Dynamical correlation effects in alkali metals

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We show that dynamical correlation effects can account for the rapid softening of the bulk-plasmon dispersion, recently observed experimentally in alkali metals.

Alkali metals have been drawing much attention in recent years as potential media to observe the exchange and correlation (xc) effects of electron gas. Since the periodic lattice potential is well screened out in these metals, the valence electrons form a nearly-free-electron system. The usual coupling parameter $r_s = d/a_0$, d being the Wigner-Seitz radius, varies from about 2 for Al to 5 for Cs. This is well outside the range of applicability for the random-phase approximation (RPA), which requires $r_s \ll 1$, and ignores the xc effects. Therefore, some of the xc effects should be observable in alkali metals. Unfortunately, weakness of the xc effects makes it very difficult to distinguish them from the small lattice-induced effects (band-structure effects). For example, the concept of charge density waves[1] in alkali metals still awaits conclusive experimental verification.

Recently, a pronounced reduced value of the group velocity of the bulk-plasmon mode for $k \to 0$ in comparison to its RPA value has been observed in alkali metals.[2] We will refer to this effect as the "softening" of the bulk-plasmon dispersion (BPD). The importance of the softening increases with decreasing electron density, i.e., with increasing r_s. For Cs the group velocity has even been found to be negative.[2] Lattice effects have been eliminated as a direct cause of this phenomenon.[2] However, theories which ignore the lattice effects but include the xc effects also have been unable to account satisfactorily for the effect. Although, in general, these theories predict that xc effects produce the softening of BPD, the predicted magnitude of the softening is much smaller than observed. Specifically, the experimental results show that an abrupt decrease of the initial slope occurs for $r_s > 4$, which is completely unaccounted for by theories that include various models of xc effects. One of the most widely used approaches is that of Singwi, Tosi, Land, and Sjölander[3] (STLS) and its modified version due to Vashishta and Singwi (VS).[4] These theories include static (frequency-independent) correlations only in determining $\epsilon(\mathbf{k},\omega)$, the dielectric response function. STLS and VS relate the static correlations to the low-frequency behavior of $\epsilon(\mathbf{k},\omega)$; a different scheme originated by Pathak and Vashishta[5] (PV) bases the static correlations on the high-frequency limit of $\epsilon(\mathbf{k},\omega)$. Neither of these approaches are able to properly treat dynamical effects that occur in the vicinity of the plasma frequency ω_p. Even a recently proposed naive dynamical theory,[6] where the frequency-dependent correlations are determined by interpolation between the low- and high-frequency, frequency-independent behaviors, is bound to miss such effects. In this Brief Report we present a plausible cause for the hitherto not included detailed dynamical correlation effects to account for the experimentally observed features of the BPD, in particular the rapid-mode softening.

We use the paradigm of the classical one-component plasma (OCP) where a similar softening of the plasmon mode was demonstrated through molecular-dynamics computer simulations[7] and, more recently, analyzed through theoretical calculations in substantial detail.[8,9] The structure of the theoretical model makes it clear that dynamical correlations *add* to the softening effect over and beyond what the static correlations contribute; the analysis also shows that it is the mode-mode interaction that plays a crucial role in generating the peculiar abrupt change around $r_s \simeq 4$. We will argue that the results obtained for the classical OCP apply, *mutatis mutandis,* to the degenerate electron-gas system as well.

The theoretical calculations concerning the one-component plasmon dispersion are based on the dynamical mean field theory (DMFT) of Golden and Kalman.[10] This theory provides a nonperturbative calculational scheme for the dielectric response function $\epsilon(\mathbf{k},\omega)$. Writing

$$\epsilon(\mathbf{k},\omega) = 1 - \phi(k)\chi(\mathbf{k},\omega), \quad \phi(k) = \frac{4\pi e^2}{k^2} \tag{1}$$

with $\chi(\mathbf{k},\omega)$, the conventional density response function, the relationship between $\chi(\mathbf{k},\omega)$ and the density response of the noninteracting gas $\chi_0(\mathbf{k},\omega)$ can be expressed as

$$\chi(\mathbf{k},\omega) = \chi_0(\mathbf{k},\omega)[1 + v(\mathbf{k},\omega)] \, . \tag{2}$$

The main structural development of the approximation scheme consists of relating the coupling function $v(\mathbf{k},\omega)$ to the quadratic density response function $\chi(\mathbf{k}_1,\omega_1;\mathbf{k}_2,\omega_2)$ through a linear operator I:

$$v(\mathbf{k},\omega) = \sum_{\mathbf{q},\mu} I(\mathbf{q},\mu) \frac{\chi(\mathbf{k}-\mathbf{q},\omega-\mu;\mathbf{q},\mu)}{\epsilon(\mathbf{k}-\mathbf{q},\omega-\mu)\epsilon(\mathbf{q},\mu)} \, . \tag{3}$$

