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LETTER TO THE EDITOR

The effect of a frequency-dependent exchange and correlation kernel on the multipole surface plasmon frequency of a bare jellium aluminium surface

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Abstract. The dynamic exchange–correlation (XC) kernel of Gross, Kohn and Iwamoto is analytically continued into the lower-half frequency plane and incorporated in a microscopic calculation of multipole surface plasmon dispersion on a jellium aluminium surface. The multipole mode found in earlier calculations using a static XC kernel is still present, the change to dynamic XC causing a small frequency shift and a more substantial percentage increase in damping.

In a recent letter [1] we calculated the dispersion relationship of a new 'multipole' surface plasmon mode of a bare jellium aluminium surface. Tsuei *et al* [2] have since shown that these modes can be observed experimentally on bare sodium and potassium surfaces. In our paper [1] we described exchange and correlation (XC) effects via a static XC kernel,

$$\mu'_{\mathrm{XC}}(n(z)) = f_{\mathrm{XC}}(\omega = 0 : n(z))$$

in the self-consistent microscopic screening equations: that is, we used the 'time-dependent local density functional' (adiabatic LDF) method [3]. Recently Gross, Kohn and Iwamoto [4] (henceforth referred to as GKI) developed a frequency-dependent XC kernel $f_{\mathrm{XC}}(\omega : n)$ for use in inhomogeneous many-electron systems. In the present letter we recalculate the multipole surface plasmon dispersion relation on bare Al using $f_{\mathrm{XC}}(\omega : n)$ instead of $f_{\mathrm{XC}}(0 : n)$: we shall refer to this as the 'dynamic local density functional' (dynamic LDF) approximation. We felt that this calculation might be especially sensitive to the XC kernel, as explained in the discussion at the end of the letter.

In order to obtain accurate values of the imaginary part Im ω_{m} of the surface plasmon frequency, our method [1] requires an analytical continuation of the bare electronic density–density response function $\chi^0(q_\parallel, z, z' : \omega)$ from the upper into the lower-half frequency plane. We performed this in our previous letter [1], taking care with cuts arising from electron–hole pair formation and photoemission. In the present case, the GKI XC kernel f_{XC} must also be analytically continued, and this can be done as follows.

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In the GKI theory, the XC kernel $f_{XC}(\omega:n)$ is a complex-valued function analytic in the upper-half frequency plane, with the following limiting values

$$f_{XC}(\omega = 0; n) = (d^2/dn^2)(n\varepsilon_{XC}(n)) \equiv f_0(n) \tag{1}$$

$$f_{XC}(\omega \to \infty; n) = -\tfrac{4}{5}n^{2/3}(d/dn)(n^{-2/3}\varepsilon_{XC}(n)) + 6n^{1/3}(d/dn)(n^{-1/3}\varepsilon_{XC}(n)) \equiv f_\infty(n) \tag{2}$$

where ε_{XC} is the XC energy per electron of a uniform electron gas of number density n. Its imaginary part is approximated by GKI as a Pade-type expression

$$\operatorname{Im} f_{XC}(\omega + i0; n) = a(n)\omega/(1 + b(n)\omega^2)^{5/4} \qquad (\omega \text{ real}) \tag{3}$$

with

$$a(n) = -c(\gamma/c)^{5/3}(f_\infty(n) - f_0(n))^{5/3} \tag{4a}$$

$$b(n) = (\gamma/c)^{4/3}(f_\infty(n) - f_0(n))^{4/3} \tag{4b}$$

$$c = 23\pi/15 \tag{4c}$$

$$\gamma = (\Gamma(\tfrac{1}{4}))^2/\sqrt{32\pi}. \tag{4d}$$

GKI proposed using the standard Kramers–Kronig relations to determine $\operatorname{Re} f_{XC}(\omega + i0)$ from equation (3) for frequencies infinitesimally above the real axis. However, because $f(z)$ is analytic and bounded in the upper half plane we have

$$f(z) = \frac{1}{2\pi i}\oint \frac{f(\nu)}{\nu - z}\,d\nu \tag{5}$$

and

$$0 = \frac{1}{2\pi i}\oint \frac{f(\nu)}{\nu - z^*}\,d\nu \tag{5a}$$

(these integrals are over the real axis closed by an 'infinite' semicircle and $\operatorname{Im} z > 0$).

Subtracting the complex conjugate of (5*a*) from (5) gives the whole GKI function $f_{XC}(\omega)$ for all values of ω with $\operatorname{Im}\omega > 0$:

$$f_{XC}(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\operatorname{Im} f_{XC}(\nu + i0)}{\nu - \omega}\,d\nu = \frac{\beta}{\pi}\int_{-\infty}^{+\infty} \frac{\nu\,d\nu}{(\nu - \omega)(\nu^2 + \alpha^2)^{5/4}} \tag{6a}$$

where

$$\alpha^2 = 1/b(n) \tag{6b}$$

$$\beta = a(n)b(n)^{-5/4}. \tag{6c}$$

To continue f_{XC} analytically into the lower half frequency plane, it is only necessary to deform the contour from $-\infty$ to $+\infty$ in equation (6*a*) ahead of the pole located at

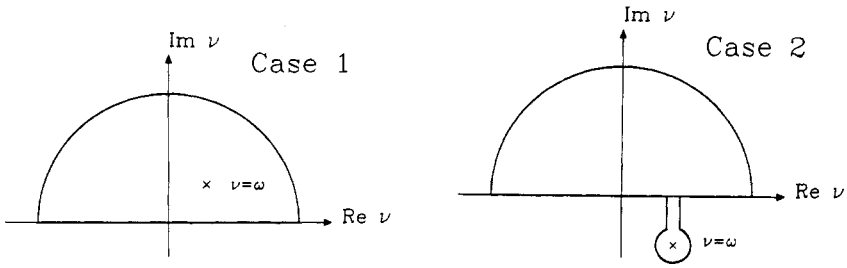

Figure 1. The contour of integration used in equation (6*a*). Case 1: the 'standard' contour used for Im $\omega > 0$. Case 2: the 'deformed' contour used for Im $\omega < 0$.

