule? We show below that if this is done it leads to a violation of the ground-state energy theorem of Ferrell [8] which states that

$$\frac{d^2E_0}{d(e^2)^2} \leqslant 0 \quad \text{at constant density} \tag{31}$$

or, equivalently

$$\frac{d}{dr_s} \bar{\gamma}(r_s) \geqslant 0 \quad . \tag{32}$$

We compare $G_{TM}(\eta)$ and $G_c(\eta)$ for small η, namely

$$G_{TM}(\eta) = \left\{ 3\left[\frac{1}{r_s}\int_0^{r_s} \bar{\gamma}(x)\,dx - \bar{\gamma}(r_s)\right] + \frac{2}{5}\bar{\gamma}(r_s)\right\} \eta^2 \tag{33}$$

and

$$G_c(\eta) = \gamma(r_s)\,\eta^2 = \left\{ -\frac{r_s}{3}\left[\frac{5\bar{\gamma}(r_s)}{r_s} - \frac{d\bar{\gamma}(r_s)}{dr_s} - \frac{5}{r_s^2}\int_0^{r_s}\bar{\gamma}(x)\,dx\right] + \right.$$

$$\left. + \left(\frac{2}{3} - \frac{1}{6} r_s \frac{\partial}{\partial r_s}\right)\bar{\gamma}(r_s)\right\} \eta^2 \quad , \tag{34}$$

which gives

$$\gamma(r_s) = 3\left[\frac{1}{r_s}\int_0^{r_s}\bar{\gamma}(x)\,dx - \bar{\gamma}(r_s)\right] + \frac{2}{5}\bar{\gamma}(r_s)$$

$$= \frac{5}{3r_s}\int_0^{r_s}\bar{\gamma}(x)\,dx - \bar{\gamma}(r_s) + \frac{r_s}{6}\frac{d\bar{\gamma}(r_s)}{dr_s} \quad . \tag{35}$$

This equation can be exactly solved giving

$$\bar{\gamma}(r_s) = \text{constant} \times r_s^t \tag{36}$$

and

$$t = -0.15 \tag{37}$$

which violates Ferrell's condition, Eq.(32).

Next, we compare the exact result of isothermal compressibility, Eq.(28), with the expression used by Vashishta and Singwi [5]. This gives

$$a = \frac{1}{2} + \frac{5\left\{\bar{\gamma}(r_s) - \frac{1}{r_s}\int_0^{r_s}\bar{\gamma}(x)\,dx\right\} - r_s\,\frac{d\bar{\gamma}(r_s)}{dr_s}}{\gamma_s\,\frac{d\bar{\gamma}(r_s)}{dr_s} + 2\bar{\gamma}(r_s)} \quad . \qquad (38)$$

It is interesting to note that the results for $\bar{\gamma}(r_s)$ from Vashishta and Singwi [5] can be fitted by Eq.(36) with $t = 0.1165$. This power law behaviour for $\bar{\gamma}(r_s)$ simplifies the expression for the parameter "a" (Eq.(38)) considerably, giving

$$a = 0.69$$

which is very close to 2/3 as used by Vashishta and Singwi [5] and is <u>independent of r_s</u>. This justifies the internal consistency of their work and explains why the compressibility sum rule is almost correctly satisfied in it.

We conclude this note by observing that the GRPA expression should be modified to satisfy these exact results. One of the possible alternatives is to assume a $(\vec{q},\omega)$ – dependent local field correction, which implies a non-local and retarded exchange correlation potential. The only work of this type is by Toigo and Woodruff [9]. But they obtain $\gamma = 1/4$, independent of r_s, in their theory. $\gamma = 1/4$ is the Hartree-Fock result and it is evident that for small $\vec{q}$ there are no correlation effects in their theory. Clearly it requires further modifications.

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