The details of the operator I and of the formalism do not concern us here: The structure of Eq. (3), however, is already indicative of the importance of the mode-mode interaction brought about by the pole structure of (3). An important contribution for the integral comes from the

double pole where both of the ϵ's vanish. For the OCP this happens for $\omega \approx \omega_p$. The enhancement of the dynamical response in the vicinity of the second harmonic of the plasma frequency is already a well-known feature of perturbation calculations.[11] Here, both the second harmonic enhancement and the altered behavior near $\omega \approx \omega_p$ are the result of the genuine dynamical correlations in the system, and thus the amplitude of the second harmonic enhancement can monitor the importance of these dynamical correlation effects in the system. This point is further elaborated below.

In order to perform any comparison between the classical OCP and the electron gas, an equivalence between the coupling parameters relevant to the two systems, $\Gamma = e^2/dk\,T$ and $r_s = d/a_0$, respectively, has to be established. There is no unique way to do this, but a rather obvious translation is provided by considering both of the parameters as the ratios of the potential energies (U) and kinetic energies (K) in the system. The kinetic energy per particle in the OCP is

$$K = \tfrac{3}{2}kT \ ,$$

while in the electron gas

$$K = \tfrac{3}{5}\varepsilon_F \ .$$

On the basis of this equivalence

$$\Gamma = 1.36 r_s \ . \tag{4}$$

We now turn to the comparison of recent experimental results on BPD with various theoretical results. Writing the plasmon dispersion in the form

$$\omega = \omega_p [1 + A(r_s) k^2] \ , \tag{5}$$

we concentrate on the quantity

$$\overline{A}(r_s) = A(r_s)/A(0) \ . \tag{6}$$

$A(0)$ is the RPA dispersion coefficient.

The experimental results of Ref. 2 are displayed in Fig. 1 as stars, together with the results of three simple theoretical approaches (solid lines), as well as those of the more elaborate DMFT (Refs. 8–10) (heavy solid line). The simple theories are (VS) the low-frequency static approximation of Vashishta and Singwi,[4] (PV) the high-frequency static approximation proposed by Pathak and Vashishta[5] (incidentally, shown recently by Kalman and Golden[12] to be correct in the strong-coupling limit, but not for intermediate coupling); and (D) the "dynamical" interpolation formula between the above two approaches of Dabrowski.[6] The results of VS and D are used in Ref. 2 to gauge the ability of existing theories to explain the experimental findings. Two striking discrepancies of the experimental results can be observed, however, when compared with these theories. The first is that the critical $r_{s,\mathrm{crit}}$ value where the group velocity becomes zero [$\overline{A}(r_{s,\mathrm{crit}}) = 0$] is much lower than predicted by any of them: VS predicts $r_{s,\mathrm{crit}} = 8.08$, while PV leads to $r_{s,\mathrm{crit}} = 12$, and the value following from the formalism of D (and calculated in Ref. 2) is in between. The experimental value is $r_{s,\mathrm{crit}} = 5.3$. The second observation is that while the experimental $\overline{A}(r_s)$ curve indicates the abrupt softening in the vicinity of $r_{s,\mathrm{crit}}$ (i.e., the $\overline{A}$ versus r_s curve drops precipitously as it approaches $r_{s,\mathrm{crit}}$), no such behavior is manifested in the predictions of any of the above theories.

We focus now on the results of the DMFT (heavy solid line). The DMFT values of $\overline{A}(r_s)$ given in Fig. 1 were calculated on the basis of the formalism of Ref. 10 in Ref. 8 and have recently been recalculated in greater detail in Ref. 9. We observe that the DMFT performs surprisingly well. It provides $r_{s,\mathrm{crit}} = 4.39$, a value much closer to the experimental one. But even more remarkable is the abrupt softening behavior, qualitatively almost identical to the one noted in relation to the experiment. Thus the careful treatment of the dynamical correlations, which is the distinguishing feature of the DMFT, seems to be crucial in obtaining reasonable agreement with experimental data.