$\nu = \omega$ as shown in figure 1. Numerical implementation of the resulting integral for f_{XC} is straightforward.

The effect of the GKI kernel on the multipole surface plasmon of Al was investigated by recalculating the complex mode frequency as in reference [1] but using the analytical continuation of $f_{XC}(\omega : n)$ of the finite-frequency GKI kernel in place of the original static kernel $f_{XC}(0 : n)$. Although GKI suggest the use of the Vosko–Wilk–Nusair [5] parametrisation for the correlation component of $\varepsilon_{XC}(n)$ we have retained the Wigner interpolation form to ensure a direct comparison with our previous work [1]. The surface parallel wavenumber, $q_\parallel$, was varied from 0.30 au to 0.025 au (zero wavenumber was not used because of numerical instability). The deep-metal cutoff, z_{left}, was varied from -15 au to -30 au and the step size dz in the discretisation of the integral equation was varied from 0.2 to 0.3 au.

For all cases treated, the real part of the multipole frequency, Re $\omega_m(q_\parallel)$ varied less than 3.1% when $f_{XC}(0 : n)$ was replaced by $f_{XC}(\omega : n)$ (with convergence parameters such as z_{left} and dz held fixed). The imaginary part, Im $\omega_m(q_\parallel)$, changed by as much as 23%, however. This effect was most pronounced for small $q_\parallel$ where the TDLDF damping is small (average of 20% for $q_\parallel = 0.025$ au) and least pronounced at large $q_\parallel$ (average of 2% for $q_\parallel = 0.3$ au) (see figure 2).

In most applications, the use of the new GKI dynamic XC kernel [4, 6] has not led to any dramatic effects. The present calculation was performed partly in the expectation that dynamic XC effects would be particularly strong for the multipole surface plasmon mode of a bare metal surface, because of its rather critical nature compared, say, with regular surface or bulk plasmons. (For example, unlike the regular 'monopole' surface plasmon whose long-wavelength frequency $\omega_s(q_\parallel = 0)$ is independent of the static surface electron profile and of many-body exchange and correlation effects, the multipole frequency is certainly sensitive to the former factor. Indeed, the natural selvage must be sufficiently thick in order to support multipole modes, and through this effect alone the multipole mode frequency $\omega_m(q_\parallel = 0)$ can depend on exchange and correlation effects since these do have an influence on the static electron density profile. The question of exchange and correlation effects on the multipole plasmon frequency for a given fixed static profile is a more subtle one.) Our data above show perhaps the largest effect (20% change in damping) yet seen [4, 6] due to the inclusion of dynamic XC effects in any inhomogeneous many-electron system. This occurs at a small surface-parallel wavenumber, $q_\parallel$, but our data are not well enough converged at small $q_\parallel$ to determine whether the multipole mode is sensitive to dynamic XC effects in the limit $q_\parallel \to 0$. Perhaps an analytic answer is available by perturbation of the dynamic screening equations about

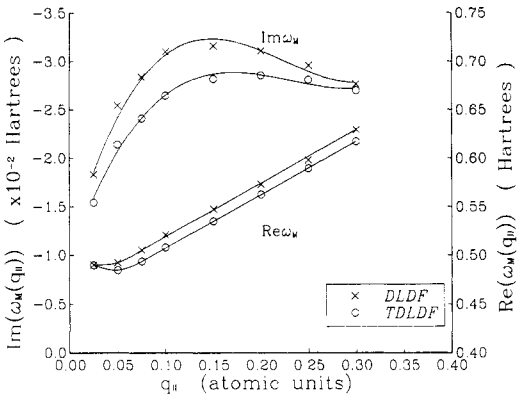

Figure 2. Changes in the real and imaginary parts of the surface plasmon dispersion relationship of the multipole mode. The data is taken for parameter values of $z_{left} = -25$ au dz = 0.25 au and $z_{right} = 10$ au. Crosses indicate the real and imaginary parts of the multipole mode frequency calculated with the dynamic (DLDF) XC kernel of Gross, Kohn and Iwamoto. Open circles indicate the mode frequency calculated with a static (TDLDF) XC kernel.

the static XC limit, or by some form of spatial moment expansion such as that of Dasgupta [7]. Alternatively, a recalculation of our screening equations with more careful attention to Friedel oscillation asymptotics [1, 8] in the bulk should be able to settle the issue, and will in any case be necessary in order to extend our multipole surface plasmon investigation to metals of lower electron density. It is for such metals that we anticipate the largest effects of dynamic, inhomogeneous exchange and correlation.

In summary, our microscopic calculations for the jellium model of a bare aluminium surface show that the multipole surface plasmon mode does not disappear when a static exchange and correlation kernel is replaced by the dynamic kernel, $f_{XC}(\omega : n)$ of Gross, Kohn and Iwamoto. Indeed there is a maximum change of 3% in real frequency for the wavenumbers $q_\parallel$ which we investigated. On the other hand, the mode damping showed perhaps the largest percentage effect (20%) yet predicted in any inhomogeneous system from the dynamic character of exchange and correlation. We speculate that even larger effects should occur for low values of the surface-parallel wavenumber $q_\parallel$ on the surface of metals, such as sodium, with a lower bulk conduction electron density.

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