The more detailed mechanism bringing this about can be identified as a kind of avalanche effect, associated with mode-mode interaction: this latter interaction which controls the mode softening, is enhanced in the neighborhood of zero group velocity, where the available phase space is enlarged; as a result, the softening of the plasmon dispersion increases, which in turn further reduces the group velocity toward its zero value. This mechanism is quite apparent from the structure of the self-consistent Eqs. (1)–(3). A corroboration of this physical model comes also from observing the amplitude of the second harmonic enhancement[9] discussed above: one notes a marked correlation between stronger enhancement and the approach to $r_{s,\mathrm{crit}}$. As one recedes to $r_s \gg r_{s,\mathrm{crit}}$ (or to $r_s \ll r_{s,\mathrm{crit}}$), the enhancement amplitude drops dramatically. Thus the importance of detailed correlations in the

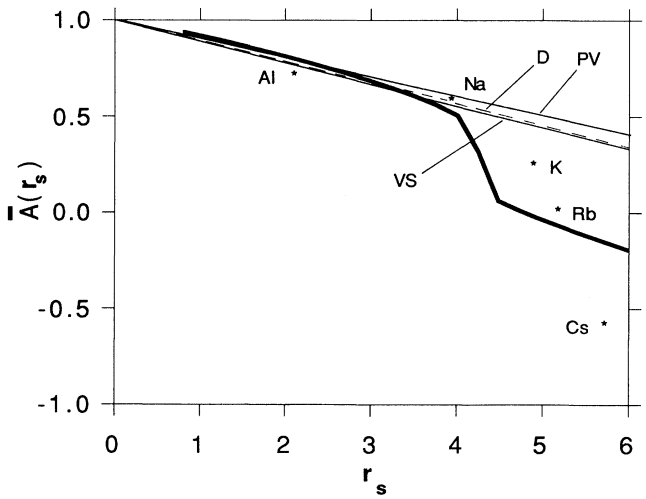

FIG. 1. Bulk-plasmon group velocity normalized to its RPA value $\overline{A}(r_s)$ vs r_s. Stars represent the experimental results: Al from Ref. 14; Na, K, Rb, and Cs from Ref. 2. Thin-solid lines are for various theories neglecting the genuine dynamical correlation effects: VS (Ref. 4), D (Ref. 6), and PV (Ref. 5). Heavy solid line is from the theory that includes the dynamical correlation effects (Refs. 8 and 9).

vicinity of $r_{s,\mathrm{crit}}$ and $\omega \simeq \omega_p$ seems to be well established.

One may wonder about the legitimacy of transplanting the results of a theory pertaining to the classical OCP into the domain of a quantum system, the degenerate electron gas. Our belief that this is not an unreasonable procedure is based on the fact that both the change from positive to negative dispersion (group velocity) with increasing coupling and the abrupt development of the softening can be explained by evoking simple physical arguments, founded on classical considerations. The development of negative dispersion is the result of the incipient quasilocalization of particles, which, in turn, entails a dispersion resembling that of the Wigner lattice, where the negative dispersion is imposed by the Kohn sum rule. As to the appearance of the abrupt softening in the vicinity of $r_{s,\mathrm{crit}}$ we have already pointed at the mode-mode interaction as the dominant dynamical process. Thus the way these two mechanisms operate should not be affected too much by the quantum nature of the system. The prominent quantum effect that distinguishes the degenerate electron gas from its classical counterpart is the exchange interaction: One would expect that the exchange has little bearing on the processes discussed. The most important effect of the exchange in an unpolarized electron gas is the *de facto* hardening of the interaction (as demonstrated, for example, by a lower $r_{s,m}$ value for Wigner crystallization[13] than expected on the basis of the $r_{s,m} \rightarrow \Gamma_m/1.36$ conversion of the OCP crystallization value, $\Gamma_m = 178$; in fact[13] $r_{s,m} \simeq 100$). Such a hardening can be accounted for by using a Γ/r_s conversion factor which is somewhat greater than 1.36. This would not affect the discrepancy between the experimental results and the predictions of the static theories, and it would only slightly change the remaining considerations of this paper.

Finally, we may wonder what happens to the plasmon mode for higher r_s and $\mathbf{k}$ values, as the slope of $\omega(\mathbf{k})$ further decreases and the extrapolated dispersion curve seems to move into the $\omega^2 < 0$ domain, heralding an unstable softening of the mode. Our analysis of the classical OCP indicates, however, that this never happens: $\omega(\mathbf{k})$ is bounded from below by ω^*, such that $\omega_p/\sqrt{3} > \omega^* > 0$, the precise value depending on the behavior of the static structure function $S(\mathbf{k})$.

Our conclusions can now be stated as follows. While there are serious discrepancies (both quantitatively and qualitatively) between recent experimental results[2] and predictions of static mean field theories[3,4,6] concerning the behavior of the bulk-plasmon dispersion coefficient for the electron gas in alkali metals, a recently developed *dynamical* mean field theory[8–10] for the classical OCP, when reinterpreted for the electron gas, provides a better quantitative agreement with the critical r_s value where the group velocity vanishes and is unique in qualitatively correctly displaying the abrupt softening of the dispersion as this critical r_s value is approached.

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